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THE RED ROAD OF THE IBERIAN EXPANSION:

Cochineal and the Global Dye Trade

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Daniel,

unquestionably it was fate.

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The Red Road of the Iberian Expansion: Cochineal and the Global Dye Trade

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Entre finais do séc. XV, início do séc. XVI, portugueses e espanhóis ampliaram os seus impérios, alargando-os ao continente americano. Enquanto os portugueses cedo se dedicaram à exploração de pau-brasil, os espanhóis estabeleceram um monopólio de cochinilha americana, a qual se tornaria num dos mais importantes produtos comerciais do Atlântico até ao séc. XIX. O desenvolvimento deste projecto doutoral combinou Química Analítica e História Económica com o objetivo de explorar o impacto deste insecto americano na circulação global de corantes, assim como a sua importância enquanto corante vermelho nos principais centros de produção têxtil na Europa e na Ásia, em relação a outros insectos corantes locais.

A investigação histórica abrangeu uma ampla leitura de publicações históricas e fontes primárias impressas, sobre o comércio ibérico transatlântico de corantes e o seu impacto nas tradições de tingimento europeias e asiáticas durante o período Moderno. Especial enfoque foi dado à aceitação da cochinilha americana em detrimento de outros insectos locais - quermes, laca e cochinilha arménia e polaca. A pesquisa histórica veio evidenciar uma adopção gradual e definida do corante americano na Europa e no Sudoeste Asiático, embora os outros insectos continuassem a ser usados, especialmente na Ásia de Leste e Sudeste.

A investigação química teve como objectivo avaliar a parte histórica relativa ao impacto do corante americano na Europa e, particularmente, na Ásia, para a qual a informação histórica disponível não era suficiente. Dado que publicações anteriores relativas à caracterização química de insectos apresentavam limitações que comprometiam a diferenciação de espécies de cochinilha em têxteis históricos, um método de cromatografia líquida de ultra eficiência (UHPLC) foi optimizado para oferecer resultados mais precisos. Subsequentemente, foram realizados tingimentos com cochinilha e kermes, através de vários parâmetros experimentais. As resultantes fibras tingidas foram caracterizadas com UHPLC, o que conduziu a significativas interpretações sobre a composição dos corantes. Além disso, o envelhecimento artificial das fibras tingidas e a sua caracterização com espectrometria de massa (MS) permitiu, pela primeira vez, a observação de compostos de foto-degradação nos corantes. Estes resultados revelaram-se semelhantes aos de fibras tingidas com cochinilha em têxteis históricos e, por isso, as fibras experimentalmente tingidas e as históricas foram comparadas através da análise discriminante com método de mínimos quadrados parciais (PLS-DA), para a identificação das espécies de cochinilha em têxteis históricos.

Ao combinar os resultados desta metodologia com os resultados para outras fibras históricas tingidas com outros corantes, e juntamente com a sua contextualização histórica, tornou-se possível atribuir interpretações assertivas sobre a data e a proveniência dos têxteis investigados. Por outro lado, interpretações históricas mais conclusivas puderam ser obtidas relativamente à dinâmica da cochinilha americana nas sociedades europeias e asiáticas durante o período colonial. Assim, a combinação interdisciplinar entre os métodos químico e estatístico desenvolvidos neste estudo, em conjunção com evidências históricas, provaram constituir uma abordagem fundamental a ser adoptada em futuros projectos relativos à caracterização de corantes de insectos em património cultural.

PALAVRAS-CHAVE: cochinilha americana; Expansão Ibérica; corantes naturais; comércio global de corantes; experiências de tingimento; envelhecimento artificial; cromatografia líquida de ultra-alta eficiência; análise discriminante com método de mínimos quadrados parciais; espectrometria de massa.

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Between the end of the 15th century and beginning of the 16th, the Portuguese and the Spanish expanded their empires to the Americas. While the Portuguese soon dedicated to the exploitation of brazilwood, the Spanish came to establish a monopoly in cochineal that would become one of the most important commercial products in the Atlantic until the 19th century. The interdisciplinary investigation presented here, combining Analytical Chemistry and Economic History, aims to explore the impact of the American insect as a commercial product in the global circulation of dyestuffs, and its importance as a red dye in the main centres of textile production in Europe and in Asia, in relation to other local insect dyes.

The historical investigation comprised a comprehensive revision of historical publications and primary printed sources regarding the Iberian transatlantic trade in dyestuffs and their impact on European and Asian dyeing traditions during the Early Modern period. Special focus was given to the acceptance of American cochineal over local insect dye sources, namely kermes, lac and Armenian and Polish cochineal. This research reveals a gradual but clear adoption of the American dyestuff in Europe and in West Asia, although local insect dyes would still have a representative role in on-going practices, especially in East and Southeast Asia.

Chemical research was pursued to evaluate the historical picture presented for the impact of the American dyestuff in Europe and, especially in Asia, to which insufficient historical information was available. Given that previous publications concerning the chemical characterization of insect dyes depicted limitations that compromised the differentiation of cochineal species in red-dyed historical textiles, an ultra high-performance liquid chromatography (UHPLC) method was optimized to deliver more accurate results. Then, experiments with cochineal and kermes dyes were undertaken following several dyeing parameters. The resulting dyed fibres were characterized with UHPLC, leading to meaningful insights about the behaviour of the colorants' dye compounds. Subsequent artificial ageing of the dyed fibres and their characterization with mass spectrometry (MS) permitted to characterize, for the first time, photo-degradation compounds in the insect's colorant. These results were reported to be similar to those for historical fibres and, for this reason, it became possible to compare the experimentally-dyed and historical fibres through partial-least squares discriminant analysis (PLS-DA), for the identification of the cochineal species used to colour the analysed historical fibres.

By combining the results of this successful approach, along with the results for other coloured historical fibres and their contextualization with historical evidence, it was possible to ascribe assertive interpretations about the date and provenance of the investigated textiles. Moreover, successful historical interpretations could be obtained about the dynamics of American cochineal in European and Asian societies throughout the colonial period. Therefore, the interdisciplinary combination of chemical and statistical methods developed here, along with historical evidence, has proven to be an important approach that should be adopted in future projects for the characterization of insect dyes in cultural heritage objects.

KEYWORDS: American cochineal; Iberian Expansion; natural dyes; global dye trade; dyeing experiments; artificial ageing; ultra high-performance liquid chromatography; partial-least squares discriminant analysis; mass spectrometry.

LIST OF ABBREVIATIONS

AGI	*Archivo General de Indias*
ARC, AHV	*Archivo de Simón Ruiz, Archivo Histórico Provincial y Universitario de Valladolid*
AGS	*Archivo General de Simancas*
NEHA	Netherlands Economic History Archives
NIPG	Netherlands Institute for Price History
EIC	East India Company
VOC	*Vereenigde Oostindische Compagnie*

HPLC	high-performance liquid chromatography
UHPLC-PDA	ultra high-performance liquid chromatography - photo-diode array detector
SST	system suitability testing
DF	dilution factor
Neff	effective plate number
LOD	limit of detection
LOQ	limit of quantification
BEH	ethylene bridged hybrid
HSS	high strength silica
ESI-MS	electrospray ionisation mass spectrometry
SEM-EDX	image scanning electron microscopy - energy dispersive X-ray spectroscopy
PCA	principal component analysis
PLS-DA	partial-least squares discriminant analysis
ESM	electronic supplementary materials

CONTENTS

AUTHOR'S NOTE

This Doctoral thesis is written in English to ease its future access to worldwide researchers. Any non-English citations taken from bibliographical references are given throughout the text in the original language in which they were written. Respective translations are made by the author into modern English and they are provided as footnotes. All citations from historical references reflect the spelling of the original documents – for instance, the use of "ſ" corresponds to the modern "s". Cited authors are usually referred to by their last name.

The majority of the dates referred to in this work are after Christian era and, for this reason, "ACE" is not indicated. In the few cases dates are before Christian era, "BCE" is properly added.

Given the wide chronology studied, generalized designations for specific territories proved challenging. Therefore, modern geographical designations are used throughout this work to ease discussion for the reader. Dynastic imperial territories (e.g. Safavid or Ottoman), which changed their borders over time, are here considered by their highest territorial occupation and by defining them according to their representative modern countries.

In the case of the Netherlands and Belgium, which as political territories have changed shape often through the centuries, it was opted to encompass both regions under the modern designation, Low Countries. Since these regions have historically evolved in separate ways, the Low Countries are divided in the text between north and south: the north roughly corresponds to the northern territories of the present-day Netherlands (people of this territory are here designated usually as Dutch); and the south comprises approximately the regions of the present-day Belgium and southern Netherlands (people of this territory are here designated usually as Flemish).

For the comparison of weights and coin currencies, these were generally converted whenever possible, although always taking into consideration possible margins of error, inherent to price fluctuations throughout time and space. For the period before the 16th century, weights given in pounds and the Italian coin currency (ducats and *soldis*) were considered, whereas for the later period, after the 16th century, the Spanish weight known as *arrobas* and coin currency (*pesos*) were used.

INTRODUCTION

Of all natural red dyes, insects have always been a valuable commodity for Europeans and Asians alike, as until the invention of synthetic dyes in the 19th century, they provided the most brilliant, rich and enduring shades of crimson red in dyed textiles. Symbols of power, status and hierarchy, these hues were very difficult to obtain owing to the complex and costly dyeing processes involved and to the scarcity of red insect dyes. Up until the end of the Medieval period, the most luxurious red fabrics were mainly dyed with kermes, lac dye and Polish and Armenian cochineal. These insects were collected from plant roots and tree branches in certain parts of Europe and Asia, and subsequently traded through well-established commercial routes between both continents to reach the main centres of textile production.

With the Iberian Expansion at the end of the 15th and beginning of the 16th century, contact with the Americas gradually led to the exploitation and circulation of valuable commodities in Europe and Asia. Among the American raw materials which were exported, dyestuffs enjoyed a significant position in the transatlantic trade throughout the colonial period: Mexico had the finest cochineal; Brazil was famous for its brazilwood; Guatemala manufactured the best American indigo; and Yucatán and other parts of Central America offered a variety of dyewoods, such as logwood.

Of all of these, American cochineal was of paramount value, ranking in price after silver and gold among exports to Spain. Indeed, this dyestuff was soon revealed to possess a much higher content of colorant than European and Asian insect sources of red, as much fewer insects were required to achieve the same shades of red. Once in Europe and Asia, local dyers began experimenting with American cochineal leading to its adoption in many centres of textile production, and its progressive rise as a staple product of trade on a global scale.

Publications over the last century have systematically affirmed that as soon as American cochineal started to appear in European and Asian markets, it rapidly penetrated the main centres of textile production, replacing other local insect sources of red dye. While the arrival and circulation of cochineal in the major cloth-producing centres of Europe is reasonably well documented, historical evidence confirming its presence in other peripheral European regions and in Asia is limited. Thus, it is possible that the presence and use of American cochineal, in relation to other insect dyes, has been over-emphasized and has even influenced interpretations of material studies of European and Asian textiles dating from the 16th century onwards.

In this Doctoral thesis, a tripartite methodology is developed combining history, textile objects from museum collections and chemistry to obtain more nuanced historical interpretations of the dynamics of American cochineal in international markets and its adoption in European and Asian dyeing practices. Emphasis was given particularly to chemical investigation of the red colorants present in a wide range and number of historical textiles, since evidence obtained from museum objects can be useful for assessing historical propositions based on limited (or even absent) historical evidence.

The historiographical revision carried out in this thesis is primarily based on primary printed sources and historical publications. The latter represent notable and substantial efforts by accomplished scholars to assess the available archival documentation concerning the trade of American cochineal, and for this reason, new research on archival documents is not a major focus of this thesis. Instead, it aims to assess the current historical picture presented in the literature and to answer some of the questions it raises by looking at material evidence and historical museum objects. Thus, by chemically identifying the American dyestuff in European and Asian textiles, dating from the Early Modern period, this thesis seeks to offer new evidence to assess the scope of the global circulation of American cochineal and the timing and extent of its penetration into local dyeing practices.

In accordance with these objectives, this thesis is organized in four major parts: firstly, it begins with an introduction to the historical background to the research problem, which explains the questions raised and the interdisciplinary approach applied in this thesis; secondly, it undertakes a broad revision of historical publications and primary printed sources associated with Spanish and Portuguese transatlantic commerce to assess market trends and processes of adoption of American cochineal in global settings, from England to China; thirdly, it develops a systematic approach to the accurate differentiation of American cochineal and other cochineal dyes in historical objects using new techniques available in the field of Analytical Chemistry; and finally, it focuses on the analysis of a large collection of samples from historical textile objects produced in Europe or Asia, mainly between the 15th and 17th centuries, to respond to the questions raised in the historical studies presented in the second part of the thesis.

The thesis opens with a chapter on *Red, Symbol of Wealth*, which demonstrates the historical importance of the colour red and its association with the exploitation, trade and dye applications of European and Asian insect dye sources, namely kermes, lac and Polish and Armenian cochineal. The historical assessment of these insect dyes is fundamental for understanding the next chapter, *American Cochineal in the Iberian Expansion*. This focuses on the historical importance of American cochineal, as well as the current status of the historical and chemical research made so far and the problems raised by their analysis. Given the difficulties involved in studying this dyestuff, the objectives of a new research methodology combining history, textile objects from museum collections and chemistry are fully discussed in Chapter 3, *Multidisciplinary Approach: History, Objects and Chemistry*. The approach described here is then developed throughout the remaining chapters of this thesis.

In this context, the second part of the thesis is completely dedicated to the history of American cochineal in European and Asian societies during the Early Modern period, as a consequence of the Iberian Expansion. This is divided into four chapters, whose themes are strongly interrelated. Chapter 4, *Cochineal in Spanish Transatlantic Commerce: Trends in Volumes and Prices*, is fundamental for understanding the importance of American cochineal, by regarding its transatlantic trade, from the perspective of Spanish colonial trade with Mexico, between its conquest in 1521 and independence in 1821. Further chapters of this work obey these time boundaries. In Chapter 5, as its title suggests, *Cochineal and Other American Dyestuffs: a Comparative Perspective* suggests, American cochineal is compared with other American dyestuffs, namely indigo, brazilwood and logwood, which were also part of the commodities traded by the Spanish and the Portuguese from the Americas. This comparison is of upmost importance for understanding the wider picture of the colonial trade in American dyestuffs in which cochineal was involved. In Chapter 6, *Cochineal and the Global Dye Trade: Penetration of International Markets*, the international importance of American cochineal is assessed. Special consideration is given here to its commerce in Europe and Asia in relation to Spanish colonial trade, as well as its geographical penetration in dyeing applications of the main centres of textile production of Europe and Asia. In order to better understand the impact of this American dyestuff on long-established traditions, this is compared with indigenous insect sources of red, kermes, lac and Polish and Armenian cochineal in Chapter 7, *Competition between Insect Dyes: Markets and Dyer's Art*.

Given the objectives of this thesis, a large set of 287 samples were investigated, mostly belonging to luxurious European and Asian historical textile objects, dating from the 15th to 17th centuries. In addition to a full analysis of their red-dyed fibres, in some cases, yellow, green, blue, pink, orange, black or brown fibres were also studied. The results obtained for such a variety of colours is revealed to be very useful for enriching the historical contextualization of the textiles, as well as for understanding the dyeing traditions typical of different regions. Furthermore, the results from the red fibres can be used as evidence for the historical trends and questions raised in the previous chapters.

Owing to the analytical limitations verified in the scientific literature concerning the chemical characterization of cochineal dyes, the next part of this thesis is dedicated to the development of an optimized analytical approach that could deliver more precise information about the source of the insects used to colour historical textiles. This third part is divided in two sections, which correspond to two papers published in ISI Web of Knowledge scientific journals, and which are presented here following the editorial guidelines of their respective journals. In both, one of the most powerful analytical techniques for compound separation currently available was used: ultra high-performance liquid chromatography coupled to photo-diode array detector (UHPLC-PDA). Chapter 8, *Evaluation between ultrahigh pressure liquid chromatography and high-performance liquid chromatography analytical methods for characterizing natural dyestuffs*, shows that the optimized UHPLC-PDA method can bring more accurate chromatographic results than the conventional HPLC method, often applied to the analysis of natural dyes in the field of cultural heritage. Moreover, the UHPLC method has shown the possibility of identifying, in one single analysis, a wide range of natural dyes used in historical textiles. In Chapter 9, *Investigation of crimson-dyed fibres for a new approach on the characterization of cochineal and kermes dyes in historical textiles*, the UHPLC method was used, along with mass spectrometry (MS) and image scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX) to investigate the colorant behaviour of cochineal and kermes insect dyes in a large set of experimentally-dyed and artificially-aged samples of silk and wool. By testing different parameters and submitting the experimentally-dyed samples to analytical techniques, it was possible to observe how the composition of the insect dye colorant was affected. Since this resulted in a large quantity of analytical results with very similar but variable dye compositions, multivariate statistical analysis (specifically, partial-least squares discriminant analysis, PLS-DA) was applied to interpret the chromatographic results and, therefore, discriminate the cochineal insect species in dyed and aged reference samples. The results of this approach confirmed the possibility of achieving accurate identifications when considering unknown species of cochineal in red historical textiles.

Therefore, the last part of this thesis, Chapter 10, *The Red Road of the Iberian Expansion*, comprises the overall review of the historical interpretations achieved earlier in this work, in relation to the results obtained from the chemical investigation of the large set of samples belonging to historical textiles. This approach not only provides more assertive interpretations about the objects analysed, namely their provenance and date of production, but also offers a more concrete perspective of the dynamics of the trade in American cochineal over the 16th and 17th centuries, and the extent of its penetration into the practices of dye workshops in Europe and Asia.

The scientific results show a gradual but clear acceptance of American cochineal in the main centres of textile production in Europe and West Asia. However, in peripheral Europe and in South and Southeast Asia, old dyeing practices continued, and native insect dyes were maintained (in agreement with the picture portrayed in the historical chapters). Therefore, the tripartite approach applied in this Doctoral thesis brings important contributions to our knowledge of the history of American cochineal, as well as of other European and Asian dyestuffs. Finally, these results open new lines of investigation for archival research, as well as for the continued chemical characterization of American cochineal and “Old World” dyestuffs in Early Modern textile objects.

CHAPTER 1

RED, SYMBOL OF WEALTH:

Historical Background

"Such extravagance in dress, such sartorial
splendour, … is far beyond the average person's
notion of luxury." John N. Munro [1]

Today we enter retail shops and purchase clothes designed in a multitude of colours and materials. These can often resist several journeys to the washing machine and come out as brilliant as the day they were bought. These are the perks of an industry that, through gradual developments and sporadic innovations extending as far back as the 16th century, has led to the affordable textiles produced today. Thus, it is hard to imagine a time when colours and fabrics were worn with restrictions and exclusively made for the consumption of an elite minority.

Such a time did exist in the Medieval and Early Modern periods, when fabrics were symbols of status and pride for the wealthy nobility and members of the high clergy. The attire one wore could say plenty about one's social condition, namely from the type and quality of the fibres used, as well as from the colour with which they were dyed. The right to wear and purchase luxury clothes was scrupulously controlled by sumptuary laws, created to dissuade excessive expenditure and extravagance; by controls on the importation of luxury products; by laws that protected local industries; and almost always with the aim of ensuring social hierarchy [2]. In the reign of King Henry VIII (r. 1509-1547) of England, it was decreed that only he and his closest family members had the right to wear purple silk and cloth of gold. In Italy, only a wealthy elite (*coccinati*) had the privilege to wear luxury red clothes [3].

These rules can in great part be explained by the sumptuous prices attributed to these clothes. Elaborate silk and woollen cloths ranked at the top of the most expensive and

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1 Munro, 1983, p. 70.

2 Greenfield, 2006, pp. 14, 22-23 and 39-44; Marichal, 2014, p. 200; Massa, 1970, p. 172; Monnas, 2008, pp. 1-2; Phipps, 2010a, p. 26.

3 Born, 1938, p. 211; Greenfield, 2006, p. 14; Monnas, 2008, p. 2; Phipps, 2010a, p. 26.

covetable fabrics. Silk fabrics like lampas and figured velvets cost more to produce than plain silks (tafettas), because they required larger amounts of materials, specific professional skills, more workers and more time. Scarlet woollen fabrics were particularly expensive, not only because of the materials used, but also because of the technical finishes applied to them after the weaving process, such as bleaching, dyeing, weighting, shearing or pressing. Silk and woollen fabrics were so expensive that "old" clothing or furnishings were frequently converted into different clothes or adapted to smaller objects, such as book covers or purses. They were also offered to the Church and then converted into liturgical garments. Fabrics dyed with expensive dyestuffs, like insect dyes, could also be converted into shearings. These were then dissolved to extract the dyestuff which was re-used to make pigments or dye new cloth [4].

Dyestuffs of animal origin constituted a major part of the cost of these textiles. They provided the deepest, most brilliant, and enduring colours, ranging from red to purple on animal fibres (silk and wool). These colours were also very difficult to obtain owing to their scarce availability in nature, the laborious work of producing and collecting the required dyestuffs, the quantity of animal ingredients necessary to obtain the colorant, and the complex and costly processes involved in dyeing with them [5]. In this chapter, the historical background of red dyestuffs of animal origin in Europe and Asia is undertaken to assess their importance as coveted sources of dye in these societies, up until the end of the Medieval period.

1.1. Royal Purple

Until the 15th century, shellfish dye extracted from a species of snail from the *Muricidae* and *Thaididae* families was the most expensive of all dyestuffs and it was highly

[4] Hofenk de Graaff, 2004, pp. 332 and 344-347; Monnas, 2008, pp. 15 and 23. Munro (1983, pp. 37, 39 and 65) explains that scarlet drapery was the most expensive of woollen cloths, because the best wool (from England) was dyed with the best red dyestuff (kermes). See also Franceschi, 2016, pp. 183-184.

[5] The research work from Munro (1983, p. 39) is essential to understand the high costs of woollen medieval textiles dyed with red dyes from animal origin: "Fees for dyeing were often a very large proportion of the final cloth price, sometimes the largest single component of total production costs. Of these dyeing costs, moreover, the raw material itself could account for 75-98 per cent". See also Munro, 1983, pp. 14 and 70; Balfour-Paul, 1998, p. 15; Born, 1938, p. 211; Donkin, 1977a, p. 848; Franceschi, 2016, p. 199; Greenfield, 2006, p. 14; Hakluyt, 1935, p. 137; Jacoby, 2004, p. 211; Lee, 1948, p. 451; Marichal, 2001, pp. 5-7, 2014, pp. 200-201; Molà, 2000, pp. 111-112.

esteemed among wealthy Phoenicians, Romans and Byzantines. The best was produced in Tyre, a Mediterranean region that gave rise to the famous designation "Tyrian purple" [6]. Over-exploitation eventually led to extinction in many Mediterranean centres of production, as large quantities of the snails were required to dye the prized "Royal" purple [7]. The industry was moreover affected by the conquest of Istanbul by the Ottoman Empire, in 1453. Since this was the last main centre under Christian rule, European access to the valuable *purpura* cloths became dependent on commerce with Asia [8].

Recipes to imitate the valuable shade of *purpura* had been long disseminated before its extinction and became increasingly important. This was possible using insect dyes, much appreciated in both Europe and Asia. Less expensive than the Mediterranean snails, insects were used instead, along with a mordant (such as alum), to dye silk and wool fabrics with deep red and crimson hues. When mixed with other dyestuffs, insects could provide a wide range of shades and, furthermore, when used with a blue dye, they could even give a purple shade, close to that of the original snails. With the fall of Istanbul and the discovery of alum mines in northern Italy, Pope Paul II (p. 1464-1471) decreed in 1467 the replacement of shellfish by scale insects to dye the garments of the Church's high clergy [9].

Besides the limited access to the "Royal" purple cloths, the profits of alum exploitation were a worthy incentive for the Vatican's textile workshops. Indeed, alum played an important role when dyeing with insect dyes, because it chemically bonds the dyestuff to the fibres, by creating a chelating reaction of fibre – aluminium – dyestuff. Without it, the dyestuff does not efficiently attach to the fabric resulting in poor colour fastness (something that is assessed by the dyeing experiments described in Chapter 9). Besides alum, other types of mordants can be used as well, such as iron sulphate or tin

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[6] Balfour-Paul, 1998, p. 14; Bender, 1947, p. 4; Cardon, 2007, pp. 571–576; Hofenk de Graaff, 2004, pp. 265–266; Munro, 1983, p. 14.

[7] Böhmer & Enez (2002, p. 233) affirm that "material from 10.000 snails was necessary to produce a single gram of the purple dyestuff", while Jacoby (2004, p. 10) states that "Twelve thousand snails of *Murex brandaris [a specific species of snail]* yield no more than 1.4 g of pure dye, enough to color only the trim of a single garment". Munro (1983, p. 14) concludes that "even the cheapest *[type of purple snail]* was far more costly than any other dyestuffs, because so many of these rare, perishable molluscs were required to produce the dyestuff". See also Balfour-Paul, 1998, p. 15; Bender, 1947, pp. 4-5; Cardon, 2000, p. 63.

[8] Bender, 1947, pp. 4-5; Böhmer & Enez, 2002, pp. 205 and 233; Brunello, 1973, p. 124; Cardon, 2007, p. 576; Greenfield, 2006, pp. 38–39; Hofenk de Graaff, 2004, pp. 55 and 265; Leggett, 1944, p. 79.

[9] Born, 1938, p. 209; Böhmer & Enez, 2002, p. 205; Brunello, 1973, p. 124; Cardon, 2000, pp. 63-64, 2007, p. 576; Greenfield, 2006, pp. 38–39; Hofenk de Graaff, 2004, p. 55; Leggett, 1944, pp. 78–79; Phipps, 2010a, p. 26; Verhecken & Wouters, 1988, p. 214. Rosetti (1969, p. 114) clearly entitles the "Cardinal shade" to describe a recipe for dyeing with kermes insects.

chloride, and this choice can influence the final colour of the fibres. Generally, dyestuffs that require a mordant reaction to bond with animal (and cellulose) fibres comprise not only insects, but also dye sources from plants (mordant dyes). On the contrary, dyeing with shellfish (vat dye) did not require a mordant, because the dyestuff was applied to the fibres in a water-soluble and reduced form (through fermentation in alkaline vats), which would then precipitate into an insoluble and resistant colour. Other dyes (direct dyes), easily soluble in water, could be directly applied to the fibres, by providing deep and brilliant colours, which tended to fade rapidly [10].

1.2. Shades of Red

In Italy, three treatises written in the 15th and the 16th centuries were largely focused on red [11]. The majority of the recipes in these sources are dedicated to the application of six types of dyestuffs, in order to achieve colour shades ranging from red to purple: madder root, orchil lichens and brazilwood (plant dyes); and kermes, cochineal and lac (insect dyes). Shades obtained with plant dyes were not as brilliant and/or lightfast as those achieved with insect dyes, and for this reason, fabrics dyed with them were less valuable [12]. Though, both plants and insect dyes were often mixed in textile centres to achieve a wide range of colours and more accessible production costs.

Brazilwood, for instance, was often mixed with other dyes in such a way that the final colour would appear similar to that achieved when using the pure expensive insect dyes. Buyers would then be deceived, since it was very hard to ascertain which dyes were used to colour the fabrics, even for experts. For instance, *paonazzo* shade (ranging from purple to

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[10] Besides insect dyes, examples of vegetable dyes that require a mordant are madder, brazilwood, logwood, weld, dyer's broom, young fustic or gallnuts. Vat dyes comprise not only shellfish, but also woad and indigo. Direct dyes include, for instance, safflower, orchil and turmeric. Information about the applications and colours obtained with these dyestuffs is given throughout this work. Cardon, 2007, pp. 4-6; Hofenk de Graaff, 2004, pp. 15-17; Kirby et al., 2014, pp. 9 and 25-28.

[11] One Florentine treatise written in the middle of the 15th century (Gargiolli, 1868); one Venetian treatise dated to the last quarter of the 15th century (Rebora, 1970); and another Venetian treatise dated to 1548 (Rosetti, 1969).

[12] According to Munro (1983, p. 39), in the Flanders markets of the mid-15th century, kermes insects could worth twenty nine times more than madder. This plant was generally the main source of red for less expensive textiles because it could be cultivated and, hence, its supply was always larger than the valuable insects. Brunello, 1973, p. 140; Cardon, 2010, pp. 107-108 and 282-283; Greenfield, 2006, pp. 45-46; Kirby, et al., 2014, p. 6; Leggett, 1944, pp. 77-78; Monnas, 2008, p. 25; Renard, 1913, p. 294.

violet) could be accomplished with all red dyes (vegetal or animal) and it was quite often mischievously adulterated [13].

In order to protect the purity of the ingredients used, Italian centres created strict statutes to regulate the dyeing of red silk fabrics throughout the 15th and 16th centuries. These statutes even prohibited sometimes the mixture of valuable dyes with cheaper plant dyes [14]. Furthermore, statutes established guidelines for the application of representative selvedges on cloths dyed with different insect dyes. This measure aimed for a better distinction between textiles dyed with different dyestuffs, since they were sold at diverse prices, but also to indicate their place of production [15]. These regulations were particularly verified in Venice, where mixtures of red dye sources, especially of vegetable origin, were firmly prohibited. Nonetheless, mixtures between cochineal and kermes insect dyes in the same bath were still common [16]. As for wool, the roots of the madder plant were routinely applied, as well as mixtures of this dye or brazilwood with insect dyes (even if sometimes forbidden) [17]. Although efforts were often made to dilute expensive insect dyes, they remained highly coveted as the best dyes for achieving strong reds.

1.3. Red Insect Dyes

Entomologically, insect dyes belong to the superfamily Coccoidea, and only few are known to be capable of supplying red dyes [18], as discussed below:

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[13] Some dyers would try to make profit by adding very little cochineal in relation to a high ratio of brazilwood. Fabrics would then be sold at the same price as if dyed with pure cochineal and, later, the colour would eventually fade. *Paonazzo* was a shade with which fraud was often complied because the mixture of dyes necessary to make it was allowed: first the silk was immersed in a red dye, and then in a blue dye bath (*vagello*) with indigo, some madder, cream of tartar (alum of lees) and bran (Molà, 2000, pp. 112-113; Brunello, 1973, p. 163). See also Bensi, 2009, p. 40; Cardon, 2007, p. 115; Gargiolli, 1868, pp. 48–51.

[14] While mixtures with insect dyes were strictly prohibited in Venice, the Genoese statutes of 1432 permit a mixture of kermes and cochineal. This was banned in 1466 (Bensi, 2009, p. 37). See also Bensi, 2009, p. 40; Brunello, 1973, pp. 137, 140 and 166; Kirby et al., 2014, p. 6; Massa, 1970, pp. 117-122; Molà, 2000, pp. 112-120; Rebora, 1970, pp. 4-6. Similar regulations were applied in French textile centres, particularly to protect the purity of silk dyed with expensive dyestuffs (Wescher, 1939, p. 620; Brunello, 1973, pp. 138 and 148).

[15] Bensi, 2009, p. 40; Massa, 1970, pp. 117-119; Molà, 2000, pp. 112, 115-117, 119 and 122; Monnas, 2008, pp. 17 and 319, 2012, p. 25. Standard selvedges were not applied in smaller textile centres, as Buss (2009, p. 46) noted for Milan.

[16] Brunello, 1973, p. 137; Buss, 2009, p. 48.

[17] Bensi, 2009, p. 39; Brunello, 1973, pp. 138 and 188; Monnas, 2012, p. 25; Munro, 1983, p. 57; Rosetti, 1969, p. 114.

[18] Donkin, 1977a, p. 848; Hofenk de Graaff, 2004, p. 53; Kondo et al., 2008, pp. 55-56; Łagowska & Golan, 2009, p. 151.

Kermes. Known since at least the middle of the 2nd millennium BCE, it was highly prized by Jews, Phoenicians, Greeks and Romans. It was regularly levied from local populations, a tradition that persisted well into the late Medieval period [19]. From several existing species of kermes, the most popular are the *Kermes vermilio* P. and the *Kermes ilicis* L. [20] species, from the Kermesidae family, which feed on oak trees, *Quercus coccifera* and *Quercus ilex*, respectively. These are plant shrubs usually found in regions around the Mediterranean and certain parts of West Asia. The collection of these insects occurred around May or June, when the adult pea-sized females, full of unborn larvae, were gathered and killed in vinegar baths or fumes. Then, the insects were dried under sun exposure, which conferred a grainy appearance to them [21]. The commercial product thus resembled a dried berry, commonly referred to as *grana* in historical documents [22].

Polish and Armenian cochineal. According to historical sources, Polish cochineal (*Porphyrophora polonica*) and Armenian cochineal (*Porphyrophora hamelii*), were extensively exploited in the regions that gave them their commercial name [23]. Nowadays, the extension of these cochineal species is known to be much larger than that evidenced by historical sources. These and another 45 species belong to the *Porphyrophora* genus

[19] Bender, 1947, p. 5; Born, 1938, pp. 211-212; Böhmer & Enez, 2002, p. 205; Cardon, 2007, p. 617; Donkin, 1977a, pp. 860-863; Greenfield, 2006, p. 47; Hofenk de Graaff, 2004, p. 55; Leggett, 1944, p. 75. Verhecken & Wouters (1988, p. 213) defend that the dyestuff used by Jews and Phoenitians was not kermes as literature affirms. According to the authors, the dyestuff was named "*karmil* or *tola' at shani* in Hebrew, which means "scarlet worm". This might refer to *Porphyrophora hamelii* (Armenian cochineal) or a related species, which are red worm-like insects, in contrast to the round brownish "berry" of kermes".

[20] Some contemporary authors assert that *Kermes ilicis* cannot provide a red colorant (Cardon, 1989, p. 5, 2007, p. 609; Verhecken & Wouters, 1988, pp. 212-213). However, analyses undertaken by Wouters & Verhecken (1991, pp. 17-20) have shown that this insect species can provide a colorant, as well as other species of kermes insects. In its turn, Molá (2000, p. 110) mentioned that this species gives, instead, beige extracts.

[21] Atasoy et al., 2001, p. 195; Beckmann, 1846, pp. 387 and 890; Bender, 1947, p. 5; Born, 1938, pp. 206-207; Böhmer & Enez, 2002, p. 205; Cardon, 2007, pp. 610-613; Donkin, 1977a, p. 859, 1977b, p. 9; Greenfield, 2006, p. 47; Martí, 1768, pp. 12-35; Molà, 2000, p. 110; Phipps, 2010a, p. 8; Verhecken & Wouters, 1988, pp. 212-213. Also, the insects could get rid of impurities and then worked into a dye pulp or a mass with vinegar, which was then commercialized as *pastel d'écarlatte.* This was four times more expensive than the separate insects (Cardon, 2007, p. 613; Verhecken & Wouters, 1988, pp. 215-216).

[22] Despite known as *grana* (or *granum, grain, graine, greyn, grana de alcarmes, grana de kermes*), *coccus* (or *coccinagrum, kokkos*), *vermiculum* (or *vermiculi, vermiculata, vermillon*) and *graine d'écarlate* (or *pastel d'écarlatte*, *scharlachbeeren*), kermes is also considered to be derived from *kirmiz*, which means "worm" in West Asia. This denomination was also used for *Porphyrophora* insects in Medieval Europe, which casts some confusion when trying to identify these dyestuffs in historical sources. Buss, 2009, pp. 48-49; Born, 1938, p. 206; Cardon, 2007, pp. 608-609; Donkin, 1977a, p. 849, 1977b, pp. 9-10; Greenfield, 2006, p. 49; Molà, 2000, p. 109; Monnas, 2012, p. 23; Munro, 1983, p. 17; Phipps, 2010a, p. 9; Verhecken, 1989, p. 389; Verhecken & Wouters, 1988, p. 214.

[23] Bensi, 2009, p. 37; Cardon, 2007, pp. 635-636; Verhecken & Wouters, 1988, p. 222.

(Margarodidae family). They are spread throughout the Palearctic region, which comprises the north of Africa, Asia above the Himalayas, and both Central and East Europe [24].

Polish cochineal was known since at least the pre-Christian era [25]. It was paid as tribute in North Europe during the Caroligian Empire, as well as to Christian monasteries, during the Medieval period [26]. The insects were collected from the roots and lower stems of several plants (mainly *Sleranthus perennis* L.), which grow in Central and East Europe, and have also been recently reported in Central and East Asia, as far as Mongolia [27]. The pregnant females and cysts were collected between May and July, by digging out the host plant and removing the insects with a trowel. The insects were then placed in vinegar or boiling water and dried in a warm oven or under the sun [28]. They were mainly collected in Russia, Ukraine and in Poland, particularly in the Ruthenia region. In Poland, this dyestuff was so important for the local economy that the month in which it was collected was given its name (*czerwiec*). There, the collection of the insects would start on June 24, the day of Saint John, which is why Polish cochineal was also known as "Saint John's blood" [29].

Armenian cochineal insects were mostly gathered in the Aras river plain near Mount Ararat. This region comprised parts of Armenia, Azerbaijan, Georgia, Iran and Turkey. The insects were used in West Asia from at least 714 BCE, year in which historical records report the presence of scarlet textiles dyed with the Armenian dyestuff among the booty plundered

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[24] For the entomologic study of *Porphyrophora* species, see Vahedi & Hodgson (2007, p. 24). See also Kondo et al., 2008, p. 56; Łagowska & Golan, 2009, p. 153.

[25] Cardon, 2007, p. 644; Donkin, 1977a, p. 855; Schmidt-Przewoźna & Przewoźny, 2010, p. 398.

[26] Beckmann, 1846, pp. 394-395; Böhmer & Enez, 2002, p. 206; Brunello, 1973, p. 153; Cardon, 2007, p. 644; Donkin, 1977a, p. 855; Gerber, 1978, p. 17; Greenfield, 2006, p. 47; Hofenk de Graaff, 2004, p. 65; Leggett, 1944, p. 81; Schmidt-Przewoźna & Przewoźny, 2010, p. 400; Verhecken & Wouters, 1988, p. 224.

[27] Atasoy et al., 2001, p. 195; Born, 1938, pp. 208-209; Böhmer & Enez, 2002, p. 206; Brunello, 1973, p. 153; Cardon, 2007, pp. 638-639; Donkin, 1977a, pp. 853-854; Molà, 2000, p. 110; Munro, 1983, p. 16; Phipps, 2010a, p. 9; Schmidt-Przewoźna & Przewoźny, 2010, p. 401; Verhecken & Wouters, 1988, p. 224.

[28] Detailed description on the harvesting process of Polish cochineal is given by Cardon (2007, pp. 640-641) and Schmidt-Przewoźna & Przewoźny (2010, p. 401). See also Atasoy et al., 2001, p. 195; Beckmann, 1846, p. 396; Born, 1938, pp. 209 and 212; Böhmer & Enez, 2002, p. 206; Brunello, 1973, p. 153; Greenfield, 2006, p. 48; Pearson, 1705, pp. 109-110; Donkin, 1977a, pp. 854-855; Łagowska & Golan, 2009, p. 158; Leggett, 1944, pp. 81-82; Munro, 1983, p. 17; Verhecken & Wouters, 1988, pp. 224-225. In the same way as made for kermes, Polish cochineal insects could be worked to a paste shaped into small balls, which was sold at higher prices than the dried insects (Cardon, 2007, p. 641; Hellot, 1750, pp. 366-367). Perhaps this can explain the two varieties of "fine" and "coarse" listed by Rosetti (1969, p. 139): the "fine" corresponds to the small balls of dyestuff, with which less quantity is needed to dye one pound of silk; whereas the "coarse" corresponds to the bulk insects (with more impurities), with which more quantity is needed to colour the same amount of silk.

[29] Brunello, 1973, p. 153; Buss, 2009, p. 49; Cardon, 2000, p. 66, 2007, pp. 639-640; Gerber, 1978, p. 17; Greenfield, 2006, pp. 47-48; Schmidt-Przewoźna & Przewoźny, 2010, pp. 398-399; Verhecken & Wouters, 1988, p. 224.

by the Assyrians, during the invasion of the kingdom of Urartu (Ararat) [30]. They were collected between mid-July and mid-September, very early in the morning, when the females would emerge from the ground to mate with males on the surface. The subsequent killing treatment was similar to that applied to kermes and to Polish cochineal [31]. Nowadays, Armenian cochineal has been found co-habiting with other *Porphyrophora* species on the roots and rhizomes of Graminae grasses, namely *Aeluropus littoralis* (Gouan), found in sandy saline soils near seas or rivers, in the dry steppes or semi-desert regions from West to East Asia [32].

Lac dye. This dyestuff has long been appreciated in Asia, where it was used to colour textiles since at least the 2nd century BCE. Historical documents report the first imports into Europe at the beginning of the Christian era, and by the Medieval period, it was commonly commercialized in Venice, along with brazilwood [33]. Lac belongs to the *Kerria* and *Paratachardina* genera (Kerridae family), geographically ascribed to South Asia and Oceania regions. Among the great variety of lac species, *Kerria lacca Kerr* is the most popular for dyeing, although other species, such as *Kerria chinensis*, might have been used as well for the same purpose [34]. Their exploitation was usually made by local populations who collected the wild insects or reared them onto twigs and fleshy young leaves of several host plants. Collected twice a year, they formed a red oval-shaped secretion resinous layer, which held a dark red liquid, the shellac and lac dye. The coated twigs of the host plants were cut before the development of the eggs, and the dyestuff was marketed containing both the resinous matter and the red dye (*sticklac*). The dyestuff could also be sold in grain form, when lac secretions were removed from the twigs [35].

[30] Böhmer, 1998, p. 36; Cardon, 2007, pp. 650-651; Donkin, 1977a, pp. 849 and 851; Kurdian, 1941, p. 105; Phipps, 2010a, p. 9.

[31] Atasoy et al., 2001, p. 195; Böhmer, 1998, p. 36; Böhmer & Enez, 2002, p. 207; Cardon, 2007, p. 648; Donkin, 1977a, p. 849; Greenfield, 2006, p. 48.

[32] Atasoy et al., 2001, p. 195; Böhmer & Enez, 2002, p. 207; Cardon, 2007, pp. 647-648; Donkin, 1977a, p. 849; Hofenk de Graaff, 2004, p. 70; Molà, 2000, p. 110; Munro, 1983, p. 16; Verhecken & Wouters, 1988, p. 227.

[33] Cardon, 2007, pp. 663-664; Donkin, 1977a, pp. 864-865, 1977b, p. 11; Hofenk de Graaff, 2004, p. 86; Verhecken & Wouters, 1988, pp. 229-230.

[34] Atasoy et al., 2001, p. 195; Brunello, 1973, p. 188; Cardon, 2007, p. 656; Donkin, 1977a, p. 864, 1977b, p. 10; Heyd, 1886, p. 625; Hofenk de Graaff, 2004, p. 86; Santos, 2010, p. 15; Verhecken & Wouters, 1988, p. 229. More entomological studies should be undertaken in order to obtain a more comprehensive knowledge on the dyeing properties of the other lac species (Santos, 2010, p. 15).

[35] For a more detailed description of the life cycle and harvesting process of lac insects see Cardon (2007, pp. 657-661). See also Atasoy et al., 2001, p. 195; Böhmer & Enez, 2002, p. 208; Donkin, 1977b, p. 11; Gerber,

1.4. The Red Dye Trade

Lac, kermes and Polish and Armenian cochineal were all extensively traded in Europe and Asia by the end of the Medieval era. In the 13th and 14th centuries, Italian dyers were experts in dyeing with kermes and, to some extent, with lac as well. Numerous references are given to the European trade of these dyes in Pegolotti's *Pratica della Mercatura*, although only two references are given for silk dyed with cochineal, traded (and perhaps made) in Cyprus and Armenia [36]. In fact, based on archival documentation, Molá (2000) reported that by 1393 a dyer from Lucca (Italy), skilled in dyeing with kermes, embarked on a long journey: first to Istanbul, then to Feodosia (Crimea) on the Black Sea, and finally to Iran, to learn the secrets on how to dye with cochineal dyes. On his way back to Italy, he brought great quantities of the dyestuff, which could be either of the Polish and the Armenian types, or both [37].

At this time, Lucca was no longer the most famous producer of silk fabrics in Europe. Due to political conflicts, many Lucchese families fled Lucca at the beginning of the 14th century to other Italian cities, such as Genoa, Bologna or Venice. These cities already had small silk workshops established and welcomed the arrival of silk merchants and skilled textile producers. Undoubtedly, the intense competition that flourished between these cities was a decisive factor in the expansion of the Italian silk industry at this time[38]. Sericulture in the north of Italy grew alongside this, but it was always necessary to import silk from other Mediterranean regions or from West Asia, not only to supplement local production, but also because diverse qualities of silk had different applications [39].

1978, pp. 19-20; Hofenk de Graaff, 2004, pp. 85-86; Leggett, 1944, pp. 90-91; Molà, 2000, p. 109; Orta, 1913, p. 241; Phipps, 2010a, p. 9; Verhecken & Wouters, 1988, p. 229.

[36] Pegolotti, 1936, pp. 59 and 78. See also Donkin, 1977a, pp. 856 and 863; Heyd, 1886, p. 350; Molà, 2000, p. 110.

[37] Molà, 2000, p. 110; Verhecken & Wouters, 1988, p. 225. At this time, the producing regions of Armenian and Polish cochineal were already specialized in dyeing textiles with them. The Spanish González de Clavijo (1928, p. 143), embarked on a journey to the West Asia between 1403 and 1406, where he noticed that "in the valleys at the foot of the *[Ararat]* mountain the *Kirmiz* worm *[Armenian cochineal]* is found, with which they *[local population]* dye the silk crimson". In addition, Schmidt-Przewoźna & Przewoźny (2010, pp. 399-400) report that Polish cochineal was produced near Poznan since the 13th century to feed the demand of a dyeing centre in a local monastery. The authors adds that the oldest registry on the export of Polish cochineal from Poland goes back to 1412, which is in agreement with the information given by Molá and Verhecken & Wouters.

[38] Brunello, 1973, p. 141; Monnas, 2008, pp. 4-7, 2012, p. 8. See also Greenfield, 2006, pp. 17-19.

[39] Monnas, 2008, pp. 5-7.

In West Asia, silk weaving techniques were long established; but in Europe, expertise in silk production was only concentrated in Italy and Spain. In the 13th century, silk was produced as well in France, in Paris and Montpellier, although on a much smaller scale. The industry would only expand in the 15th century when Italian experts settled in Tours and Lyon [40]. Instead, in the 14th century, Paris was the main supplier of woollen tapestries in Europe. Other Northern European centres of wool production were internationally renowned as well, namely in the south of the Low Countries, at Tournai, Brussels, Ghent, Leuven or Malines. In Italy, Florence was renowned for its woollen cloths, followed by some other Italian cities [41].

As the popularity of silk and woollen cloths grew, merchants sought to make them available everywhere. Venetians, Genoese and Pisans created outposts in Istanbul and in key centres of West Asia. The Mediterranean ports in the Levant region, such as Damascus and Beirut, as well as Alexandria, were important stations for the exchange of European and Asian goods, Fig. 1.1. There, Italian merchants traded woollen and silk fabrics for raw silk, Islamic carpets, spices (cloves and nutmegs) and dyestuffs (lac dye, indigo, dragonsblood or saffron) [42]. These products came from distant regions, such as India, China, Japan and Indonesia, either down the Silk Road, crossing southern Russia, Afghanistan, Iran and Turkey; or alternatively, by sea routes, crossing Egypt to the Red Sea and the Iranian Gulf, transported by Chinese, Indian and Arab merchants, Fig. 1.2 [43].

[40] Brunello, 1973, p. 127; Monnas, 2008, p. 4, 2012, pp. 11-12; Wescher, 1939, p. 620.
[41] Brunello, 1973, pp. 129, 135 and 156; Franceschi, 2016, p. 183; Marichal, 2014, p. 201; Monnas, 2008, pp. 5-6; Munro, 1983, pp. 17 and 30; Spufford, 2010, p. 17. Not many historical treatises on dyeing are available to this period and the list is shortened if counting only those which mention the use of insect dyes. Apart the abovementioned Italian treatises (Gargiolli, 1868; Rebora, 1970; Rosetti, 1969), two more from this period were reported with the use of insect dyes. They both come from famous European centres of textile production: one was published in Brussels in 1513 and it gives reference to the use of *greyn*, meaning kermes (Frencken, 1934, pp. 29, 43 and 105; see also Brunello, 1973, p. 178; Hofenk de Graaff, 2004, p. 327); the other is a Spanish treatise from 1491, where kermes is referred to as *grana* (Comamala & Llave, 2011, pp. 169, 177, 239 and 241). Other historical sources (principally of German origin), related to dyeing for this time, are mainly dedicated to domestic practices. These were carried out in more isolated European regions such as monasteries, where textile production was carried out at a small scale. At these places, local fibres and dyestuffs were applied, rather than costly imported materials, such as insect dyes. Although these dyestuffs have not been reported in "domestic" literature, German monasteries still received tributes of Polish cochineal from locals (Brunello, 1973, pp. 153-154; Kirby et al., 2014, pp. 36-37). See also Verhecken & Wouters, 1988, p. 208.
[42] Monnas, 2008, p. 8; Spufford, 2010, pp. 12-13.
[43] Spufford, 2010, pp. 14 and 18.

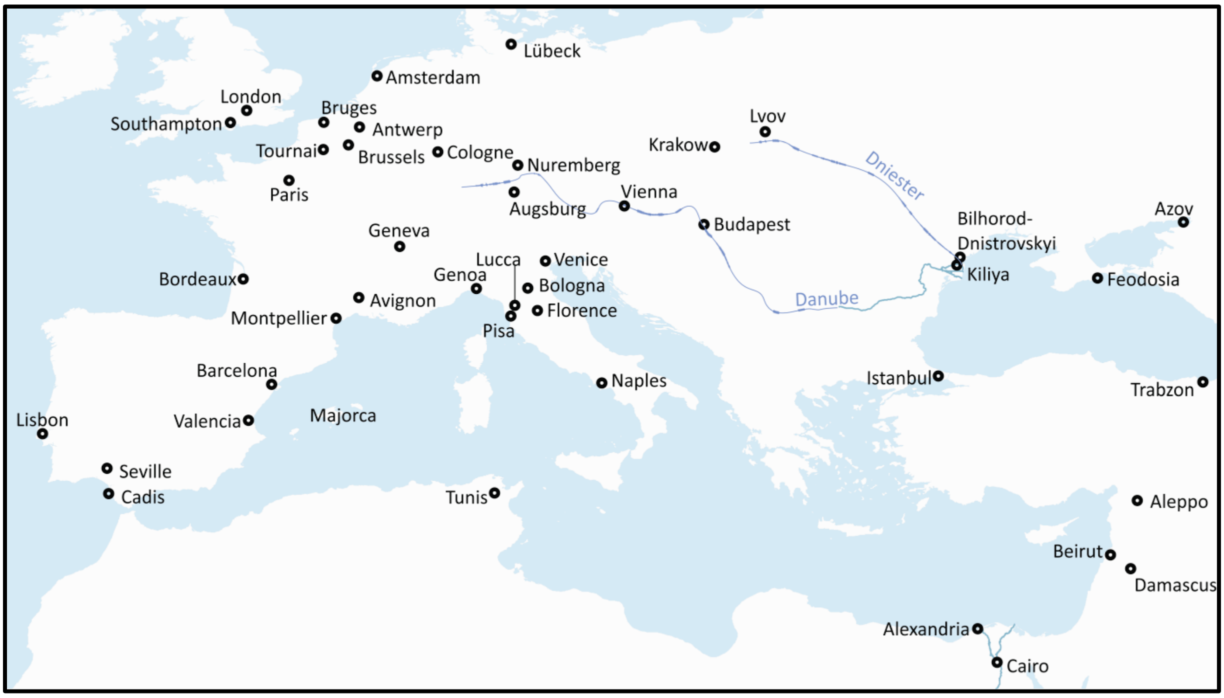

Fig. 1.1. Map of the main European textile production and/or commercial centres, as well as ports of connection to the principal Asian trade routes, from the 13th to the 16th centuries.

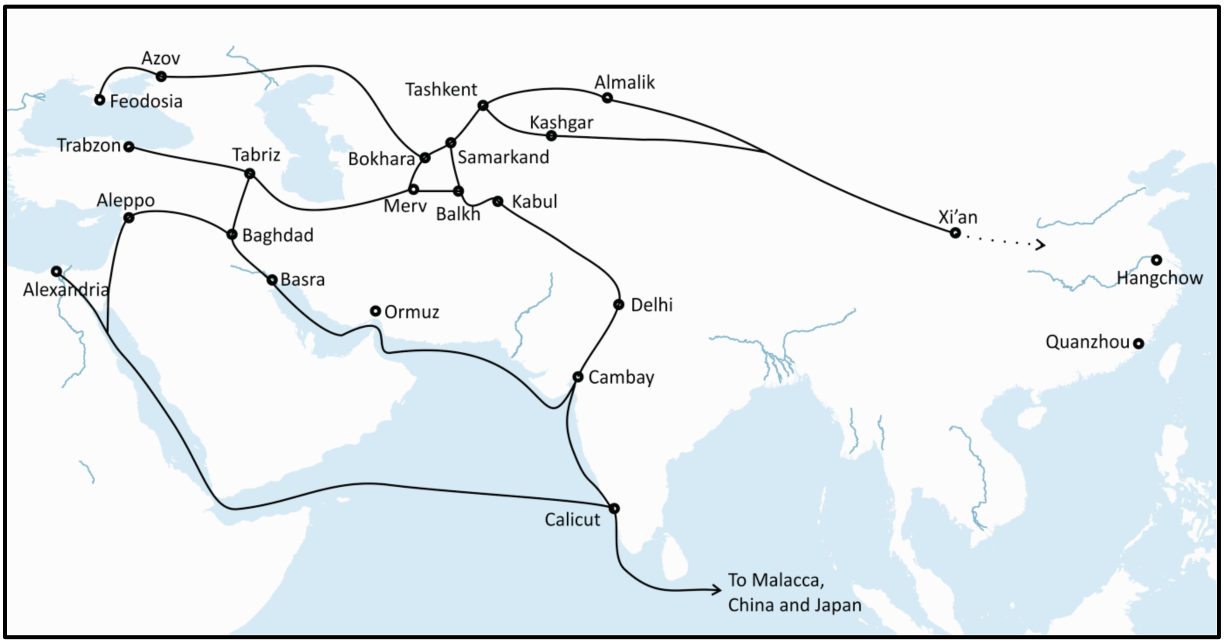

Fig. 1.2. Map of relevant Medieval Asian trade routes [44].

[44] Idem, p. 11.

Throughout Europe, import-export companies settled in strategic ports in Italy (Florence, Venice, Genoa, Pisa), France (Paris, Montpellier, Avignon), Spain (Barcelona), England (London), south Low Countries (Bruges, Antwerp) and Switzerland (Geneva) (Fig. 1.1). In North Europe, during the 15th century, Bruges was the most important commercial entrepôt but, after 1480, due to political instability in the region, Antwerp gained increasing significance and, hence, merchants from Italy, Portugal, Spain, England and other countries moved there. Also, in London, merchant communities of Italians, Scots, Germans, Spanish and French proliferated. German merchants, too, settled in Poland (Krakow) [45].

To connect north and south, sea routes, mainly controlled by the Italians (principally Genoese and Venetians), crossed the Mediterranean and the Atlantic to reach London and the Low Countries, as well as Poland and Russia, especially in the 15th century. Italian merchants navigated to the ports of Trabzon (Turkey) and Azov (Russia) in the Black Sea. From this sea, and through Kiliya and Bilhorod-Dnistrovskyi (Ukraine), they could also go up the Danube or Dniester rivers into Central Europe [46]. When sea trade was no longer safe after the end of the 15th century, land routes still connected Central Europe to all corners, which were largely controlled by Jews and German traders [47].

On the one hand, these routes connecting European regions, as well as Europe with Asia, encouraged the growing circulation of luxury goods and the spread of European cloths to wealthy courts everywhere in Europe and West Asia. On the other hand, while textiles flowed away from Italian and Flemish production centres, there must have been a vast appetite for materials in these thriving industries. Besides the obvious example of silk and wool production and the channelling of these products to the main centres of textile manufacturing, a suitable example of continuous demand and markets response can be found in the trade of insect dyes.

Lac dye was mainly produced in India and other regions of South Asia, such as Burma and Cambodia. From there it was exported to China, Iran and other parts of the continent, as well as to Europe, through the main trade routes. Based on Datini's merchant valuations and bills of lading, DeLancey reports that lac dye was commonly marketed in Alexandria, Beirut,

[45] Brunello, 1973, pp. 134-135; Monnas, 2008, pp. 8-12; Spufford, 2010, pp. 14-16.
[46] Brunello, 1973, pp. 134-135; Cardon, 2007, p. 644; Spufford, 2010, pp. 17-18.
[47] Cardon, 2007, p. 644; Donkin, 1977a, p. 863; Spufford, 2010, p. 18.

Damascus, Low Countries, Barcelona, Venice, Genoa, and Pisa, between 1379 and 1405 [48]. However, in Europe, lac was not as famous to dye silk as other insect dyes, because extracting the colorant was a highly complex process. In Genoa, for instance, it was even banned from local workshops in 1466. Regardless, it was still used in Perugia by 1531 and it was prolifically applied in Turkish velvets [49].

Kermes was predominantly collected in Spain (especially Valencia), Maghreb (Morocco, Algeria, Tunisia and Libya), south of France (Provence and Languedoc) and Greece (Corinth and Crete) - the latter provided the highest quality, as crimson shades could be obtained with fewer insects. From these producing regions, kermes was shipped to the main European centres and to the Levant, from where it would reach the inner lands of West Asia [50]. For example, in the 14th century, a company in Florence bought several shipments of kermes: in 1349, a total of 319 pounds of dyestuff was brought from Corinth to Florence; in 1353, c. 937 pounds were brought to the same city from Montpellier; and in 1357, 1 272 pounds were bought in Marseilles to be shipped to Bruges. At this time, the dyestuff sold in Florence or Paris was on average valued at c. 0.8 – 1 gold florins per pound, although this price could vary depending on the region of production, the method of preparation and the yield of harvest [51]. In Spain and in France, given its abundance, kermes was not only exported, but it was also the chief source of red in local textile centres: Spanish silks dyed with kermes were exported to Italy in 1450, whereas wollen cloths produced in Narbonne were exported to the Levant in the 13th century [52].

As for Polish and Armenian cochineal, after the first experiments of Italian dyers at the end of the 14th century, they became bulk merchandises and the primary sources for

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[48] DeLancey, 2010, pp. 77 and 80.

[49] Bensi, 2009, p. 39; Greenfield, 2006, pp. 46-47; Massa, 1970, pp. 118-119; Molà, 2000, p. 112; Monnas, 2012, p. 23; Rebora, 1970, p. 5; Verhecken & Wouters, 1988, p. 230. Its application for dyeing textiles is moreover mentioned in one Venetian treatise, dated to the end of the 15th century (Rebora, 1970, p. 120).

[50] Bensi, 2009, p. 37; Born, 1938, pp. 213-214; Donkin, 1977a, p. 863; Rosetti, 1969, p. 136. According to an Italian treatise from the middle of the 15th century, kermes from the region of Sintra, in Portugal (*grana di Cintri*), would have been traded in Italy as well, and it was even considered of better quality than the Spanish (Gargiolli, 1868, pp. 109 and 134; see also Sequeira, 2014, p. 114). Also, Power & Postan (2006, p. 215) mention that the trade in kermes to Bristol (England) was mainly coming from Portugal, rather than Spain. Exploitation of Portuguese kermes in this period was actually made at large proportions, and, besides meant for export (to Italy, England or Germany), it was used as well in local workshops to produce rich silk and woollen textiles (Braga, 1998, pp. 184-186, 2001, pp. 104-105; Ferreira, 2010, p. 1; Sequeira, 2014, pp. 112-114; Silva & Carmona, 1988, p. 6).

[51] Cardon, 2007, pp. 612-613. One florin would be similar to one ducat in terms of weight in gold (c. 3,536 g) or 124 *soldi* (Molà, 2000, p. IX; Morrisson, 2001, p. 226).

[52] Bensi, 2009, p. 37; Cardon, 2007, p. 618; Donkin, 1977a, p. 863.

dyeing red silk in Italy, during the following century. In some textile producing centres of North Europe, Polish cochineal was adopted as well. Both insect dyes were commercially known everywhere by several variants of the Arabic "worm" (which was also applied confusingly to kermes) [53], and were not only used widely by local populations, but thoroughly traded between Europe and Asia, reaching the most famous centres of textile production [54].

In Poland, for instance, Polish cochineal was bred in Owinska, in the outskirts of Poznan, since 1242. Production was led by the local monastery, which had a textile centre too. The majority of the cochineal harvest was sent to Poznan, where merchants dealt with international buyers from Nuremberg or Italy. From there, Polish cochineal was sent to the major European centres of textile production, in Italy and in the south of the Low Countries. From Italy, it was also dispatched to the Asian trade routes, through which it reached the dye workshops of Turkey and other parts of West Asia [55].

Armenian cochineal was widely applied on silk, woollen cloths and carpets in the dye workshops of West Asia. Near Ararat (the main exploitation region), Artashat and Dvin were renowned cities for the manufacture of fine textiles, many of them dyed with the Armenian insects. In addition to the Asian land routes that led to Europe and Iran, shipments of the dyestuff also reached the Black and the Caspian Seas, through the Aras river [56].

The final price of clothes dyed with cochineal dyes was at least twice as expensive as those that were dyed with kermes. In 1397, to dye one light pound of silk to make warp and weft threads would cost a Venetian dyer about 3.5 ducats using kermes, while with cochineal this price would practically double (8 ducats). For one light pound of silk intended for warp pile threads, an even higher amount of colorant was necessary as this is more visible than either warp or weft threads. Hence, the cost to the dyer was about 5.5 ducats

[53] *Vermiculo*, kermes, *krmi, kirmiz, karmir, karmil, kirmizi, carmes, carmusi, carmasio, cermesi, chermes, chermisi, crimsyn, cremesi, cremex, cremexi, cramoisi, cremesi, chermesi, coccus, etc*. Cardon, 2007, pp. 608-609; Donkin, 1977a, pp. 851 and 863; Greenfield, 2006, p. 49; Hofenk de Graaff, 2004, pp. 64 and 70; Kurdian, 1941, pp. 105-106; Molà, 2000, p. 109; Munro, 1983, p. 18; Renard, 1913, p. 294; Verhecken & Wouters, 1988, pp. 214-215 and 228-229.

[54] Cardon, 2007, pp. 644-645 and 651-652; Donkin, 1977a, pp. 852-853 and 856; Hofenk de Graaff, 2004, p. 71; Łagowska & Golan, 2009, pp. 158-159; Verhecken & Wouters, 1988, p. 225; Schmidt-Przewoźna & Przewoźny, 2010, pp. 398-399.

[55] Schmidt-Przewoźna & Przewoźny, 2010, pp. 398-400. See also Cardon, 2007, pp. 644-645; Verhecken & Wouters, 1988, p. 226. Production of Polish cochineal was furthermore controlled by local monasteries in Germany during the 13th century (Cardon, 2007, p. 639).

[56] Donkin, 1977a, pp. 852-853; Kurdian, 1941, p. 105.

with kermes, and 11 ducats with cochineal. In 1429, Florentine dyers were paying a price 50 times lower (c. 12 *soldi* for kermes and 25 for cochineal), most likely because there was a higher availability of these dyestuffs in the Italian markets. Similar prices were also registered in the middle of the century and, in this case too, the price was double for dyeing with cochineal [57].

These differences in costs might be related to different types of dye preparation and harvest yields. Cochineal and kermes dyestuffs sold in dried form were soaked for several days and then filtered (to remove all impurities) and grinded into a paste. In the case of cochineal dyes, silk needed to be immersed in several dye baths at least two or three times to obtain the desired colour. The process of dyeing with kermes was far simpler, as only one dye bath was sufficient. Moreover, in order to obtain crimson shades for one pound of silk, circa four pounds of Polish cochineal were required. This was a great amount if it is considered that one person could only collect about 2.1 - 3.5 ounces per day. In comparison, one person could collect up to two pounds of kermes insects in a single day, whereas to dye one pound of silk with an intense red, c. 1.5 - 2.5 pounds of kermes would be needed [58].

In other words, dyeing one pound of silk with four pounds of Polish cochineal corresponded to the harvest of a single person over twenty days. If considering that a deep crimson was only achieved with three dye baths, the total amount of Polish cochineal required (12 pounds) was equivalent to the work yielded by the same person over the course of two months. By contrast, with kermes, a deep red hue could be achieved on one pound of silk with only one dye bath, and this required only the yield of a little more than one person's workday. Therefore, given the low dye content of cochineal insects and their scarce availability, they were always much less advantageous than kermes.

However, fabrics dyed with kermes exhibited red-orange shades, lac imparted a dark blood red shade, and cochineal, a purplish or blue-toned red (crimson), close to that of the legendary shellfish purple. At the end of the day, the expensive prices of crimson purple fabrics dyed with cochineal still had an intrinsic symbolic value, which the wealthy elites

[57] Molà, 2000, p. 359; Gargiolli, 1868, p. 78. One light pound is equivalent to 12 ounces or c. 301 g (Molá, 2000, p. IX; Cardon 2000, pp. 72-73); one regular pound corresponds to c. 453 g. See also Brunello, 1973, p. 164.

[58] Cardon, 2007, p. 612; Łagowska & Golan, 2009, p. 158; Verhecken & Wouters, 1988, p. 225. One pound is considered to correspond to 16 ounces. See also Born, 1938, p. 212; Brunello, 1973, pp. 153-154; Cardon, 2007, pp. 642-643; Gargiolli, 1868, pp. 31-37; Leggett, 1944, pp. 81-82; Jacoby, 2004, p. 211; Molà, 2000, p. 111; Rebora, 1970, pp. 72-78; Rosetti, 1969, pp. 134-139; Verhecken & Wouters, 1988, p. 227.

were more than willing to pay for. Therefore, it is not surprising that Italian dyers kept on dyeing their most elaborate silk with cochineal [59], whereas kermes was principally used to dye wool scarlet [60].

As previously observed for kermes varieties, the quality between cochineal dyes varied as well. Insects of Polish cochineal (*chermesi minuto*), though considered to be smaller and to provide less beautiful shades than those of the Armenian variety (*chermesi grosso*), have a higher concentration of colorant, which made them more valuable. Indeed, Armenian cochineal, despite easier to collect, presents a very high content of fatty compounds, which hinder the dyeing process. For this reason, twice as many Armenian insects were necessary to obtain the same crimson shade as from Polish cochineal. Nevertheless, Armenian cochineal was still very appreciated and it was particularly used to dye smaller fabrics [61].

As quality between these insects varied, so did prices. Cardon (2000) conducted archival research on the account books of the Venetian merchant Giacomo Badoer, and found annotations for the trade in cochineal dyes in Istanbul between 1436-1440, immediately before its fall to the Ottomans. There, the merchant bought a great deal of cochineal and became famous for his interest in this product. For good prices, he usually

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[59] Bensi, 2009, p. 38; Cardon, 2000, p. 642; Greenfield, 2006, p. 48; Molà, 2000, p. 111; Rosetti, 1969, pp. 108 and 123-124. Cardon (2007, p. 642) states that Polish cochineal insects "were better suited for use in dyeing lighter, precious silk textiles than large, heavy pieces of cloth. They were largely ignored by all the great woollen cloth centres". Nonetheless, two Italian treatises (Gargiolli, 1868, pp. 35-37 and 49-51; Rosetti, 1969, pp. 133-136 and 144-145) still describe recipes where the use of kermes is suggested to dye silk in crimson. In regions like Spain where there was an abundance of kermes, it is expectable that this would be the main source to dye silk fabrics, rather than the imported costly cochineal dyes (Brunello, 1973, p. 154).

[60] Munro accomplished a remarkable work in characterizing medieval scarlet clothes. He states that these evolved in such way that, by the Middle Ages, they represented the most fine and expensive woollen draperies dyed with kermes and made of English wool. They were "indisputably the most costly of all woollens *[…]* presumably they were also the most extensively finished" (Munro, 1983, pp. 25 and 37). Cardon (2007, p. 642) adds: "crimson *[cochineal]* represents for silk what kermes scarlet is for wool", although the author also reports that, if cochineal was to be applied on wool, only half of the amount generally used on silk would be necessary to obtain an acceptable colour. See also Brunello, 1973, p. 188; Cardon, 2007, pp. 614-615; Franceschi, 2016, pp. 183-184; Kirby et al., 2014, p. 7; Monnas, 2008, p. 25, 2012, p. 23; Rosetti, 1969, pp. 108-109, 114 and 123-124.

[61] Cardon, 2007, pp. 649-650; Verhecken & Wouters, 1988, pp. 222 and 224. A similar argument was given in the 15th century (Gargiolli, 1868, p. 32): *e se vuoi vedere se è di meno perfezione il grosso che 'l minute, pon mente che dua libre di grosso tingono per una di minuto, ma il grosso tigne più gentile e più vivo che il minuto, ma fa minore colore* ["and if you want to see if Armenian cochineal is less perfect than the Polish, bear in mind that two pounds of Armenian dye make one of Polish, but the Armenian dyes are more gentle and bright than the Polish, but make less colour"]. See also Bensi, 2009, p. 38; Böhmer & Enez, 2002, p. 208; Buss, 2009, p. 49; Cardon, 2000, pp. 67 and 70; Donkin, 1977a, pp. 849 and 851; Gargiolli, 1868, p. 134; Greenfield, 2006, p. 48; Kirby et al., 2014, p. 8; Kurdian, 1941, p. 106; Munro, 1983, p. 16; Rebora, 1970, p. 77.

placed orders through intermediaries and commissaries who collected the merchandise directly from the dye-producing regions. In 1437, Badoer bought Polish cochineal (*cremexe rosesco*) valued at about 75 *soldi* per light pound and Armenian cochineal coming from Trabzon (*cremexi di vini*) valued at a lower price, about 56 *soldi* per light pound [62]. In 1438, the merchant bought a shipment of *cremexi savaxi*, which Cardon attributes to be the same as *cremesino schiavo* or *raguseo minuto* (Polish cochineal) [63]. Also, the author hypothetically attributes its origin to a region near Belgrade and close to the Sava river, from where it could have been channelled to Dubrovnik (Croatia) up the course of the river Drina, or down the Sava and then the Danube, ending up in Istanbul [64].

All shipments purchased by Badoer were sent to Venice to be sold at even higher prices. During the four years spent in Istanbul, the merchant bought a total of 4 400 light pounds of cochineal, equivalent to 824 515.3 ducats, either paid for in gold or in bartered manufactured woollen and silk cloth (most of it Italian). This was brought to East Europe and to Asia and, supposedly, a good part had been dyed with cochineal insects originally coming from those regions [65]. Nonetheless, since the insects have a low colorant strength, then the Polish insects would merely dye, at best, about 349.5 light pounds of silk, and the less expensive Armenian insects, about 125.3 light pounds of silk [66].

Although Badoers' purchases seem gigantic, they are just numbers for only one merchant. Based on Poznan's tax registries, Schmidt-Przewoźna & Przewoźny (2010) report that in 1515 an Italian merchant bought c. 7 726 pounds of Polish cochineal and, in 1540,

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[62] Cardon, 2000, pp. 67-68. The author makes a general estimation to compare the price of eight Circassian young healthy slaves, purchased at the same time as the cochineal shipment: if, in average, each slave would have weighed about 183 pounds, and knowing that each would have cost about 30.4 ducats, then their price per pound would be about 21 *soldi*, a price four times cheaper than one light pound of Armenian cochineal. Similar nomenclature on cochineal dyes is found in one Italian treatise from the middle of the 15th century. This treatise furthermore demonstrates that the Polish cochineal was not only more expensive than the Armenian, but also than kermes (Gargiolli, 1868, p. 109). See also Cardon, 2007, p. 645.

[63] These varieties are also mentioned by Rosetti (1969, pp. 139 and 194) and, because of the amounts suggested to dye one pound of silk, they may certainly correspond to Polish cochineal. A Levant variety is also suggested and this too may be Polish cochineal, since its quantity is similar to the aforementioned varieties. This Levant cochineal was possibly sent from Poland and Germany to Venice, and from there, to Asia, through the Levant. See also Bensi, 2009, p. 38; Buss, 2009, p. 49; Cardon, 2007, p. 645; Donkin, 1977a, p. 856.

[64] Cardon, 2000, pp. 69-70, 2007, p. 645.

[65] Idem, pp. 70-71.

[66] The calculations from Cardon (2000, pp. 71) are based on Rebora (1970, pp. 76–79) and Rosetti (1969, p. 47), where it is considered that for dyeing one pound of silk, six to nine pounds of Polish cochineal, or 12 to 14 pounds of Armenian cochineal, are necessary.

another foreign merchant exported almost 24 282 pounds of the valuable dyestuff. In 1534, a record of 66 225 pounds was sold in Poznan, mostly to merchants from Augsburg [67].

With the launch of the Portuguese expansion in the fifteenth century, maritime routes with Asia were established, while Portuguese and Spanish settlements started to flourish in the recently reached Americas in the early 16th century. This permitted the import of new merchandise and, consequently, the flow of overseas dyestuffs from the Americas into Europe and Asia. The production of red textiles, as well as the composition of the local trade of dye sources in these regions, would start undergoing a subtle but gradual change over the following century.

[67] Schmidt-Przewoźna & Przewoźny, 2010, pp. 399-400.

CHAPTER 2

AMERICAN COCHINEAL IN THE IBERIAN EXPANSION:

Questions for Research

Uno de los mas preciosos frutos que se crian en
nuestras Indias Occidentales, es la grana
cochinilla, mercadería igual con el oro y plata.
Felipe III (r. 1598-1621), 1620 [1]

With the Iberian Expansion at the turn to the 16th century, European commercial contacts were extended, firstly towards the East by the Portuguese, with the establishment of the maritime Cape route leading to the Indian Ocean and Asia, and then shortly thereafter, towards the West, by way of the transatlantic route to the Americas, also followed by the Spanish. From the Americas, the Spanish then crossed the Pacific Ocean to reach the Philippines and, thence, Asia. Throughout the 16th century, Asian, American and African products arrived in the Iberian Peninsula along these routes and, from there, were re-shipped to Europe. The English, Dutch and French also entered the long-distance trade later in the century and, subsequently, goods no longer passed exclusively through the Iberian Peninsula. At the same time, European merchants continued trading in the Mediterranean, namely in Tétouan, Istanbul, the Levant region and Cairo, connecting Europe, North Africa and Asia. Istanbul connected the Mediterranean to Turkey and the Caspian region, through the Black Sea; the Levant ports gave way to the Silk Road that headed to the interior of Asia overland, namely to Iran, and thenceforth India; and Cairo was the door to access sea routes from the Red Sea and the Persian Gulf, hence connecting Europe with the Indian Ocean, Fig. 2.1 [2].

[1] ["One of the most precious fruits breeding in our West Indies, is the cochineal, a merchandize equal to gold and silver"] (Boix, 1841, p. 314).
[2] Alden, 1965, pp. 37-39; Balfour-Paul, 1998, pp. 41, 44 and 50-51; Darling, 2006, pp. 176-177; Donkin, 1977a, p. 865, 1977b, pp. 38-39; Gillespie, 1920, p. 132; Lane, 1940, pp. 581, 587-589; Lee, 1951, p. 211; Masson, 1896, pp. 129, 373-374 and 386; Pieper, 1998, pp. 364-365; Spufford, 2010, pp. 15 and 18.

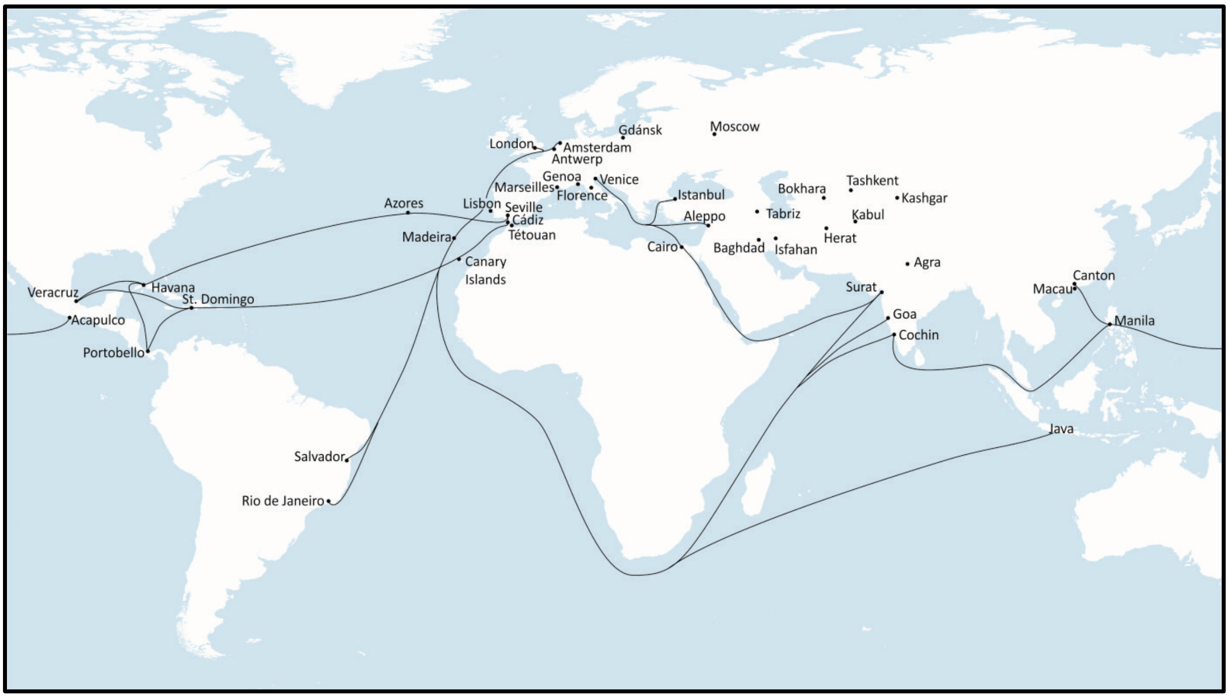

Fig. 2.1. Map of the principal maritime trade routes between the 16th and the 18th centuries [3].

In the Americas, incentives from settlers and merchants gradually led to the exploitation and circulation of valuable commodities that would boost the European economy in the 16th century. Undeniably, the vast amounts of gold and silver crossing the Atlantic Ocean became the primary gears for European interest in the Americas, and consequently, for the local development of colonial settlements [4]. Spanish and Portuguese merchants not only focused on the bullion available, but also took advantage of local products, and introduced and propagated European animals and plants, mainly in response to the demands of European and Asian markets [5]. Indeed, the majority of the American merchandise that arrived in Lisbon, Seville or Cadis, comprised raw materials that were chiefly produced by the colonies to supply international needs [6].

[3] Bethell, 1988, p. 49; Burkholder & Johnson, 1998, p. 135; Garavaglia & Marchena, 2005, I, p. 294; Mazín, 2007, pp. 24 and 112; Parry, 1990, p. 228.

[4] Baskes, 2000, p. 9; Braudel, 1982, p. 196; Brunello, 1973, pp. 194-195; Garavaglia & Marchena, 2005, I, pp. 250-251; Hamilton, 1948, p. 34; MacLeod, 1984, pp. 355-367; Parry, 1990, pp. 115-116; Phillips, 1990, p. 83; Pieper, 1998, p. 360; Spufford, 2010, p. 18.

[5] Bagú, 1949, pp. 65-66; Baskes, 2000, p. 9; Garavaglia & Marchena, 2005, I, pp. 259-260; Heers, 1961, p. 3; McAlister, 1984, p. 234; Parry, 1990, p. 115; Phillips, 1990, pp. 76 and 78-79; Ulloa, 2010, pp. 95–96.

[6] Chaunu & Chaunu, 1956, VI$_1$, pp. 98-108; Chevalier, 1943, pp. 327-330; Fuentes, 1997, pp. 212-214 and 236; Garavaglia & Marchena, 2005, I, pp. 259-260; González, I, 1976, pp. 338 and 343; MacLeod, 1984, p. 355;

American commodities regularly flowed into the Iberian Peninsula, and from there to the rest of Europe and then Asia: silver, gold, pearls, cochineal, indigo, sugar, hides, cocoa, tobacco, exotic woods (brazilwood, logwood and others), medicinal drugs (sarsaparilla or canafistula), and many other minor items [7]. By far, the most valuable products traded across the transatlantic routes were silver and gold, followed by non-metallic goods. McAlister asserts that for the 16th-century Spanish Americas "major exports in order of value (in *pesos de oro* of 450 *maravedis* each) were: precious metals, 14 141 216 (1566-70); hides, 583 438 (1568-70); cochineal, 478 856 (1568-70); and sugar, 268 040 (1568-70). Secondary exports consisted mainly of dyewoods and other products". From these, the total value of non-metallic merchandise corresponded to c. 14%. However, such percentage would change throughout the colonial period. By the beginning of the 17th century, non-metallic merchandise brought from Mexico to Spain represented 40 to 50% of the total bulk, whereas in the second half of the 18th century, only 25% [8].

From these products, dyestuffs enjoyed an increasing position, especially American cochineal, which had a paramount value among exports to Spain. If considering the 14% of non-metallic merchandise, the value of cochineal represented about 41.6% of it, indigo 10%, and dyewoods (among other cheaper products) 8.8% [9]. While the best cochineal was produced in Mexico, Brazil was famous for its brazilwood, Guatemala for indigo, and Yucatán and other parts of Central America, for dyewoods in general. Once in Europe, and thence Asia, American dyestuffs would gradually be accepted in local textile industries [10]. For the purposes of this thesis, it is important to generally understand the importance and value of American cochineal for the Spanish Empire and European and Asian societies.

Mazín, 2007, p. 113; McAlister, 1984, pp. 234 and 370; Parry, 1990, p. 124; Phillips, 1990, pp. 78-79; Pieper, 1998, pp. 360 and 362.

[7] Burkholder & Johnson, 1998, p. 144; Chaunu & Chaunu, 1956, VI_1, pp. 98-108; Chevalier, 1943, pp. 327-330; Fuentes, 1997, pp. 212-214 and 236; Garavaglia & Marchena, 2005, I, pp. 259-260; González, 1976, I, pp. 338; MacLeod, 1984, pp. 355-356; McAlister, 1984, pp. 234 and 370; Parry, 1990, p. 124; Phillips, 1990, pp. 78-79.

[8] González, 1976, I, p. 342; Lee, 1948, p. 449; Mazín, 2007, pp. 113 and 117; McAlister, 1984, p. 247; Morineau, 1985, p. 103; Sanz, 1979, p. 545.

[9] Sanz, 1979, pp. 545-546.

[10] Brunello, 1973, pp. 195-196; Leix, 1937b, pp. 20-21; Garavaglia & Marchena, 2005, I, pp. 259-260; Lee, 1948, p. 449; Marichal, 2001, p. 18; Sanz, 1979, p. 548.

2.1. A New Red Dye: American cochineal

Dactylopius coccus, also known as "American cochineal", along with nine species, is part of *Dactylopius* genus, Dactylopiidae family [11]. This insect is a domesticated cochineal species, grown on the surface of cactuses belonging to the *Opuntia* genus [12]. This species exhibits larger dimensions, extended lifespan, higher dye content and more vulnerability than the other *Dactylopius* species, which are often entitled "wild" cochineal. Given these contrasting characteristics, contemporary entomologists believe that *D. coccus* is the result of the optimal breeding of another *Dactylopius* species in ancient pre-Colombian cultures [13]. Although considered to possess a lower grade of dyestuff, wild cochineal insects were used for the same purposes as *D. coccus*. According to Cardon, *cette cochenille silvestre ou campessianne est toujours plus menue que la fine et a un air plus rouillé. La couleur qu'elle donne est toujours plus solide, mais elle n'a jamais autant d'éclat. On compte 3 livres de cochenille silvestre pour 1 livre de cochenille fine* [14]*.* Wild insects also breed on the surface of *Opuntia* cactuses and the harvest follows similar procedures for both varieties: the females are collected when they are about to lay their eggs and this may occur at least three times a year for *D. coccus*, and throughout the year for the wild insects [15]. The preparation of the

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[11] *D. austrinus, D. confertus, D. salmianus* and *D. zimmermanni* are attributed to South America, while *D. opuntiae, D. bassi, D. confusus* and *D. tomentosus* are ascribed to North America. *D. ceylonicus and D. coccus* have been attributed to both American regions (Chávez-Moreno et al., 2009, p. 3338; Portillo, 2005, p. 2; Rodríguez et al., 2001, p. 73), although recent ecologic and genetic work on *D. coccus* has pointed out its geographic origins to Oaxaca, Mexico (Dam et al., 2015, pp. 307-308). Rodríguez et al. (2001, p. 73) only points to the existence of nine *Dactylopius* species, while Portillo (2005, p. 2) and Chávez-Moreno et al. (2009, p. 3338) mention that *D. bassi* might be a synonym for other *Dactylopius* species. Further entomological and chemical studies should be carried out on this cochineal species. See also Kondo et al., 2008, p. 56; Łagowska & Golan, 2009, p. 153.

[12] Baskes, 2000, p. 9, 2005, pp. 192-193; Camargo, 1998, pp. 286-287; Cardon, 2007, p. 620; Donkin, 1977b, p. 14; Gerber, 1978, p. 23; Lee, 1948, p. 450, 1951, p. 206; Marichal, 2001, p. 15; Phipps, 2010a, p. 10; Portillo, 2005, p. 1; Verhecken & Wouters, 1988, p. 209.

[13] A good comparison between the domesticated and the wild species is given by Cardon (2007, pp. 620 and 632-634), Donkin (1977b, pp. 14 and 32) and Humboldt (1822, III, pp. 66-70). See also Baskes, 2000, pp. 9-10; Chávez-Moreno et al., 2009, p. 3338; Born, 1938, pp. 216-217; Lee, 1948, p. 451; MacLeod, 1973, p. 171; Munro, 1983, p. 63; Phipps, 2010a, p. 10; Portillo, 2005, pp. 1-2; Ramírez, 1831, pp. 267-268; Roquero, 2006, p. 140; Silva & Bosa, 2006, p. 478.

[14] ["this sylvester or campeachy cochineal is always smaller than the domestic cochineal and has a more rusty appearance. The colour is always faster, but it never has as much brilliance. Three pounds of sylvester cochineal are needed instead of one pound of domestic cochineal"] (Cardon, 2007, p. 634). Jordán (1963, p. 16) adds that the wild cochineal is not suitable to dye silk, instead it damages it. See also Jordán, 1963, p. 302; Pearson, 1705, pp. 160 and 280.

[15] For a thorough understanding on the life cycle of *Dactylopius* and the careful rearing of *D. coccus*, see Cardon, 2007, pp. 620-623; Cervantes, 1944, pp. 165-174; Donkin, 1977b, pp. 14-17; Humboldt, 1822, III, pp. 72-78; Ramírez, 1831, pp. 251-267 and 271-286; Réaumur, 1737, pp. 120-126. See also Baskes, 2000, pp. 10-11; Bender, 1947, p. 5; Dampier, 1699, pp. 228-229; Jordán, 1963, pp. 12-13; Juan & Ulloa, 1748, pp. 445-446; Lee,

dyestuff can be achieved through several methods, which were considered to influence the quality of the colorant [16].

Originally collected in Central and South America, *Dactylopius* insects were traded and locally applied as red dyes by pre-Colombian cultures, since at least the 2th century ACE [17]. In spite of its early use among the American populations, it was only after the Iberian Expansion, at the beginning of the 16th century, that Europe and Asia had contact with the American dyestuff. Certainly, when the Spanish reached Mexico in 1519, members of Hernán Cortés expedition noticed that the indigenous people were using a red dye obtained from cochineal insects raised on the surface of cactuses: *y quando ſlegamos á la gran plaça, que ſe dize el Tatelulco* [in City of Mexico], *como no auiamos viſto tal coſa, quedamos admirados de la multitud de gente y mercaderias que en eſla auia* [...] *é vendian mucha grana debaxo de los portales que eſtavan en aquella plaça* [18]. Soon afterwards, the Spanish

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1948, pp. 450-451 and 466-467; MacLeod, 1973, pp. 170-171; Marichal, 2001, p. 14, 2014, p. 199; Phipps, 2010a, p. 14; Roquero, 2006, p. 141; Sanz, 1979, pp. 552-554; Verhecken & Wouters, 1988, pp. 209-210.

[16] The most common procedure for preparing cochineal dyes consists on spreading the collected females over mats, exposing them to hot sun. This results in a product of whitish "grainy" appearance, which was commercially known as "silver cochineal", and which was believed to be the best. Other methods were used as well, although they were considered to produce dyestuffs of lower quality. For detailed information on these several methods see Cervantes (1944, pp. 174–176). See also Bender, 1947, p. 5; Cardon, 2007, p. 623; Born, 1938, p. 216; Donkin, 1977b, pp. 17-19; Humboldt, 1822, III, pp. 78–79; Juan & Ulloa, 1748, pp. 446-447; Lee, 1948, pp. 467–468; Marichal, 2001, p. 15, 2014, p. 199; Ramírez, 1831, pp. 286-290; Roquero, 2006, p. 139; Sanz, 1979, pp. 554-555; Verhecken & Wouters, 1988, p. 210.

[17] The earliest textile witnesses, in which *Dactylopius* cochineal presence was reported, were found in a necropolis site of Paracas civilization (c. 500 BCE - ACE 200), in the southern region of Peru. Analyses undertaken by contemporary chemical researchers on the red dyes belonging to textiles from subsequent South American cultures have shown that these insects were increasingly applied in American dyeing practices in the following centuries. Cardon, 2007, pp. 630 and 635; Donkin, 1977b, p. 32; Phipps, 2010a, pp. 12 and 18-26; Saito et al., 2003, p. 85; Wallert, 1996, pp. 859-860; Wouters & Rosario-Chirinos, 1992, pp. 238 and 249-253; Zhang et al., 2007, pp. 1576–1577 and 1581. For Central America, little is known about the use of cochineal species by Pre-Colombian cultures, as very few textiles have survived to this day. Although Humboldt (1822, III, p. 62) asserts that "the rearing of the cochineal, (*Grana Nochiztli,*) *[…]* goes beyond the incursions of the Toltec tribes" (10th century), one of the unique testimonies that may truly assert the application of *Dactylopius* insects in Central America is the *Matrícula de tributos*. This historical document demonstrates that cochineal was part of a list of taxes levied by the Aztec Empire to the conquered territories in Southern Mexico, during the beginning of the 16th century (prior to the arrival of the Spanish). See Cardon, 2007, p. 629; Born, 1938, p. 217; Coll-Hurtado, 1998, p. 72; Donkin, 1977b, p. 21; Lee, 1948, p. 452; MacLeod, 1973, p. 171; Phipps, 2010a, p. 12; Roquero, 2006, p. 140; Silva & Bosa, 2006, p. 478; Ulloa, 2010, p. 97.

[18] ["and when we arrived to the great square, which is called *Tatelulco [in City of Mexico], since we have not seen something like this, we were admired by the crowd of people and merchandize there […]* and they sold much cochineal under the portals that were in that square"] (Castillo, 1632, p. 70). Born (1938, p. 214) and Brunello (1973, pp. 198-199), followed by Schweppe & Roosen-Runge (1986, p. 261), suggest that the Spanish had their first contacts with Mexican indigenous cultures, and, necessarily, with the American cochineal, in 1512. So far, no historical source could corroborate this information. Nevertheless, Garavaglia & Marchena (2005, I, p. 131) assert that the conquerors Yanéz Pinzón y Lepe and Juan Díaz de Sólis had been exploring the coasts of Honduras and Yucatan (Mexico) since 1508. It is possible that, during these early expeditions, the

monarch Carlos I (r. 1516-1556) received knowledge of the American insect, through correspondence with Cortés as well as the arrival of red Aztec clothes, cochineal insects and other American products in Seville. After this, it did not take long for the monarch to perceive the profitable potential of the red dyestuff [19].

By presenting dyeing properties similar to kermes, the American product became known as *grana* [20]. This is clearly demonstrated in reports sent to Spain, where predictions about its breeding and commercialization were outlined, shortly after the conquest of the City of Mexico in 1521. Indeed, in 1523, Carlos I sent instructions to Cortés: *Y haviendo tenido el Rei noticia, que en Nueva Eſpaña nacía Grana en abundancia, i que traìda à Caſtilla, podia redundar en mucho provecho para las Rentas Reales, mandò al Governador, que lo miraſe, i hicieſe coger, i aviſaſe luego, ſi eſto era verdad,i que le parecia, que para benefeciarla ſe podia hacer* [21].

2.2. Production, Circulation and Acceptance

Despite the vested interests of the Spanish Crown, the output of American cochineal for international trade was inadequate in the first years of occupation, as expected for a territory that had mainly been producing the dyestuff to respond to local demand [22].

Spanish conquerors could have been in contact with the locals and, hence, with cochineal. See also Baskes, 2000, p. 11; Castillo, 1928, pp. 298-299; Donkin, 1977b, p. 23; Lee, 1948, pp. 453-454; Ulloa, 2010, p. 96.

[19] Castillo (1928, p. 216) mentions the offer of "two hundred pieces of cloth, richly worked with feathers and other patterns" (much of them possibly dyed with the American insect) from the Aztec Emperor Moctezuma II (r. 1502-1520) to Cortés, in 1519. The reception of these gifts at the Spanish Court is described in Folsom (1843, pp. 35-36 and 74). See also Chávez-Moreno et al., 2009, p. 3345; Comellas, 1992, p. 173; Donkin, 1977b, p. 23; Lee, 1948, p. 454; Marichal, 2014, p. 198.

[20] Baskes, 2000, p. 11; Born, 1938, p. 214; Gerber, 1978, p. 26; Marichal, 2001, p. 14; Munro, 1983, p. 63; Roquero, 2006, p. 137; Ulloa, 2010, p. 96; Verhecken & Wouters, 1988, p. 210.

[21] ["as the King got news that in New Spain *[Americas]* cochineal was produced in abundance, and that brought to Castille *[Spain]*, could result in great benefit to the Royal Revenue, he ordered to the Governor, that he would see, collect, and let him know soon if this was true and what he would think about it, so that it could be possible to take advantage of it"] (Tordesillas, 1726, pp. 153–154). See also Donkin, 1977b, p. 23; Leggett, 1944, p. 85. Later in the same year, another letter from Carlos I to Diego de Sámano, the royal official from the province of Vitoria Garayana (Pánuco), requests the shipment of American insects to Spain, as well as information about their potential use for dyeing and trade (Donkin, 1977b, p. 23). See also Beckmann, 1846, p. 397; Born, 1938, p. 217; Brunello, 1973, p. 199; Chávez-Moreno et al., 2009, p. 3345; Gerber, 1978, p. 25; Jordán, 1963, p. 15; Lee, 1948, p. 454; Marichal, 2001, p. 2; Phillips, 1990, pp. 75-76; Phipps, 2010a, pp. 26-27; Sanz, 1979, p. 560.

[22] *Esta grana cochinilla se criaba y cogía en el tiempo de la infidelidad de los indios en poca cantidad porque no tenían salida de ella* ["This cochineal was raised and picked up sparingly at the time of the infidelity of the indigenous people because they had no demand"] (Cervantes, 1944, p. 164). See also Donkin, 1977b, p. 23; Lee, 1948, pp. 454 and 457, 1951, pp. 206 and 218.

Nevertheless, the Spanish progressively promoted its exploitation [23] by levying the dyestuff from local producers under the royal tribute system, since as early as the 1530's [24], as well as through the *repartimiento* system. This "was a forced system of production and consumption driven by the coercive authority of Crown officials that was designed to draw reluctant Indians into the market at unfavorable terms. *[…]* Officials of the Spanish Crown used the political power of their offices to force Indians to buy European items that they neither needed nor wanted and to produce marketable commodities with which to pay for these *forced purchases*. Prices in this exchange were always exceedingly unfavorable to the Indians" [25]. In other words, the system was "an institution designed to overcome the inherent riskiness of providing credit to poor, widely dispersed Indians under the peculiar cross-cultural conditions of colonial Mexico" [26].

In this context, an increasing number of Mexican regions, especially in the provinces of Oaxaca, Puebla and Jalisco, would become specialized centres of domesticated cochineal [27]. Wild insects were chiefly collected in the Mexican province of Chiapas, but also

[23] Don Sebastián Ramírez de Fuenleal (g. 1531-1535), and later Don Martin Enriquez de Almanza (g. 1568-1580) and Don Pedro Moya de Contreras (g. 1583-1585), were some of the first governors of Nueva España who incited the expansion of cochineal production for international markets (Cervantes, 1944, p. 164; Chevalier, 1963, p. 193; Donkin, 1977b, pp. 24-25; Jordán, 1963, p. 15; Lee, 1948, pp. 455 and 457-458; Sanz, 1979, pp. 560-561). Coll-Hurtado (1998, p. 72) affirms that, from 1531 (Donkin (1977b, pp. 23-24) points to the 1540's) a progressive impulse on the insect exploitation was incentivized by the Spanish authorities and by the religious Dominican order. See also Baskes, 2000, p. 11; Gibson, 1967, p. 149; Hamnett, 1971a, p. 10; Heers, 1961, p. 6; Jordán, 1963, pp. 15-16; Lee, 1948, pp. 455-457 and 463, 1951, p. 218; Sanz, 1979, p. 549; Silva & Bosa, 2006, p. 478. It is interesting to notice that some historical sources erroneously assert that the Spanish taught the Mexicans to raise cochineal: *la Cochinilla, cuyo uso no conocian*, *hasta que le aprendieron de los Españoles* ["cochineal, whose use was not known, until learnt from the Spanish"] (Rivadeneyra, 1988, p. 204); *pues aunque los Indios la tenian, no hacian el cafo de ella, que los Caftellanos les han enfeñado* ["yet the indigenous had cochineal, they did not value it, it was the Castilians *[Spanish]* who taught them"] (Tordesillas, 1726, p. 169). However, it is likely that, in some regions of Mexico, cochineal was not produced, though it was acknowledged (Donkin, 1977b, pp. 23-24). Spanish authorities would have had then encouraged the interest of indigenous people for rearing the insect, as mentioned by Burgoa (1989, p. 279) for the Mixteca region, in Oaxaca: *Nuestros primitivos religiosos* […] *les persuadieron al cultivo de los nopales, que es planta que se da en los campos, y en sus pencas cría Nuestro Señor la cochinilla, de que se engendra la grana, que ha enriquecido a estas Indias* ["our primitive religious persuaded them to grow cactus, which is plant that grows in the fields, and on their pads Our Lord breeds cochineal, from which dyestuff is generated, which has enriched these Indies"]. These incentives are understandable if it is considered the growing demand for the American dyestuff in Europe. See also Jordán, 1963, p. 15.

[24] Coll-Hurtado, 1998, p. 74; Donkin, 1977b, p. 24; Lee, 1948, p. 454; MacLeod, 1973, p. 171; Marichal, 2014, pp. 199 and 208.

[25] Baskes, 2005, pp. 187–188.

[26] Idem, p. 190. See also Gibson, 1964, p. 354; Marichal, 2014, p. 209; Silva & Bosa, 2006, pp. 479-480.

[27] Tlaxcala was the primary centre for cochineal production throughout the 16th and 17th centuries. However, owing to the efforts of Spanish authorities, cochineal production would mainly increase and concentrate in Mixteca (Oaxaca), until the 19th century. Guadalajara, in the Jalisco province, as well as Chiapas also had an important role in the cochineal production for international markets. See Baskes, 2000, pp. 11-12; Born, 1938,

in Guatemala, Honduras, Nicaragua, Ecuador, Peru and Argentina. These, along with the domesticated variety, occupied an important place in transatlantic cargoes [28].

The most creative schemes for profiting from this business frequently led to the adulteration of the dyestuff in commercial consignments. For instance, foreign matter was often added to the dyestuff batches in order to increase the weight of the final product. Additionally, lower grades of *D. coccus* or wild cochineal could be mixed with the superior *D. coccus*, to obtain higher profits from its sales [29]. In response, the Spanish authorities created an effective controlling system to ensure the quality of the dyestuff, while keeping a tight control on European foreigners visiting the Spanish colonies and imposing severe regulations against the export of living insects from the Americas. In a decree, the Spanish king D. Felipe II (r. 1556-1598) declares that *Ningun Eſtrangero pueda en las Indias por ſi, ni por interpoſitas perſonas reſcatar oro, ni plata, ni cochinilla en tiangues, ſerias, ó mercados, ni en otra ninguna parte, pena de perder lo que aſsi contratare, y la mitad de todos ſus bienes, aplicados á nueſtra Camara, y Fiſco, aun que tenga lincencia general para tratar, y contrataren las Indias* [30]*.* In this way, the cochineal monopoly and its revenue would remain assured to the Spanish treasury.

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p. 217; Brunello, 1973, p. 199; Camargo, 1998, p. 286; Cervantes, 1944, p. 164; Chaunu & Chaunu, 1956, VII_1, pp. 771-772; Chevalier, 1963, p. 193; Coll-Hurtado, 1998, p. 74; Donkin, 1977b, pp. 24-27; Fuentes, 1997, p. 213; Gibson, 1964, p. 354; Hamnett, 1971b, p. 59; Heers, 1961, p. 8; Jordán, 1963, pp. 12 and 16; Juan & Ulloa, 1748, p. 448; Lee, 1948, pp. 452 and 464-465; Marichal, 2001, pp. 15-16, 2014, p. 199; Roquero, 2006, p. 141; Sanz, 1979, pp. 549 and 560; Silva & Bosa, 2006, p. 479; Tordesillas, 1726, p. 170. It is worthwhile mentioning the testimony of some European travellers who were in these regions by this time: "the commodity of Cochinilla groweth in greatest abundance about the towne of Pueblo de los Angeles *[city of Puebla]*; *[…]* there are *[…]* three other great cities, the one named Tepiaca *[Tepeaca, Puebla]*, a very famous city, Waxazingo *[?]*, and Tichamachalco *[Tecamachalco, Puebla]*: all these in times past belonged to the kingdome of Tlaxalla: and from these cities they bring most of their Cochinilla into Spaine (Hakluyt, 1904, pp. 360 and 363). Berra (1960, p. 180) adds: *La grana o cochinilla* […] *era criada con abundancia en los tiempos antiguos en el Mixtecapan* [Oaxaca]*, entre los tzapoteca, y cerca de Chalollan* [Cholula, Puebla] *y de Huexotzinco* [Huejotzingo, Puebla] [Cochineal *[...]* was raised with wealth in ancient times in the Mixtecapan *[Oaxaca]*, among *tzapoteca* people, and near Chalollan *[Cholula, Puebla]* and Huexotzinco *[Huejotzingo, Puebla]*].

[28] Cardon, 2007, p. 635; Chaunu & Chaunu, 1956, VI_2, pp. 982-983; Donkin, 1977b, pp. 29-30 and 37; Jordán, 1963, pp. 10, 12 and 16-17; Lee, 1948, p. 450; MacLeod, 1973, pp. 171-172 and 174-175; Marichal, 2001, p. 14, 2014, p. 199; Morineau, 1969, pp. 161-165; Sanz, 1979, p. 560.

[29] These and other deceiving methods are meticulously described in Cervantes (1944, pp. 176–179); and in Anonymous (1883, pp. 67-68). See also Cardon, 2007, p. 634; Coll-Hurtado, 1998, p. 79; Donkin, 1977b, p. 18; Gibson, 1967, p. 150; Hamnett, 1971a, p. 10; Humboldt, 1822, III, p. 79; Jordán, 1963, pp. 14-15; Lee, 1948, p. 470; Sanz, 1979, pp. 563-564; Tordesillas, 1726, p. 170.

[30] ["No foreigner can be in the Indies on his own, neither people to collect gold, silver or cochineal in markets or fairs, neither other place, otherwise will lose anything bought, and the half of his belongings, donated to our Council and Treasury, even if he has licence to buy and contract in the Indies"] (Paredes, 1681, p. 12). See also Brunello, 1973, p. 199; Born, 1938, p. 217; Cervantes, 1944, pp. 179-182; Chávez-Moreno et al., 2009, pp. 3346-3347; Coll-Hurtado, 1998, pp. 72 and 79; Donkin, 1977b, pp. 25 and 52; Gibson, 1967, p. 150; Hamnett, 1971a,

Some years after the first cargoes of American cochineal began arriving in Spain [31], news of the existence of an insect that could provide brilliant and vibrant crimson shades in textiles gradually spread across Europe and Asia. This dyestuff could achieve a wide range of hues, and some of them were close to those achieved by the native European and Asian cochineal dyes. In contrast to the "Old World" insects, its high dye content meant that fewer insects had to be used in the dyeing processes: "the savings brought about by the adoption of the new dyestuff were truly revolutionary: $1^{3/4}$ pounds of cochineal – 7% of the weight of the cloth – would now give a scarlet that, using kermes, had so far required the same weight in insects as of cloth or, at the very minimum, 71.5%!" [32]. In other words, to dye the same quantity of cloth a deep shade of red now required about ten times less of the American insects than when using Eurasian kermes [33]. This had important economic implications for European and Asian textile production. Indeed, knowledge of its economic advantages quickly spread, and with it, increased demand in European and Asian textile manufacturing centres. As a result, a gradual revolution started to occur in local dyeing traditions and European and Asian insect sources of red started to be relegated to a secondary plane [34].

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p. 10; Heers, 1961, p. 7; Humboldt, 1822, III, p. 79; Lee, 1948, pp. 450, 1951, pp. 217-218; Leggett, 1944, pp. 85-86; Marichal, 2001, p. 18; Roquero, 2006, p. 141; Sanz, 1979, pp. 564-565 and 569; Ulloa, 2010, p. 96.

[31] A debating question seems to persist about when American cochineal started to be regularly brought from the Americas to Seville, with the commercial transatlantic cargoes. While Lee (1948, p. 454) states that the first cochineal cargoes arrived in Seville in 1526, Donkin (1977b, p. 37) defends that the reference for this year is not well supported by the historical sources used by Lee - Gillespie (1920, p. 133), based on Reinhardt (1911, pp. 118-119). Instead, Donkin indicates the year of 1543, although he also suggests that small quantities of the American insect were most probably shipped to Spain in the 1520's and 1530's. It is undeniable, however, that cochineal became part of the royal tribute system in the 1530's, which means that it was regularly sent to Spain at an early date. For instance, Lee (1948, p. 454) reports a royal tax of circa 252 *arrobas* of cochineal in 1536, only for Guaxuapa (located in the southeast of Mexico City). Dutton (1992, p. 40) mentions the wrecks from the Spanish vessel Santa Maria de Yciar, which had sunk in 1541 and was found in 1991: this was bringing to Spain 4 barrels containing 800 arrobas of American cochineal. With this information, it is conceivable to suppose that the American dyestuff could be regularly traded across the Atlantic from the 1530's, although not in great amounts. See also Lee, 1951, pp. 206 and 224.

[32] Cardon, 2007, p. 628.

[33] Lee (1951, p. 206): "Cochineal possessed from ten to twelve times the dyeing properties of kermes; it also produced colors far superior in brilliancy and fastness"; Munro (1983, pp. 63-64): "It was certainly far more abundant in supply; and furthermore it yielded a richer, more powerful dye, so that far smaller quantities were required per cloth. *[…]* About 10 to 17 per cent of the average amount of kermes per cloth used in the medieval Flemish draperies"; and Férnandez (1778, p. 151): *Kermes dá menos sustancia que la referida Cochnilla, y sus colores que produce no son de tan superior calidad en la hermosura, como los de esta, pero sí en la firmeza* ["kermes gives less substance than the aforementioned Cochineal, and the colors it produces are not as superior in quality and beauty, like those of this, but yes in strength"]. See also Böhmer, 1998, pp. 37-38; Hofenk de Graaff, 2004, p. 77; Lee, 1948, p. 451; Kirby et al., 2014, p. 6; Molà, 2000, p. 120.

[34] Cardon, 2007, p. 618; Chávez-Moreno et al., 2009, p. 3345; Donkin, 1977b, p. 37; Heers, 1961, p. 5; Hofenk de Graaff, 2004, p. 55; Lee, 1948, p. 449; Leggett, 1944, p. 85.

Mainly due to its exponential popularity in textile dyeing, American cochineal became one of the most sought-after and expensive luxury dyestuffs during the colonial period, and, certainly, a great source of income to Spain, as shall be later demonstrated in this thesis [35]. Indeed, among the transatlantic shiploads, cochineal was valued only second to gold and silver, and the most important in comparison to other natural products [36]. It was so important that one convoy arriving in Brussels from Spain in 1565 was described as the "cochineal fleet" [37].

Publications over the last century have systematically affirmed that as soon as American cochineal arrived in Europe in the 16th century, it was swiftly assimilated into the main centres of textile production, replacing other local insect sources of red dye [38]. Some publications have suggested that a rapid acceptance also occurred when the American product was traded to Asia [39]. However, a revision of this literature below shows that while the wide circulation and adoption of cochineal has been reasonably well documented for certain parts of Europe, information confirming its presence in other European and Asian markets and, in particular, textile workshops, is really quite restrictive.

[35] Cervantes (1944, p. 163), in 1599, writes that cochineal *es un genero que casi iguala a la plata, la cual se saca de estos reinos* [Americas] *para los de Castilla; y solia que en cada flota se sacaban diez y doce mil arrobas de la dicha grana* ["is a genre that almost equals the silver, which is derived from these kingdoms *[Americas]* to Spain; and in each fleet ten and twenty thousand *arrobas* of cochineal were brought"]. Although Donkin (1977b, p. 25) affirms that Cervantes certainly exaggerated, there is no doubt that "Cochineal became an increasingly important item in the export trade of New Spain in the second half of the sixteenth century *[…] [it]* stood in second place by value of all goods exported from the Spanish territories in the New World" (Donkin, 1977b, p. 37). Also, Lee (1948, p. 462): "Spanish writers were fascinated with this concentrated source of wealth from the Indies, and they were prone to make exaggerated statements concerning its value. *[…] grana* ranked next to silver among Mexico's exports by 1600". Lee, 1951, p. 224: "the crimson-hued insect from Mexico had become, during the course of the century, a precious commodity in international trade". See also Chávez-Moreno et al., 2009, p. 3347; Fuentes, 1997, p. 213, 1980, p. 336; Lee, 1951, p. 205; Salazar, 1875, p. 149; Silva & Bosa, 2006, p. 478.

[36] Parry, 1990, p. 243; Lee, 1948, pp. 462-463. Chaunu (1956, $VIII_1$, p. 771) states that *la cochenille constitue, dans la hiérarchie des valeurs, le deuxième poste des exportatons du Mexique, très loin derrière, certes, mais après l'argent* ["cochineal is, in the hierarchy of values, the second place of Mexico's exports, far behind, certainly, but after the money"].

[37] Rigg, 1916, p. 18 Jul., 1565 [327].

[38] Donkin (1977a, p. 857), "In the cloth-working centres of western Europe particularly, the American product gradually supplanted Polish cochineal"; Donkin (1977b, p. 37), "It partly displaced the older product *[kermes]*, at least in the main cloth-producing centers of western Europe, before the end of the sixteenth century"; Hofenk de Graaff & Roelofs (1976, p. 33): "It is evident from various sources that 50 years after the discovery of America cochineal had captured the European market and had virtually completely ousted kermes"; Munro (1983, p. 63): "From about the 1560s *[…]*, cochineal began displacing kermes in the textile-dyeing of most European countries"*;* Phipps (2010b, p. 2): "Cochineal *[…]* was in abundant supply and easy to use, and it quickly supplanted all other red dyestuffs *[in Europe and Asia]*". See also Lee, 1951, p. 224.

[39] Donkin, 1977a, p. 867; Lee, 1951, p. 211; Phipps, 2010b, p. 81.

2.3. Problems for Research

Given the discrepancies between the affirmative statements of the literature and the uneven historical information available, important historical questions are raised about whether American cochineal was promptly accepted in Europe and Asia as attested, and especially the extent of its impact on the trade and use of local insect sources of red. Understanding the challenges presented by the historiography, the nomenclature used, as well as the current state of material studies of dyes in textiles, is necessary to develop an appropriate methodology for a new programme of research.

Historiography. In general, historical publications over the past century have given little importance to dyestuffs, despite their importance for trade and society. As regards American cochineal, some economic studies have been dedicated to its production and trade in the Spanish colonial context [40]. Few other studies have focused on its international circulation to respond to European and Asian market demand, or its application in local dyeing industries [41]. A revision of these latter studies reveals several limitations that impede a full appraisal of the subject.

For instance, the works of Robin A. Donkin (1977a,b) and Raymond Lee (1948, 1951) can be considered good examples of how archival and primary printed sources have been used to look at the dynamics of American cochineal as a staple commodity in the main mercantile routes, long established in Europe and Asia. Based on historical evidence, they make a strong argument for the widespread and profuse diffusion of the American insect and, consequently, to the replacement of local European and Asian insect sources of dye. For instance, Lee claims: "It seems apparent that the New World dyestuff *[American cochineal]* was readily accepted by European dyers, the inertia of traditional methods and vested interests being negligible" [42].

Indeed, the authors' main argument seems to be somewhat inconsistent, considering that historical information is very small (or even absent), when it comes to dating or localizing cochineal in certain European and Asian markets or textile industries. For example,

[40] Chaunu & Chaunu, 1956; Donkin, 1977b; Fuentes, 1980; González, 1976; Hamnett, 1971a; Lee, 1948; Morineau, 1969, 1985; Phillips, 1990; Sanz, 1979; Silva & Bosa, 2006; Smith, 1959.
[41] Donkin, 1977b; Lee, 1951; Marichal, 2014; Pieper, 1998.
[42] Lee, 1951, p. 224. See also footnote 38.

Donkin and Lee principally follow the historical registries of European regions which had a preponderant role in the trade and use of American cochineal (Spain, France, Italy, Low Countries and England), and fail to consider neighbouring regions, such as Portugal. This makes it difficult to assess whether there is an absence of sources for these latter regions or, alternatively, whether they did not make a significant contribution to the trade in American cochineal. Moreover, there exists a notion of swift acceptance which has been perceived from data for exports and imports; however, this was not necessarily the case, as commercial data registered in one territory does not imply that the American product was immediately adopted there, by local dyeing centres.

To this day, Donkin and Lee have frequently been cited in contemporary publications dedicated to the historical study of American cochineal, such as Marichal (2014), Molá (2000), Munro (1983), Cardon (2007), among others used in this thesis. While these works bring well contextualized historical information that complement Donkin's and Lee's works, it must be emphasized that the overall information given by all these publications is still scattered and requires systematic review.

As for the impact of American cochineal on European and Asian insect red varieties, it is reasonable to suppose that, even if the American dyestuff was accepted in local dyeing practices, other insect sources could still be part of the dyer's repertoire. Actually, Donkin mentions that considerable amounts of Polish cochineal were still sent to Venice at the end of the 18th century, although he also adds that this dyestuff was supplanted by the American insect in the textile manufacturing centres of Western Europe [43].

Therefore, a full historical appraisal still needs to be undertaken about the consequences of the trade in European and Asian insects and their dyeing applications, during and after the 16th century. Up until now, few historical works have attempted to focus on the history of these insect dyes [44], and attention is chiefly given to their historical context in medieval times, because information on their circulation is more frequent for this period than for the Early Modern one. Moreover, when regarding their dye applications, historical evidence is predominantly found in medieval dye treatises, which are quite rare. This rarity can be attributed to the fact that knowledge on dyeing and other artisanal

[43] Donkin, 1977a, p. 857.
[44] Cardon, 2000, 2007; Donkin, 1977a; Molá, 2000; Verhecken & Wouters, 1988.

activities was reserved to a minority of masters, who would only share (orally) their secrets and expertise with their sons, apprentices or guilds, who were directly involved in the industry [45]. In Europe, since most of the silk production was carried out in Italy before the 16th century, it is understandable that some of the few existing recipes that explain how to dye with these insects are principally of Italian origin, as discussed in Chapter 1 [46].

Nomenclature. In medieval sources and in mercantile records, insect dyes are often discussed using different designations, in diverse languages. Also, the opposite situation can happen, when historical sources use the same designation for different dyestuffs. For this reason, their differentiation is sometimes unclear in contemporary works, which can result in erroneous interpretations [47]. A similar situation is furthermore observed when considering confusion in nomenclature between kermes and American cochineal in some historical documents dating from the 16th century onwards [48]. Therefore, it is noteworthy to emphasize that when one comes across a historical source, the interpretation of the nomenclature used should principally be supported by any additional information present, namely place of production, pattern of commerce, price, applications, amount required to dye one fabric, among others.

[45] Brunello, 1973, p. 183; Hofenk de Graaff, 2004, p. 324; Rosetti, 1969, p. xiv.

[46] Gargiolli, 1868; Rebora, 1970; Rosetti, 1969.

[47] A discussion about nomenclature and problems associated with distinguishing insect dyes in historical documentation is given by Verhecken & Wouters (1988, pp. 214-215, 226 and 228-229). They contest affirmations given by Rosetti (1969, p. 94), who was actually not a dyer, but still collected recipes and information on dyeing and dyestuffs from Italian cloth production centres. Rosetti appears to confuse between kermes and cochineal, by mentioning that "the grain of Armenia is numbered among the good". Here, "grain" should refer to cochineal, although this designation is always used for kermes. In the same chapter, he states that "the best of all are those *[grain]* that are gathered from the ground, because they fall by being most ripe". Again, this is likely to be cochineal, because it had to be collected from the ground, whereas kermes would not fall from the oak trees - instead, it would be rid of the cysts as soon as it would grow into larva stage. Also, Leggett (1944, pp. 80-82), Beckmann (1846, p. 388) and Brunello (1973, pp. 123 and 153) are examples of common misunderstanding of these dyestuffs, as they consider Polish and/or Armenian cochineal dyes as varieties of kermes, thus hindering historical interpretations. Also, Donkin (1977a, p. 860) reveals confusion about the insect dye reported in one historical source: "The Jewish community in Cairo in the 13th century included dyers specializing in crimson (*qirmizini*) *[…]*, notably for silk, but whether the agent was kermes or Polish cochineal (shipped from Venice) cannot be determined". See also Donkin, 1977a, p. 849, 1977b, p. 10; Greenfield, 2006, p. 49; Hofenk de Graaff, 2004, p. 65; Munro, 1983, pp. 17-18.

[48] Gerber, 1978, p. 14: "Once *[American]* cochineal had entered the markets of Europe there ensued a rather short-lived struggle between kermes and cochineal for supremacy. *[…]* There remained the confusion in terms of "grain" - the word being applied to both dye insects". See also Phipps, 2010a, p. 44.

Recently, Molá and Cardon, based on historical primary material, have commonly referred to cochineal insects as "kermes", and to kermes insects as "grain" [49]. These designations are literal translations of the nomenclature used in historical sources, as summarized in Table 2.1. However, and despite these terms being in agreement with historical evidence, the present names "cochineal" and "kermes" are too ingrained in the scientific mentality to be replaced now by "kermes" and "grain", respectively. In fact, based on the work of Molá, a recent study has already misinterpreted the historical nomenclature, by treating "kermes" as kermes ("grain"), and not as cochineal [50].

Table 2.1. European and Asian nomenclature and regions of collection of insect dyes, reported in historical publications.

Present name	**Historical nomenclature**	**Geographical collection**
Kermes (*K. vermillio*)	*grana, grain, graine, grein, granum, vermilion*	Mediterranean coast and certain parts of West Asia
Polish cochineal (*P. polonica*)	"Saint John's blood", Polish or German kermes, *Johannisblut*, *Pohlnische Purpurkörner*, *sura, sure, suere*, *czerwiec*, *chervets*, kamaschken, *chremesi minuto* [small], *cremexe rosesco*, *cremexi savaxi*, *cremesino schiavo*, *raguseo minuto*	Central and Eastern Europe
Armenian cochineal (*P. hamelli*)	*chremesi grosso* [big], *cremexi di vini, vordan karmir*	Armenia, Turkey (Ararat) and Azerbaijan
Lac dye (*Kerria lacca*)	*lacca, lacha, lacham, gomma laca, gum-lac, East-Indian cochineal*	South Asia and Oceania islands
American cochineal (*D. coccus* and "wild")	*cochineal*, *cochinilla*, *grana*, *grana fina*, *sylvestra, campesina, mesteque, cochenille, cremisi d'India, cremese, kermez, karmiz, kyrmisi, cormeli, oudez*	Central and South America

Table 2.1 displays the five most popular types of insect dyes specific to certain regions around the world, according to historical sources. From these five, three are cochineal dyes. However, currently there are 57 cochineal species entomologically identified, a number far beyond the three most famous cochineal dyes discussed extensively

[49] Molá, 2000, p. 109; Cardon, 2007, pp. 608-609, 645 and 651. In agreement to this, Pearson (1705, p. 108), translating the German *Ars tinctoria fundamentalis* from 1683: "of the Word *Carmaſin* i. e. Crimſon; *[…]* which is likewiſe eſteemed the principal Silk Dye; *[…]* the Name of Chermes, rather appears to be given to theſe Berries *[Polish or Armenian cochineal insects]* by the *Arabians*, than the *Greeks*, ſince he informs us, that in the *Phœnician* Tongue, the Worm was called Chermes". See also Hofenk de Graaff, 2004, pp. 64 and 70.
[50] Phipps, 2010a, p. 32.

in the historical literature. Hence, and as mentioned earlier in Chapters 1 and 2, there are: 47 *Porphyrophora* species, including the Polish (*Porphyrophora polonica*) and the Armenian (*Porphyrophora hamelii*) [51], and 10 *Dactylopius* species, counting with the domesticated American (*Dactylopius coccus*) [52].

As historical sources for the American insects are generally more abundant than those for European and Asian insect dyes, it is possible to know more details about the trade of "wild" *Dactylopius* species (the exact species remains unknown, however), other than American cochineal. These, too, were shipped to Europe and Asia, but as inferior products [53]. Few publications discriminate the remittances of the different types of American cochineal and their prices. These usually use the nomenclature *grana fina* (or *D. coccus*), *grana silvestre* (wild cochineal species) and *grana campesina* (wild cochineal species from Campeche) [54]. However, estimates made in the majority of Economic History studies usually consider the overall volume of all types of cochineal shipped from the Americas annually, which presents problems for distinguishing the importance and role of the various types.

Studies on Dye Identification. Based on the historical arguments from Donkin and Lee, chemists such as Judith Hofenk de Graaff & Wilma Roelofs (1972 and 1976), and more recently the conservator Elena Phipps (2010a and 2010b), dedicated their investigation to the historical contextualization of American cochineal in European and Asian dyeing practices. For this, chemical studies were carried out to determine the presence of red insect sources in historical textiles, through the interdisciplinary conjunction of historical interpretations and chemical analyses. In this way, such publications aimed to provide more supportive interpretations, which were not achievable simply through historiography.

When studying historical textiles, provenance, chronology and historical context are fundamental questions for understanding their production and for answering enquiries

[51] Vahedi & Hodgson, 2007, p. 24.

[52] Chávez-Moreno et al., 2009, p. 3338; Portillo, 2005, p. 2.

[53] Chaunu & Chaunu, 1956, VI_2, pp. 982-983; Donkin, 1977b, pp. 29-30; Cardon, 2007, p. 635; Jordán, 1963, pp. 16-17; MacLeod, 1973, pp. 171-172 and 174-175; Morineau, 1969, pp. 161-165; Sanz, 1979, p. 560.

[54] For instance, Chaunu (1956, VI_2, p. 983) ascribes the shipment of 4 458 arrobas of *grana fina*, 1 288 arrobas of *grana silvestre* and 144 arrobas of *grana campesina* from Spain to Venice, in 1618. Donkin (1977b, p. 37) mentions that Seville received 6 000-6 500 arrobas of *grana fina* and each of 1 500 arrobas of *grana silvestre* and *grana campesina,* in 1619. Also, González (1976, 2, pp. 222-275) distinguishes estimates for two types of American cochineal traded in the transatlantic routes, *grana fina* and wild cochineal.

about their preservation and authenticity. They can be answered using art historical methodologies, namely iconography, style, technological examination and possible connections with archival sources, such as inventories. They can also be answered using analytical chemistry techniques applied to the materials present in the textiles. For instance, since insect dyes are specific to certain regions around the world, it is possible to chemically ascribe the origin of the red colorant found in some historical textiles and the results can then be used to characterize their date and provenance.

Following this principle, the analytical confirmation of the use of American cochineal in European and Asian historical textiles helped Hofenk de Graaff & Roelofs and, later, Phipps, to develop more precise historical interpretations about the dynamics of this dyestuff in Europe and Asia. In this context, Hofenk de Graaff & Roelofs analysed 250 red samples from European textile objects [55], whereas Phipps analysed 100 red samples from European, American and Asian textiles [56]. With this approach, it was possible to regard historical textiles as a way of connecting artistic production between different cultures, through the global circulation of insect dyes. However, owing to the limitations of the chemical methods used to perform the chemical analyses, these studies encountered difficulties in distinguishing the cochineal varieties in the examined historical textiles. For instance, when investigating the red historical textiles belonging to the collection of the Metropolitan Museum of Art, Phipps was not able to discriminate between American and Armenian dyes in many of the red fibres from the analysed textiles [57].

Insect dyes are discriminated using an analytical separation technique, generally high-performance liquid chromatography (HPLC), coupled to a UV-visible detector. With the visual examination and the quantification of the compounds ratio in the resulting chromatograms (Fig. 2.2), it is possible to characterize the insect dyes [58]. These compounds become part of a reference library which is then used to identify them in dye extracts from historical textiles.

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[55] Hofenk de Graaff & Roelofs, 1972, p. 1.
[56] Phipps & Shibayama, 2010, p. 2. See also Phipps, 2010a,b.
[57] Phipps, 2010a, pp. 31 and 41; Phipps & Shibayama, 2010, p. 8. Verhecken & Wouters (1988, p. 208) interpret the results obtained in the work of Hofenk de Graaff & Roelofs (1972) and, referring to the attribution of cochineal in 16th-century European historical textiles, they conclude that: "these *[results]* however might partly refer to another dye (Ararat cochineal?), or not all her samples were correctly dated, since she finds a number of *[American]* cochineal-dyed textiles that are prior to the discovery of America".
[58] Verhecken & Wouters, 1988, p. 208; Wouters, 1985, pp. 123-125; Wouters & Verhecken, 1989a, pp. 191 and 193-195; Wouters & Verhecken, 1989b, pp. 396-398, 400-404 and 406-409.

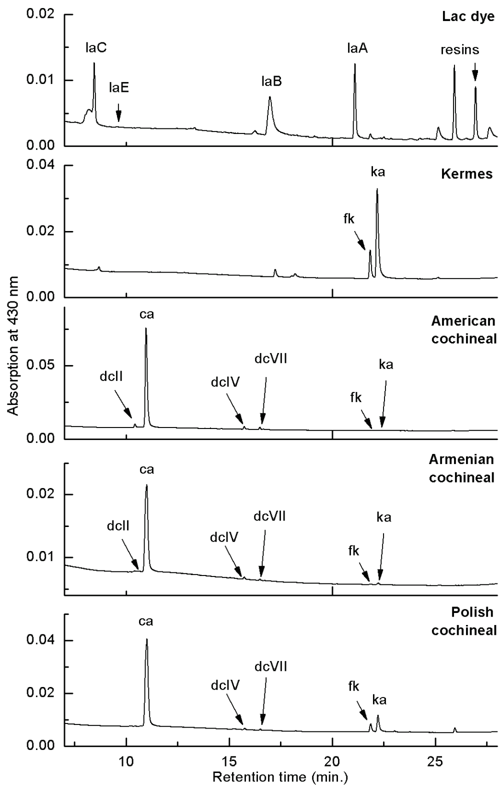

Fig. 2.2. Representative UHPLC chromatograms of red insect dyes.

In Fig. 2.2, it is possible to observe that the differentiation of kermes or lac dye is straightforward, given that different compounds are present: lac dye, with laccaic acids (given the nomenclature, la) and resins; and kermes, with flavokermesic acid (fk) and kermesic acid (ka) compounds. With cochineal species, this becomes more difficult, owing to a very similar dye composition: dcII (not present in Polish cochineal), carminic acid, dcIV, dcVII, fk and ka. Hence, given the variable ratios of the minor compounds dcII, fk and ka, their areas are often used to differentiate the insect species. This method was successfully applied to characterize the cochineal source in wool and cotton historical samples, but not in silk [59]. Silk is, in fact, the most frequent substrate to which cochineal dyes were applied in European and Asian red-dyed textiles dating from the 15th to the 17th centuries.

Moreover, the analytical procedure can influence the chromatographic results, since the poor resolution of chromatograms can substantially hinder their interpretation, and thus, the distinction of American and Armenian cochineal dyes in historical textiles [60]. The interpretation of the chromatographic results can be furthermore complicated by the fact that historical textiles were often dyed with more than just one insect dye or with other dyestuffs, such as the vegetable dyes brazilwood and madder [61].

Given these limitations and their influence on the acquired analytical results, Hofenk de Graaff & Roelofs and Phipps tended to rely on the historical literature available. For this reason, it is possible that their attributions of the presence of American cochineal in European and Asian historical textiles, dating from the 16th century onwards, may have been over-emphasized. Indeed, the argument for swift and complete integration of the

[59] Wouters & Verhecken, 1989a, pp. 191, 193-195 and 197.
[60] Serrano et al., 2011, p. 736.
[61] Verhecken & Wouters, 1988, p. 208.

American dyestuff has become so deeply ingrained in the literature that it now requires reappraisal in this Doctoral thesis.

Having identified a number of limitations in the literature concerning the historical study of insect dyes, their historical nomenclature and their chemical characterization in textile objects, it is important to develop a multidisciplinary approach that can offer more comprehensive data to assess this perceived revolution in trade and dyeing practices.

CHAPTER 3

MULTIDISCIPLINARY APPROACH:
History, Objects and Chemistry

"It is absolutely essential … to assess the speed and scope of assimilation of this dyestuff *[American cochineal]*" Serrano et al. [1]

Bearing in mind the historical antecedents for the cultural importance of insect dyes in textile traditions across Eurasia and the Americas, and the problems of research described in the previous chapter concerning the circulation and adoption of American cochineal with the advent of the Iberian Expansion, a multidisciplinary approach was developed for this Doctoral thesis. Here, history, textile objects and chemistry are brought together to achieve a more comprehensive understanding of the dynamics of the American dyestuff in international markets and its influence on European and Asian dyeing practices. In short, it aspires to attain more complete answers for two central questions: firstly, how was American cochineal disseminated in Europe and in Asia after the rise of the Iberian Expansion; and secondly, what was its impact in European and Asian textile dyeing centres. While the first question principally concerns the mechanisms of its trade and, to a lesser extent, its production in the Americas, the second focuses on its reception and influence on dyeing practices, especially the extent of its adoption in relation to other red insect dyes.

The historical part of this thesis takes a wide perspective and looks at historical publications dating from the past century, which mainly evaluate archival documentation. It does not undertake a full revision of all the primary sources considered by these publications. Such a task would be far beyond the scope of this project, which is primarily concerned with comparing the results of recent historical knowledge with what can be learned from other sources, namely extant textile objects and their dye materials, both of which have received little recognition to date as sources of information for historical discussions.

[1] Serrano et al., 2011, p. 743.

Hence, given the interdisciplinary nature of this thesis, considerable emphasis is dedicated to establishing the chemical composition of dyes from a wide range of European and Asian historical textile objects, in order to provide concrete material evidence that can support (or deny) historical conclusions. These conclusions have been based on data provided by historical sources, which can sometimes be limited in scope due to issues relating to the production of these documents and their survival. In other words, this thesis is mainly concerned with attempting to verify the extent of the global circulation of American cochineal and its penetration in international markets through the chemical study of historical textiles. Ultimately, it intends to bring a fresh contribution to the fairly sizeable body of historical work carried out until now, by shedding new light on old questions and, hopefully, raise questions that may stimulate a renewed interest in future historical and archival research.

This chapter explains the objectives of this project and how the three areas of research – history, objects and chemistry – are brought together in a multidisciplinary approach. It begins with an overview of the historiographical background to the thesis, before turning to the objects studied and finally to the challenges of undertaking chemical research.

3.1. History

The historical analysis presented here is principally based on the collection and appraisal of historical publications and primary printed sources, and aims at a comprehensive picture of the historical information currently available on the trade and use of American cochineal as a red textile dye. This bibliography is used to evaluate demand and supply, exchange routes, key commercial centres, volumes and prices, as well as the regularity and instability of trade (due to political, economic or cultural circumstances), and ultimately the extent of influence of American cochineal on European and Asian markets and dyeing traditions.

Principally, this appraisal is focused on a group of contemporary historical publications dating from the past century and listed as Major Bibliography below. Analysing and comparing the data offered in these works was an important focus of this thesis. They look mainly at archival documentation related to the international trade of American cochineal, which requires confronting different types of data and methods of study, especially concerning volumes and prices (discussed in the next section):

- Lee (1948): this publication focuses on the production of cochineal and its transatlantic trade until 1600, and comprises a thorough characterization of its importance for Spanish commerce and contribution to Mexico's economy. The references consulted by Raymond Lee, comprise mainly historical publications and printed primary sources from representative Spanish authors, writing about the American dyestuff during the colonial era. However, information concerning volumes and prices of cochineal exports is small.

- Donkin (1977b): this paper characterizes American cochineal in a broader perspective, by considering its production, worldwide trade and propagation to appraise its historical importance for the societies of the Americas, Europe and Asia. Information is mostly obtained from printed primary sources and historical publications. Records of volumes and prices for cochineal colonial exports are succinct and generally follow those from the work of Lee.

- Chaunu & Chaunu (1956): this is an Economic History study about the Spanish Empire, from the 16th to the first half of the 17th century. It is based on detailed archival research of the composition, volume and price evolution of cargoes from the Americas to Seville. Regarding American dyestuffs, the research undertaken looks at historical publications, printed primary sources and, principally, archival documentation belonging to the *Casa da Contratación* and the *Indiferente General* collections at the *Archivo General de Indias* (AGI), in Seville. Such documentation comprises, for example, accounts of custom taxes [2] collected in the ports of Seville, evaluations of the registries made by the agents at the *Casa da Contratación*, or trade letters exchanged by merchants.

- Prada (1961) and Martín (1965): these two studies in Economic History assess the trade exports from Seville to Antwerp (Prada) and from Seville to Florence (Martín), during the 16th century. For this, they undertake archival research based on correspondence between Spanish and European merchants, held at the *Comercio* section of the *Archivo de*

[2] Mainly *avería* documents that helped to finance armed escorts for the fleets, and *almojarifazgo* taxes on the exports from Seville (Chaunu & Chaunu, 1956, VI_1, pp. 101 and 109). See also Lee, 1951, p. 219; Tejada, 1853, p. 12.

Simón Ruiz, belonging to the *Archivo Histórico Provincial y Universitario de Valladolid* (ARC, AHV). Since in both European cities there was a vast demand for natural dyes in local dyeing industries, the consulted archival correspondence comprises many references to the trade of American cochineal, including details about international demand and information about the prices at which the valuable dyestuff was sold in Antwerp and in Florence (sometimes only predictions). For the study of the commerce between Seville and Antwerp, correspondence mentioning cochineal is dated between 1563 and 1598, whereas for the commerce between Seville and Florence, records are dated between 1571 and 1585.

- Sanz (1979): this work is dedicated to the commercial connections between Spain and the Americas, during the second half of the 16th century. For assessing the trade of American dyestuffs in this period, the author uses historical publications, printed primary sources, Chaunu & Chaunu's registries from the AGI, and records from archival sources held at the *Consejo y Juntas de Hacienda* and the *Cuntadorías Generales* collections of the *Archivo General de Simancas* (AGS). Volumes and prices available for cochineal in the transatlantic trade are particularly extensive. The author also traces the commerce of cochineal between Seville, Antwerp and Florence to assess the influence of European demand over the price of the insect dye in Seville. For this, research is based on the same archival documentation from the A.R.C., A.H.V., which had been used previously by Martín and Prada.

- Morineau (1969): this study is a collection of excerpts from historical publications (including the work of Chaunu & Chaunu) and printed primary sources concerning the shipment of American goods to Europe between 1580 and 1660. This also includes the revision of European newspapers dated to the 17th and 18th centuries. Trade composition and registries for cochineal and indigo arriving to Spain between 1580 and 1620 are given here. Some records are given for dyewoods as well. Although information on these dyestuffs is missing for the years after 1620, registries can still be found when considering descriptions of bounties seized by pirate and privateer assaults on the Spanish fleets.

- Morineau (1985): this more extensive work focuses on American bullion and its influence over the development of capitalism in Modern Europe. It is supported by historical publications (including 17th- and 18th-century European newspapers), printed primary sources and archival documentation. Registries for volumes and prices are given for American products in Spain, between the 16th and 18th centuries. These include the data given for American cochineal and indigo published in 1969, as well as for the period ranging 1757 and 1779. Yet, information is missing for the years between 1620 and 1757 and, for this reason, Morineau undertakes a review of historical sources to assess the economic and commercial circumstances that have caused this conundrum.

- Fuentes (1980): this work is particularly focused on the transatlantic commerce of American products during the second half of the 17th century, and is based on archival documentation belonging to the AGI. However, and as shall be discussed further in this work, this is an era for which archival sources are scarce [3]. For this reason, Fuentes assesses possible historical interpretations to explain the reduced number of historical sources; the irregular transatlantic communications; the increased rates of smuggling and pirate/privateering; and the landing of American cargoes in Cádiz (besides Seville). Trade records for American cochineal, indigo and dyewoods are characterized, although very few remittances are ascribed for cochineal.

- González (1976): regards the Spanish commerce between 1717 and 1778, a period in which Cádiz becomes the official port of communication with the Americas. Here, an assessment is made on the improvements of colonial production and transatlantic commerce, resulting from political and economic Spanish reforms. This is based on historical publications, printed primary publications and AGI documentation, namely the registries of fleets and mixed vessels belonging to the *Contratación* section and the records of loose documents. With these sources, relative volumes and prices of American products are given, including American cochineal (*grana fina* and wild), indigo and dyewoods.

- Hamnett (1971a): this study discusses the production of American cochineal for international markets between 1750 and 1820, and its economic importance to Oaxaca, the major centre of cochineal production. Historical contextualization on political and economic reforms is given to understand the decrease and near extinction of Oaxaca's cochineal industry in the 19th century. In this context, volumes and prices referring to the exports of the American dyestuff are divided into two distinct periods: the first, concerning shipments

[3] Fuentes, 1980, p. 1: *El reinado de Carlos II continúa siendo una de las grandes incógnitas de nuestra historia. Es como si la tremenda crisis que embargo aquellos años se hubiera proyectado en el tiempo provocando el bache historiográfico que padecemos* ["The reign of Carlos II (r. 1665-1700) remains one of the great misteries of our history. It is as if the tremendous crisis that comprised those years was projected in time causing the historiographical hole we bear"].

sent to Cádiz between 1760 and 1772; and the second, shipments leaving Vera Cruz to Europe between 1796 and 1820, as a consequence of the establishment of free trade with the Americas. Such data is mostly extracted from Tejada's work (1853), although archival documentation belonging to the AGI is considered here as well.

- Phillips (1990): evaluates the Spanish and the Portuguese colonial trade with the Americas regarding the period between 1450 and 1750, to assess the yearly shifts in cargo volumes, according to political and economic changes within the Iberian Peninsula. General contextualization is given for the trade of American dyestuffs, although only records for the volumes of American cochineal are provided. These records are given for the period ranging 1556 and 1776, but information is missing for the years between 1620 and 1717, given the small availability of registered trade during this period, as assessed by Fuentes (1980). This work is essentially based on the abovementioned historical publications.

- Silva & Bosa (2006): study about the evolution of the importance of American cochineal in international markets during the colonial era. Special focus is given to the years ranging from 1758 to 1857, period in which the insect's production and trade started to decline in Mexico, in parallel to its growth in Canary Islands. Volumes of export are given for the years between 1758 and 1849 [4], and they are based on primary printed sources with annual registries made by local authorities in Oaxaca.

- Posthumus (1946): characterizes the market prices and rates of exchange in Amsterdam from the 16th century until the First World War, based on archival documentation belonging to the Netherlands Economic History Archives (NEHA), the Netherlands Institute for Price History (NIPG) and state and municipal archives of the Netherlands, but also from Brussels, Gdánsk, Florence, Copenhagen, Seville, Stockholm and Vienna. This work includes detailed information on the prices of several commodities traded in Amsterdam, including American cochineal, to which prices are available between 1589 and 1843 [4].

- Baskes (2000): this study is primarily focused on the evaluation of the *repartimiento* relationship between the Mexican indigenous people and the Spanish authorities, between 1750 and 1821. To do so, the author assesses the local production system of American

[4] Owing to the time boundaries defined in this thesis, only the records until 1820 are considered here.

cochineal as well as its transatlantic trade, while enhancing the insect's production at the beginning of the 19th century. Furthermore, this study comprises an evaluation of the commerce of cochineal in Europe, by assessing the prices at the markets of London and Amsterdam, in relation to those in Mexico. Whereas the latter are mostly obtained from Mexican archival documentation, the former are from the works of Posthumus and of Tooke & Newmarch (1838).

Volumes and Prices. An important component of the historical analysis undertaken in this thesis involves the collation and interpretation of volumes and prices to assess trends in supply and demand. The above-mentioned publications are based on different, or sometimes the same, historical sources: custom taxes and annual evaluations of custom registries; correspondence from European merchants; commercial newspapers; annual predictions on the amounts and prices of dyestuffs; and other commercial resources available in archival collections. Following these primary sources, the published works generally present annual relative estimates of volumes and prices of American cochineal (Appendix 1, Tables 1 and 2). A revision of these published estimates enables an overall evaluation and historical contextualization of the trade of American dyestuffs throughout the Early Modern period.

However, it is important to note that weights of measure and price currencies can vary between publications. To enable a proper comparison between values given throughout time and space, units were converted whenever possible in this work. Also, since these values are estimates, they always have a margin of error which is not regarded here, because the main objective of this thesis is to look at periodical tendencies of volumes of trade and prices through time. For this reason, when converting estimates into general currencies or weights to ease comparison, published index numbers were used.

Hence, cochineal, indigo and other insect dyes discussed in this part of this thesis, for which volumes were represented in pounds in the literature, were converted into Spanish *arrobas* (11.5 kg), with each *arroba* corresponding to 25 pounds (lb), and one ounce to 1/16 of 1 lb [5]. American cochineal and indigo were often shipped in bags of *zurróns*, although the

[5] Baskes, 2000, p. 3; Hamnett, 1971, p. VIII; Lee, 1951, p. 206; MacLeod, 1984, p. X; Prada, 1961, p. 237.

weight of these bags could roughly vary. For instance, cochineal *zurróns* could weigh between 7 to 9 *arrobas*, but some historical publications can sometimes consider other smaller weights as well [6]. For comparison meanings in this study and to ensure homogeneity with the majority of the publications available, one *zurrón* of cochineal was considered to weight 9 *arrobas*. Dyewoods (brazilwood or logwod) were usually traded in hundredweights (*quintals*) and they corresponded to c. 4 *arrobas* or 100 lb [7].

Price currencies encountered in historical publications were converted into Spanish *pesos* whenever possible, following published currency index numbers for the period in study, as indicated in Table 3.1. However, it is noteworthy to emphasize that currency conversions undertaken did not consider coin fluctuations over time. This means that mean average annual prices indicated in the historical part of this thesis (based on figures from Appendix 1, Tables 1 and 2) always have some margin of error and should not be considered a reflection of the intrinsic value of the dyestuffs. Instead, average annual prices principally aim to indicate the dyestuffs' relative value in international trade.

This implies that the extensive methods used in Economic History studies were not applied here, namely precise conversions or comparisons between prices in local currencies and weights in local measures, as well as their inflation over time. Despite this margin of error, the data can nevertheless provide substantial interpretations and comments about the importance (and relative cost) of dyestuffs in international trade, their availability in key ports and their supply and demand in European and Asian markets.

[6] Baskes, 2000, p. 145; González, 1976, II, p. 223; Hamnett, 1971, pp. VIII and 32; Heers, 1961, p. 9; Lee, 1951, p. 206; Magán, 1963, p. 83; Morineau, 1985, p. 423; Phillips, 1990, p. 39; Vasco, 1963, p. 57.
[7] Baskes, 2000, p. 3; MacLeod, 1984, p. X.

Table 3.1. Currency index numbers for the general exchange between European prices encountered in the literature, for the period in study [8].

Seville and Cádiz	**London**
1 *ducado* = 375 *maravedis* (*mrs.*) 1 *peso* (*de plata*) = 8 *reales de plata* = 272 *mrs.* 1 *real de plata* = 34 *mrs.*	1 pound (£) = 20 shillings (s.) = 240 pence (d.) 1 s. = 12 d. 1 Spanish *peso* = c. 4.20 s. (c. 4.70 s. in the 18th cent.)
Lisbon	**Paris**
1 *canto* = 1 000 *milréis* (1 000$000) 1 *milrei* (1$000) = 1 000 *réis* 1 *cruzado* = 400 *réis* (480 *réis* in the 18th cent.) = 1 Spanish *ducado*	1 *livre tournois* = 20 *sous* = 240 *deniers* 1 *livre* = 0.66 Spanish *pesos* (16th cent.) 1 English £ = 24 *livres* = c. 4.26 Spanish *pesos* (18th cent.)
Florence	**Antwerp**
1 *ducat* = 6 *livres* = 124 *soldis* (*di piccoli*) 1 *livre* = 20 *soldis* 1 Florentine *ducat* = 385 Spanish *mrs*. 1 Florentine *livre* = c. 0.24 Spanish *pesos*	1 *ponden Vlaamsh* (£ Vl.) = 20 *schellingen* = 240 *grooten* 100 *grooten* = 281.61 Spanish mrs. (17th cent.) 1 £ Vl. = c. 4.6 Spanish *pesos* (16th cent.) and c. 2.48 *pesos* (17th cent.)
Amsterdam	
1 *gulden* = 20 *stuivers* = 240 *grooten* 1 £ Vl. = 6 *gulden* = c. 2.48 Spanish *pesos*	

Historical themes. While bearing in mind these observations for the construction of the historical part of the thesis, and by considering historical information found in contemporary publications and primary printed sources related to the international circulation and dye applications of American cochineal, four themes emerge as the most relevant, and are developed in subsequent chapters: chronological trends observed in volumes and prices; the role of cochineal in the wider context of the transatlantic trade in American dyestuffs; the spatial reception of cochineal in international markets and dye workshops; and finally its impact in relation to other red insect dye sources.

The first study, presented in Chapter 4, aims to examine the growing importance of cochineal for the Spanish Empire, in terms of its colonial trade as well as its production, which is inherently associated with international demand. Hence, this study looks at the

[8] Baskes, 2000, p. 3; Bethell, 1988, p. VIII; Hamnett, 1971, p. VIII; MacLeod, 1984, p. X; Posthumus, 1946, pp. LIV–LVI and 585-586; Prada, 1961, pp. 238-239; Raynal, 1783, III, p. 356.

historical situation surrounding cochineal in the Spanish transatlantic commerce, by considering the evaluation of volume and price tendencies for this dyestuff during four periods, defined here as “economic impulse”, “economic crisis”, “reforms” and “decline”. These terms are considered useful for dividing and characterizing the diverse chronological phases identified through examining the historical evolution of the Spanish trade in American cochineal (as it has been presented in the literature to date). These four phases correspond to the three centuries of Spanish occupation of Mexico, the main centre of cochineal production during the colonial period. This time range is somewhat equivalent to the Early Modern period, and is bounded in this thesis by the conquest of the City of Mexico in 1521, and the official year of Mexico’s Independence in 1821. This more or less coincides as well with Portuguese colonial occupation of Brazil, between 1500 and 1822. The revision of trends in volumes and prices for the Spanish trade in cochineal conducted here indicates an exponential increase of its importance in transatlantic communications, while also demonstrating that historical publications are not always able to provide sufficient figures for a full analysis of some specific chronological periods.

The second study, presented in Chapter 5, primarily looks at American cochineal in wider perspective, by comparing it with other major American dyestuffs traded in the Spanish and Portuguese transatlantic routes, namely indigo, brazilwood and logwood, to better assess its role and position in transatlantic trade patterns, especially of dyestuffs. This study is strongly connected to the previous one, as it establishes very important historical relationships, in terms of volumes and prices, which are shared between cochineal and the other dyestuffs exported from the Americas. Although, this study enhances understanding of the absence of figures reported for cochineal in the previous chapter, it is also important to look at cochineal in the global context, by assessing its dissemination beyond the Atlantic Ocean.

Hence, the third study, presented in Chapter 6, looks at the reception and integration of cochineal in international markets and centres of textile production, in order to assess current historical interpretations and conclusions about the geographical spread of American cochineal in Europe and Asia with the advent of the Iberian Expansion. This study considers the most controversial parts of the literature, by comparing the historical information assessed in Chapters 4 and 5 for the Spanish transatlantic trade in cochineal, in relation to the interpretations found in historical sources related to its commerce in European and Asian regions. Based on these sources, very important interpretations are achieved here about cochineal's diffusion and acceptance in Europe and Asia, which require complimentary information, namely by comparing the dye applications of the American insect dye in relation to other red insect dyes in European and Asian dye workshops.

The fourth and final study, presented in Chapter 7, looks at the integration of American cochineal in European and Asian dyeing practices, by comparing it with "Old World" insect dyes, specifically kermes, lac and Armenian and Polish cochineal. Here, the geographical extent to which the American red dye penetrated European and Asian dyeing practices is considered, by looking at its influence (or not) on the trade and application of the other insect dye sources. Non-commercial historical information used here, and in Chapter 6, is chiefly obtained from primary printed sources, such as recipes and treatises on dyeing, as well as historical publications that analyse sumptuary legislation, guilds statutes and other sources related to old dyeing practices.

By comparing the historical interpretations attained in Chapter 6, it becomes clear in this study that, despite the diffusion of American cochineal, indigenous insect dyes were still considered to be important sources of red for Europeans and Asians alike, throughout the Early Modern period. However, it is worth noticing that only limited historical evidence was encountered for the trade and dyeing applications of American cochineal and other insect dyes in certain European regions, and particularly in Asia. For this reason, it is of upmost importance to assess alternative research approaches that can offer additional information to assess the historical arguments made in the literature.

3.2. Textile Objects for Material Study

Historical textile objects and their dye materials can represent an important source of information to support historical interpretations provided by archival documentation, or even to clarify ambiguous hypotheses, to which historical evidence is not always accessible. In this context, knowledge of the confirmed presence of insect dyes in historical textiles can provide worthy contributions to understanding the extent of their trade, uses and applications in diverse European and Asian contexts. Therefore, determining the exact species of cochineal in historical textiles not only constitutes irrefutable proof of the veracity of historical documents and interpretations, but also helps assessing the dissemination of American cochineal in territories, for which only scarce or incomplete data is available (or for which information is missing altogether). This is the case of Iran, for which little historical material is currently available for understanding when the American insect reached the region, and how it was received in local dye workshops (as shall be discussed in Chapter 6).

The confirmation of the existence of insect dyes in historical textiles depends on their accurate assessment through chemical analyses. However, and as described in Chapter 2, analytical limitations have been identified in scientific publications concerning the chemical characterization of insect dyes, particularly cochineal species, in historical textiles. Indeed, due to these limitations, the precise characterization of the cochineal species present in historical textiles has often been inconclusive.

For this reason, an analytical approach was developed in this thesis to overcome the limits of currently available scientific methodologies. This comprises an important contribution towards the main objective of this work, as it enables the possibility of achieving accurate chemical characterizations of cochineal dyes in historical textiles. Based on the successful results accomplished with this approach (described in the Chemistry part, below), an extensive comparative investigation of the dyestuffs present in a large group of historical textiles is undertaken.

Selection of Historical Textiles. A systematic revision of scientific publications allowed a comprehensive overview of the type of textiles in which cochineal dyes have been detected so far, thus bringing insights about which objects should be selected for the current study. Hence, it became apparent that it was necessary to look at a wide number and range of textiles, produced in European and Asian regions between the 15th and the 17th centuries. The option for this time frame aimed to bring significant interpretations about two distinct periods: before the arrival of American cochineal to Europe and Asia (15th century); and then, its arrival and gradual adoption in those regions (16th and 17th centuries). As for the range of European and Asian territories, these mainly comprised centres of textile production, renowned at this time for producing abundant luxury textiles, dyed with expensive dyestuffs, like American cochineal and other insect dyes: in Europe, these were found in Italy, Spain, France and the north and South of the Low Countries; whereas in Asia, they were established in Turkey, Iran, India and China, especially under court sponsorship. By studying textiles produced in these different periods and regions, it was expected that successful comparisons could be attained between American cochineal and "Old World" insects, and thus, bring conclusive perspectives concerning the impact of the dissemination of American cochineal.

Although provenance and date were essential for defining the group of textiles to be investigated in this thesis, other features needed to be considered as well. Hence, the selection was made on the basis of a visual assessment of the potential presence of cochineal dyes, and thus, the defining feature connecting all of the textiles investigated here is the presence of yarns with a strong and vivid red or crimson colour, which is often used for large background areas, and occasionally, for smaller decorative motifs.

As previously mentioned in Chapter 1, rich European silk clothes were often dyed with cochineal, whereas for wool, kermes was the most commonly used insect dye (or the roots of madder, depending on the quality of the textile). In Asian cultures, the choice of insect dyes would likely shift to lac dye, as shall be discussed further in this work. Based on this knowledge, and since the objective of this thesis is to look at the geographical spread of American cochineal, the majority of the textiles examined comprise red luxurious silk fabrics (rather than woollen ones), of which more than half are velvets (Appendix 2). Made exclusively or almost entirely of silk, these velvets have elaborate designs and complex weaving structures, and are often decorated with gilt-metal and silver threads, and dyed with the finest available dyestuffs. Other rich fabrics like damasks, lampas, taffetas, brocades, *brocatelles*, satins and even silk carpets are also included. In addition, a small group of woollen textiles was considered as well.

Today, a great number of these textiles are only fragments, but back in their heyday, they were parts of the clothes that endowed power to the wealthy nobility of Europe and Asia, by dressing them, decorating their courtly homes, and even by following them into the afterlife. Besides textile fragments, the selection of textiles investigated in this thesis includes banners, covers, shields, table-cloths, cushions, carpets, Islamic prayer carpets, tapestries, among others items. Furthermore, in Europe, rich textiles and decorative strips were also used in the manufacture of the apparel of the high clergy, and thus, chasubles, copes, capes, pluvial, dalmatics and altar frontals were also examined.

Since the majority of the textiles considered here are rich, elaborate objects, a great number were expected to have been produced in the main European and Asian centres of textile production. However, it was expected that textiles produced in other regions, and exhibiting the red shades potentially indicative of the presence of insect dyes, should be obtained for this study as well. Unfortunately, this was not always possible due to an absence of specimens. In general, museum collections reflect the geographical distribution of textile manufacturing in the main European and Asian centres, where production was mostly dependent on international demand.

Therefore, nowadays, it is common to find Italian luxurious insect-dyed silk fabrics in European museum collections, whereas very few comparable examples from other European regions, for instance. Even so, when these are available, their access is often dependent on museum considerations, namely if they are on exhibition, or if they are eligible for sampling. Given the scope of this thesis, efforts were undertaken to reach as many European and Asian regions as possible, although it was not possible to sample red insect-dyed examples from everywhere. For this, a more detailed survey and the selection of a wider number of textiles in cultural heritage institutions would be necessary.

Taking this limitation into consideration, it must be acknowledged that this thesis can only provide a small picture of the true impact of American cochineal in Europe and Asia. Nevertheless, as we shall see, the results do constitute fundamental support for complementing the historical interpretations discussed in the historical chapters and even shed light on periods and circumstances for which historical documentation is entirely lacking.

Historical textile samples. The samples analysed in this project comprise 287 in total, belonging to 115 European and Asian historical textiles, as well as one Peruvian example, held at sixteen cultural heritage institutions (Table 2). All of these textiles were manufactured between the late Medieval period and the 17th century, i.e., before and immediately after the arrival of American cochineal to the textiles' producing regions.

Although special focus was put on silk, 46 wool samples were considered as well in the total of 287 (Appendix 2).

Table 2. Abbreviations list of cultural heritage institutions holding historical textiles, which fibre samples were investigated in this project (Appendix 2).

Donor	Abbreviations
Abegg Stiftung, Riggisberg, Switzerland	AS
Catharijneconvent Museum, Utrecht, The Netherlands	ABM
Calouste Gulbenkian Museum, Lisbon, Portugal	CGM
Deutsche Textilmuseum, Krefeld, Germany	DTM
Historisch Museum, Bern, Switzerland	HMB
Kungl. Livrustkammaren, Stockholm, Sweden	KLS
Schweiz Landesmuseum, Zurich, Switzerland	LM
Österreichisches Museum für Angewandte Kunst, Austria, Wien	MAK
The Metropolitan Museum of Art, New York, U.S.A.	MET
Musée des Tissus et Musée des Arts Décoratifs, Lyon, France	MT
Museu Nacional de Arte Antiga, Lisbon, Portugal	MNAA
Palácio de Vila Viçosa, Portugal	PVV
Rijksmuseum, Amsterdam, The Netherlands	RMA
Schule für Gestaltung auf der Lyss, Basel, Switzerland	SGL
Muzeum Narodowe w Warszawie, Warsaw, Poland	SZT
Victoria and Albert Museum, London, United Kingdom	V&A

A great part of these historical samples were obtained through an ARCHLAB Access project, belonging to the European consortium CHARISMA. ARCHLAB Access granted the possibility of conducting archival research on many reports and publications concerning the identification of insect dyes in historical textiles and oil paintings, belonging to associate institutions, namely the British Museum, National Gallery of London and the Netherlands Cultural Heritage Agency (RCE) (Appendix 3). Given the selection features mentioned above (provenance, date, colour, type of textile and type of fibre), 108 samples held at the RCE archives were considered. These samples belong to 55 historical textiles, and they had been donated to this institution for dyestuff identification by Hofenk de Graaff & Roelofs, in the 1970's [9]. Since these samples had been already analysed by these researchers, the presence of kermes and cochineal dyes was known. However, because these had been characterized

[9] Hofenk de Graaff & Roelofs, 1972, 1975, 1976.

using thin-layer chromatography (TLC), it was expected that more accurate chromatographic results would be obtained here, following the analytical method developed in the Chemical part of this thesis.

Moreover, given that the majority of these samples belong to European textiles, it was necessary to obtain more samples, especially examples of Asian origin. Hence, 179 samples from 61 historical textiles were obtained through direct contact with cultural heritage institutions. While the majority of these samples had not been analysed, and thus, the dye source present was unknown, samples belonging to Asian historical textiles from the CGM and the MNAA had been assessed by HPLC in an earlier project [10]. In order to obtain comparable chromatographic results with those from other textiles analysed in the present work, these CGM and MNAA samples were re-analysed.

Although focus is given to red samples, other yellow, green, blue, pink, orange, black or brown fibres are also part of the total of 287 samples investigated in this project. However, for the European textiles, few non-red fibres were considered, mainly because many studies on dye identification have dedicated to them previously, and thus, little information would be added. By contrast, not many studies on dye identification are available for Asian textiles, so information on non-red fibres could provide helpful insights into the history of these textiles and dyeing applications in different Asian regions (in relation to those practiced in Europe as well). For instance, yellow dyes can provide significant information about the provenance of the textiles. Indeed, since yellow-dye plants tend to be widely available and are endemic to specific regions around the world, they could be collected nearby centres of textile production (and thus, not submitted to long-distance trade).

Once the representative samples were gathered, conditions were met to perform their chemical dyestuff characterization. However, limitations of current analytical procedures have been identified in the scientific literature for the chromatographic characterization of cochineal dyestuffs. For this reason, it was important to develop an optimized analytical method that could deliver more precise identifications about the source of insects used to colour historical textile objects, and thus, lead to supportive historical interpretations for the European and Asian dissemination of American cochineal.

[10] Serrano et al., 2011.

3.3. Chemistry

The historical diffusion of American cochineal in Europe and in Asia can be evaluated by the chemical investigation of red insect dyes present in historical textiles, for which both provenance and date are known, as demonstrated by Hofenk de Graaff & Roelofs and, later, Phipps, as described in Chapter 2. Given the evolution of chemical analysis described in the latter chapter and the limitations that have emerged concerning current difficulties in discriminating cochineal species, this part of the thesis aimed to develop improved analytical conditions to obtain an accurate chemical characterization of the cochineal dyes most popularly used in historical textiles, namely American, Polish and Armenian cochineal (*D. coccus, P. polonica* and *P. hamelii*). These insects, along with lac dye and kermes, were typically found in major European and Asian markets and, conceivably, dyers would want to use the best insect dyes available when dyeing the most elaborate and expensive textiles.

By achieving an accurate chemical characterization of cochineal dyes, it can become possible to identify which of the textile objects investigated in this thesis had been dyed with American cochineal or with other insect dyes. Hence, and according to the date and provenance of the textiles, the interpretation of the analytical results can bring very important contributions for understanding the historical penetration of American cochineal into European and Asian regions, during and after the 16th century.

Following these premises, through the continuation of a research project previously started as a Master's thesis [11], the Chemistry part of this Doctoral thesis comprises a chemical investigation undertaken in two phases: 1) the development of an analytical method that provides superior chemical characterization of cochineal and other natural dyes usually present in historical textiles; and 2) the chemical investigation of the composition of cochineal dyes in dyed textiles and historical objects, in order to provide accurate chemical results that lead to more accurate historical interpretations about the regional applications of American cochineal, during the Early Modern period.

The first phase of research, presented in Chapter 8, concerns the optimization of an analytical method using ultra high-performance liquid chromatography coupled to photo-diode array detector (UHPLC-PDA) for the identification, in one single analysis, of a wide

[11] Serrano, 2010; Serrano et al., 2011; Serrano et al., 2013.

range of dye compounds with closely related and/or different physicochemical properties, belonging to natural dyestuffs. By adopting a more precise analytical method than others currently available in the field of dyestuff analysis, usually using HPLC, it is aimed here to acquire UHPLC results that can provide more accurate information about dye sources present in textile objects, namely cochineal species or mixtures of these with other insect sources of red, for example.

Therefore, a literature review was undertaken of case studies regarding the characterization and identification of natural dyestuffs in historical textiles using HPLC and on case studies using UHPLC in diverse fields of research (pharmacy, food industry or environment preservation), in order to assess the most proper parameters for transferring analytical conditions from HPLC to UHPLC. Based on the results of the literature review, the UHPLC method optimization included the test of different gradient elution programs on seven UHPLC columns, with different dimensions and stationary phases, as well as the application of several separation solvents (i.e. mobile phases), flow rates, temperatures and running times. The optimized UHPLC method was then compared to an HPLC method and the efficiency of both chromatographic systems was evaluated.

This research demonstrated that the UHPLC method can display significant chromatographic improvements over HPLC, by providing better detection limits and higher efficiency of separation and resolution, thus contributing for a better characterization and identification of minor components in complex biological samples. This is extremely valuable for obtaining more precise chromatographic information about cochineal species. Hence, a reference library was created using this optimized method by analysing c. 85 representative compounds usually present in natural dyestuffs, for later characterization of unidentified dye sources present in historical works of art [12].

In the second phase of research, presented in Chapter 9, the optimized UHPLC-PDA method was used, along with mass spectrometry (MS) and image scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX), to investigate a large set of experimentally-dyed and artificially aged contemporary samples of silk and wool, the most elected fibres for dyeing with insect dyes in Europe and Asia. This approach aimed to assess the fastness of the dyes and whether the colorant ratio could be affected by the dyeing

[12] See Appendix 4.

procedure and possible ageing mechanisms. Once acknowledged the stability of the cochineal dyes, it would be possible to ascertain if cochineal species could be characterized in historical textiles.

For this, UHPLC-PDA analyses of dye extracts from insect dyes were compared with those of experimentally-dyed samples. These were prepared following diverse parameters for mordanting and dyeing, such as types of water, temperature, bath duration, pH, concentrations, laboratory-grade ingredients and insect dyes - kermes and American, Polish and Armenian cochineal [13]. The choice for these parameters was based on the extensive revision of contemporary publications and historical recipes, dated between the 15th and 18th centuries.

All chromatographic data obtained with the UHPLC-PDA analyses of the insect dyes and the experimentally-dyed samples was examined but, given the great amount of analyses made and the samples' very similar but variable dye composition, multivariate statistical analyses were indispensable. Hence, with the collaboration of Andre van den Doel (Radboud Universiteit Nijmegen, The Netherlands), partial-least squares discriminant analysis (PLS-DA) was used to model the chromatographic data and, therefore, discriminate the cochineal insect species, as well as their correspondent dyed fibres [14]. This data was moreover compared with a selection of experimentally-dyed fibres that had been submitted to artificial ageing [15]. This was a crucial step to verify possible differences in colorant composition due to degradation processes and, furthermore, establish comparisons with the composition of historical cochineal-dyed fibres.

Along with UHPLC-MS and SEM-EDX, PLS-DA results on UHPLC-PDA data demonstrated the possibility of successfully obtaining close comparisons between the experimentally-dyed and the artificially-aged samples with the historical fibres. Hence, red samples from the group of historical textile objects described above, were analysed with UHPLC-PDA [16], in order to obtain important historical interpretations about the insect dyes used, in the context of the textiles date and provenance. Ultimately, this was an important

[13] See Appendices 5, 6 and 7.
[14] See Appendix 5.
[15] See Appendix 8.
[16] See also Appendices 2 and 5.

contribution to establish new interpretations about the impact of the American dyestuff on well-established European and Asian dyeing traditions from the 16th century onwards.

The results of the two above-mentioned phases of research have been published in ISI Web of Knowledge scientific journals, and they are presented in this thesis following the editorial guidelines of their respective journals. Since they have been submitted to a peer-review process, no changes have been made to their structure, content or bibliographical organization. Hence, they are close reproductions of the original publications. The Electronic Supplementary Materials (ESM) mentioned in these papers have been converted into Appendices 4 and 5, and additional supporting material has also been added to this thesis, as Appendices 6, 7 and 8.

Finally, the successful results of these two studies lead to the final part of this thesis, which involves an interdisciplinary discussion that connects the chemical results obtained through dye characterization of the textile object samples with the interpretations achieved through the historical analysis, in order to propose more conclusive interpretations about the historical dissemination and adoption of American cochineal, in relation to other dyestuffs, during the Early Modern period.

Thus, following the structural organization for the approach described above, the four succeeding chapters of this work are dedicated to the historical investigation of American cochineal; these are then followed by two chapters, devoted to improving the chemical characterization of cochineal dyes in textiles objects; and lastly, the final chapter consolidates the historical and chemical results on the historical objects, through a multidisciplinary analysis that aims to offer supporting evidence for the historical knowledge of American cochineal for Early Modern European and Asian societies.

CHAPTER 4

COCHINEAL IN SPANISH TRANSATLANTIC COMMERCE:

Trends in Volumes and Prices

"The history of this mad race for cochineal is a window onto
another world … To obtain it, men sacked ships,
turned spy and courted death." Amy B. Greenfield [1]

From 1503, Seville and (officially) from 1717, Cádiz, constituted the only Spanish ports allowed to communicate with the Americas until 1790. This strict monopoly system was controlled by the royal Spanish authorities, while the *Casa da Contratación* registered and taxed all the products sent to and received from the Americas. Facing the exponential European demand and the growing variety of American consignments, this institution created a system of annual convoys (*Carrera das Indias*) in 1564, which carried the American shipments. Protected with galleons against the French, English and Dutch corsairs in the transatlantic routes, the annual fleet system travelled at specific times of the year, permitting communication between the merchants in Spain and the main American ports of St. Domingo, Nombre de Dios, Vera Cruz and Havana [2].

In Mexico, the cochineal trade was based on a close relationship between merchants and local authorities, who obtained the dyestuff from indigenous communities. Dyestuff consignments were dispatched from Vera Cruz to Seville (and Cádiz), and from Acapulco to Asia, via the Philippines. Once in Europe and Asia, the American dyestuff was extensively traded in the most important mercantile routes, both by sea and by land [3], as attested by the numerous references made to this product in commercial correspondence exchanged by

[1] Greenfield, 2006, p. 15.

[2] From Nombre de Dios and, after 1598, from Portobello, official land routes connected the trade between Seville and Peru. Baskes, 2000, pp. 154-155; Burkholder & Johnson, 1998, pp. 146-147; Chevalier, 1943, p. 323; Crevea, 1906, pp. 523-524; Donkin, 1977b, pp. 37-38 and 52; Garavaglia & Marchena, 2005, I, pp. 260 and 295-296; Hamilton, 1948, p. 41; Hamnett, 1971a, p. 24; Herrera, 1883, pp. 448-449; Lee, 1951, pp. 206-207 and 214; MacLeod, 1984, pp. 341-342 and 350-351; Mazín, 2007, pp. 109-113; McAlister, 1984, pp. 233-234; Parry, 1990, pp. 53-57 and 128-130; Phillips, 1990, pp. 76-78.

[3] Crevea, 1906, pp. 524-525; Donkin, 1977b, pp. 38-39; Lee, 1951, p. 207; Marichal, 2014, p. 207.

countless merchants [4]. Based in Seville and later in Cádiz, these English, Flemish, French, Greek or Italian merchants represented essential intermediaries for the distribution of the American products around Europe and Asia [5]. During the 16th century, the Portuguese too had a monopoly system of trade with Asian regions and with Brazil, in which products were channelled to the *Casa da Mina* in Lisbon. From there, they were re-exported to the rest of Europe, especially north to Antwerp [6].

Figs. 4.1 to 4.4 depict average plots for relative annual volumes and prices registered (or estimated) by historical publications for the transatlantic trade of American cochineal during the colonial period (Appendix 1, Tables 1 and 2) [7]. Since this data is based on the registry of the irregular arrival of remittances to Seville or Cádiz and predictions made by merchants, general fluctuations and possible margins of error should be taken into consideration. Moreover, a graph could not be constructed for the period between 1620 and 1717, because very few records for cochineal have been found as yet in historical documentation, as also noted by Fuentes (1980) and Phillips (1990).

Since historical documentation does not often discriminate the different grades of cochineal sent to Spain, Figs. 4.1 and 4.2 include their overall volume: the domesticated *grana fina* from Oaxaca and adjacent regions (usually named according to its provenance, “Tlaxcala” or “Mixteca”); and the wild or *silvestre* variety, collected in the Yucatán Peninsula (“Campeche” cochineal) and other Mexican regions, as well as in Honduras, Nicaragua, Costa Rica, Guatemala, Ecuador, Havana, Peru and Argentina [8].

Although the proportion of the wild variety could add up to almost a quarter of the total amount of cochineal sent to Spain at times during the 18th century, it more often represented smaller (or even null) percentages of the total cochineal brought annually in the

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[4] Martín, 1965; Prada, 1961. See also Baskes, 2013, p. 159; Lee, 1951, pp. 210-211; Marichal, 2001, p. 19, 2014, p. 205.
[5] Baskes, 2000, p. 171; Crevea, 1906, p. 456; Herrera, 1883, p. 444; Lee, 1951, pp. 207 and 210; Sanz, 1979, p. 549.
[6] Lane, 1940, p. 589.
[7] Registries from Vera Cruz are characterized by Hamnett and Silva & Bosa. Relative values from Phillips and Silva & Bosa correspond to the average of volumes registered every four years (Appendix 1, Tables 1 and 2). Chaunu & Chaunu, 1956, VI_2, pp. 980-981, 984-987 and 1039-1051; Donkin, 1977b, p. 37; González, 1976, pp. 222–275; Hamnett, 1971, p. 175; Lee, 1948, pp. 458-463; Morineau, 1969, p. 336, 1985, pp. 103 and 422; Phillips, 1990, pp. 80-81; Sanz, 1979, pp. 550, 556-560, 574 and 579-580; Silva & Bosa, 2006, p. 485.
[8] Baskes, 2000, pp. 11-12; Chaunu & Chaunu, 1956, VI_1, p. 99, VI_2, pp. 980-981; Donkin, 1977b, p. 29; Jordán, 1963, p. 12; Lee, 1948, p. 465; Marichal, 2001, p. 14; Pérez-Garcia, 2016, pp. 199-200; Tordesillas, 1726, VIII, p. 170; Vasco, 1963, p. 64.

transatlantic shipments. Indeed, the majority of the bulk was occupied by the *grana fina*, especially because this was always considered to possess a much higher colorant content [9]. For this reason, its prices were generally much higher than those for the wild insects.

Hence, given the small number of price records available for wild cochineal, and in order to avoid high standard deviations between the existing prices of both cochineal varieties, Figs. 4.3 and 4.4 only depict relative prices of *grana fina*. Nevertheless, it is worthwhile mentioning that the few records of wild cochineal must not be underestimated: in 1618, in a shipment sent from Spain to Venice, one *arroba* of *fina* would have cost about 121 *pesos*, one of *silvestre,* 96 *pesos*, and one of *Campeche* (or *campesina*), 40 *pesos* [10].

Figs. 4.1 to 4.4 display annual fluctuations, occurring when there was abundance or shortage of available merchandise in Spain. For instance, in shortage years prices could skyrocket depending on the level of international demand. Annual availability and, inherently, irregular arrival of remittances were directly related to production and trade.

As regards production, cochineal was directly influenced by weather conditions, namely floods, storms or dry seasons; insect plagues and other animal predators; epidemics, diseases and starving periods affecting the yield of human labour; and other political or economic events that could lead to the abandon or decimation of entire crops [11]. These factors are not fully discussed in this study, as focus is put on international trade. However, excellent work on this subject has been published by Baskes (2000) and Hamnett (1971a).

[9] Baskes, 2000, p. 12; Chaunu & Chaunu, 1956, VI_2, pp. 980-981; González, 1976, II, pp. 222–275; Morineau, 1969, pp. 164–165, 1985, pp. 494–495; Raynal, 1783, III, p. 356; Tordesillas, 1726, VIII, p. 170.

[10] Chaunu & Chaunu, 1956, VI_2, p. 983. See also Morineau, 1969, pp. 161 and 163. Lee (1951, p. 221) adds: "*Grana* sold out of French prizes in 1626 was classified by the English as Mestera (Mixteca?) worth 33s. 4d. per pound *[c. 198 pesos per arroba]*; Tesiala (Tlaxcala?) at 30s. *[c. 179 pesos per arroba]*; Campeiana (campesino?) at 6s. *[c. 36 pesos per arroba]*; and Silvester (silvestre?) at 5s. *[c. 30 pesos per arroba]*". In Chiapas (Mexico), wild cochineal valued one third of the price of *grana fina* (Donkin, 1977b, p. 29). In the middle of the 18th century, shipments to Europe included *fina*, along with cheaper *granilla* (fragments of *fina* or smaller individuals), *silvestre* and dust (*polvo,* produced during the killing treatment and sold along with other impurities from the insects) (Morineau, 1985, pp. 494-495; Raynal, 1783, III, p. 356; Réaumur, 1737, p. 125). See also Jordán, 1963, appendix 1; Born, 1938, p. 216; Magán, 1963, p. 85; Paganucci, 1762, p. 324; Pérez-Garcia, 2016, pp. 199 and 201; Serrano et al., 2013, p. 138; Vasco, 1963, p. 66.

[11] Alden, 1965, p. 42; Balfour-Paul, 1998, pp. 46-47 and 64; Donkin, 1977b, pp. 28-29; Hamnett, 1971b, p. 59; Jordán, 1963, p. 37; MacLeod, 1984, p. 367; McAlister, 1984, p. 247; Parry, 1990, p. 118.

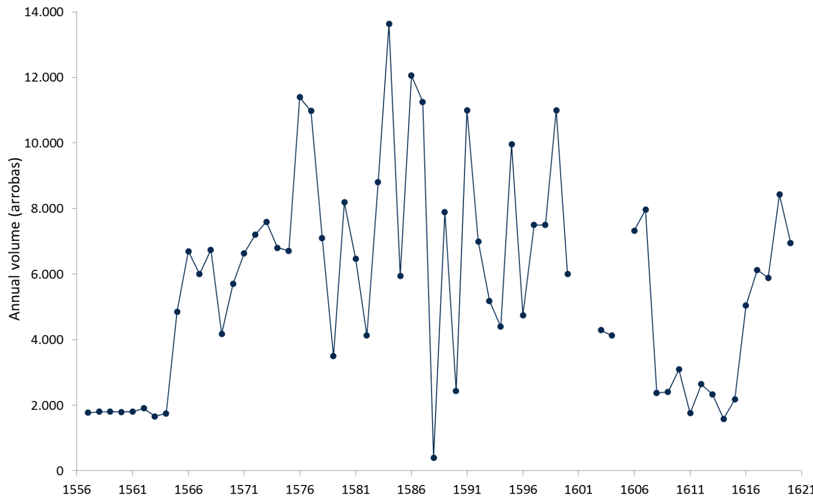

Fig. 4.1. Average of annual transatlantic volumes (*arrobas*) of American cochineal (all insect grades) from historical publications, 1557 - 1620 - Appendix 1, Table 1.

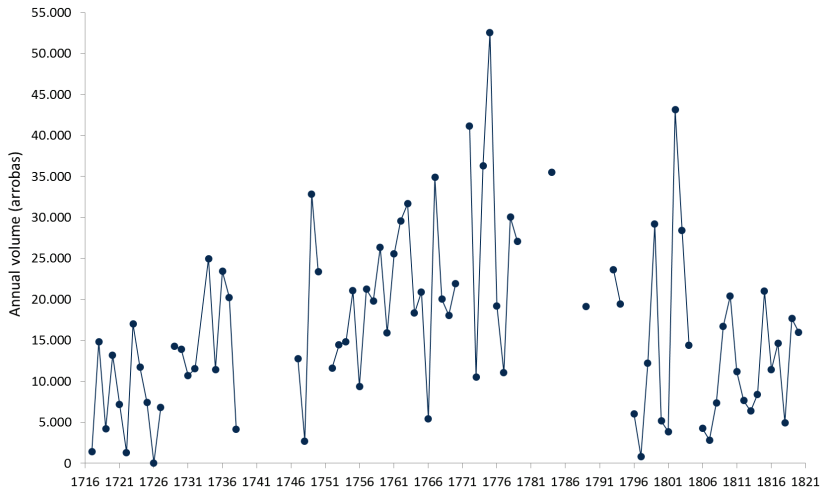

Fig. 4.2. Average of annual transatlantic volumes (*arrobas*) of American cochineal (all insect grades) from historical publications, 1717 - 1820 - Appendix 1, Table 1.

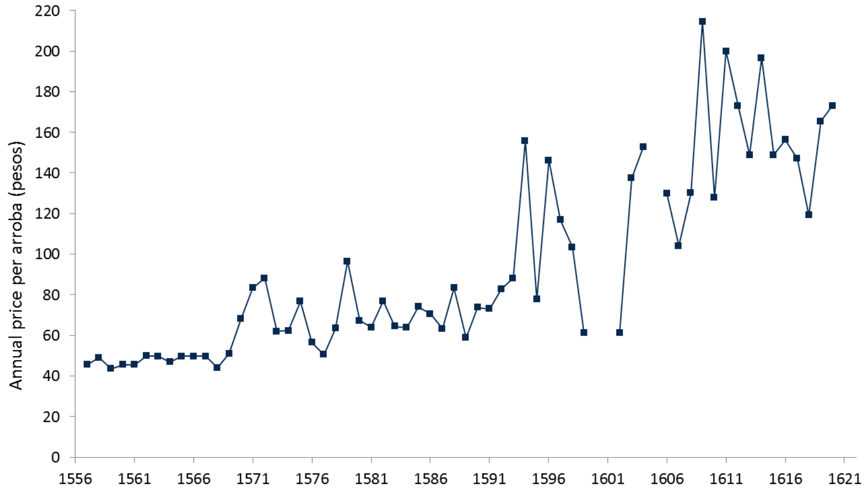

Fig. 4.3. Average of annual transatlantic prices (*pesos*) per *arroba* of American cochineal (*grana fina*), 1557 - 1620 – Appendix 1, Table 2.

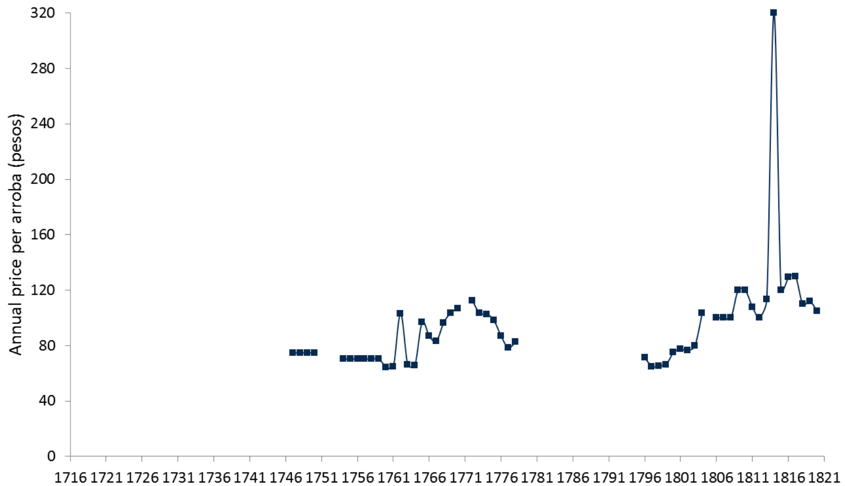

Fig. 4.4. Average of annual transatlantic prices (*pesos*) per *arroba* of American cochineal (*grana fina*), 1747 - 1820 - Appendix 1, Table 2.

As for trade, dyestuffs travelled long distances across the globe, from the original centres of production to the final destinations, constantly exchanging hands between countless merchants. In the process, the amount of available merchandise was dependent upon the demand of the product; quantity of fleets yearly travelling to and from the Americas; abundance of dyestuff brought in the vessels; rate of smuggling; and many other vicissitudes that could disturb the transatlantic course, such as storms, wars and pirate or privateer assaults [12].

English, French and Dutch seizures to the Iberian fleets were especially frequent during periods of war. In those times, communication between the Iberian Peninsula and the Americas was often interrupted and, hence, imports arriving in Lisbon, Seville or Cádiz were considerably shortened or even lacking in some years. As a result, cochineal prices increased, due to constant demand for it in international markets, its limited availability and the high insurances levied for its unstable transatlantic transport [13]. Furthermore, due to conflicts and wars between Spain and England, for instance, the English Crown supported privateering plunder of American shipments crossing the Atlantic in the Spanish fleets [14]. Dutch and French too chased the American cargoes, especially after they started settling along with the English in the Caribbean islands throughout the 17th century. Indeed, in 1615, Captain John Smith was made prisoner in a French pirate vessel and reported the arrest of "fiftie Chests of Cutchanele" among other commodities from another Spanish ship [15].

To avoid losing their best cargoes to the enemy, the Spanish often dispatched cochineal and other prized consignments separately in several vessels sailing from the Americas to Spain, or alternatively, via sloop ships. These were faster than the convoys of the *Carrera de Indias* fleet system, which were accompanied by the large but slow war galleons of the Spanish Crown. The main job of these sloop ships was to exchange

[12] Baskes, 2000, p. 160; Burkholder & Johnson, 1998, p. 155; Fuentes, 1980, p. 2; Hamnett, 1971a, p. 2; Lee, 1951, pp. 212-214; MacLeod, 1984, pp. 374 and 376; McAlister, 1984, p. 247; Parry, 1990, p. 118; Prada, 1961, p. 102; Sanz, 1979, pp. 571-572 and 578-579; Souza, 1939, p. 181.

[13] Baskes, 2000, pp. 139 and 158; Lee, 1951, pp. 212-214; Magán, 1963, p. 84; Morineau, 1969, p. 147.

[14] Baskes, 2013, p. 161; Greenfield, 2006, pp. 147-151; Lee, 1951, pp. 212–214; Lemon, 1865, pp. 588 and 702. In 1589, an English privateer ship apprehended from a vessel coming from Mexico "sixe chests of Cochinell, every chest houlding one hundred pound weight *[c. 24 arrobas]*". Two years later, another English ship brought a cargo of 16 chests of cochineal, among other precious commodities taken from a Spanish boat (Hakluyt, 1904, VII, pp. 20 and 60).

[15] Smith, 1910, p. 738. See also Greenfield, 2006, p. 146; MacLeod, 1984, pp. 377-381; Phillips, 1990, p. 89.

correspondence with the Americas and, although the transport of commercial products was virtually forbidden, valuable products would have a safer and faster journey [16].

Moreover, and despite the fact that Seville was the official port for trade of American products, smuggling would take place among corrupted Crown officials and merchants, in Vera Cruz or other ports of the Atlantic. Hence, they would declare lesser products than those they actually dealt with, and/or use trade routes which were not supervised. Obviously, more profitable investments were achieved, rather than facing the heavy taxes imposed by the Spanish Crown [17]. In this context, throughout the second half of the 16th century, European merchants were buying cochineal from Spanish ships stopping in Portugal (Azores or mainland), while heading to Seville [18]. However, although smuggling was a very important part of the transatlantic commerce, very few records of this practice are currently available (because it was illegal) [19].

Once in Spain, cochineal prices depended not only on demand and availability, but also on the greed of merchants and investors involved in its trade. Like precious metals, alum or pepper, cochineal was a valuable and easily transportable product, which through financial gambling could bring enormous profits or heavy losses. Hence, leading merchants and bankers would invest large sums of money in financial speculations concerning cochineal, while attempting to corner its market. In the 16th century, cochineal's trade was generally controlled by Spanish and Italian merchant bankers, who connected Seville and Cádiz with Genoa, Livorno or Florence. In this context, much correspondence regarding production, distribution and consumption of cochineal was exchanged between the involved parties [20]. These would attempt to buy the whole stock of cochineal in Seville and other European ports and, by holding the bulk, they would try to manipulate the price of cochineal to sky-high values, until a new shipment would arrive in Seville. However, sometimes demand in one specific year could be low and, as a result, such a strategy would simply fail.

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[16] Crevea, 1906, p. 524; Greenfield, 2006, p. 153; Lee, 1951, pp. 214; Martín, 1965, p. CXXVI; Sanz, 1979, pp. 572-573.
[17] Bagú, 1949, pp. 121-122; Burkholder & Johnson, 1998, p. 146-147; Fuentes, 1997, p. 216; Garavaglia & Marchena, 2005, I, pp. 294 and 310-312; Lee, 1951, pp. 219-220; MacLeod, 1973, pp. 264 and 384, 1984, pp. 376 and 380-381; McAlister, 1984, pp. 374-375; Morineau, 1985, p. 219; Phillips, 1990, p. 85.
[18] Lee, 1951, pp. 213-214. See also Gage, 1655, p. 80.
[19] Garavaglia & Marchena, 2005, I, p. 310; McAlister, 1984, p. 375.
[20] Braudel, 1982, pp. 421–423; Brown, 1894, Venice August 26, 1587 [572], 1904, Madrid, Nov. 3, 1608 [357]; Greenfield, 2006, p. 105; Lee, 1951, pp. 210-211; Marichal, 2014, p. 205; Sanz, 1979, pp. 581.

Efforts to corner the market in cochineal kept occurring well into the 18th century, not only by Europeans but also by Mexican merchants [21].

To understand all these factors for the transatlantic trade of cochineal and the small availability of records for the 17th century, it is important to evaluate the commercial trends (in bulk and price) shown in Figs. 4.1 to 4.4. This evaluation is divided in four periods, termed after the diverse chronological phases that have been identified when studying the literature regarding Spanish trade in American cochineal.

4.1. Period of Economic Impulse

Shipments of cochineal started to be brought to Spain from at least the 1520s onwards, although historical publications mention that *Casa de Contratación* commercial records begun in the 1550s [22]. Fig. 4.1 shows that remittances were quite small at first, not exceeding 2 000 *arrobas* per year. A gradual increase of volume is observable in the following decades, reaching a peak of 14 000 *arrobas* by 1584 [23]. At the same time, Fig. 4.3 shows the increasing value of cochineal throughout the second half of the century: until 1569, one *arroba* was worth c. 50 *pesos*; from 1570, its annual average was around 70 *pesos*; and by the end of the century, it was over 100 *pesos* [24]. This increase in volume and price are proportionally related to the increase of production in Mexico stimulated by the Spanish authorities, as well as to the growing quantities crossing the Atlantic and the exponential demand in Seville to feed the European and (soon) the Asian dye houses.

As described above, annual average fluctuations are intrinsic to the commerce of American cochineal. For instance, in 1584 the total cargo of estimated cochineal was c. 14 000 *arrobas*; this quickly dropped to c. 6 000 *arrobas* in the following year; it rose again to

[21] Greenfield, 2006, p. 105; Marichal, 2014, pp. 205-206. According to Hamnett (1971a, p. 10): “the increasing demand for the product *[cochineal]*, and the heavy profits received from it, encouraged extremes of fraud and speculation within New Spain *[Mexico]* itself”.
[22] Regulations to dye with American cochineal in Spain date to 1528 (Lee, 1951, p. 218; Phillips, 1990, p. 79).
[23] Between 1565 and 1598, Seville received a total of 259 000 *arrobas* of cochineal worth 19 413 653 *pesos*, which represents 20% of the value of the gold and silver imported from Mexico during the same period (Sanz, 1979, p. 551).
[24] For 1575, Hamnett (1971a, p. 10) reports that cochineal would be sold in Mexico at about 37 *pesos* per *arroba*. Fig. 4.3 shows that in Seville this price was practically the double.

c. 12 000 *arrobas* in 1586; in 1587, it dropped once more [25]; in 1588, mere 400 *arrobas* arrived to Spain; and, in 1589, the shipment increased again to 7 900 *arrobas* [26]. If fluctuations are not considered in the following years, shipments follow a more or less constant pattern of c. 8 000 *arrobas* per year until the end of the century [27].

Fluctuations in prices are directly connected to volumes: in 1576 and 1577, large cargoes of cochineal arrived to Seville, and hence, cochineal abundance led to a decrease in its price. In the two following years, smaller amounts were available and, consequently, its price increased. If demand was small, independently of how much cochineal was arriving in one year, prices would obviously drop, as demonstrated by Sanz for 1580 [28].

Given the war conflicts between Spain and England that endured practically the whole half of the 16th century, privateering in the Atlantic also contributed to the variation in volumes and prices registered in Seville. Smuggling too, had its effect: in 1568, 7 491 *arrobas* of cochineal left Mexico and only 6 742 *arrobas* entered Seville. For this and the next two years, the rate of unregistered trade (from smuggling or privateering) did not surpass 10%, and in 1571 this was even below 4% [29]. This rate, however, would increase in the 17th century, when a series of events led the Spanish Empire into a long period of economic crisis.

4.2. Period of Economic Crisis

After the prosperous decades of the second half of the 16th century, the markets of Seville started suffering a decrement of American cargoes of cochineal. Indeed, Fig. 4.1 shows that cochineal shipments steeply decrease to an average amount of c. 2 000 *arrobas*

[25] For this year, Chaunu & Chaunu give 25 000 *arrobas*, whereas other authors indicate a decrease in volume (Appendix 1, Table 1). Also, Fuentes (1997, p. 213) reports only 6 740 *arrobas*, while Acosta (1792, p. 245), writes in 1590: *son la cochinilla tan afamada de Indias, com que tiñen la grana fina; déjanlos secar, y así secos los traen a España, que es una rica y gruesa mercadería; vale la arroba de esta cochinilla o grana, muchos ducados. En la flota del año de ochenta y siete vinieron cinco mil y seiscientas y setenta y sete arrobas de grana, que montaron doscientos y ochenta y tres mil, y setecientos y cincuenta pesos, y de ordinario viene cada año semejante riqueza* ["it is the famous cochineal from *Indias*, with which they dye fine scarlet; they are dried, and once dried they bring them to Spain, which is a rich and bulk good; each *arroba* of this cochineal is worth many ducats. In the fleet of the year 1587 came 5 667 *arrobas* of *grana*, which mounted 283 750 *pesos [c. 68 pesos per arroba]*, and usually comes every year such wealth"].

[26] Fuentes (1997, p. 213) reports a total of 7 070 *arrobas* for this year.

[27] Chevalier (1943, p. 328) states that 7 000 *arrobas* of cochineal were sent to Seville in 1598, a very similar remittance to those reported in Fig. 4.1.

[28] Sanz, 1979, pp. 556-559 and 578-579.

[29] Chaunu & Chaunu, 1956, VI_2, p. 984. See also Phillips, 1990, p. 85.

per year at the beginning of the 17th century. Due to a shortage of availability, prices increase up to 200 *pesos* per *arroba* by 1609, Fig. 4.2 [30]. However, despite the rise of available cochineal in the following years, annual average prices do not go below 100 *pesos* [31]. This must be linked to a change in the royal Spanish taxation policies: besides the several duties already applied in Mexico and in Seville to the trade and transport of cochineal, after 1608 an additional tariff of 10 *ducados* (c. 14 *pesos*) was imposed to each *arroba* exported from Spain. In the next decades, this was to bring an overall growth of tax evasion [32].

Such intensification of the royal Spanish duties is perhaps explained by the large expenditure in war campaigns by the Crown. Since the 16th century, the French, English and Dutch had ambitions to play an increasing role in the overseas trade, due to the very restrictive regulations and overcharged taxations practiced in Seville. Moved by these and other political motivations, they were involved in constant war conflicts with Spain. When that happened, transatlantic communications between Spain and the Americas could be practically interrupted, a situation that was furthermore aroused by privateers sponsored by home governments [33]. This situation, along with higher royal taxes, led frustrated merchants to turn to smuggling and, hence, less American shiploads arrived to Spain, thus contributing to the decline of the nation's economy [34].

Spain's high taxes and poor economy may be connected as well with the fact that, during the 17th century, there was a shortage of demand for silver in European markets. With the mining boom in the Americas and increasing exports to Europe throughout the 16th century, a fall in the value of money eventually occurred. This, in turn, reduced the market demand for silver. In the Americas, mines started to have higher expenses than returns, which was sufficient to stop production. Consequently, the export of bullion decreased, and so did the export of non-metallic crops like cochineal or indigo. Indeed,

[30] Galdácano, 1917, pp. 167-168; Lee, 1951, pp. 219-220; Marichal, 2014, p. 204.
[31] Marichal, 2014, p. 204.
[32] Baskes, 2000, p. 171; Galdácano, 1917, pp. 167-168; Lee, 1948, p. 459, 1951, pp. 219-220. Lisbon, by then under Spanish rule, became a common spot for cochineal contraband (Chaunu & Chaunu, 1956, VI_1, p. 100).
[33] Baskes, 2000, p. 139; Fuentes, 1980, p. 2; Herrera, 1883, pp. 446-449; Phillips, 1990, p. 89.
[34] Fuentes, 1980, p. 9; Wallerstein, 2011, pp. 150-151.

owing to the drop in profits for the yearly transatlantic runs, the Spanish fleets started to cross the Atlantic more sporadically [35].

For contemporary researchers, this period is rather problematic, not only because of the smaller amount of official commerce, but also because the high rates of smuggling implied unregistered trade. Therefore, the amount of archival resources available today is very small or even completely absent [36].

Morineau reports the arrival of c. 7 200 *arrobas* of cochineal to Seville in 1621 [37] and, for the following year, 6 325 *arrobas* to Cádiz. In 1623, one of the American shipments reaching Seville carried a total of 3 714 *arrobas*, while c. 1 655 *arrobas* (wild variety) was ascribed for 1624. Morineau also accounts for other arrivals in the same year, although the volume of the shipments is not specified. In fact, the author states that in this year cochineal only represented 3.7% of the total of shipments. The last record of cochineal is given for 1633, with c. 4 872 *arrobas* [38]. In the forthcoming years, Morineau is only able to give remittances for indigo and dyewoods, among other products.

Chaunu & Chaunu do not give volumes for the years after 1620, perhaps because they are not sufficiently complete to draw secure estimates. However, they provide relative prices: in 1621, one *arroba* of cochineal was estimated in Seville at 110 *pesos*, while two years later this value dropped to 81 *pesos*. An increase to 125 *pesos* was brought in 1624, remaining the same in the following year. In 1627 the price rose again to 132 *pesos* and, in 1633, suffered a small drop to 129 *pesos*. In 1636 and 1637, it dropped again to 110 *pesos,* and in 1648, to 100 *pesos* [39]. These prices can give an idea of which years cochineal was shipped in more or less abundance to Europe, since they can be directly connected to the

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[35] Wallerstein, 2011, pp. 16-17, 106, 149-150 and 276. See also Davis, 1973, p. 161; Phillips, 1990, pp. 83-88.

[36] McAlister (1984, p. 375): "It is impossible to calculate, even roughly, the volume and value of trade conducted outside the bounds of the Spanish mercantile regime. In the Indies, Spanish defrauders kept no public books of their transactions, and the records of foreign contrabandists are widely scattered in public and private archives. It maybe guessed that by mid-seventeenth century smuggling accounted for better than half of the commerce of the Spanish Caribbean". Morineau (1985, p. 219) adds: *l'enregistrement des trésors américains par les autorités espagnoles se dégrada sérieusement dans la première moitié du XVII^{e} siècle* ["the registration of American treasures by the Spanish authorities are seriously deteriorated in the first half of the 17th century"]. See also Fuentes, 1980, p. 5; Marichal, 2014, p. 204.

[37] Morineau, 1969, p. 165. Here, the amount of cochineal was given in *rubbi*, a measure of weight used in the centre of Italy and which varied from city to city. For comparison meanings, it was considered the *rubbo* of Genova, which was equivalent to c. 0.7 *arrobas*.

[38] Morineau, 1969, pp. 164-172 and 185-186; 1985, p. 67. For 1624, the 1 655 *arrobas* of wild cochineal were estimated in 3.1 *pesos* per *arroba*, whereas *grana fina* received was so small that it was not even quantified.

[39] Chaunu & Chaunu, 1956, VI_2, pp. 1050-1051.

product's availability. Moreover, since these prices are somewhat lower than those registered in the first decades of the century (Fig. 4.1), it is possible to assume that 1) Europe was receiving higher amounts than those reported by Morineau; and 2) prices practiced in Seville were possibly lowered to keep up competition with unofficial trade, which prices were exempt of Spanish duties [40].

Besides contraband, pirates and privateering during war had an important influence for the influx of cochineal into Europe. Only between 1623 and 1625, about eighty Dutch ships were sent to the Americas to attack the *Carrera das Indias* fleets [41]. Also, a Dutch document dated to 1628 gives a list of several American products that were captured by Dutch privateers when Spanish fleets were heading to Seville. This includes a significant amount of cochineal-dyed textiles, 242 boxes (c. 1 162 *arrobas*), 364 lumps, along with packs and chests of cochineal [42]. It is worthwhile noticing that neither Chaunu & Chaunu nor Morineau found records of cochineal in Seville's documentation for this year. Further in the century, in a letter addressed from Jamaica in 1679, cochineal is mentioned among the English capture of Spanish goods, which were later sent to England [43].

At this time, political efforts in Spain were undertaken to recover the economy, and American exports increased again; although most of these exports were made by European merchants, rather than by Spanish. Official remittances of cochineal arriving to Spain were even lesser than in the first half of the century, which might be explained by a continued option for contraband [44]. Although Morineau mentions one official shipment of cochineal arriving in Spain in 1658-1659 (no volume specified) [45], Fuentes gives several, but meagre, records for the years between 1650 and 1697 (Appendix 1, Table 1). About these records, the author states: *Sin embargo es realmente sorprendente la caída de las importaciones de grana en la segunda mitad del siglo XVII: en cincuenta años no hemos podido contabilizar*

[40] In the 1610's, cochineal was worth 60 times more than an equivalent weight of sugar and, in the 1630's, it was only worth 30 times that value (Marichal, 2014, p. 204).
[41] Lee, 1951, p. 213.
[42] Morineau, 1969, p. 175. The boxes would correspond to c. 4.8 *arrobas* each (1969, p. 336). The packs may correspond to the American *zurrónes,* while the lumps might have been the *pane* or *macno,* which were compact cakes of cochineal, usually the wild variety mixed with alum and other herbs (Donkin, 1977b, pp. 33 and 35; Roquero, 2006, p. 139). However, Roquero (2006, p. 139) and Jordán (1963, p. 14) assume that these cakes were made for local consumption in Latin America, rather than for the international trade.
[43] Sainsbury & Fortescue, 1896, 18th Oct. Jamaica [1150].
[44] Phillips, 1990, pp. 91 and 94.
[45] Morineau, 1969, pp. 206-207.

más que 649 arrobas. Cantidad realmente insignificante si la comparamos con las importaciones de los años 1619 y 1620, fechas en las que se importan respectivamente 8 306 y 7 160 arrobas [46].

By the end of the 17th century, cochineal was no longer part of the Spanish commerce. Although the heavy taxations in Spain were the principal reason to curtail commerce [47], low wages and harsh labour conditions imposed on the indigenous producers in Mexico may have had a crucial impact as well [48]. Regardless of the absence of great volumes and prices, it is still possible to identify cochineal as an important trade item in this period. The fact that the Spanish Crown set its taxes even higher to help subsidizing war campaigns is already a very good example. However, this becomes even clearer when considering the European trade of cochineal outside Spain, as shall be discussed later in this work. In Spain, cochineal eventually found its way back again into the markets of Cádiz during the 18th century, when economic reforms started to be implemented by the government to encourage the production of the American dyestuff, as well as maintenance of a constant transatlantic flow.

4.3. Period of Reforms

The end of the 17th century was marked by the commencement of a new political conjuncture, which was characterized by various attempts to establish reforms and

[46] ["Yet it is really surprising the drop in imports of cochineal in the second half of the 17th century: in fifty years we could not count more than 649 *arrobas*. Really insignificant amount when compared to the imports from the years 1619 and 1620, dates in which 8 306 and 7 160 *arrobas* are imported, respectively"]. Fuentes, 1980, p. 336.

[47] Fuentes (1980, p. 336) concludes that *según el Consejo de Indias (que recoge el sentir del Consulado de Comercio de Sevilla) se dejó de importar como consecuencia de la firme oposición de los comerciantes sevillanos al establecimiento de la renta de la grana, medida antipopular, que provocaría la perdida de la renta "por no haberse traído ninguna /grana/ en los años siguientes" a su establecimiento* ["according to the Council of Indies (which represents the decisions of the Consulate of Commerce of Seville) the import of *[cochineal]* was ceased because of the strong opposition of Seville's merchants to the application of a cochineal tax, loathed measure, which would be lost "for not having brought none / cochineal / in subsequent years" to their property"].

[48] Jordán, 1963, pp. 17 and 92: *Un buen día los indios se cansaron y de común acuerdo destruyeron sus plantíos; esto sucedió en la segunda mitad del siglo XVII* […] *en Otumba, Cholula, Tepeaca, Guejocingo* [Huejotzingo] *y Tlaxcala, en donde despedazaron y quemaron las nopaleras por no ser esclavos de la codicia de los alcaldes mayores ni colectarla para éstos a corto precio* ["One day the Indians got tired and agreed to destroy their plantations *[of cochineal]*; this happened in the second half of the 17th century *[…]* in Otumba, Cholula, Tepeaca, Guejocingo *[Huejotzingo]* and Tlaxcala, where they tore and burned cactus because they were not slaves of the greed of the *alcaldes mayores [Crown officials]* and neither collect it for these at short price"]. See also Coll-Hurtado, 1998, p. 74.

economic impulses in the Spanish Empire. Consequently, this would have a direct impact on the volume of trade and the price of cochineal throughout the 18th century.

In this context, the *Casa de Contratación* transferred the official fleet system from Seville to Cádiz in 1680, and then in 1717, its headquarters. This institution was no longer useful in Seville as most of the trade had been practiced in Cádiz for many years already. With Cádiz directly facing the sea, the large vessels of the *Carrera de Indias* could easily unload their shipments there. Access to Seville was hindered by the small dimensions of the river Guadalquivir, which is why the merchandise needed to be first unloaded in San Lúcar and then transported up the river in smaller vessels, or by land with mules [49].

With the new reforms, regulations were also created throughout the century to reduce smuggling and pirate raids. After 1769, several prohibitions that once served the monopolistic purposes of the Spanish trade were lifted, leading to a decrease of contraband and the progressive flourishing of free trade between the Americas, other Spanish ports and the international markets in general. Free trade would progressively replace the *Carrera de Indias* fleets system, which would be discontinued in 1789, while the *Casa de Contratación* would close in the following year [50]. Even so, Cádiz kept representing the main Spanish port for American commerce [51].

On the other side of the Atlantic, the reorganization of local American businesses aimed to reinforce the *repartimiento* system, and thus, raise cochineal production to respond international demand [52]. In spite of a lack of records for the first years of the century, which were characterized by the War of Spanish Succession (1701-1713), Fig. 4.2 shows that volumes exported to Spain follow a steady increase until the end of the 1730s, if fluctuations are not considered. Interestingly, the year in which these registries begin coincides with the year in which the *Casa de Contratación* is moved to Cádiz. By the end of

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[49] Girard, 2006, pp. 68-93; Phillips, 1990, p. 90.
[50] Fisher, 1985, p. 36; Mazín, 2007, pp. 31-33; Parry, 1990, pp. 281-285; Phillips, 1990, pp. 95-96.
[51] Baskes, 2000, pp. 154-155; Burkholder & Johnson, 1998, p. 257; Chapman, 1933, p. 207; Fisher, 1985, p. 49; Garavaglia & Marchena, 2005, II, p. 308; Mazín, 2007, p. 114; Parry, 1990, pp. 316-317; Phillips, 1990, p. 98.
[52] Baskes, 2005, p. 193; Jordán, 1963, p. 20. González (1976, II, p. 339) affirms that *el nivel bruto de las importaciones* [to Seville] *sufre un incremento espectacular en la segunda mitad del siglo XVIII que puede cifrarse en los porcentajes de aumentos: productos tintóreos aumentaron en un 344%, el tabaco en un 91%, el cacao en 626%, el azúcar en un 2 401%, el cobre en un 2 609% y los productos medicinales en un 402%* ["the gross level of imports *[to Seville]* suffers a dramatic increase in the second half of the 18th century that can be estimated at increasing percentages: dyestuffs increased by 344%, tobacco by 91%, cocoa in 626%, sugar in 2 401%, copper in 2 609% and medicinal products in 402%."].

the 1730's, figures are interrupted for almost a decade, which is connected with a war period that affected transatlantic trade, but made possible for European ships to trade directly with the Americas [53]. Nonetheless, between 1740 and 1745, c. 84 843 *arrobas* of cochineal were brought to Cádiz, making an average of c. 14 140 *arrobas* per year [54]. In 1722, cochineal was worth 100 *pesos* in producing regions of Mexico, but given a rise in production, this price was lowered to c. 44-50 *pesos* per *arroba* by 1740-1742 - a price which was 1.5 times cheaper than that registered in Cádiz at this time. In 1771, each *arroba* in Vera Cruz was around 100 *pesos*, a more close value to that registered in Cádiz (Fig. 4.4). This demonstrates that, between Mexico and Cádiz, the value of cochineal could increase substantially in some years, depending on taxations, tariffs or insurances imposed to its export and transport (especially in times of war) [55].

Cochineal exports increased practically ten times throughout the 18th century, reaching their highest point in 1775 (Fig. 4.2). In Fig. 4.4, it is evident that cochineal prices became two times cheaper than those registered at the beginning of the 17th century, when prohibitive taxes were practiced in Spain. However, prices and volumes of trade are never exempt of fluctuations. Indeed, during the Seven Years' War (1754-1763), the constant interruption of the transatlantic communications led to a decrease in cochineal prices in Mexico and an increase of prices in Europe, especially after the English captured Havana (1762), a key port for trade with Spain. When peace returned in 1763, prices moved upwards again, as trade in the Atlantic re-opened. Similarly, as Atlantic wars with the English resumed once more between 1779 and 1783, and between 1796 and 1805, transatlantic Spanish exports were interrupted again or assaulted by the English, thus bringing a negative impact on its production and trade [56]. After this, the last quarter of the century and the first decades of the 19th century would bring a downward trend in the trade of Mexican cochineal.

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[53] Vasco (1963, p. 47) mentions that *en la ciudad de Antequera* [Oaxaca] *no había caudales a causa de estar cerrado el comercio con Europa por las guerras que en ella había* ["in the city of Antequera *[Oaxaca]* there was no flow *[of cochineal]* because trade with Europe was closed by the wars there"]. See also Phillips, 1990, p. 96.
[54] Morineau (1985, p. 375) refers to 9 427 *zurróns* of cochineal.
[55] Ducasse, 1978, p. 31; Hamnett, 1971a, p. 30; Magán 1963, p. 74; Vasco, 1963, p. 47.
[56] Baskes, 2000, p. 139, 2013, pp. 148-150 and 159-161; Fisher, 1985, p. 63; Hamnett, 1971b, p. 30; Magán, 1963, p. 74; Marichal, 2014, pp. 210 and 213; Vasco, 1963, p. 47. See also Gay, 1890, pp. 362-363; Jordán, 1963, p. 28; Lee, 1951, p. 220.

4.4. Period of Decline

In the last decades of the 18th century, a series of events led to the gradual decline of cochineal production in Mexico. First, there were military conflicts between Spain and England, bringing the consequent blockade of transatlantic connections, between 1779 and 1783. In the same decade, a local crisis started to grow among the Mexican populations. This would bring crucial consequences to the local production and the export of cochineal.

After the abolishment of the *repartimiento* system in 1786, the creation of the System of Intendancies was not well accepted among the Mexican authorities. By ending the royal monopoly regime of production that allowed the control of indigenous people, the System of Intendancies came to interfere with the social organization that had been settled far back to the beginning of the 16th century [57]. As a result, indigenous people progressively abandoned cochineal to dedicate freely to other local industries. This was especially verified after a devastating crisis of famine and disease that overwhelmed Mexico between 1779-1780 and 1785-1787, bringing a boost to the production of maize and other food crops. Meanwhile, Spanish producers of cochineal, who emerged in the cochineal business throughout the century, came to fear attempts by local authorities to apply taxes upon their product, making cochineal a non-profitable enterprise [58]. At the same time, demand in Europe for cochineal dropped and merchants gradually lost interest in the product, since it was no longer profitable [59].

Following these events, the production of cochineal, as well as annual exports, started to drop in the last decades of the century [60]. For this period, the price of cochineal per *arroba* in Cádiz could vary between 80 and 150 *pesos*, depending on war years [61]. Mexican exports kept on slowly declining in the first two decades of the 19th century, not surpassing an average of 20 000 *arrobas* per year. However, prices increased (Fig. 4.4), firstly because of the Napoleonic occupation of Spain between 1808 and 1814, and then because of the wars of independence in Mexico, causing a shortage of cochineal in Veracruz and in

[57] Baskes, 2005, pp. 188 and 205. According to this system, the "subordinate administrators, the local Subdelegates, were expected to maintain themselves from a 5 per cent levy from the Indian tribute income" (Hamnett, 1971a, p. 63). Jordán (1963, pp.28-29) states that, before, such levy was about 50%. See also Coll-Hurtado, 1998, pp. 79-80; Silva & Bosa, 2006, p. 480.
[58] Baskes, 2000, p. 179; Hamnett, 1971b, pp. 59 and 61-62; Marichal, 2014, p. 210.
[59] Baskes, 2000, pp. 180-183.
[60] Hamnett, 1971b, p. 174; Jordán, 1963, appendix 1.
[61] Marichal, 2014, pp. 204.

international markets [62]. Furthermore, it is possible that, given the war in Europe, contraband might have been intensified, while merchant firms in Europe and in Mexico could have cornered the market, thus forcing prices to rise [63].

After 1821, when Mexico was finally freed of Spanish control, the price of cochineal started dropping. This is likely due to the appearance of new centres of cochineal production in other regions around the world, now competing with Oaxaca in international markets [64].

For over three centuries, the Spanish kept secret about the production of cochineal in Mexico, by strictly forbidding the export of living insects from that region and by closely controlling the visits of foreigners in Mexico. This might be the origin of the common belief that American cochineal was a dried berry. Although some sources of the 16th and 17th centuries were very accurate in describing the American insect [65], such belief endured practically until the 19th century [66]. In this way, the Spanish kept a safe monopoly, since other nations were not aware of the dyestuff's true source and were not able to properly search for it in other American regions [67].

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[62] Baskes, 2000, pp. 142-143; Marichal, 2014, pp. 211 and 213; McCulloch, 1835, p. 301. These events are particularly observed for 1814, when the average price of cochineal was c. 320 *pesos* per *arroba*.

[63] Baskes, 2000, p. 142; Marichal, 2014, pp. 211 and 213.

[64] Marichal, 2001, p. 24, 2014, pp. 211 and 213; Silva & Bosa, 2006, pp. 482-483.

[65] Sahagún (1963, p. 239): "This cochineal is an insect; it is a worm. The cochineal *nopal* is the breeding place of this cochineal. It lives, it hatches on the nopal like a little fly, a little insect."; and Camargo (1998, p. 287): *la grana cochinilla, la cual es cosa viva, a manera del gusano de la seda* ["cochineal, which is a living thing, like the silkworm"]. See also Donkin, 1977b, pp. 44-45; Jordán, 1963, p. 11; Laet, 1988, p. 123; Rivadeneyra, 1988, p. 204.

[66] Ramírez (1831a, pp. 247-248): *Los estrangeros que han escrito sobre grana no merecen aprecio, son unos mutuos copistas, que engañan á muchos de sus lectores, porque se hallan en sus libros* […] *informe de algunos que han vivido en Oajaca* ["The foreigners who have written about cochineal do not deserve appreciation, they are mutual copyists, who deceive many readers, because their books mention the voices *[…]* of who received report of some that lived in Oaxaca"]; Juan & Ulloa (1748, p. 444): *La Grana, ò Cochinilla huvo tiempo, en que ſe* creyó *ſer Fruto, ò Semilla de ciertos Arboles, ò Plantas; originandoſe acaſo eſta opinion de la confuſa idèa de criarſe en ellos, y de carecerſe de todas las luces, tocantes al modo de ſu propagación* ["Cochineal had a time when it was believed to be a Fruit, or Seed of certain Trees, or Plants; this opinión was occasionally originated by the confusing idea of its breeding on them, and by missing all explanations in respect to which propagation"]*;* and Champlain (1859, p. 25), who lived in Mexico between 1599 and 1602: "*[cochineal]* grows in the fields as peas do elsewhere. It comes from a fruit the size of a walnut which is full of seed within". See also Beckmann, 1846, pp. 397-399; Brunello, 1973, p. 199; Donkin, 1977b, pp. 44-45 and 52; Hakluyt, 1904, IX, pp. 358 and 360; Jordán, 1963, p. 11; Lee, 1948, p. 451, 1951, pp. 217-218; Leggett, 1944, pp. 86-88; Pomet, 1748, pp. 16 and 19; Ramírez, 1831a, pp. 247-249; Ulloa, 2010, p. 96.

[67] Champlain, 1859, pp. 25-26; Lee, 1951, p. 217.

By the 18th century, empirical knowledge on the insect was more developed [68]. Several foreigners attempted to smuggle the American insect outside the Spanish colonies to breed it in several regions around the world. Species of *Dactylopius* and host cactuses were brought from Latin America to be reared in British India, Dutch Indonesia, the French Caribbean or Algeria [69]. The most famous story is the one from the French botanist Thierry de Menonville who, in 1777, sought to smuggle cochineal from Mexico to Haiti to propagate it for export. Unfortunately, soon after his successful endeavour, he died of sickness and his cochineal culture was abandoned [70].

In the meantime, several attempts had been undertaken to produce cochineal in Brazil. The Portuguese Crown and the Brazilian authorities encouraged the research and publication of scientific works about this dyestuff's rearing and preparation. Since 1782, the Brazilian culture of wild cochineal was particularly successful in the region of Santa Catarina. Though, due to a lack of funding and technical knowledge on how to rear and prepare the insects, the Brazilians eventually abandoned the business. Anyhow, it is worthwhile mentioning that, inspired by Menonville, the Portuguese also sent an envoy to the Spanish Americas in 1798, which was supposed to collect information and live insects to be bred in Brazil [71].

Guatemala, Nicaragua, Salvador or Peru also started to dedicate themselves to rearing of *grana fina*, achieving successful results and becoming important export centres in the first half of the 19th century. These would only find competition with the Canary Islands, where the Spanish encouraged the development of the industry [72]. Despite international competition and the inherent drop of prices, Mexicans kept on with their production for decades [73]. However, from 1856, chemical industries in Germany developed more pure and cheaper sources of red dye, the first synthetic red aniline dyes. This was the start of the gradual revolution of dye industries, leading to the replacement of natural dyes by synthetic

[68] Donkin, 1977b, p. 45; Kellman, 2010, p. 373; Leeuwenhoek, 1996, pp. 321-353; Réaumur, 1737, pp. 114-116 and 127-135.
[69] Anderson, 1791, pp. 3-4, 12, 18-19, 47, 49-50 and 52; Balfour, 1885, p. 757; Cardon, 2007, p. 631; Donkin, 1977b, pp. 46-50; Heers, 1961, pp. 16-17; Itier, 1848, pp. 339–342; Lee, 1951, p. 218; McCulloch, 1835, p. 301; Phipps, 2010, p. 41; Verhecken & Wouters, 1988, p. 210.
[70] Menonville, 1812, pp. 753-876. See also Edelstein, 1958, pp. 67-74; Marichal, 2014, pp. 212-213.
[71] Ferraz, 2007, pp. 1034-1035; Reis, 2014, pp. 45-49; Zaroski, 2013, pp. 330-337 and 342.
[72] Cardon, 2007, p. 631; Carvajal, 1812, pp. 23-24; Donkin, 1977b, pp. 30-31; Dunlop, 1847, pp. 123-146; Jordán, 1963, p. 10; Marichal, 2001, pp. 23-24, 2014, pp. 211 and 213; Silva & Bosa, 2006, pp. 483 and 485.
[73] Marichal, 2014, pp. 211 and 213; McCulloch, 1835, p. 301.

ones. Eventually, cochineal, once one of the most important and lucrative products traded worldwide, was withdrawn to a secondary plain. Today, it enjoys a revival, and is being produced to be used as a colorant in the food and cosmetic industries [74].

Conclusions. Since its first shipments from the Americas after the 1520's, cochineal achieved wide international popularity within decades. The analysis of published relative annual volumes for this American product has shown that, by the end of the 16th century, its production in Mexico increased as much as seven times to respond the demand of European merchants based in Seville. In the middle of the 18th century, this ratio was even higher, with production almost reaching a fourfold in relation to the 16th century.

The high value of cochineal made it a very profitable commodity during practically the entire colonial era, because the Spanish kept its production restricted to Mexico, as well as the monopoly of its trade. Therefore, as its popularity grew, so did its price, especially after the Spanish Crown increased taxations over its trade at the beginning of the 17th century, to help subsidize its international conflicts.

This brought a very important change to the patterns of transatlantic trade for the American dyestuff, during the rest of the century. Indeed, merchants soon started smuggling cochineal into the European markets to avoid the heavy tariffs imposed in Seville. Also, warfare with other European nations frequently led to privateering assaults (supported by home governments) on the Spanish mercantile fleets crossing the Atlantic. Hence, despite the fact that cochineal was not registered in Seville for many years during the 17th century, as noted by several contemporary studies, it is possible to presume that it was still entering Europe and Asia, as shall be demonstrated later in this work.

Although military conflicts and contraband were particularly crucial for the Spanish trade of cochineal in the 17th century, they were also a constant for the most part of the colonial period. These, among other factors connected to production and trade, are fundamental for understanding the historical context of the annual commercial trends verified for the published relative volumes and prices of cochineal examined here. On the one hand, during times of war, there was often a shortage of cochineal available in the

[74] Cardon, 2007, p. 631; Hofenk de Graaff, 2004, pp. 12-13; Jordán, 1963, p. 10; Marichal, 2001, p. 24.

markets of Seville, due to a blockade of communications between Spain and the Americas. As a result, and depending on the demand for this product, the prices would sharply rise. On the other hand, abundant availability of the product in European markets, especially in years of peace or intense contraband, would increase competition, thus lowering prices. This shows that there is a clear relationship between availability, demand and prices in the transatlantic commerce of American cochineal.

This relationship is very important to assess the historical importance of this dyestuff, but it is not complete without considering it in a broader context. Indeed, a wider picture of the Iberian commerce, which takes into consideration the export of other significant American dyestuffs such as indigo, brazilwood and logwood, in comparison to cochineal, can offer additional support for the importance of the American red dyestuff in transatlantic trade.

CHAPTER 5

COCHINEAL AND OTHER AMERICAN DYESTUFFS:

A Comparative Perspective

"Cochineal was distinguished from the other *[American]* dyes
because of its greater (and more specialized)
demand and higher prices." Carlos Marichal [1]

Besides cochineal, other noteworthy American dyestuffs, namely indigo, brazilwood and logwood, were part of the maritime routes crossing the Atlantic towards Spain and Portugal, during the colonial period. A historical contextualization of these dyestuffs can lead to interpretations regarding their transatlantic trade; their impact on long-established European and Asian dyeing traditions; and how they competed with local dye sources. Furthermore, by comparing these dyestuffs with cochineal, it is possible to achieve a wider historical perspective of the transatlantic patterns of trade in American dyestuffs, as well as enhance the importance of cochineal in Atlantic communications.

Bearing this in mind, comparisons between American dyestuffs are considered here not only in terms of their relative volumes and value in the Iberian shipments coming from the Americas, but also their dye applications, quality and availability in Europe and in Asia.

With regard to their dye applications, and depending on the materials to be dyed and the desired final colour, the percentage of brazilwood (per weight of fabric) required to dye one piece of cloth can vary between 17 and 33%; logwood, 15 to 100%; indigo, 3 to 30 % or, for an intense dark blue, c. 83%; and American cochineal, only 0.5 to 7%. This means that, for example, to dye a fabric with a brilliant and deep shade of red, large amounts of brazilwood are necessary, in relation to much smaller quantities of cochineal [2]. Apart from its colorant yield, cochineal is also of better quality than brazilwood, as it has improved fastness properties.

[1] Marichal, 2014, p. 205.
[2] Cardon, 2007, pp. 283-285, 269-272, 347-352 and 652-628.

In terms of availability, and excluding other wild insect species, American cochineal was only available in specific regions of Mexico all through the colonial period. The other dyestuffs, however, were generally exploited in several American and Asian regions, thus displaying a higher availability and lower prices. Adding to the fact that cochineal required special expertise in terms of production, preparation and dyeing procedures, this dyestuff was, at all times, more valuable than the other American dyes, as demonstrated below.

Consequently, a comparison between published relative volumes and prices for these dyestuffs in the transatlantic commerce is undertaken, in order to establish their relative importance during the Early Modern period.

5.1. Indigo

This is a blue dyestuff prepared from several species of plants belonging to the *Indigofera* genus that grow in tropical and subtropical regions of Africa, Asia, the Americas and Australia. From these, the most popular is the *Indigofera tinctoria* L., which is possibly native to India and it was gradually introduced to several parts of the world in the course of the centuries [3]. Other *Indigofera* species were used as well for dyeing practices: the *I. arrecta* Hochst. ex. A. Rich, the *I. articulata* Gouan or the *I. coerulea* Roxb., abundant in Africa and later introduced into Asian territories, such as India and Indonesia; or the *I. suffruticosa* Miller and the *I. micheliana* Rose endemic to Central and South America [4].

This dyestuff was probably used in India since at least the 1st millennium BCE. Knowledge of its manufacture and consumption may have spread to other Asian regions by way of the Silk Road, and small amounts of it were reaching Europe possibly by the 2nd century BCE [5]; although woad (*Isatis tinctoria* L.) was the main source of blue in European dye workshops well until the 16th century. This was a crop commodity mainly grown in the Low Countries, Italy, France, England, Germany and other parts of Europe. Indigo, however, was an Asian product imported to Europe and, until the end of the Medieval era, it was

[3] Alden, 1965, pp. 36-37; Balfour-Paul, 1998, p. 91; Bender, 1947, p. 3; Cardon, 2007, pp. 353-355; Hofenk de Graaff, 2004, p. 253; Smith, 1959, p. 181.
[4] Balfour-Paul, 1998, pp. 91-92; Böhmer & Enez, 2002, p. 223; Cardon, 2007, pp. 355-357; Roquero, 2006, pp. 151–152.
[5] Balfour-Paul, 1998, p. 18; Bender, 1947, p. 3; Brunello, 1973, p. 144; Cardon, 2007, pp. 362-363; Hofenk de Graaff, 2004, p. 253; Roquero, 2006, p. 155.

considered a luxury item, suitable for paints, cosmetics, medicines and other small applications [6]. Both dyes were often associated with wealth and prestige by Europeans and Asians alike, given the range of blues and fast colours achieved with them [7].

In France and Germany, where woad was one of the major sources of wealth, indigo was met from the start with strong resistance [8]. However, in late medieval Italy and Spain, the long-standing connections with the Islamic world enabled the entry of increasing amounts of indigo brought from North Africa and Asia. There, this dyestuff was eventually integrated into local dyeing practices alongside with woad, which was produced locally or imported from France and Germany [9].

During and after the 16th century, with the establishment of maritime trade routes around Africa, the Portuguese and later the English and the Dutch, started importing into Europe abundant amounts of indigo from India, Iran and Indonesia. On the other side of the Atlantic, the Spanish too started to produce the blue dyestuff to respond to European demand. Hence, while production was amplified in Asia and the Americas, more and more indigo became gradually available in Europe, and consequently, its price became more accessible to European dyers, who soon realized that it was more economical than woad, as it had a higher dye content [10].

However, due to the influence of European woad producers and the initial lack of expertise on how to use indigo, this was prohibited in some parts of Europe, and throughout the entire 16th century, under the belief that it would ruin woollen fabrics. Even so, by the

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[6] According to Balfour-Paul (1998, p. 23), "Romans used native woad for blue dyeing, for with imported indigo pigment at twenty *denarii* a pound, around fifteen times the average daily wage, the several pounds required for a dye vat would have been prohibitive". In the 13th century, indigo was still considered a luxury dyestuff, suitable to paint medieval works of art. It was marketed in the ports of Venice, Genoa, Bologna, Marseilles and London. Alden, 1965, p. 37; Bensi, 2009, pp. 37 and 41; Balfour-Paul, 1998, p. 27; Brunello, 1973, p. 144; Cardon, 2007, p. 364; Hofenk de Graaff, 2004, pp. 245 and 325; Kirby, 2010, p. 342; Roquero, 2006, p. 156; Spufford, 2010, p. 10.

[7] Cardon, 2007, p. 335.

[8] Balfour-Paul, 1998, pp. 33-35; Böhmer & Enez, 2002, p. 225; Brunello, 1973, p. 145; Cardon, 2007, p. 363; Heers, 1961, p. 5; Hofenk de Graaff, 2004, pp. 240 and 245; Wescher, 1939, pp. 624-625.

[9] Alden, 1965, p. 37; Balfour-Paul, 1998, p. 28; Brunello, 1973, pp. 145 and 189-190; Spufford, 2010, pp. 10-11.

[10] Leix (1937b, p. 21): "The great advantage of indigo over the native woad consists in a concentration of pigment equal to ten times that of its rival". Also, Lee (1951, p. 221): "Four pounds of indigo (costing an average of 5 s. per pound) and 133 pounds of woad (costing £2 10s. per hundredweight *[or 2 s. per pound]*) were required for *[dyeing a deep blue wool fabric]*" in the English dyeing industries, from the beginning of the 17th century. See also Alden, 1965, pp. 37-39; Balfour-Paul, 1998, pp. 41, 44, 50-51 and 156; Brunello, 1973, p. 196; Cardon, 2007, p. 364; Gillespie, 1920, p. 132; Hofenk de Graaff, 2004, p. 253; Roquero, 2006, p. 156; Sanz, 1979, p. 588.

end of the century, imported recipes from Istanbul were being applied in Venetian and Genoese workshops to dye clothes with American indigo [11]. In the rest of Europe, woad producing countries attempted to protect their industry, by establishing strict regulations and forbidding the import of indigo. Regardless, the foreign dyestuff continued to flow into European dye workshops, while demand for woad progressively declined and, eventually, its production as well [12].

In the Americas, indigo had been long used by the indigenous populations, before the Spanish caught interest in it. From 1558, they started to encourage its production and furthermore introduced and naturalized Asian indigo species. While in Asia indigo production was controlled by coerced locals, in the Americas production relied on imported African slaves and American indigenous people, who submitted the plants to a laborious process to extract and prepare the dyestuff. Throughout the colonial period, indigo was produced in the Pacific coast of Guatemala, Honduras, Nicaragua, Mexico (Yucatán, Michoacán and Chiapas), Caribbean, El Salvador, Ecuador, Venezuela, Panama and Peru [13]. From all these regions, Guatemala was the primary producing region. Its indigo, known as *flor* (*I. suffruticosa*) was one of the most valuable products exported from Central America [14].

American indigo exports started in the early 1570s, mainly from Mexico, Honduras and Guatemala [15]. By this time, American cochineal already had a significant role in the transatlantic trade, for at least two decades. In spite of inherent annual fluctuations, average

[11] Hofenk de Graaff, 2004, p. 329; Molà, 2000, p. 130.

[12] In Languedoc (France), woad producers had enough political strength to influence the ban of indigo imports in 1598. Only by 1737, when its advantages were well known, indigo was officially allowed in French dye workshops. In Germany, the import of indigo (known there as "devil's eye") was forbidden since 1577. In England, by 1581, indigo was solely allowed in woad vats to obtain black colours. Though, a complete ban was soon applied and it endured well until 1660. As for the north of the Low Countries, prohibitions started in 1587, but by 1615 indigo was generally accepted. See Abrantes, 1888, p. 46; Alden, 1965, pp. 38 and 42; Balfour-Paul, 1998, pp. 27 and 55-57; Bender, 1947, p. 3; Böhmer & Enez, 2002, p. 225; Brunello, 1973, pp. 145, 189-190 and 196-197; Cardon, 2007, p. 365; Gillespie, 1920, p. 132; Heers, 1961, p. 5; Hofenk de Graaff, 2004, pp. 240, 245-246, 253 and 329; Leix, 1937a, p. 15, 1937b, p. 20; Pieper, 1998, p. 379; Sanz, 1979, p. 596.

[13] Several attempts were initially undertaken to naturalize woad in Central America, although they were unsuccessful. Abrantes, 1888, p. 46; Alden, 1965, pp. 39-40; Balfour-Paul, 1998, pp. 63 and 54; Brunello, 1973, p. 196; Cardon, 2007, pp. 355-356 and 364; Fuentes, 1980, p. 332; Heers, 1961, p. 4; Hofenk de Graaff, 2004, p. 253; Roquero, 2006, pp. 151-155; Sanz, 1979, pp. 588-589 and 592-593; Smith, 1959, pp. 181-182. For a detailed description of the process of indigo preparation: Alden, 1965, p. 36; Bender, 1947, p. 3; Cardon, 2007, pp. 336 and 341-344; Ramírez, 1831a, pp. 191-202; Roquero, 2006, pp. 157-163; Smith, 1959, pp. 183-184.

[14] Mexico produced lower grades and small amounts of indigo. The bulk shipped in Vera Cruz was mainly from Honduras and Guatemala. Alden, 1965, p. 40; Balfour-Paul, 1998, pp. 63-65; Fuentes, 1980, p. 332; Marichal, 2001, p. 18, 2014, p. 205; Morineau, 1985, p. 393; Sanz, 1979, p. 592; Smith, 1959, pp. 182 and 199-200.

[15] Chaunu & Chaunu, 1956, VI_2, pp. 988-993; Sanz, 1979, p. 591; Smith, 1959, p. 197.

exports of indigo did not surpass the 2 000 *arrobas* per year until the end of the century [16], whereas annual remittances of cochineal rarely went below 4 000 *arrobas* for this period. Moreover, prices for indigo were no higher than 59 *pesos* per *arroba*, whereas cochineal prices generally doubled this [17]. Despite presenting a lower price than cochineal, indigo was still quite valuable: from 1576, it represented 10% of the total annual value of non-metallic American goods arriving in Seville – cochineal represented 41.6% [18].

In the first decades of the 17th century, exports of indigo practically increased as much as ten times, exceeding those of cochineal [19]. Prices, however, did not change substantially in relation to previous years, while prices for cochineal were exceptionally high, due to additional taxes in Seville [20]. This clearly enhanced the value of cochineal over indigo: given the Spanish monopoly on cochineal in Mexico, the Crown opted to levy extra tariffs on it rather than on indigo, since this would find competition with the Asian variety available in other European markets.

By 1643, American indigo exports were reaching c. 50 000 *arrobas* in the markets of Seville, valued at c. 14 *pesos* per *arroba*, a much lower price than that registered at the beginning of the century [21]. This is perhaps due to the increasing availability of the blue dyestuff in European markets (from the Americas and from Asia). For this period, records for the arrival of cochineal in Seville are not available; but, in 1648, it was valued at 100 *pesos* per *arroba* [22], a price about seven times higher than that of indigo.

During the rest of the century, and with few intermittences, annual shipments no higher than 16 500 *arrobas* of indigo kept on being sent to Spain, mainly from Honduras, but also in small amounts from Mexico and the Panama Isthmus [23]. This demonstrates that demand for indigo in Spanish markets continued, whereas cochineal was entering Europe via unofficial routes (contraband, pirate raids or privateering).

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[16] Acosta, 1792, p. 245; Alden, 1965, p. 40; Chaunu & Chaunu, 1956, VIII$_1$, p. 771; Phillips, 1990, p. 79; Roquero, 2006, p. 156; Sanz, 1979, p. 591; Smith, 1959, p. 197.
[17] Chaunu & Chaunu, 1956, VI$_2$, pp. 988-993; Chevalier, 1943, pp. 327-328; Fuentes, 1997, p. 236.
[18] Sanz, 1979, p. 546. Furthermore, when indigo reached its zenith during the colonial period, it could be even exchanged 'pound for pound' for African slaves (Balfour-Paul, 1998, p. 60).
[19] Alden, 1965, p. 40; Chaunu & Chaunu, 1956, VI$_2$, pp. 988-993; Fuentes, 1980, p. 330; Morineau, 1969, p. 336; Smith, 1959, p. 197.
[20] Chaunu & Chaunu, 1956, VI$_2$, pp. 988-983.
[21] This remittance might indicate that indigo was embargoed at American warehouses for several years before sent to Seville. Chaunu & Chaunu, 1956, VI$_2$, pp. 988-983; Fuentes, 1980, p. 330; Smith, 1959, p. 197.
[22] Chaunu & Chaunu, 1956, VI$_2$, pp. 1050-1051.
[23] Fuentes, 1980, pp. 332 and 509-510.

During the 18th century, and as previously observed for cochineal, American production of indigo was intensified, especially in Guatemala [24]. At this time, Guatemalan indigo was considered the best quality indigo produced in the Americas and it was mostly consumed in Spain and Peru, as well as in the Low Countries, Italy and England [25]. Despite the inevitable annual fluctuations, remittances to Spain increased greatly throughout the century, reaching a peak in 1769, with c. 56 479 *arrobas,* and in 1802, with c. 59 223 *arrobas* [26]. Export peaks of cochineal were not far from these, as they reached an annual average of c. 52 576 *arrobas* in 1775. In terms of value, one *arroba* of the blue dyestuff was sensibly valued in c. 50 *pesos* in Cádiz during 1748 [27], while cochineal kept a higher rank, valuing up to two times more.

From the middle of the 17th century, the French and the English too started producing indigo in their recently occupied colonies - the French in Haiti, Guadalupe, Martinique and Louisiana; and the English in Jamaica, Barbados, Montserrat, Georgia, and later, South Carolina. Indigo from these territories, along with that from Brazil and North America, expansively contributed to respond to the demand of worldwide markets [28]. At this time, American indigo was so popular that it was even re-shipped from Europe to West Asia, where it was used along with the Asian variety in local dye workshops [29].

As Guatemala and Honduras continued to be major Spanish producers during the course of the 18th century, Louisiana reached an average output of 22 000 *arrobas* per year in the 1790s; the French Caribbean, c. 156 528 *arrobas* in 1771; and Georgia exported more than 2 000 *arrobas* of indigo in peak years [30]. Nevertheless, the English, like the Portuguese, were largely focused on the trade of indigo with Asia during most of the colonial period.

Even so, after the 1640s, when woad production declined in the Azores and much of the monopoly trade with Asia was lost to the English and the Dutch, the Portuguese

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[24] Smith, 1959, p. 198.
[25] Balfour-Paul, 1998, p. 64; Morineau, 1985, p. 393; Pieper, 1998, p. 363; Smith, 1959, p. 199.
[26] González, 1976, II, pp. 222-271; Morineau, 1969, p. 336, 1985, p. 375; Smith, 1959, pp. 197 and 199.
[27] Morineau, 1985, pp. 495-496; Raynal, 1783, III, p. 349, IV, p. 78.
[28] Alden (1965, p. 40): "only the French colony of Saint Domingue *[Haiti]* exceeded Guatemala in the quality and volume of indigo that it produced". Alden, 1965, pp. 41-45; Balfour-Paul, 1998, pp. 66-69; Cardon, 2007, pp. 365-366; Hofenk de Graaff, 2004, p. 253; Pieper, 1998, p. 363-364 and 371; Roquero, 2006, p. 156.
[29] Balfour-Paul, 1998, p. 52; Pieper, 1998, p. 365; Roquero, 2006, p. 156.
[30] Prolific plantations of indigo particularly increased in Haiti from the second half of the 18th century and until the end of the colonial epoch. Balfour-Paul, 1998, pp. 68-69; Cardon, 2007, p. 635; Pieper, 1998, p. 364; Roquero, 2006, p. 156.

attempted to produce indigo in Brazil [31]. However, it was only from the second half of the 18th century that exploitation was truly stimulated for home and international demand [32]. From Rio de Janeiro, but also from the regions of Pará and Bahia, c. 5 800 *arrobas* of indigo were sent to Lisbon in 1779, while this value practically doubled in 1796. Along with indigo brought from Asia, the Brazilian dyestuff was either used locally or re-exported to other European regions, where it was held in high demand, especially because of the interruption of transatlantic communications with their own colonies, due to international conflicts, such as the Napoleonic wars [33]. Even so, it is worthwhile noticing that despite the frequent blockades of its transatlantic shipments, Spain was still receiving cochineal and indigo from the Americas at this time.

At the beginning of the 19th century, indigo production in Brazil drastically decreased. This was due to the cumulative debt of the Portuguese Crown to Brazilian producers; the high speculation of indigo prices; the availability of better grades of dyestuff (from Asia and other American regions) in international markets after the Napoleonic wars; or the frequent adulteration of the product to increase its weight and prices. Therefore, given the high risk of this crop, Brazilian producers turned to more profitable industries [34].

Meanwhile, England was fostering a revival of indigo production in India, especially in Bengal, while American territories started fighting for independence. As Asian indigo became progressively available in international markets, the price for the dyestuff dropped and, consequently, its production in Guatemala, Honduras and other Spanish colonies [35]. The Asian dyestuff, along with woad, kept on being used in the dye vats of many European centres of textile production, until they were replaced by synthetic indigo and the anilines, developed in the 19th century [36].

[31] Alden, 1965, p. 46; Balfour-Paul, 1998, p. 65; Bethell, 1988, p. 122.
[32] At this time, Portugal was mostly importing indigo from Spain to feed its expanding textile industries in the two principal centres of Portalegre and Covilhã. Alden, 1965, pp. 46 and 48; Balfour-Paul, 1998, p. 65; Braga, 2001, pp. 121-122; Bethell, 1988, p. 268; Pesavento, 2006, pp. 3-4; Reis, 2014, pp. 49-50.
[33] Abrantes, 1888, pp. 55-56; Alden, 1965, pp. 53 and 55-56; Balfour-Paul, 1998, p. 65; Pesavento, 2006, pp. 8 and 11-12; Reis, 2014, p. 50.
[34] Abrantes, 1888, pp. 48-49 and 58-59; Alden, 1965, pp. 54-57; Balfour-Paul, 1998, p. 65; Pesavento, 2006, pp. 12-13 and 17.
[35] Abrantes, 1888, pp. 47-49; Alden, 1965, pp. 575-579; Balfour-Paul, 1998, pp. 65 and 70; Smith, 1959, p. 198.
[36] Leix, 1937b, p. 20; Balfour-Paul, 1998, pp. 38 and 65; Roquero, 2006, p. 156.

Conclusions. In the course of the colonial period, indigo produced in the Spanish Americas followed a somewhat similar path to American cochineal. Incentives for its production started a few decades later than cochineal, but it quickly reached high popularity (especially the *flor* variety from Guatemala), as soon as European dyers recognized its advantages over woad, in the first half of the 17th century. American cochineal too had penetrated into European dye workshops in the second half of the 16th century, after showing clear advantages over the European and the Asian insect dyes, as shall be demonstrated further in this work.

During the 17th century, cochineal was brought to Europe through alternative routes, so that merchants could avoid the heavy taxes charged by the Spanish Crown on its trade. Indigo, in its turn, was annually arriving to Seville, thus indicating a more stable commercial situation than cochineal. In the 18th century, new trade measures and intensification in production of both cochineal and indigo reflected a period of prosperity for the Spanish Empire, which resulted in annual peak exports in the second half of the century.

The price of indigo, however, was always lower than that of the valuable cochineal, particularly because of availability. While the Spanish monopoly on cochineal allowed merchants to keep its cost high at all times, Spanish indigo always faced competition from other indigo varieties produced in Asia and other parts of the Americas that were occupied by the French, English or Portuguese. Availability, along with quality, is the main reason why brazilwood and logwood were also cheaper than cochineal at all times.

5.2. Brazilwood and Logwood

Brazilwood takes its name from the fiery red colours obtained with it, which resemble glowing coals (*brasas*). Species of this dyewood belong to the Leguminosae family and they are endemic to several parts of the globe. The most popular species used in dyeing practices were the *Caesalpinia sappan* L., found in tropical regions of South Asia [37], and the *Caesalpinia echinata* L., grown in tropical parts of the Americas [38].

[37] *C. sappan* is found in central and southern India, Sumatra, Thailand, Malaysia, Burma, southern China and Japan. Barragán, 2013, p. 8; Brunello, 1973, pp. 130-131; Cardon, 2007, pp. 275-276; Hofenk de Graaff, 2004, pp. 142-143; Leggett, 1944, pp. 49-50; Nowik, 2001, p. 129; Roquero, 2006, p. 120; Souza, 1939, pp. 82 and 84.

[38] Also known as *Caesalpinia vesicaria* Vell., *ibirapitanga* or Pernambuco wood. Cardon, 2007, p. 276; Hofenk de Graaff, 2004, p. 143; Simonsen, 1938, pp. 95-96; Souza, 1939, p. 39-40; Varnhagen, 1854, p. 21.

C. sappan was used in Asian dyeing traditions since at least the 2nd century BCE, and it started to be imported into Europe possibly in the 11th century [39]. Throughout the rest of the Medieval period, this dye wood became commonly marketed in the main European medieval ports. However, the brilliant and strong shades of red achieved with brazilwood have low lightfastness properties. Adding to its higher availability, this explains why this dyestuff was cheaper than insect dyes, for instance [40]. Even so, and although brazilwood was tightly regulated and forbidden to be used alone (poor fastness), European dyers used it in mixtures with insect dyes or madder, to dye fabrics with more vivid shades of red [41].

With the Iberian Expansion, the Portuguese and Spanish found a great abundance of the wood in the Americas which was revealed to possess dyeing properties similar to those of the Asian variety. Hence, a year after the expedition of Pedro Álvares Cabral landed in Brazil in 1500, the Portuguese established a royal monopoly for the exploitation of the local dyewood (*C. echinata*) [42]. This native dyewood was quickly welcomed in European dye workshops and demand for it rose in international markets. As a result, Brazil (originally named Terra de Vera Cruz ou da Santa Cruz) was soon baptized after the famous dyestuff [43].

Exploitation was cheap, since it was made by the indigenous people and later by African slaves, wherever the trees were growing: along the coastal region between Cabo Frio, in Rio de Janeiro, and the Cape of São Roque, in the North Rio Grande [44]. The trunks were prepared and cut into logs for being transported to the coast to be shipped to the *Casa*

[39] Brunello, 1973, p. 131; Cardon, 2007, p. 286; Hofenk de Graaff, 2004, p. 142; Nowik, 2001, p. 129; Roquero, 2006, p. 119; Simonsen, 1938, p. 85; Souza, 1939, p. 82.
[40] Brunello, 1973, p. 137; Cardon, 2007, pp. 282-283; Hofenk de Graaff, 2004, p. 142; Jacoby, 2004, p. 211; Leggett, 1944, pp. 49 and 77-78; Roquero, 2006, pp. 119 and 124; Rosetti, 1969, p. XV; Simonsen, 1938, p. 85; Souza, 1939, p. 82.
[41] Adrosko, 1971, p. 25; Brunello, 1973, p. 137; Cardon, 2007, pp. 282-284; Souza, 1939, p. 177.
[42] This royal monopoly initially consisted in the Portuguese Crown renting, for three years, its exploitation and trade to a Portuguese new Christian, D. Fernão de Loronha. Later on, the contract was extended to other private tenants and renewed a couple of times. Abreu, 1907, p. 26; Barragán, 2013, p. 9; Bagú, 1949, p. 66; Cardon, 2007, p. 287; Chaunu, 1984, p. 160; Garavaglia & Marchena, 2005, II, p. 380; Simonsen, 1938, p. 86; Souza, 1939, pp. 103-111.
[43] Abreu, 1907, p. 27; Brunello, 1973, pp. 130 and 198; Cardon, 2007, pp. 275 and 287; Rocha, et al., 2007, pp. 751, 761 and 763; Roquero, 2006, p. 120; Salvador, 1918, p. 15; Simonsen, 1938, p. 85; Souza, 1939, pp. 97-101.
[44] Abreu, 1907, p. 27; Cardon, 2007, p. 276; P. Chaunu, 1984, pp. 158-159; Gândavo, 1576, p. 18; Heers, 1961, p. 3; Rocha et al., 2007, p. 752; Simonsen, 1938, pp. 98-99; Sousa, 1879, pp. 41-42 and 103; Souza, 1939, pp. 81, 86 and 173.

da Mina in Lisbon [45]. Once there, at least a small portion may have been destined to local industries[46]. But, in fact, the vast majority of the redwood arriving to Lisbon was re-exported to Antwerp, as well as to Spain and Italy and, later in the 17th and the 18th centuries, mostly to London [47]. Due to their expansive textile industry, the French too had a high interest in brazilwood. For this reason, smugglers, pirates and privateers followed later on by the English and Spanish, frequently seized Portuguese ships or landed on the Brazilian coast to bargain with the indigenous people [48].

The Spanish started their exploitation of red dyewoods during their initial expeditions to the Caribbean islands, after the first voyage of Cristóbal Colón into the Hispaniola in 1492 [49]. After the preliminary period of exploration and conquest, further colonial settlements allowed the exploitation of dyewoods practically all over the Spanish Americas: *C. echinata* L., in Jamaica; *C. violacea* (Miller) Standl., near Buenos Aires; and *Haemotoxylum brasiletto* Karst., in Mexico, Colombia, Venezuela, Cuba, Hispaniola or Curaçao. From these species, *C. echinata* was considered to be the best [50].

Logwood (*Haematoxylum campechianum* L.) soon revealed to be distinguishable from the abovementioned dyewoods. While brazilwood mainly provided shades of yellow, pink and red on fabrics, logwood provided a wide range of reds, violets, blues, greens and deep blacks. Commercially known as Campeche wood - because it was exploited in the Campeche Bay and other swampy regions of the Yucatán peninsula - logwood was heavily exported by the Spanish to respond to international demand [51].

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[45] For a detailed description of brazilwood trees, and their exploitation and preparation during the colonial period, see Cardon, 2007, p. 280; Chaunu, 1984, p. 159; Léry, 1578, pp. 195-196; Roquero, 2006, p. 124; Simonsen, 1938, pp. 89 and 99; Souza, 1939, pp. 70-71 and 170-176.

[46] Braga, 2001, pp. 121-122; Sequeira, 2014, p. 120; Souza, 1939, pp. 176-177; *Regimento da fabrica dos panos de Portugal,…* , 1690, p. 32.

[47] Cardon, 2007, p. 287; Souza, 1939, pp. 110 and 176-178.

[48] Bethell, 1988, p. 10; Cardon, 2007, pp. 287-288; Garavaglia & Marchena, 2005, II, p. 380; Léry, 1578, pp. 195, 380 and 394; Simonsen, 1938, pp. 89-90; Souza, 1939, pp. 119-120.

[49] Cardon, 2007, pp. 286-287; Roquero, 2006, p. 121; Simonsen, 1938, p. 85; Souza, 1939, p. 85; Varnhagen, 1854, p. 21.

[50] *C. violacea* (or *C. brasiliensis*), exploited as well in Brazil, possesses half of the dye content of the *C. echinata*. *H. brasiletto* (or peachwood, Nicaragua wood, or Santa Martha wood) has even lower amount of colorant. Barragán, 2013, p. 9; Cardon, 2007, pp. 278-279; Chaunu, 1984, p. 159; Comellas, 1992, p. 173; Fuentes, 1980, pp. 334 and 336; Hofenk de Graaff, 2004, p. 143; Roquero, 2006, pp. 121 and 123; Sanz, 1979, p. 598; Simonsen, 1938, pp. 95-96; Souza, 1939, pp. 85-86.

[51] Later in the colonial period, logwood was furthermore exploited in the regions of Tabasco and northern Chiapas (Mexico), as well as in the regions of Péten (Guatemala), the north of the Belize, the north coast of South America and the Antilles. Bender, 1947, p. 3; Brunello, 1973, p. 197; Cardon, 2007, pp. 263-266; Fuentes,

Like brazilwood, its exploitation was made by the indigenous people of the Americas and by African slaves. After prepared, the wood was sent to the main American ports to be shipped to Spain, and thenceforth, to Europe. From the late 16th century, the English too had a preponderant role in sending this dyewood to Europe, through corsair interceptions of the Spanish fleets and the raid of Spanish exploitation spots, such as the Campeche Bay [52].

Once in Europe, the new dyestuff quickly met strong popularity in textile producing centres, mostly owing to its low price and versatility to achieve a wide range of colours, especially intense black and blue shades. Indeed, black had become a fashionable colour all over Europe, particularly among Catholic and Protestant followers [53].

Until the 16th century, black fabrics were obtained through laborious processes of mixing several dyes; madder and woad gave a brownish black (*brunetta*), for instance. Another method was to use high concentrations of plant tannins in combination with iron sulphate, which was extremely harmful to the textiles fibres [54]. With logwood, achieving black became easier and, for this reason, this dyestuff was widely accepted throughout Europe. However, dyers soon realized that it had low fastness properties [55], which is why it became severely regulated and, sometimes, even prohibited. Notwithstanding, it kept conquering European workshops by displacing old dyeing practices, along with another new technique, which combined woad or indigo with plant tannins and iron sulphate [56]. Indeed, in 1579, Richard Hakluyt instructed an English master dyer that, on his financed journey to

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1980, pp. 327 and 330; Hofenk de Graaff, 2004, p. 235; Marichal, 2001, p. 19; Molà, 2000, p. 130; Roquero, 2006, p. 123; Sanz, 1979, p. 600.

[52] Cardon, 2007, pp. 266-267; Gillespie, 1920, p. 133.

[53] Schneider (1978) provides an extensive assessment on the historical context of black in European dress. See also Balfour-Paul, 1998, p. 55; Cardon, 2007, pp. 268-271; Marichal, 2014, p. 205; Roquero, 2006, p. 126.

[54] Balfour-Paul, 1998, p. 30; Bensi, 2009, p. 40; Cardon, 2007, pp. 115, 271 and 374; Hofenk de Graaff, 2004, p. 287; Monnas, 2008, p. 24; Schneider, 1978, p. 425.

[55] Balfour-Paul, 1998, p. 55; Cardon, 2007, p. 268; Hofenk de Graaff, 2004, pp. 235 and 328-329; Molà, 2000, p. 131; Roquero, 2006, p. 126; Schneider, 1978, pp. 430-431.

[56] In some European dye workshops, logwood should be accompanied by other dyestuffs, namely madder or brazilwood. In the North Low Countries and in England, its application on fabrics was even temporarily forbidden. In this context, Balfour-Paul (1998, p. 57) states: "In 1581, *[…]* an Act was passed which authorized searchers to burn any logwood found in an *[English]* dye-house". Severe penalties were also instituted from 1592 to 1607, to Venetian dyers who attempted to use this dyestuff (Molà, 2000, p. 131). See also Bender, 1947, p. 3; Brunello, 1973, p. 197; Cardon, 2007, p. 268; Gillespie, 1920, p. 133; Hofenk de Graaff, 2004, pp. 235 and 330-331.

Iran, he should try to learn how to properly dye with logwood, "so shall we not need to buy oade *[woad]* so deere, to the enriching of our enemies" [57].

In the 17th century, after settling in Jamaica and in the Bahamas, the English cultivated logwood trees intended for international markets. The Spanish too cultivated this dyewood in Hispaniola (Dominican Republic), Cuba and Martinique during the 18th century. The Caribbean in fact was revealed to have a suitable environment for breeding logwood and, soon enough, it became one of the main exports from this part of the Americas to feed the insatiable demand of European textile industries, during the Industrial Revolution [58].

Remittances of brazilwood in the Portuguese transatlantic trade were relatively small in the first half of the 16th century, perhaps because of conflicts with indigenous people and with French pirates and privateers, who frequently visited the Brazilian coast to trade brazilwood with the natives [59]. Even so, in the first years after the Portuguese arrived in Brazil, approximately 20 000 *quintals* were annually imported to the *Casa da Mina* in Lisbon. From there, most of the brazilwood cargoes were re-exported to other European regions at c. 2.5 - 3 (Venetian) ducats per *quintal* (c. 3.5 - 4 *pesos*) [60]. After 1570, with the development of sugar production, the import of forced human labour into the Americas and new methods of exploiting wood, the industry started to expand, and so did exports [61]. By the end of the century, brazilwood monopoly was granting around 200 000 *cruzados* (c. 280 000 *pesos*) to the Portuguese government [62]. At this time and in the first years of the 17th century, Lisbon annually received between 5 000 and 10 000 *quintals* of the dyewood. If contraband (mainly practiced by the French) is considered, this estimate might well be doubled [63]. In Lisbon, each *quintal* of dyestuff was sold at 4 000 *réis* (c. 14 *pesos*) [64]. Meanwhile, in Seville, the equivalent weight of one *quintal* (4 *arrobas*) of American cochineal would cost at least 240 *pesos*, a price about 17 times higher than brazilwood.

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[57] Hakluyt, 1935, p. 139.
[58] Barragán, 2013, p. 11; Burkholder & Johnson, 1998, p. 156; Balfour-Paul, 1998, p. 55; Bender, 1947, p. 3; Cardon, 2007, pp. 264 and 274; Hofenk de Graaff, 2004, p. 235.
[59] Abreu, 1907, p. 48; Cardon, 2007, p. 288; Simonsen, 1938, p. 98; Staden, 1955, pp. 99-101.
[60] Bagú, 1949, pp. 66-67; Simonsen, 1938, pp. 97-98; Souza, 1939, pp. 110 and 112.
[61] Chaunu, 1984, p. 159; Souza, 1939, p. 144.
[62] Souza, 1939, p. 192.
[63] Bethell, 1988, p. 98; Chaunu, 1984, pp. 159-160; McAlister, 1984, p. 384.
[64] Souza, 1939, p. 181.

During the 17th century, owing to over-production and exhaustion of available resources, as well as reduction in prices due to international competition, the Portuguese government imposed regulations for brazilwood exploitation and commerce. As a result, shipments fell by half until the middle of the century, whereas prices dropped after 1625 [65]. The Dutch occupation of several Brazilian regions from 1630 and the subsequent conflicts with the Portuguese also contributed to the decrease of brazilwood shipments to Portugal. Even so, from the territories occupied by the Dutch, a total of 23 239 *quintals* were exported to the Netherlands between 1631 and 1651 [66].

In the Spanish Americas, brazilwood exploitation was relatively modest in the 16th century, exceeding very few times the annual average of 1 000 *quintals*. This is acceptable when considering that international demand was also supplied by Asian and Brazilian wood. For logwood though, the only regions in the world for producing it were in Central America and Caribbean, which explains its relatively high volumes in Spanish transatlantic shipments, reaching a peak of 13 000 *quintals* in 1587 [67]. Nevertheless, and even though brazilwood exported from the Spanish Americas was considered to be of inferior quality (colorant yield) and three to five times cheaper than the wood from Brazil, it was always more expensive than logwood: in Seville, until the beginning of the 17th century, the price of one quintal of the former could vary between 2.55 and 4.4 *pesos*, whereas the latter, between 1 and 2.44 *pesos* [68]. In comparison, the cheapest cochineal registered in Seville in this period was worth 44 *pesos* per *arroba* (176 *pesos* per *quintal*), a price 40 times more expensive than the most expensive *quintal* of brazilwood from the Spanish Americas.

In the following decades of the 17th century, prices for logwood and brazilwood from the Spanish Americas did not significantly change, despite the fall registered for the brazilwood sold in Lisbon. Even so, prices slightly increased for specific years: in 1633, logwood was sold at 3.7 *pesos* per quintal, while in 1648, good quality brazilwood (probably from Mexico) was sold at 5.15 *pesos* per quintal [69]. This brazilwood was about 80 times cheaper than the cochineal sold in Seville in the same year (100 *pesos* per *arroba*).

[65] Chaunu, 1984, pp. 159-160; McAlister, 1984, p. 384.
[66] Cardon, 2007, p. 288; Burkholder & Johnson, 1998, pp. 155-156; Souza, 1939, pp. 164 and 167-168.
[67] Cardon, 2007, pp. 266-267; Chaunu & Chaunu, 1956, VI_2, pp. 994-1001; Morineau, 1969, p. 143; Sanz, 1979, pp. 598-599.
[68] Barragán, 2013, pp. 87-88; Chaunu & Chaunu, 1956, VI_2, pp. 998-1000.
[69] Chaunu & Chaunu, 1956, VI_2, pp. 1039-1051.

Despite annual fluctuations, logwood kept its leading position, representing 36.5% of the total of the imports to Spain in the 1650s. At this time, prices for brazilwood slightly increased, perhaps because of an international shortage of this product. In 1657, the Mexican variety was worth 9 *pesos* per *quintal*, while an inferior grade from Santa Marta (Colombia) was valued in 7.35 *pesos* per *quintal* [70].

For the rest of the century, annual remittances for both dyewoods generally decreased, perhaps owing to higher rates of contraband and pirate or privateer raids. Nonetheless, both dyewoods continued to be officially shipped to Seville at this time, which indicates that demand in Spanish markets continued, as also reported for indigo, but not for cochineal. However, prices for logwood did not proportionally increase in response to its reduced availability: in 1675, one *quintal* was sold at 2.5 *pesos,* and in 1598, at 1.9 *pesos* [71].

In the 18th century, exports suffered an increment, as a result of the amplification of American production to respond to international demand (as did with cochineal and indigo). This is especially verified for 1753, when exports of logwood reached a maximum of 30 877 *quintals*. In the same year, brazilwood achieved an export peak of 3 771 *quintals* [72]. In the Spanish markets, Mexican brazilwood was now valued at 2.5 *pesos* per *quintal*; Colombian brazilwood, at 2.6 *pesos*; and logwood, at 1.9 *pesos* per *quintal* [73]. Cochineal, in is turn, was valued in 70 *pesos* per *arroba,* a price about 110 times more expensive than brazilwood. At the same time, and despite the growing transatlantic Spanish freights, the English were also bringing 8 127 *quintals* of smuggled logwood from Honduras to England in 1750 [74].

As for Portugal, shipments of brazilwood kept on flowing to Europe, although many Brazilians had abandoned its exploitation to dedicate themselves to sugar production, throughout the 17th century [75]. Regardless, in 1711, Brazil exported to Portugal wood valued in 48 000 *contos* (c. 2.917 *pesos*) and, in 1747, 21 493 *quintals* [76]. In the beginning of the 19th century, exploitation and export of dyewoods in Brazil and in Spanish Americas for the benefit of the Iberian Peninsula continued until these regions achieved political

[70] Fuentes, 1980, p. 334.
[71] French, English and Dutch settled in the Caribbean, frequently visited the Spanish American continent to deal directly with producers of brazilwood. Barragán, 2013, pp. 13-14 and 45; Fuentes, 1980, pp. 329-331.
[72] González, 1976, II, pp. 222-271.
[73] Morineau, 1985, pp. 494-496; Raynal, 1783, pp. III, 357, IV, 66.
[74] Cardon, 2007, p. 267.
[75] Idem, p. 288; Chaunu, 1984, p. 160.
[76] Antonil, 1711, p. 191; Morineau, 1985, p. 208.

independence [77]. After that, brazilwood continued to be exported as long as natural dyes were used. As for logwood, since mordanting methods improved in about 1840, it kept its chief role in worldwide centres of textile production well into the 20th century, competing with synthetic dyes [78].

Conclusions. In opposition to indigo and cochineal, brazilwood and logwood did not have to compete with locally available dye sources when they arrived in Europe in the early 16th century. Therefore, they quickly found ready markets and were rapidly assimilated into local centres of textile production. The dyeing properties of brazilwood were already known, due to the use of the imported Asian variety since Medieval times; but the colorant from logwood was new to European dyers. After gladly welcoming this new dyestuff into their practices, they soon realized that it had poor fastness properties, similar to those of brazilwood.

In the 17th century, as previously seen for indigo, dyewoods continued being part of the Spanish transatlantic routes. In the meantime, high taxes drove cochineal out of the markets of Seville. During the 18th century, dyewoods too were heavily exploited for the international markets, but the amount of brazilwood exported from the Spanish Americas could never compete in size with the shipments from Brazil.

Indeed, the dyewood from Brazil surpassed that coming from the Spanish Americas both in quality and in prices. Moreover, despite the fact that logwood was only available in specific parts of the Americas (and the world) a monopoly on this dyestuff was never as lucrative as that of cochineal. In fact, logwood was even cheaper than brazilwood produced in the Spanish Americas. This is mainly related to two factors: 1) quality, since great amounts of dyewoods were necessary to achieve suitable colours and they had poor lightfastness, in relation to cochineal and indigo; and 2) availability and easy methods of exploitation, in contrast to the constant nurturing of cochineal insects, or the laborious dyestuff treatment of indigo plants. Hence, this explains the high volumes and cheap prices of brazilwood and logwood annually shipped to the Iberian Peninsula, in relation to that of cochineal.

[77] Souza, 1939, pp. 193-195.
[78] Cardon, 2007, pp. 268-269 and 288; Souza, 1939, p. 29

These considerations along with those previously ascribed for indigo give a clear image of the importance of cochineal in the Atlantic context. This is particularly true when contemplating the commercial situation of these dyestuffs in the 17th century. Given the Spanish monopoly on cochineal, its esteemed value and high international demand, the Crown imposed extra tariffs on its trade in Seville. This strategic move eventually led European merchants to obtain it through alternative routes and means, and in the second half of the century, the dyestuff was no longer part of Spanish transatlantic shipments. As for the other American dyestuffs, given their wide availability, lower prices in relation to cochineal and/or competition with similar varieties, any additional taxes would have been counter-productive for the Spanish Crown.

By comparing the historical trends observed in the commerce of American cochineal (discussed in the previous chapter) with the situations of other American dyestuffs here, a richer and broader picture of the importance of cochineal for Spanish transatlantic commerce is possible. Indeed, throughout the colonial period, cochineal was, at all times, more valuable than the other dyestuffs. However, further insights can complement the historical conclusions made thus far, by considering the global circulation of the American insect beyond the borders of the Spanish Empire, as well as its acceptance in the main European and Asian centres of textile production, as discussed in the next chapter.

CHAPTER 6

COCHINEAL AND THE GLOBAL DYE TRADE:

Penetration of International Markets

Cochinilla, que es grana preciosísima, la cual, desde estas partes [Americas]*,*
se reparte por todo el mundo. Cervantes de Salazar [1]

While many riches arrived in Europe, coming from many parts of America, Asia and Africa, the monopoly on American cochineal was successfully maintained in Mexico, by the Spanish throughout the entire colonial period. In Europe, it was only officially obtainable through Seville and later Cádiz, the only official ports trading with the Spanish Americas during the colonial period. From there, it was sent to North Europe, as well as to the Mediterranean. From both regions, cochineal was re-shipped to eastern territories, reaching the Silk Route and, thence, to West and Central Asia or, through the maritime routes, to Southeast Asia. Alternatively, it could be shipped directly from Mexico to Asia, by way of the trans-Pacific circuit. Depending on the demand of local industries and the politico-economic situation, European and Asian regions gradually began to adopt the new dyestuff.

The main focus of this chapter concerns the degree and extent of circulation and acceptance of the American dyestuff in Europe and in Asia, throughout the Early Modern period. Hence, cochineal is assessed here as a commercial product in international markets, and as a dyestuff in local dye workshops.

This chapter is a continuation of the historical background offered in Chapters 1 and 2, and further aims to support the conclusions attained in the historical studies about cochineal in the transatlantic context, presented in Chapters 4 and 5. It looks principally at cochineal's geographical spread, especially in the main centres of textile production, where luxury textiles were manufactured and, thus, where the most expensive and high quality dyestuffs were applied. In this context, two sections comprise this chapter, one focused on European territories, and another, on Asian ones.

[1] ["Cochineal, which is highly precious and which, from these parts (Americas), it is distributed worldwide"] (Salazar, 1914, p. 13).

6.1. American cochineal in Europe

The most famous European territories of textile production during the 16th century were Spain, the south of the Low Countries, France and Italy, as discussed in Chapter 1. Connected by sea and land routes, these territories constantly communicated with each other, thus facilitating the dissemination of the American red dye through well-established trade conduits and encouraging its experimentation in dye workshops. Later, with the overseas expansion of England and the north of the Low Countries during the 17th century, these regions achieved international importance, which enhanced textile production and made local textile industries in eager to also take advantage of the new American dyestuff.

Spain. Dyeing with American cochineal in Spain must have commenced sometime after 1523, when the Spanish king started enquiring about it from Cortés, as described in Chapter 2. After that, small shipments of insects must have been brought from Mexico to feed a then flourishing textile industry. As of 1528, regulation measures were implemented and the use of the American dyestuff was restricted to the finest textiles, while mixtures with inferior dyes, like madder, were forbidden [2]. Production of these textiles was mostly carried out in Segovia and within the boundaries of Spain [3]. Wool, silk and dyestuffs were produced as well in Mexico, but textiles produced in that region were not allowed to be exported to Spain. They were sent instead to Peru [4].

In these first years, cochineal may have been only used in Spain, given to its limited production in Mexico, small transatlantic shipments and demand from Spanish workshops. However, in about two decades, the Spanish cloth production declined, owing to a lack of specialized workers and high prices of the produced clothes. Consequently, local demand for cochineal fell and merchants started to re-export it, especially now that production was being incentivized in Mexico and annual vessels were crossing the Atlantic with an abundance of American dyes [5].

[2] Lee, 1951, p. 218.
[3] Marichal, 2014, p. 200.
[4] Hakluyt, 1935, p. 107; Marichal, 2014, p. 200.
[5] Greenfield, 2006, p. 99; Lee, 1951, p. 206. During the 18th-century, Spain continued to export mainly dyestuffs and other raw materials meant for textile production; although it kept being strongly dependent from the import of finished clothes (Pérez-Garcia, 2016,pp. 187-188).

Low Countries (South). Politically linked to Spain from 1535, the Low Countries might have been one of the first European territories to receive consignments of American cochineal [6]. In the 16th century, Antwerp was the main commercial hub in the north of Europe, where a wide range of commodities were available, produced locally or in transit from elsewhere. Most of the trade with the Mediterranean was made through Antwerp, where goods came by sea or overland, crossing the Alps. The English used it to export their woollen cloths; the Portuguese and the Spanish, to sell Asian and American products; and the Germans, to channel all those products, through the land routes they controlled in Central Europe. Once in Italy, products were re-shipped from Venice to the Levant, and thence, towards the caravan and maritime Asian routes [7].

Although shipments of American cochineal were reported in Antwerp's markets in 1552 [8], it is possible that this product was arriving there years before, along with other foreign and expensive dyestuffs and pigments. Given the esteemed value of cochineal, small volumes could have been brought by courier in closed packages. As these were shipped in small quantities intended for "personal" use, they were usually free of duties. This may explain an absence of records for cochineal's entry into the region. Commodities obtained in this way were commonly imported on behalf of the Crown as diplomatic presents, for instance [9]. Regardless, there is no doubt that by 1567, Ludovico Guicciardini describes American cochineal as a common product in the exports of Antwerp [10] and, in 1571, about a third of the amount of cochineal arriving in Seville was re-shipped to Antwerp – if considering the volumes represented in Fig. 4.1 from Chapter 4, this amount would correspond to about 2 210 *arrobas* [11].

The Flemish had a well-established textile industry, especially the tapestry workshops in Antwerp. The city housed a large community of dyeing centres, where vast quantities of

[6] Donkin, 1977b, p. 38.
[7] Anderson, 1801, II, pp. 108-109; Davis, 1973, pp. 32-34; Kirby, 2010, p. 342; Lee, 1951, p. 209; Pieper, 1998, p. 366; Spufford, 2010, p. 18; Vermeylen, 2010, pp. 356 and 360.
[8] Between April 1552 and August 1554, Antwerp received a total of American cochineal valued in 15 186 *guilders* (c. 6 276 Spanish *pesos*). This would roughly correspond to 140 *arrobas* of cochineal, if considering the relatively stable prices registered in Seville by the end of the decade (45 pesos per *arroba*). From all dyestuffs imported, American cochineal was only followed by that of brazilwood, worth 13 074 *guilders* (c. 5 404 *pesos*) - most of it was likely to be of Brazilian origin (Vermeylen, 2010, p. 360). See also Goris, 1925, pp. 262-263; Lee, 1951, p. 209.
[9] Kirby, 2010, p. 349; Vermeylen, 2010, p. 357.
[10] Guicciardini, 1593, pp. 34-35.
[11] Prada, 1961, p. 101.

Flemish and English unfinished cloths were brought to receive colour [12]. First experiments with American cochineal were carried out by the Flemish Pieter Coecke for the local tapestry industries. This may have happened before 1543, as by this time Flemish dyers were brought to Mexico to assist the Spanish in mastering the use of local dyestuffs (cochineal among them). From Antwerp, knowledge about dyeing with American cochineal was soon spread all over the Low Countries and Europe [13].

France. By the mid-16th century, great quantities of the American insect were sent from Antwerp to the main French markets of Paris, Rouen, Malines, Lyon, Marseilles and Bordeaux. In return, brazilwood was brought to Antwerp by French merchants [14]. They were also established in Seville and Cádiz, where they sold a great amount of French drapery to the Spanish, while shipping cochineal and other American products to French ports. From there, cochineal was re-shipped either to Antwerp or to London [15].

In France, cochineal and other rich dyestuffs were mostly employed in the textile centres of Rouen and Nantes, where fine textiles were produced. However, owing to the civil war, these centres, along with the emerging Gobelin dye works, were halted. As a result, imports of dyestuffs were curtailed throughout the rest of the century [16]. It was only at the beginning of the 17th century that the main ports were re-opened, namely St. Malo, Dieppe, Rouen, Nantes, Bordeaux and Le Havre-de-Grace [17]. To improve the debilitated textile industry, the chief minister of finance Jean Baptiste Colbert (g. 1665-1683) undertook efforts to boost production; increase textile quality; and promote the use and production of French raw materials, such as kermes and madder, rather than imported American cochineal. In 1662, Colbert, on the behalf of the French Crown, purchased the Gobelin workshops where the manufacture of tapestries and upholsteries was encouraged [18].

In the second half of the 16th century French authorities believed that the popularity of American cochineal could endanger the production of local dyes and, for this reason, it

[12] Anderson, 1801, II, p. 108; Vermeylen, 2010, p. 357.
[13] Lee, 1951, p. 222.
[14] Idem, 1951, pp. 208-209; Marichal, 2014, p. 202; Vermeylen, 2010, pp. 360-361.
[15] Anderson, 1801, III, p. 6; Lee, 1951, p. 209; Sanz, 1979, pp. 584 and 586.
[16] Brunello, 1973, p. 186; Lee, 1951, pp. 208 and 223; Sanz, 1979, pp. 586-587.
[17] Lee, 1951, p. 208.
[18] Brunello, 1973, p. 200; Hofenk de Graaff, 2004, pp. 6 and 54-55; Phipps, 2010, p. 33.

was highly taxed and thus used mainly in luxury fabrics [19]. Notwithstanding, the *Instruction générale pour la teinture des laines* from Colbert, originally published in 1671, demonstrates that the American dyestuff was well integrated in French dyeing practices by the second half of the 17th century, since it was essential to obtain four of the seven most popular shades of red produced in the *grand teint* French dyeing centres [20]. Moreover, by 1686, a sixth of all the cochineal that arrived in Spain was sent to France [21]. This reference is very interesting, given that no available records can confirm cochineal's arrival this year in the markets of Seville. However, Fuentes mentions that, in 1685, a small amount of 63 *arrobas* of cochineal was registered in Seville (Appendix 1). Although this is a small quantity, it is likely that much greater volumes were circulating in Europe at the time. Hence, it is possible to presume that cochineal shipped from Spain to France was being smuggled, for example, from Cádiz.

Italy. From the ports of Antwerp, considerable quantities of the American insect were sent to Ancona, Venice and Milan by 1567 [22]; although cochineal was known in Italy already in 1542, when the Duke of Tuscany, Cosimo I, sponsored Lapo da Diacceto to secretly investigate dyeing techniques with American cochineal, without interference of other interested parties and guild statutes [23]. One year later, the dyestuff was being mentioned in the reform of the cotton and silk guild statutes of Perugia, when it became officially part of the group of red dyes used by local dyers [24]. At the same time, other cities like Florence, Lucca and Milan were adopting the American dyestuff as well [25].

In Genoa, on the contrary, authorities strictly prohibited silk dyeing with the American insect, given their concerns about the effects that the new dyestuff could bring to the quality of their products. By 1550, local entrepreneurs were petitioning to freely use the dyestuff, as it was well accepted and commonly used in every Italian silk industry. In fact, the

[19] Lee, 1951, p. 215.
[20] Colbert, 1672, pp. 22-25. See also Hellot, 1750, pp. 241 and 276-354.
[21] Lee, 1951, p. 209.
[22] Guicciardini, 1593, pp. 34-35. In 1565, Matthioli (1565, p. 1031) mentions the import of American cochineal. Though, the dyestuff was already marketed in Venice by 1543 and, by 1575, it was being dispatched to Florence directly from Spain. Atasoy et al., 2001, p. 196; Lee, 1951, pp. 209-210; Vermeylen, 2010, p. 360.
[23] Galluzzi, 1841, pp. 198-199. See also Bensi, 2012, p. 31; Molà, 2000, p. 121.
[24] Bensi, 2012, p. 31; Molà, 2000, p. 121.
[25] Monnas, 2012, p. 23.

fabrics dyed with the new American dyestuff were in much demand all over Europe and, for this reason, Genoa's market fell in relation to international competition [26].

Although Italian dye works were still using the European and Asian insect dyes, American cochineal permitted the production of cheaper textiles - smaller amount of insects and simpler dyeing expertise to achieve the same colours. Inherently, this insect was bringing down the price of crimson textiles in international markets, thus leaving the expensive Genoese textiles at a distinct disadvantage [27]. For this reason, the Genoese authorities had no choice but to grant the use of the American dyestuff. However, on one condition: since crimson hues from insect dyes were very difficult to differentiate and production costs varied considerably between them, American cochineal ought never to be mixed with other insects, and fabrics should be differentiated with selvedges or seals [28].

In Venice too, some resistance to American cochineal was initially met, after it was introduced to the city in 1543. One year later, once its advantages in terms of quality and costs of production had been demonstrated, the American insect was accepted in the silk industry [29]. As in Genoa, authorities decreed in 1557 the application of selvedges to assist with discriminating the fabrics dyed with different insect dyes [30].

As for the Venetian woollen industry, resistance to the American insect was stronger, perhaps because European and Asian cochineal dyes had not been traditionally used on wool. Instead, the popular Venetian scarlet had long been dyed with kermes, which was moreover a source of income to several Italian producing regions. Hence, American cochineal was firmly forbidden in wool workshops from 1558 and, during the 1560's, while Italy was receiving wool dyed with American cochineal from Antwerp, wool dyed with

[26] Bensi, 2012, p. 31; Cardon, 2007, p. 613; Massa, 1970, pp. 122-123; Molà, 2000, pp. 121-122; Monnas, 2008, pp. 25-26, 2012, p. 23.

[27] Cardon, 2007, p. 613; Lee, 1951, p. 210; Monnas, 2008, pp. 25-26, 2012, p. 23; Marichal, 2014, p. 202.

[28] Massa, 1970, pp. 122-123; Molà, 2000, pp. 121-122; Monnas, 2008, pp. 17 and 369; Phipps, 2010, p. 32.

[29] Bensi, 2012, p. 31; Molà, 2000, pp. 122-125. Interestingly, Rosetti's work (1969), formerly dated to 1548, does not mention American cochineal. The year of 1540 has been suggested to be a more acceptable date for this publication (Brunello, 1973, p. 184). In fact, it is known that Rosetti was not a dyer, but instead he worked at the Venetian arsenal, provisioning all raw materials arriving to the city. If he had come cross with the American dyestuff, either through the Venetian ports or through his collection of dyer's recipes in Italian workshops (Naples, Rome, Florence, Genoa, Venice and other Italian regions), it seems likely that he would have mentioned it (Idem, pp. 192-193). Although Brunello (Idem, p. 189) and Verhecken & Wouters (1988, p. 226) suggest that Rosetti indeed mentions the American insect ("crimson of the West"), the quantity given to dye one pound of silk is very close to that suggested for the European and Asian dyestuffs (Rosetti, 1969, p. 139), thus excluding such possibility.

[30] Molà, 2000, p. 129. See also Monnas, 2012, p. 23.

kermes was sent to Flemish markets. Nevertheless, Venetian dyers (like in many other Italian cities) started using the American dyestuff to make cheaper imitations of the expensive kermes-dyed cloths. These cheaper fabrics were then exported to Istanbul and to the Levant, along with shipments of the American dyestuff brought from Seville. By the end of the century, dyeing with American cochineal on wool had become such a common practice in the Venetian works that any prohibitions concerning this insect had become obsolete [31].

During the second half of the 16th century, the luxury textile industries of Italy, France and the south of the Low Countries were the main consumers of American cochineal and other expensive dyes [32]. Based on the prices of cochineal in Antwerp, Florence, and at a small extension, Amsterdam, it is possible to gain an idea of the relative value of this dyestuff in Europe, throughout the second half of the 16th century and the beginning of the 17th century [33].

In Fig. 6.1, it is clear that prices of cochineal in Florence and Antwerp follow the same rising trend in relation to those of Seville; although they are generally doubled, which indicates the additional costs of transport and export/import tariffs, as well as profits that merchants could get from its sale. As previously discussed in Chapters 4 and 5, price fluctuations can be highly dependable of production, demand, transport and political conditions. In the European markets, these transatlantic circumstances must be taken into consideration, as well as the political and economic contextualization of local markets and to where they were re-exporting the dyestuff [34]. For instance, in 1581 there was small demand for cochineal in the Levant and so prices dropped in Florence, since a good part of the dyestuff was annually re-exported there [35]. In Antwerp, by 1590, prices dropped even further because English privateers ransacked great amounts of cochineal from Spanish fleets and were selling it at low prices. However, in 1595, prices reached a peak of 87.5 Flemish *sous* per pound (c. 503 Spanish *pesos* per *arroba*) in Antwerp, because there had been a low

[31] For instance, American cochineal was used to dye red felt hats, or *fezzes,* which were mostly exported to Istanbul. Brunello, 1973, pp. 199-200; Lee, 1951, p. 210; Marichal, 2014, p. 202; Molà, 2000, pp. 128-130; Prada, 1961, p. 101.
[32] Marichal, 2014, p. 202; Martín, 1965, pp. CXXV and CXXVII; Molà, 2000, p. 128.
[33] Posthumus, 1946, pp. 420-422; Prada, 1961, pp. 254-255; Sanz, 1979, pp. 562-563 and 566-568. See also Crevea, 1906, p. 456; Lee, 1951, p. 210; Marichal, 2014, p. 202; Mun, 1895, p. 66.
[34] Martín, 1965, pp. XVI and CXXVII; Prada, 1961, pp. 102 and 255-256.
[35] Prada, 1961, p. 102; Sanz, 1979, p. 562.

availability of cochineal since the previous year (Fig. 4.1 in Chapter 4) and demand was now incredibly high [36].

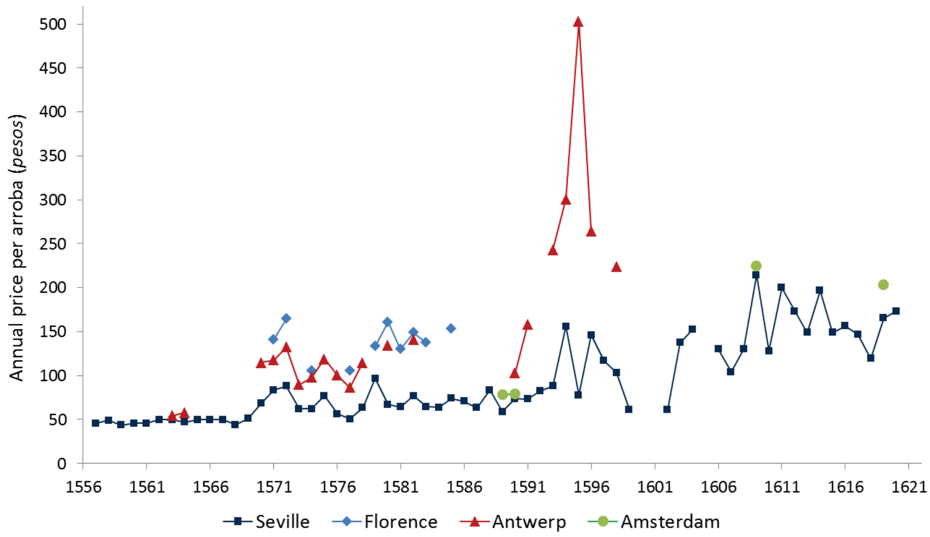

Fig. 6.1. Transatlantic and European relative prices (*pesos*) per *arroba* of American cochineal (*grana fina*), 1557 - 1620 – Appendix 1, Table 2.

Political and religious turbulences and warfare with the Spanish throughout the second half of the 16th century led to the eventual fall of Antwerp as the main commercial port. At times, maritime communications were interrupted, but cochineal was still reaching the city by land, from France. This situation eventually led to a shift in the majority of North European commerce to Amsterdam [37], along with the migration of many Flemish dyers to other parts of Europe, like London and Amsterdam. Until then, these cities had not had the international popularity of Antwerp or Florence for the trade of dyestuffs, precisely because of their small textile industries. However, once established, the Flemish dyers helped boost local production by sharing their dyeing expertise [38]. This seems to be somewhat visible in

[36] In 1589, cochineal was sold in the English markets at 26 s. per pound (c. 155 *pesos* per *arroba*). In 1598, like in Antwerp, prices ranged between 30 - 40 s. per pound (c. 178.6 – 238 *pesos* per *arroba*) but, soon afterwards, they would drop again to 16 s. per pound (c. 95 *pesos* per *arroba*) due to a higher availability of cochineal that had been looted by English privateers from Spanish fleets. This may explain why no registries are given for cochineal in Seville in the following years. Lee, 1951, p. 221; Prada, 1961, p. 102; Sanz, 1979, pp. 575-576.

[37] Donkin, 1977b, p. 38; Hofenk de Graaff, 2004, p. 5; Lee, 1951, p. 209; Prada, 1961, p. 255; Spufford, 2010, p. 18.

[38] Brunello, 1973, p. 186; Hofenk de Graaff, 2004, pp. 5, 55, 328 and 332; Lee, 1951, p. 222; Sanz, 1979, p. 585; Schneider, 1978, p. 435; Vermeylen, 2010, p. 361.

Fig. 6.1: prices for cochineal in Amsterdam are relatively low throughout the second half of the 16th century and, in the 17th century, when dyeing works start expanding, demand for the American dyestuff increases, and so does its price; although more conclusive data is given for the following decades.

As for Italy, with the international trade routes now being controlled by other Europeans, Italian merchants gradually lost the main control of the international trade. Despite the constant flow of dyestuffs into the region, Italy became somewhat isolated from major developments in European textile industries. Actually, while the quality of the Italian silk textiles kept their renowned excellence, international markets were flooded with cheaper and lighter textiles, some of them poor imitations of the Italian fabrics. This eventually brought a decrease on demand for the Italian manufacture and, by the 18th century, Italy's international produce was practically ceased [39].

England. London was a dominant port in the 16th century, which was connected by mercantile routes with Rouen, Calais, Antwerp, Middelburg, Emden, Seville and, later in the century, Italy. Trade in textiles and foreign dyestuffs was monopolized by the Company of Merchant Adventurers, who brought shipments of American cochineal from Antwerp [40]. This was possibly imported to England in 1558, the same year in which the dyestuff was described by an English merchant. However, official imports from Spain are only registered from 1569, when it started to be unloaded at the docks of Portsmouth [41].

Given the then flourishing English textile industries and the general discontentment of dyers towards the inferior quality of local dyestuffs, American dyestuffs were in high demand in English markets [42]. Indeed, aiming for international recognition for their fabrics, the English authorities sent dyers abroad to learn new techniques. For instance, in 1579,

[39] Brunello, 1973, p. 195; Heers, 1961, p. 10; Hofenk de Graaff, 2004, pp. 10-11; McNeil, 1974, p. 217; Schneider, 1978, pp. 436-437.
[40] Kirby, 2010, p. 342; Vermeylen, 2010, p. 361.
[41] Donkin, 1977b, p. 38; Green, 1871, p. 174; Lee, 1951, pp. 207-208.
[42] Balfour-Paul, 1998, pp. 36-37; Brunello, 1973, p. 147; Lee, 1951, pp. 207-208; Marichal, 2014, p. 202; Page, 1907, pp. 261-262; Schneider, 1978, p. 428.

Richard Hakluyt provided instructions to an English master dyer who was about to undertake a journey to Iran to learn about dyeing techniques and the materials used there [43].

In spite of their emergent dyeing skills, the English continued to produce cheap, poorly dyed and finished fabrics which, even so, found ready markets abroad. The most fine woollen textiles kept on being annually exported to the Low Countries, where they were coloured with cochineal shades [44]. Attempts were made to prohibit the export of undyed cloths, as well as to find sustainable sources of dyes that could free the English from the Spanish trade in dyestuffs. In this context, instructions were drawn up to find new dyes sources, especially cochineal, in expeditions carried out in the Americas [45].

Despite these English investments, American dyestuffs, among other products, were largely imported from Spain during the 16th century, and even with the conflicts between both nations. Although commerce was hindered, English merchants residing in Spain still sent cochineal to England. This relationship continued throughout most of the colonial period, because of English dyers' high demand for American dyestuffs [46]. In addition, and to respond to home demand, English pirates and privateers frequently raided the Spanish fleets crossing the Atlantic [47]. Cochineal brought to England by this route was in such a magnitude that Thomas Gage declared in 1648: "No Nation is more warlike and high ſpirited then the Engliſh, whoſe very clothes were fiery; wearing more ſcarlet then any nation in the World; *[…]* their coming ſo much with their ſhips to the *Indian* Coaſts to fight with the *Spaniards*; and that as they delighted to go in red, and to be like the Sun, ſo naturally they were brought to those Seas to ſingle out ſuch ſhips as from *America* carried with the rich Commodity of

[43] Hakluyt, 1935, pp. 137-139.
[44] Fairlie, 1965, p. 489; Gillespie, 1920, pp. 133-134; Israel, 2002, p. 117; Phipps, 2010, pp. 28-29; Schneider, 1978, p. 435.
[45] Lee, 1951, pp. 216-217; Schneider, 1978, p. 435. In 1578, Hakluyt (1904, VII, p. 247) gives instructions for an expedition about to be undertaken: "if you can find the berrie of Cochenile with which we colour Stamelles, or any Roote, Berrie, Fruite, wood or earth fitte for dying, you winne a notable thing fitte for our state of clothing. This Cochenile is natural in the West Indies on that firme."
[46] Cochineal was one of the six main imports from Spain to England in 1621. Green, 1967, p. 327; Hamnett, 1971a, p. 25; Lee, 1951, p. 208; McLachlan, 1940, p. 10; Page, 1907, pp. 261-262; Pieper, 1998, p. 365.
[47] Lee, 1951, p. 212. Correspondence dated from 1569 describes the English capture of three Spanish ships, containing 600 cases (400 *arrobas*?) of cochineal, among many other goods. This was sold in England at 7s. 6d. per pound, or c. 44.6 *pesos* per *arroba*, a price close to that registered in Seville at that time. In 1571, the English captured other large number of prizes from Portuguese and Spanish transatlantic convoys, containing 250 *arrobas* of cochineal (Martin, 1899, 20th Dec. Paris [570], 22nd Dec. Paris [571], 23rd Dec., 1571 [573]).

Chochinill, whereof they make more uſe then *Spain* it ſelf to die their cloaths and Coats withal" [48].

English efforts to achieve an internationally-recognized (and cheap) textile industry came later in the 18th century, through a new branch of textile production: cotton printing. India had long been known for its export of large quantities of textiles to Europe, among them many cotton cloths with calico prints. Knowledge of the techniques for printing cotton was firstly applied in England and, in the 18th century, they were fully established all over Europe. Since cochineal is chemically more suitable to colour animal fibres, its use was not appropriate to print on cotton (vegetable fibres). Madder, however, gave better results, especially to obtain the Asian shade of Turkey red, which had been unknown to Europeans until the middle of the 18th century. This inevitably brought some decrease to the demand of American cochineal (still suitable for woollen fabrics) and a renewed interest for madder production in Northern European regions [49].

Low Countries (North). From the end of the 16th century, Amsterdam was a thriving centre in the overseas trade, by supplying the range of goods previously available in Antwerp. Direct maritime trade routes were established throughout Europe, reaching Italy and the Levant, as well as the Indian Ocean, through the Cape route. Despite political conflicts with the Spanish between the 16th and 17th centuries, American cochineal and indigo shipments glided to and from Amsterdam [50].

In contrast to the south of the Low Countries, American cochineal (and, before that, other European and Asian insects) did not come into use in Dutch centres of textile production before the end of the 16th century. This was mainly due to government prohibitions that favoured madder as the official source of red, given its economic importance for local farmers, especially in Zeeland. Besides madder, the only additional red source allowed in Dutch dyeing centres was brazilwood, initially imported from Asia, and then, from the Americas. This was allowed for purple and brown colours. However, after

[48] Gage, 1655, p. 100.
[49] Balfour-Paul, 1998, p. 48; Cardon, 2007, pp. 115-116; Fairlie, 1965, pp. 489 and 491-492; Gillespie, 1920, pp. 134-135; Hofenk de Graaff, 2004, pp. 7, 9-10 and 112; Pérez-Garcia, 2016, p. 216; Pieper, 1998, pp. 371-379; Riello, 2009, pp. 264, 268, 280 and 286; Schneider, 1978, p. 436.
[50] Kirby, 2010, p. 343; Lee, 1951, p. 210; Phillips, 1990, p. 87; Spufford, 2010, p. 18.

Flemish dyers moved into the region, insect dyes became more popular dyestuffs to dye fine woollen fabrics [51]. Hence, from the beginning of the 17th century, the Dutch started dominating the European markets with their fine scarlet wool, which was not only produced locally but also imported in raw state from England or Spain [52]. Since this wool was mainly dyed with American cochineal, it is not surprising the abundance of price records available for this dyestuff in the markets of Amsterdam, during the course of the 17th and beginning of the 18th centuries (Fig. 6.2) [53].

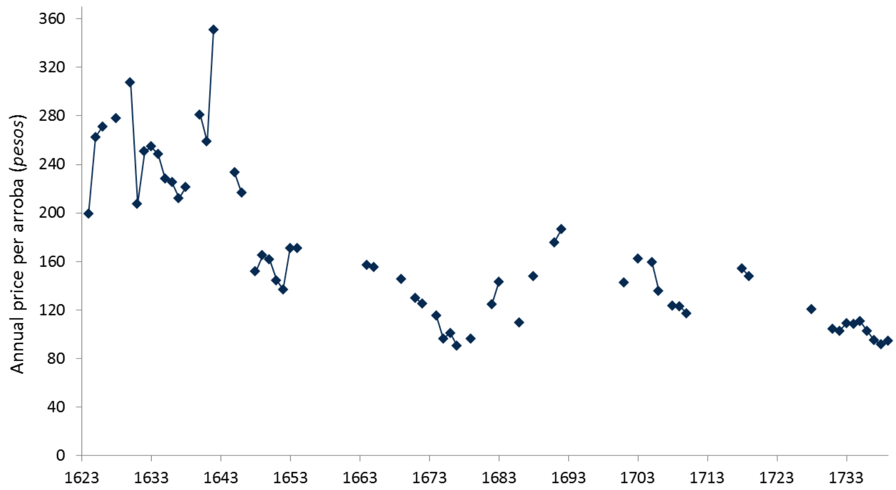

Fig. 6.2. Relative prices (*pesos*) per *arroba* of American cochineal (*grana fina*), in Amsterdam, 1624 - 1738 – Appendix 1, Table 2.

These records clearly reinforce the fact that, even after registries of cochineal practically ceased in Spain during the 17th century, the dyestuff continued entering Europe. Despite the interruptions for several years and the inherent fluctuations, Fig. 6.2 provides a clear idea of the relative value of cochineal throughout the century. Indeed, until 1629, prices could vary between 16 and 57%. In 1642, prices reached a zenith of 33.9 *gulden* per pound (c. 351 *pesos* per *arroba*), which might not only be related to the elevated tariffs charged to the export of the dyestuff from Seville, but especially to the war conflicts with Spain. In the meantime, England was enjoying a better political situation, and English

[51] Hofenk de Graaff, 2004, pp. 55, 324-328 and 331; Posthumus & Nie, 1936, pp. 215-216.
[52] Israel, 1995, pp. 199-201; Lee, 1951, p. 223-224; Posthumus & Nie, 1936, p. 229.
[53] Posthumus, 1946, pp. 420-422.

merchants were selling the dyestuff at cheaper prices by registering, in 1626, 33 s. per pound (c. 196 *pesos* per *arroba*). When peace treaties were drawn in 1648, cochineal prices dropped by one third in the markets of Amsterdam, whereas in London, they kept around 32 s. per pound (c. 190 *pesos* per *arroba*). These prices, either in England or in Amsterdam, were generally 1.5 times more expensive than those in Seville at this time, likely because of extra commercial tariffs. For the following decades, prices in Amsterdam varied up to 20%, which show some degree of stability in local markets [54]. Since prices do not steeply rise during this period and until the beginning of the 18th century, it is possible to suggest that the Dutch may have had easy access to relatively high amounts of the American dyestuff (probably through privateering in the Caribbean), as opposed to the small records encountered for Seville.

Alternatively, it is possible that this depression in prices might be related as well with the spread of production of cotton prints in Dutch and French centres of textile production, while madder exploitation was intensified in these regions. The growing importance of this vegetable dyestuff in European dyeing industries was such that, during some decades of the second half of the 18th century, it became temporarily more expensive than cochineal [55]. Notwithstanding, cochineal was far from losing its value in the European fashion, and this is clear in Fig. 6.3, where relative annual prices for Amsterdam and London can be compared with those registered in Cádiz and in Vera Cruz, during the 18th century and the beginning of the 19th century [56].

For the first half of the 18th century, prices in Cádiz and Amsterdam generally follow similar trends and they can even be related closely, especially during peaceful periods. However, during the Seven Years' War (1754-1763) with England, Spain suffered interruptions in its transatlantic trade, especially caused by pirates and privateering. As a result, this led to a shortage of cochineal and the rise of prices in European markets and, inherently, in Amsterdam. Until the end of the century, closely related prices between Amsterdam and London indicate that cochineal commonly flowed between both cities,

[54] Israel, 1995, pp. 199-201; Lee, 1951, pp. 220-221; Steckley, 1984, Letters 1648 [1], 1649 [2, 5b] and 1650 [13b]. See also Pérez-Garcia, 2016, p. 204.
[55] Pieper, 1998, pp. 371-381; Posthumus, 1946, pp. 420-423.
[56] Posthumus, 1946, pp. 420-422; Tooke & Newmarch, 1838, p. 400.

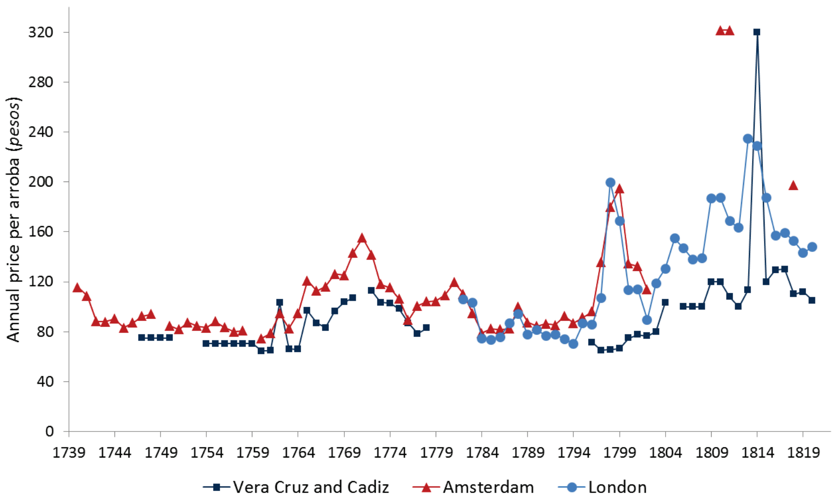

Fig. 6.3. Transatlantic and European prices (*pesos*) per *arroba* of American cochineal (*grana fina*), 1740 - 1820 – Appendix 1, Table 2.

although it is clear that high availability of the product and low demand have brought down prices. From the last years of the century, the French Revolution, the Napoleonic wars and the English war blockades to the Spanish transatlantic trade, halted availability and raised cochineal prices. In Vera Cruz, on the contrary, prices were kept low because of stagnation of transatlantic communications. When markets opened again and transatlantic connections were resumed, prices in Vera Cruz increased accordingly with the constant demand in Europe [57]. Even so, Mexican wars for independence were now causing a lack of cochineal production, which may explain why prices were kept high in Vera Cruz, and consequently, in London and in Amsterdam.

Textile centres in other parts of Europe may not have met the expansion of England, Low Countries, France or Italy. Nevertheless, in more isolated places, monasteries, for instance, may have kept an important role by producing for local needs. In more cosmopolitan environments, local textile centres were sufficiently developed to meet local demand as well. In such places, it is likely that local fibres and dyestuffs were used, rather than the more costly imported materials (not at an industrial level, at least).

German merchants were not in direct contact with the overseas trade with Asia or the Americas. Instead, Hamburg and Leipzig received shipments from Italy, coming overland

[57] Baskes, 2000, pp. 139-141, 160 and 182, 2013, pp. 83-84; Ducasse, 1978, p. 301; Pérez-Garcia, 2016, p. 209.

through Augsburg towards north and crossing the Alps. German merchants also used the Central European land routes to reach Antwerp and later Amsterdam. By sea, they reached the ports of England and France. The import of American dyestuffs into Germany, although not as prominent as that reported for the above-mentioned European regions, was registered. In the beginning of the 17th century, indigo, brazilwood and other dyewoods from the Americas were being mainly imported from Portugal and Spain. However, in the 18th century, England gained a major role for providing Germany with American dyestuffs, obtained from the English American possessions or from trade with Spain. As for cochineal, Spain continued to be Germany's main supplier during the colonial period, whereas Portugal kept its importance in supplying brazilwood [58].

In local German centres of textile production, foreign dyestuffs, like indigo or cochineal, initially met a fierce competition with local dyes, namely woad and madder, which were highly important for sustaining local economies. Perhaps for this reason, old dyeing traditions were kept active longer than in other European regions, like England, where there was a common discontentment with local dye sources. Until the 16th century, madder and woad represented important cash crops for the local populations and for the economy of Germany, but also of France, Low Countries and, to a small extent, Italy and Spain [59].

As observed above, with the advent of colonialism and overseas trade, most of these territories sought to feed the demand of their textile industries, which in turn were producing for international demand, at an industrial scale. Although Spain had short-lived international recognition for its textile production, it still held a significant part of the bulk of dyestuffs entering Europe. Germany, in its turn, did not have a strong textile industry that demanded exquisite and expensive dyes, nor a direct connection that would allow merchants to buy great quantities of them at advantageous prices. Hence, it is not at all surprising to see the strong competition that brazilwood and cochineal encountered when faced with native German madder, or indigo with woad, while in other countries like France and North Low Countries both foreign and native dyes co-existed in the dyer's vats.

As for Portugal, American cochineal must have made its entry onto the scene by at least the time of the Spanish occupation in 1580. In that year, Durante Rodríguez, a

[58] Anderson, 1801, II, pp. 108-109; Lee, 1951, pp. 210-211; Pieper, 1998, p. 366; Spufford, 2010, p. 18; Vermeylen, 2010, pp. 356 and 361.
[59] Pieper, 1998, p. 366.

Portuguese merchant, certainly profited from this Iberian union. Based in Seville, he secured consignments of cochineal through a possible relative, Simón Rodríguez, who was established in Mexico [60]. Whether Durante sold his cochineal shipments to other European merchants or brought it home is not acknowledged. Moreover, while historical evidence demonstrates the use of locally produced kermes (*grãa*) to produce red dyes in Portuguese textile centres, no reference is found for the American or any other kind of cochineal [61]. In fact, textile production carried out in Portugal at this time was mainly intended for local consumption [62], and thus, the locally-available kermes would have been enough to meet the industry's demand. In the 18th century, American cochineal was certainly imported to be used as lake pigment for painting purposes, along with lakes from brazilwood and local kermes [63].

Conclusions. In the 1520's, American cochineal started arriving in Spain and it was soon accepted in local centres of textile production. However, in a time span of two decades, Spanish textile production declined and merchants sought to bring the American dyestuff to other European markets. Therefore, in the early 1540's, cochineal was being tested in the dye works of the south of the Low Countries and Italy and, in few years, it became a common merchandise in the markets of the main European cloth-producing centres.

Even so, in some European regions, such as France, the north of the Low Countries or some parts of Italy, cochineal was seen initially as a threat to the local production and trade of red dyestuffs, namely madder and kermes, and to the quality and price of the manufactured textiles. Hence, imposed regulations aimed to highly tax its trade and control (or even forbid) its dyeing applications, throughout the second half of the 16th century. By the 17th century, given its economic advantages and colour possibilities over locally

[60] Idem, p. 366; Lee, 1951, p. 207.

[61] Other sources of red, namely brazilwood (*Braſil*, from Brazil), madder (*ruiva,* from Spain or Flanders) and dragon's blood (from Azores and Madeira) are mentioned as well. Braga, 1998, pp. 184-186, 2001, p. 105; *Regimento da fabrica dos panos de Portugal…*, 1690, pp. 26–27 and 32; Sequeira, 2014, pp. 112-113, 115 and 120.

[62] Although it has been reported that reasonble numbers of Portuguese textiles were exported during this period, they were far from rivalling with those from the major European centres of textile production (Sequeira, 2014, pp. 153, 167 and 183). Later in the 18th century, textile production significantly increased through the encouragement of the Portuguese government, and indeed, considerable quantities of linens, cottons and silks were mostly sent to Brazil (Braga, 1998, pp. 184-186, 2001, pp. 104-105 and 109).

[63] Cruz, 2009, pp. 392-393.

available red dyestuffs, American cochineal was widely accepted to dye fine silk and woollen textiles.

The high value of this insect dye made it a very profitable commodity which was commercialized by wealthy merchants until the 19th century, as indicated by the relative prices examined in this chapter. Here, it is demonstrated that the political and economic conjuncture of European markets to where the American dyestuff was traded influenced its prices (due to war conflicts, for instance). Moreover, these prices also show a close relationship to those practiced by the Spanish (Chapters 4 and 5), which were highly dependent on Mexican production, international demand, transport and Spanish political and economic circumstances, namely periods of war (privateering) and extensive contraband. Therefore, in order to understand the circulation of cochineal throughout the Early Modern period, it is important to consider the wider picture of European commerce, and not only restrict it to Spain.

Indeed, the absence of 17th-century registries for Spanish commerce, highlighted in Chapters 4 and 5, can be explained in the context of the burgeoning international trade undertaken by other European empires at this time. While cochineal was missing from the markets of Seville, it was, meanwhile, being channelled to the north of the Low Countries and England, through transatlantic privateering and contraband. Both of these regions developed a high demand for American dyes in their centres of textile production, which had been expanding since Flemish dyers fled there, after political and religious conflicts in the south of the Low Countries, at the end of the 16th century.

Textile centres in other parts of Europe did not witness the expansion that occurred in England, the Low Countries, France or Italy and, thus, it is possible that their use of American cochineal was limited. In fact, the local textile manufacturing centres of these regions relied on locally available dyestuffs, which were sufficient to meet local demand and available expertise. This seems to have been the case of Germany and Portugal, where madder and kermes, respectively, played important roles in assuring local economies. In more easterly parts of Europe, through political or commercial connections to West Asia, American cochineal probably had a more preponderant role, as shall be assessed further in Chapter 10. As for Asia, a few decades after American cochineal started to be accepted in the main European centres of textile production, it was soon disseminated to important commercial centres of the Islamic world.

6.2. American cochineal in Asia

During the course of the Early Modern period, American cochineal was re-exported from Europe to Asia by way of the land routes of the Silk Road; sea routes of the Red Sea and the Persian Gulf; or by the Cape route, around the horn of Africa to the Indian Ocean. In the early 17th century, the latter route was mostly used by the vessels of the Portuguese, English (East India Company, EIC, founded in 1600) and Dutch (*Vereenigde Oostindische Compagnie*, VOC, since 1602). Moreover, it was channelled directly from the Americas to Asia by the Spanish, via the Pacific Ocean [64]. Increasingly considered a valuable commodity for the most sumptuous textiles, the American insect gradually became available in the most important cities of Turkey, North Africa, Iran, India and China.

Turkey and the Levant. Sahagún, in 1570, affirms that cochineal *llega hasta la China y hasta Turquía*, *[and] casi por todo el Mundo es preciada y tenida en mucho* [65]. Whether or not this was true already by 1570, it is a fact that Venice had old commercial links with Istanbul, the Levant and other parts of West Asia, as well as an established tradition of international trade in dyestuffs [66]. Italy had a long-standing relationship with the Ottoman Empire, which contributed to the interchange of artistic knowledge between both territories and, hence, the application of common practices for textile production. Although the Ottoman court workshops, in Bursa (15th and 16th centuries) and in Istanbul (after the middle of the 16th century), produced fabrics of high quality in both designs and manufacturing, the court came to appreciate the Italian production, in the late 15th and early 16th centuries. Hence, Italian silk-weaving workshops extensively produced Ottoman-style fabrics for export to the Turkish market, which, in turn, resulted in the introduction of Italian artistic influences into the pattern layouts and artistic motifs of Ottoman textiles. As a

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[64] Balfour-Paul, 1998, pp. 44 and 50-51; Donkin, 1977a, p. 865, 1977b, pp. 38-39; Lee, 1951, p. 211; Masson, 1896, pp. 129, 373-374 and 386; Spufford, 2010, p. 18.
[65] Sahagun, 1956, p. 341 ["reaches China and Turkey, *[and]* almost all around the world it is appreciated and much considered].
[66] Donkin, 1977a, p. 865; Sanz, 1979, p. 585.

result, an extraordinary similarity between textiles from both places evolved, namely through the use of similar materials and shared compositions and motifs [67].

In this context, it is likely that American cochineal may have been brought to this region, along with textiles dyed with it, a few years after it started being adopted in Italian dyeing centres. By 1572, the Venetians were undoubtedly bringing the dyestuff to Istanbul and to the Levant. Alternatively, cochineal travelled from Antwerp to Turkey with Eastern European merchants, reaching first Moscow or Gdánsk by sea and river, and then again being re-shipped to the Black Sea towards its final destination, Istanbul [68].

Cochineal was also shipped to Turkey and to the Levant by merchants from other parts of Europe [69]. In 1573, it was sent by the French, from Marseilles to the Levant, and by 1580, most of the cochineal exported from Florence was also sent to that region [70]. In 1582, Bernardino De Mendoza writes from London to the Spanish king warning that an English vessel was about to set sail to Istanbul, bringing from the English queen "a grand present of cochineal and other things to the Turk *[sultan]*" [71]. During the 17th century, both Dutch and English merchants were bringing the dyestuff along with other products to the Levant, to Turkey and to Tunis [72]. In 1605, the Portuguese Jewish Teixeira writes that "much cochineal" was brought from Venice to Aleppo [73]. John Sanderson, a traveller and company agent, suggests in 1586 that consignments of the American dyestuff should be sent to Cairo and, in 1597, he reports it in Beyoğlu (district of Istanbul). By then, it was also used in the dyeing industry of Fez (Morocco), where it was being sold at a price similar to that in Seville [74]. By the middle of the 17th century, cochineal was a regular commodity brought annually to the Levant [75].

[67] The similarities of the textiles from both regions can hinder iconographic assessments for their provenance attribution. Though, the woven structures usually remain characteristically Italian or Turkish and, thus, it is possible to distinguish them through technological examinations. Atasoy et al., 2001, pp. 18-19 and 155-156; Baker, 1995, p. 92; Böhmer, 1997, p. 156; Carboni, 2007, pp. 188-189 and 196-197; Monnas, 2012, pp. 11-13.
[68] Prada, 1961, p. 102; Sanz, 1979, p. 585. See also Atasoy et al., 2001, pp. 176-177.
[69] Atasoy et al., 2001, p. 159; Prada, 1961, p. 102; Sanz, 1979, pp. 585 and 587.
[70] Sanz, 1979, pp. 562 and 585-586.
[71] Hume, 1896, 10th Nov. London [294].
[72] Huet, 1719, p. 107; Kadi, 2012, p. 183; Roberts, 1677, pp. 69 and 107.
[73] Teixeira, 1902, p. 119.
[74] Sanderson, 1931, pp. 131 and 169. See also Atasoy et al., 2001, p. 196; Donkin, 1977a, pp. 865-866, 1977b, p. 38; Lee, 1951, p. 211; Sanz, 1979, p. 585.
[75] Anderson, 2015, p. 353; Baladouni & Makepeace, 1998, p. XXIII.

Iran. One of the first records of shipments of American cochineal in Iran might be the one brought by the diplomatic mission led by García de Silva y Figueroa in 1614, sent by the king of Spain, Phillip III (r. 1598 - 1621), to the Safavid Shah 'Abbas I (r. 1587 - 1629). Among a large number of valuable gifts offered to the emperor, were five large barrels filled with 30 *arrobas* of the American insect, worth 4 000 ducats (c. 184 *pesos* per *arroba*) [76], a value close to the prices registered in Seville at this time. However, it is possible of course that the American insect was being supplied years before to the Iranian markets and to centres of textile production from Yazd, Tabriz, Isfahan, Kashan or Kirman, through other mechanisms. Indeed, in spite of almost constant war with Turkey throughout the 15th and 16th centuries, the economy of the Safavid Empire was dependent on the Ottomans, not just because they were important consumers of Iranian silk, but also because they controlled the main gates to European markets [77]. Hence, the American dyestuff could have been brought into the region through the contact with merchants from Turkey or North Africa.

Even so, historical evidence for the trade of this insect dye into the region is certainly reported for the first years of the 17th century. In 1618, the English were bringing the dyestuff into the region and, in 1619, the dyestuff was sold in Isfahan, having been brought by the Portuguese [78]. In 1626, the same city was selling cochineal, brought by the Dutch from Venice and Istanbul. Its price was settled at £3.25 per pound (c. 387 *pesos* per *arroba*), a price almost three times more expensive than that reported in Seville at the same time. This price not only depended on the shipped quantity available, but also on which trade routes were used [79]. By then, cochineal was already being used in the main Safavid centres of textile production, such as Tabriz, Isfahan or the provinces of Kerman and Khorasan, where manufacturers had long been using lac dye from South Asia [80].

India. From the second half of the 16th century, under the rule of Emperor Akbar (r. 1556 - 1605) and his cosmopolitan court, the arts of Mughal India started to achieve great

[76] Pinto, 2011, pp. 265-266 and 277; Simpson, 2010, p. 39. See also Anderson, 2015, p. 353. Some decades before, in 1581, an English traveler reported the trade of "Cochonillio" in Shiraz. This could either be the American dyestuff or, alternatively, an Asian variety (Purchas, 1905, p. 461). See also Donkin, 1977b, p. 39.
[77] Atasoy et al., 2001, pp. 155-157 and 182-189; Baker, 1995, pp. 107-111 and 120; Sardar, 2013, pp. 67 and 69.
[78] Sainsbury, 1870a, April [339], 1870b, Oct. 16 Ispahan [753].
[79] Sainsbury, 1884, Ispahan June 14 [330].
[80] Donkin, 1977a, p. 866.

artistic development. At this time, Iranian artists moved to the region and local artistic production became strongly influenced by Safavid models. Famous textile production centres were located in the provinces of Gujarat (Surat, Ahmedabad, Cambay), Punjab (Lahore, current Pakistan) Bengal and Dhaka (current Bangladesh). In these centres, velvets, brocades, satins, carpets, rugs and rich cottons were produced, not only for the most important court palaces in Delhi, Lahore and Agra, but also for the lucrative textile trade, conducted by agents of the Mughal emperors with Southeast Asia and later Europe, especially in the 17th and 18th centuries [81].

After establishing commercial relationships and a textile factory in Surat in the first years of the 17th century, the English EIC started importing cochineal from Europe to India through the Cape route [82]. Though, demand for it was small in Indian markets, which might be related to the competition not only from the locally available lac dye, but also from mercantile land routes connecting the north of India with Iran. There, cheaper cochineal was coming through land routes crossing Turkey and North Africa [83]. This cheaper cochineal was likely the American variety, but it could also have been another type of cochineal brought from Russia through inland routes, as shall be discussed later in this work.

Sir Thomas Roe, the first accredited English ambassador to the Mughal Court, wrote to the English Factors in 1617 from Mandore, in Surat. In his letter, he advised that the American dyestuff would be better sold in Surat, because in Mandore competition was raised by the presence of cochineal being sold in the "Persian Seray" (an inn for travellers and merchants, roadside to trade routes). One month later, in another letter to the factors in Surat, Roe considers that cochineal "is no commodity for ordinary markets and *[…]* too dear ever to be a commodity for this country" [84]. In another month, the EIC was informed that the American dyestuff was being used in Agra "in mean quantity" [85]. Again, in 1618, the dyestuff was reported in Ahmedabad, but it was "sold below cost", whereas in 1619 and 1620, its sale was reported in Surat, but advised against further shipments, since it was

[81] Walker, 1997, pp. 3-5 and 8; Riello & Roy, 2009, pp. 4-6 and 219; Shibayama, et al., 2015, p. 2.
[82] Donkin, 1977a, p. 866, 1977b, p. 39; Phipps, 2010, p. 45; Walker, 1997, p. 15. Alden (1965, p. 38) and Balfour-Paul (1998, p. 45) also mention the English relationship with Surat for the trade of Indian indigo into England, for the then growing English textile industry.
[83] Donkin, 1977a, p. 866, 1977b, p. 39; Foster, 1906, p. 169; Lee, 1951, p. 211; Sainsbury, 1870f, Dec. 25 near Lahore [790].
[84] Foster, 1902, pp. 123-124 and 149.
[85] Idem, p. 254. See also Sainsbury, 1870c, Dec. 20 Agra [220].

unprofitable [86]. In 1634, cochineal was still reported in Indian markets, sold by both English and Dutch, though with not much success [87]. By now, the Dutch also were bringing cochineal to other points of Asia, such as Indonesia [88].

The English small trade in India for cochineal was not only related to competition. Sir Thomas Roe mentions that, in 1618, cochineal was brought by merchants from Iran to India and it was only sold in the markets of Sind. He adds that this dyestuff was not much known in India [89]. Later on, reforms applied by the Mughal Emperor Aurangzeb (r. 1658-1707) banned the use of cochineal and safflower from several textile centres [90], which indicates that old dyeing traditions continued to hold a strong place in Indian workshops. Nevertheless, in 1663, Armenian merchants were buying the American dyestuff in England to sell it in India and Iran, through English convoys sailing down the Cape route [91].

China and other ports of Asia. Another way to reach the outposts of Asian markets, was the sea route that was established by the Spanish in the 1570's, between Acapulco (initially from Barra de Navidad and other small ports along the west shores of Mexico), and Manila, in the Philippines. This route was connected by the Manila galleon which annually brought silver, cochineal and other merchandise. Owing to this transpacific route, Manila became one of the most important international entrepôts up until the 19th century [92]. There, cochineal was so important for the Asian merchants that the Spanish were even using it as currency for exchange in the second half of the 18th century [93].

American cochineal was already available in China around 1700, when the Chinese Emperor, K'ang-hsi (r. 1661-1722), described it as a better source of red than the local lac dye [94]. The American dyestuff may have been brought into the region and to Japan since the 16th century by the Spanish, through the transpacific route. It was likely brought to Japan as

[86] Foster, 1906, pp. 21, 54, 78 and 184-185. See also Sainsbury, 1870d, Feb. 15 Ahmedabad [272], 1870e, March 12 Surat [624].
[87] Sainsbury, 1892a, Mar. 5-7 [544], 1892b, Nov. 27 Ispahan [624].
[88] Balfour-Paul, 1998, p. 44; Phipps, 2010, p. 41.
[89] Roe, 1899, p. 488. See also Donkin, 1977a, p. 866.
[90] Donkin, 1977a, p. 866.
[91] Baladouni & Makepeace, 1998, pp. 57-58; Anderson, 2015, pp. 353-354.
[92] Burkholder & Johnson, 1998, p. 146; Donkin, 1977a, p. 865, 1977b, p. 39; Hakluyt, 1935, pp. 99 and 109; Hamilton, 1948, p. 42; Lee, 1951, p. 211; Marichal, 2014, p. 207; Phipps, 2010, p. 40; Tejada, 1853, pp. 16-17.
[93] Raynal, 1783, III, p. 83.
[94] K'ang-Hsi, 1779, pp. 477-478.

well by Portuguese and Italian missionaries at this time. By then, its price was reported to be so high that it even reached several times the price of the same weight of gold. For this reason, the American dyestuff may have been mostly used for small applications, such as painting, rather than for dyeing [95].

In the 18th and 19th centuries, cochineal was reported in Canton, where European merchant ships docked annually, such as English, French, Dutch, Swedish and Danish [96]. Its price was probably cheaper now, given the affluence of European merchants who sought to increase its availability in Asian markets. Indeed, in the middle of the 19th century, it was commonly used for dyeing Chinese textiles [97]. At this time, from Canton (via Manila) or directly from Europe, the American dyestuff was reaching the main ports of India (Surat, Bombay, Madras or Calcutta), the Persian Gulf, Vietnam, Cambodia, Siam, Japan, the north of India and beyond, to the inland regions of Central Asia [98].

Conclusions. Since the first shipments from the Americas, cochineal achieved wide popularity within a few decades in the most important ports and centres of textile production in Europe and the Islamic world, and at a much slower pace, in Central, Southeast and East Asia.

In Turkey and in the Levant, owing to long-lasting commercial and cultural connections with Italy, American cochineal was brought into the region, soon after it was acknowledged in Italian dye works, sometime during or immediately after the 1540's. From Turkish markets, cochineal may have been transported to the markets and textile producing centres of Iran, given the regular mercantile communications between both regions. Later in

[95] Anderson, 2015, p. 354; Lee-Whitman, 1982, p. 24; Yu & Liu, 2013, p. 20. In personal correspondence, Jing Han (Centre for Textile Conservation and Technical Art History, History of Art, University of Glasgow, Scotland) informed that American cochineal has not been so far reported in 16th to 18th-century historical Chinese documents, namely dye recipes, documents of the central government (warehouse dyes lists) and local records/accounts on dyestuffs. See also Han, 2016, pp. 231 and 296.
[96] Anderson, 2015, p. 354; Lee-Whitman, 1982, pp. 39 and 41; McCulloch, 1835, pp. 234 and 242; Viana, 1903, pp. 274-275. According to Balfour-Paul (1998, p. 48), the Danish settled their commercial company in 1602 in the Coromandel coast in India, while the French, in 1664.
[97] Hedde, et al., 1848, pp. 192 and 194.
[98] Kuropatkin & Gowan, 1882, p. 74; Milburn, 1813, I, pp. 145, 147, 155, 160, 182 and 211–212, II, pp. 45, 51, 145, 150, 433, 444, 454 and 485; Moorcroft & Trebeck, 1841, p. 175; Pritchard, 1957, p. 131; Viana, 1903, p. 306. See also Donkin, 1977a, p. 867, 1977b, pp. 39-40; Lee, 1951, p. 212; Phipps, 2010, pp. 40-41. Aitchison (1874, p. 140), in the second half of the century, states that American cochineal was transported from the sea coast of India to Kashmir, and thence, to the markets of Leh, in the north of India.

the century, and throughout the following one, trading relationships with other European territories, such as Portugal, England or the north of the Low Countries, may have led to the dissemination of cochineal into West Asia as well, either through the Red Sea and Persian Gulf routes beginning in North Africa; or through the Cape route from Europe.

Despite links to international trade, the main centres of textile production in India and China do not seem to have accepted American cochineal as swiftly as those of West Asia and Europe. In the early 17th century, the American dyestuff brought by sea to Indian commercial seaports was facing competition with the same product, sold at cheaper prices, being imported by way of the land routes connecting the north of India with Iran. At the same time, the Spanish were bringing it to the Philippines, and re-shipping it from there to China. However, either because of its initial high price or because of long-standing dye traditions that still used locally available lac dye, cochineal only penetrated into Indian and Chinese dye workshops somewhat later, as shall be discussed further in Chapter 10.

Indeed, by the second half of the 18th century, global circulation of American cochineal between Europe and Asia is well illustrated by Anderson, who provides English imports and exports for this dyestuff [99]. From his testimony, it is possible to conclude that England received the bulk of its cochineal from Spain, as well as smaller amounts from Florida, Virginia and Maryland (United States), and from the Low Countries. From England, the dyestuff was re-exported to Denmark, Sweden, Norway, (back to) the Low Countries, France, Germany, Ireland, Italy, Portugal, Russia, and further afield, to Turkey and the English Empire in India. This offers only a glimpse of how much of the dyestuff these places were receiving, either from England or elsewhere – for dyeing, painting or medicinal applications [100].

Therefore, one can imagine that many of the textiles manufactured in Asia and exported to Europe could have been dyed with American cochineal at this time. This shows the global trade involved in the textile industry: while cochineal travelled great distances across the world from the Americas to Europe and then to Asia, it also made its way back from Asia to Europe, in the form of Chinese, Indonesian, Indian or Iranian textiles. However, other local sources of red dye would have been available also in dyeing centres, and for this

[99] Anderson, 1801, IV, p. 450.
[100] Idem, I, p. 524. See also Anderson, 2015, pp. 339 and 344; Greenfield, 2006, pp. 110-114; McCulloch, 1835, pp. 894 and 897; Pomet, 1748, p. 18.

reason, it is fundamental to assess their importance for dyers, once American cochineal became available. Such a comparison can demonstrate in a more conclusive way the extension of the geographical impact of the American dyestuff across European and Asian textile industries and, therefore, emphasize the growth of its global importance throughout the Early Modern period.

CHAPTER 7

COMPETITION BETWEEN INSECT DYES:

Markets and Dyer's Art

"*[American cochineal]* quickly supplanted all

other red dyestuffs." Elena Phipps [1]

As American cochineal became an increasingly important commodity in European and Asian commerce, its popularity in dyeing centres and in dyeing treatises grew alongside [2]. Although other insect sources of red could still be marketed and used for dyeing purposes, references to them in historical sources after the 16th century became scarcer. This is directly related to the advantages offered by the American dyestuff, which was at least ten times cheaper, yielded more colorant and gave more intense shades of red [3]. This chapter undertakes a comparison between the trajectory of the American insect and "Old World" insect dyes, namely kermes, lac and Armenian and Polish cochineal, to determine the geographical extent of the adoption of American cochineal into European and Asian dyeing practices, and consequently, its impact on the trade and dye applications of local insect dye sources. This study constitutes the final part of the historical section of this work, and hence, following the interpretations obtained in the previous chapters, aims to present a more comprehensive perspective about the importance of American cochineal in Early Modern European and Asian societies.

Hence, it is divided geographically, and looks, firstly, at the relationship between the American insect and European kermes and Polish cochineal; before turning to a comparison between the same and Asian lac dye and cochineal. By reviewing the historical context of these dyestuffs in this way, it is possible to elucidate a more complete picture of the process

[1] Phipps, 2010a, p. 2.

[2] Multiple references to American cochineal are found in many treatises dated during and after the 16th century, not only to obtain red shades (crimson or scarlet) but also to achieve many other colours (Berthollet, 1791; Férnandez, 1778; Hellot, 1750; Hofenk de Graaff, 2004; Macquer, 1808; Pearson, 1705; Posthumus & Nie, 1936; Talier, 1805; Verhecken, 2013).

[3] Hofenk de Graaff, 2004, p. 55; Lee, 1951, p. 210; Schmidt-Przewoźna & Przewoźny, 2010, p. 402; Verhecken & Wouters, 1988, p. 214.

of their replacement by American cochineal. The chapter ends by arguing for a need for complimentary data to properly assess the results of these historical studies and proposes the incorporation of material cultural and dye science.

7.1. Kermes and Polish cochineal

In the middle of the 16th century, American cochineal was found in the major European ports and, while dyers were starting to accept it in the main centres of textile production, painters were using it as well, by mixing it with kermes in their lake pigments [4]. As the American dyestuff was slowly stepping into local practices and its annual remittances from Mexico were still small in relation to those registered later in the century, kermes was still being produced on a large scale in France and was commonly co-existing with the American insect in the markets of Antwerp [5].

Indeed, despite the advantages of the American product and growing transatlantic imports of it, kermes continued to be highly considered by Europeans. Between 1567 and 1568, London imported a total of 2 510 pounds of *grain* (or kermes, c. 100 *arrobas*) and 350 pounds of American cochineal (c. 14 *arrobas*). Also in the 1560's, kermes was co-existing with American cochineal in the markets of Venice, while clothes exported from Ancona and Milan were still dyed with the old materials [6]. In Turkey, people still collected kermes throughout the century to pay as duty to the Ottoman court [7].

Nevertheless, American cochineal began to be part of local dyeing practices. *De' secreti del reverendo donno Alessio Piemontese* from 1558, mentions the use of *tre once* [*cremeſi*] *per ogni libra di ſeta* [8], which seems to be a somewhat smaller amount of dyestuff, in relation to that usually suggested for kermes and Polish and Armenian cochineal (see Chapter 1). This could be American cochineal given the mid-16th-century date of the

[4] Benavente, 1988, p. 250.
[5] Cardon, 2007, p. 613; Goris, 1925, pp. 262-625. See also Lee, 1951, p. 209.
[6] Donkin, 1977a, p. 865; Kirby, et al., 2014, p. 5; Sanz, 1979, p. 561.
[7] Atasoy et al., 2001, p. 195; Böhmer, 1997, p. 156.
[8] ["three ounces *[crimson]* for each pound of silk"] Ruscelli, 1558, pp. 287-288. See also Kirby, et al., 2014, pp. 37-38.

treatise [9]. In fact, a similar amount of *cremese* is proposed for dyeing silk in the *Nuovo Plico d'ogni sorta di tincture*, published in 1680. This *cremese* is likely to be American cochineal, given the nomenclature for other dyestuffs and amounts described in other recipes of this manuscript. For instance, it suggests the use of *grana* (kermes) to dye a woollen hat; as well as six ounces of *grana di Spagna* (also kermes) per pound of (woollen) cloth, to dye a Venetian scarlet shade. The amount of *grana* recommended here (six ounces) to dye wool is double that mentioned when using *cremese* to dye silk (three ounces). Therefore, and since wool generally requires less colorant than silk to obtain deep red shades, it is clear that the designation *cremese* does not correspond here to kermes. Instead, in another recipe of the same manuscript, American cochineal is referred to as *cocceniglia, cioè cremese* [10]. Hence, it is quite possible that American cochineal was also used in the 1558 Italian recipe.

At this time too, in the *Instruction générale pour la teinture des laines* from Colbert, originally published in 1671, kermes (*vermillon* or *graine d'écarlatte*) and American cochineal are mentioned together as *drogues colorants qui doivent eſtre employees ſeulement par les* [French] *Teinturiers du grand & bon teint* [11]. Kermes, still grown in the regions of Provence, Languedoc and Roussillon in the second half of the 17th century, is described in the *Instruction* as one of the ingredients used to obtain two of the seven most popular shades of red produced in *grand teint* French dyeing centres, *eſcarlatte de Frãce* and *demy graine* (mixture of kermes and madder). As mentioned in the previous chapter, from these seven shades, four were also obtained with American cochineal: *rouge carmoiſy, demy cramoiſy* (mixture of cochineal and madder), *ecarlatte de cochenille ou façon de Hollande* and *eſcarlatte de Frãce* - in this case, cochineal was used, instead of kermes. The other two colours were acquired with madder [12].

In the middle of the 18th century, Hellot in his *L'art de la teinture des laines*, defines American cochineal as a common ingredient to achieve red and other colours. As for kermes, one recipe describes how to dye French scarlet with it, although Hellot adds that this colour

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[9] To dye one pound of silk, it was needed at least 4 pounds of the best *cremesi* (European/Asian cochineal), and at least 1.5 pounds of the best *grain* (kermes) (see Chapter 1). Instead, 3 ounces would be a more suitable amount for American cochineal (see Chapter 2).

[10] Talier, 1805, pp. 59, 62-63, 73 and 111. Italian commercial records also refer to the American dyestuff as *cremese* (Morineau, 1969, p. 165) or *cremessi* (Brown, 1904, Madrid, Nov. 3, 1608 [357]).

[11] ["drug dyes that must be solely employed by the Dyeing of great and good tints"] (Colbert, 1672, pp. 2 and 76-77).

[12] Colbert, 1672, pp. 23-25 and 178. See also Pomet, 1748, p. 20.

was now known better as Venetian scarlet, since it was, as along with kermes, most frequently utilized in that Italian city, rather than in France. Indeed, Hellot complains that French dyers were barely aware of kermes and, for his experiments, he had to visit Languedoc (kermes producing region) and buy it himself, for the merchants of Paris only had small amounts for medicinal purposes. Regardless, he informs that kermes was exported from Marseilles to the Levant and chiefly to Tunis and Algiers [13].

In 1791, Berthollet in his *Elements de l'art de la teinture*, besides typically indicating the use of cochineal, also describes a recipe to dye wool with kermes, which was then mainly collected in Languedoc, Spain and Portugal. By then, its price in France ranged between 30 - 40 *sous* per pound of dried insects (c. 7 – 9 *pesos* per *arroba*), a price almost ten times cheaper than that registered for American cochineal at this time – though a textile dyed with kermes would be as or more expensive as one dyed with the American variety, since more insects were required to obtain a similar colour. Even so, kermes was still applied by French dyers and much of the kermes used in France was imported from the Levant. Moreover, French textiles dyed with this insect or with American cochineal were sent to that region [14].

In Spain, in the middle of the 18th century, Férnandez in his *Tratato instructivo, y práctico sobre el arte de la tintura*, also mentions the use of kermes in 18th-century Spanish dyeing practices, in spite of the wide use of American cochineal. In fact, kermes is recommended to colour wool, whereas American cochineal is considered more appropriate to dye silk [15] – in accordance with medieval dyeing traditions discussed earlier in Chapter 1. Moreover, Férnandez informs us that kermes was still exported from Spain, as international markets were demanding it [16]. Indeed, its production kept on being considered an important factor for local economies, as shown by *Memorias … sobre la grana Kermes de España* [17].

[13] Hellot, 1750, pp. 244-276. See also Verhecken, 1989, p. 389. At this period, great quantities of kermes were indeed reported in the Languedoc region (Cardon, 2007, p. 613). Pomet (1748, p. 20), in the end of the 17th century, mentions that the people of Languedoc were selling kermes to apothecaries, who made syrup with it and then re-sold the remainder to dyers. See also Diderot & D'Alembert, 1772, pp. 319-321; Paganucci, 1762, p. 477.
[14] Buti, 2008, pp. 10-11; Berthollet, 1791, pp. 205-212.
[15] Férnandez, 1778, pp. 109, 147 and 151.
[16] Férnandez, 1778, p. 150: *Con la grana Kermes, que se coge en abundancia en España, y se llevan los Estrangeros para el Tinte de sus manufaƐturas, se pueden hacer muy buenos colores en Lanas, usando de ella en la misma forma que se usa la Cochinilla para los colores de escarlatas* ["With kermes, which is caught in abundance in Spain and the foreigners take it for dyeing their manufactures, very good colours can be made on wools, using it in the same way as the cochineal for scarlet colours"].
[17] Martí, 1768.

As for the Low Countries, kermes imported from the south of France and other Mediterranean regions was still being applied at the beginning of the 17th century. Written between 1619 and 1623, the *Conste des ververs* from the Flemish dyer Henrick Coghen mentions the use of kermes (besides American cochineal) in the dyeing practices of Leuven [18]. Nearby, in the north of the Low Countries, another manuscript dated to the first quarter of the century also describes the use of kermes, as well as cochineal. At this time, and as demonstrated in the previous chapter, the imports of cochineal were growing to feed the expanding textile industry of the north of the Low Countries. Later in the century, perhaps after recognizing the advantages of the American dyestuff over kermes (both imported products), the Dutch authorities started to consider kermes an inferior product and, therefore, banned it from local dye workshops [19].

Moreover, an English translation of the Colbert's *Instruction*, dating from 1705, adds a note mentioning that "in our *[English]* Dyeries the Chermes Berries are but little uſed, for moſt Reds are Dyed with Cochineal" [20]. This clearly demonstrates that, by the beginning of the 18th century, American cochineal was well integrated in English dyeing practices, but kermes was no longer being used in workshops, at least in considerable quantities.

As late as 1794, the Mexican Alzate y Ramírez affirms that American cochineal, due to its higher quality and yield, eventually brought about the obliteration of dyeing with kermes, which had become something rarely practiced [21]. Although this could have been true for Northern European countries, it was not the case for territories surrounding the Mediterranean, where kermes was still produced, as demonstrated above. In fact, in Portugal, kermes produced locally was favoured still by the end of the 17th century, while imported American cochineal seems to have not been part of local dyeing traditions [22]. In the 18th century, the American dyestuff was applied as a lake pigment in paintings, as was kermes [23].

At the end of the 18th century, Beckmann, based on the testimony of contemporary travellers, indicates that kermes was being collected in Crete and in the Levant (as also

[18] Verhecken, 2013, p. 61.
[19] Hofenk de Graaff, 2004, pp. 56-57; Posthumus & Nie, 1936, pp. 218-228 and 231-233.
[20] Pearson, 1705, p. 168.
[21] Ramírez, 1831a, p. 302.
[22] *Regimento da fabrica dos panos de Portugal…*, 1690, pp. 26–27.
[23] Cruz, 2009, pp. 392-393.

mentioned by Hellot and Berthollet) and that most of it was being sent to Venice [24]. There, the insect continued to be used in workshops alongside American cochineal. International trade in kermes continued until the late 19th century and, as recently as 1988, kermes from Algeria was still reported in one Tunisian dye house [25].

In opposition to kermes, it is noteworthy that few of the above-mentioned dye treatises mention Polish (or Armenian) cochineal dyes. In fact, Hellot, in 1750, states that Polish cochineal cannot be used to obtain the same shades as with the American variety or with kermes. This is perhaps because here it is meant only for wool. Hellot adds that the Polish dye is much more expensive than the finest American cochineal, since it does not yield a fifth part of its colour. Hence, he concludes that this may be the reason why its commerce has lessened, as well as its name in most European cities [26]. Macquer, a few years later, in his *Art de la teinture en soie* only mentions recipes to dye with American cochineal [27] and, by the end of the century, Berthollet affirms that “no uſe is made of it in Europe”, and that “there are many other inſeɛts which alſo afford a red colour; *[…]* but from the advantages offered by cochineal, they have fallen into negleɛt or diſuſe” [28]. Nevertheless, both Hellot and Berthollet still provide recipes for kermes, which was widely produced in France by then.

One century earlier, an English translation of the German *Ars tinctoria fundamentalis* from 1683, adds a note mentioning that Polish and Armenian cochineal are not applied in England anymore: “*Polygonum*, in *Engliſh* Knot-graſs, is very well known to be of two ſorts, *viz*. large and ſmall, and there are different ſorts of each, tho' they are not commonly applied to any particular uſe”[29].

Schmidt-Przewoźna & Przewoźny (2010), based on Polish archival documentation, clearly demonstrate a decline in the production and trade of Polish cochineal, already in the middle of the 16th century. In 1539, export figures still show average levels, but in about eight years they vanish from the lists of products traded from Poznan and Wroclaw. A few years later, a similar crisis is seen in the Polish drapery industry. As the popularity of

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[24] Beckmann, 1846, p. 388.
[25] In 1830-1840, kermes was still exploited in some parts of Spain, as well as in Argelia. Heers, 1961, p. 13; McCulloch, 1835, p. 739; Verhecken, 1989, p. 390; Verhecken & Wouters, 1988, p. 214.
[26] Hellot, 1750, pp. 368-369.
[27] Macquer, 1763, pp. 76-93.
[28] Berthollet, 1791, pp. 212-213.
[29] Pearson, 1705, pp. 107-108.

American cochineal increased internationally, the demand for Polish dyed clothes diminished, thus forcing producers and buyers to lower their prices. Consequently, while dye producers started adding foreign components to the dyestuff, textile manufacturers began counterfeiting the fabrics. Adulteration hampered the dyeing efficiency and the quality of the finished textiles and, as a result, demand for Polish cochineal-dyed textiles progressively ceased [30].

By 1566, the insect was no longer profitable in Gdánsk and all over Poland and adjacent regions, it became less and less profitable. Eventually, fields formerly propagated with perennial knawel (the plant the insect fed on) were adapted for growing cereals and other crops of higher economic value. In a few regions, however, its breeding was still preserved, namely near Lezajsk and Belz, or fields nearby forests [31].

Nevertheless, in 1671, Bernitz wrote that Polish cochineal was found in abundance near Warsaw, as well as in Germany and Ukraine, especially in sandy regions. This was being sold by the lords of those lands to Jews, who collected it for sale to Armenian and Turkish merchants, who brought it to their nations to dye woollen and silk cloths. German merchants were also collecting it to sell to the Dutch, who were buying it at high prices in Gdánsk. Back home, Dutch dyers were mixing it with the American variety to obtain *Scarlatum & Carbaſinum* shades. By contrast, kermes was no longer allowed in Dutch centres of textile production at this time. Besides its dyeing applications, Polish cochineal imported by Jews and Armenians was also used in Iran to prepare carmine lakes [32].

Close to Poznan, the nuns of the Owinska monastery kept on breeding the Polish insect until the religious order was closed in the 18th century [33]. Its exploitation in Poland and adjacent countries like Germany was likewise reported at the end of the 17th century.

[30] The luxurious price of textiles dyed with Polish cochineal was not only related to its colorant yield, which was much smaller than that of American cochineal. The dyestuff itself was very expensive because of its exhausting harvest. Entire villages were engaged in this task, but they obtained small amounts. Indeed, to collect only 1 pound of Polish cochineal, it was needed to uproot at least 104 thousand plants, each of which only holding about ten insects. Schmidt-Przewoźna & Przewoźny, 2010, pp. 401-403.

[31] Schmidt-Przewoźna & Przewoźny, 2010, p. 403.

[32] Bernitz, 1681, pp. 144-145. See also Born, 1938, p. 212; Cardon, 2007, p. 640; Donkin, 1977a, p. 856; Hellot, 1750, pp. 367-368; Pearson, 1705, pp. 109-110; Verhecken & Wouters, 1988, p. 227. In a Dutch treatise from the first quarter of the 17th century, Polish cochineal is listed as *greyn met haer pastel uut Duytslant* ("kermes with its paste from Germany") and, in relation to several types of kermes, it is considered the worst – the best is the kermes paste from Turkey and Syria - followed by the Spanish and the French (Posthumus & Nie, 1936, pp. 232-233).

[33] Schmidt-Przewoźna & Przewoźny, 2010, p. 400.

By 1792, annual exports were still sent to Venice (as was kermes), and in the 19th century, its commerce and dye applications were still reported in Eastern European countries, namely in Poland and Ukraine, and in the most important markets of West Asia, such as in Turkey and Armenia [34]. In Poland, a renewed interest for this dyestuff and old dyeing techniques with it were furthermore revived at the beginning of the 19th century, although it was soon acknowledged that it was not economically viable [35].

Conclusions. From this review of historical dye treatises and historical information on trade, it is possible to conclude that, in the cloth-working centres of Europe, the American product slowly supplanted kermes and Polish cochineal, though not entirely.

Especially in kermes-growing territories around the Mediterranean Sea, this dyestuff continued to have some importance for local economies, as production was not only undertaken for the consumption of local centres of textile production, but also for export. This included places like Greece and other southern European regions, which did not possess internationally renowned textile centres, but could produce kermes for local needs and export purposes. Indeed, until the 19th century, it kept on being internationally traded to meet the demand of dyeing centres, which could not be fully served by home production. By contrast, northern European countries, which had to import kermes, soon started to rely solely upon American cochineal, since it offered more economic advantages and possibilities.

In the same way, although international demand for Polish cochineal and for textiles dyed with it drastically decreased in Europe during the 16th century, the dyestuff continued to be employed in Eastern Europe, including Ukraine, as well as some parts of West Asia, where it was also imported [36]. In Italy, specifically in Venice, kermes and Polish cochineal continued to co-exist with American cochineal in dye workshops until the 18th century.

Following long-standing traditions going back to Medieval times (Chapter 1), Venice, and other territories around the Mediterranean Sea, preferred to employ kermes on wool to

[34] Balfour, 1885, p. 758; Beckmann, 1846, pp. 395-396; Donkin 1977a, p. 857; Łagowska & Golan, 2009, p. 158; Pearson, 1705, p. 109; Schmidt-Przewoźna & Przewoźny, 2010, p. 405.
[35] Schmidt-Przewoźna & Przewoźny, 2010, p. 405.
[36] Donkin, 1977a, p. 857.

obtain, for example, the vivid orange red Venetian (or French) scarlet; though American cochineal could also be employed to obtain the same colour. Nevertheless, the American insect, as with the Polish variety, was more often preferred for achieving pinkish red shades on silk. Hence, perhaps because of its red orange hues, kermes was never overthrown from many southern European dye workshops, before the 19th century.

As for Polish cochineal, despite its disadvantages both in terms of production and dyeing, it continued to be brought to Venice (and even to the north of the Low Countries), as well as to West Asia. However, it is probable that it was no longer used in such sizeable quantities as up until the 16th century. Instead, it was now considered a compliment to the American variety, and mixed with it, to improve the final colour of the dyed textile.

These observations demonstrate that - despite the fact that American cochineal flooded international markets and revolutionized practices in European dye workshops by facilitating the production of cheaper textiles and a wider range of colour possibilities - in some parts of Europe, the old materials and traditions were never completely obliterated, as some scholars have tended to affirm over the past century. Moreover, this scenario is also verified for Asian insect dyes.

7.2. Lac dye and Asian cochineal

During and after the 16th century, lac dye maintained a small role in most European dyeing centres, although it was still used as a lake pigment [37]. For instance, Hellot, writing in the mid-17th century, describes his experiments on dyeing scarlet with lac dye [38]. At the end of the 18th century and throughout the 19th century, the English were also importing this dyestuff from India, which was used to some extent to colour fabrics, besides being applied as a pigment or as lacquer [39].

[37] Bensi, 2012, p. 31; Hofenk de Graaff, 2004, p. 52. Garcia da Orta (1913, pp. 247 and 249) describes its trade to Portugal and other parts of Europe in the second half of the 16th century.

[38] Hellot, 1750, pp. 354-364. Berthollet (1791, pp. 213-217) also mentions dyeing with lac dye, but using tin and a mixture with American cochineal.

[39] Hofenk de Graaff, 2004, pp. 52-53 and 85-86; McCulloch, 1835, p. 301; Simmonds, 1880, p. 3795; Verhecken & Wouters, 1988, p. 230.

In Asia, lac dye was traded regularly, and it was profusely applied in Asian centres of textile production [40]. Indeed, and as stated in the previous chapter, when American cochineal started gradually appearing in local Asian markets, lac seems to have represented a competitor to it entering local dyeing practices, especially in territories where lac was produced, such as India and China. Although the available historical evidence for confirming these propositions is small or even rare, scientific research shall be undertaken in this work to verify them.

As for Armenian cochineal, apart from the occasional historical mention that it was no longer used in Europe, no other information is available, which may point to its absence in European trade and dyeing practices, somewhere after American cochineal was adopted in European dyeing centres [41]. Given its small yield, difficulties presented to extracting the colorant, and distant trade (Polish cochineal, by contrast, was coming from nearby regions and had more colorant), it seems acceptable to assume that it was no longer worthy of use in European textile centres.

However, there is no doubt that the application of the Armenian dyestuff continued in Asia, despite the gradual availability of American cochineal in the main centres of textile production, discussed in the previous chapter. In 1686, Sir John Chardin in his travel through Iran, documented that the citizens of Marand were collecting *Cocheneel Quermis* "for any longer time then only eight days in the Summer" (the time that endures the insects' mating season) [42]. This was possibly used in local dyeing or painting practices or, alternatively, exported to other Asian regions. Indeed, in 1776, Turkish dyers were still using it [43] and, in 1834, Parrot addressed its use for dyeing in Iran and other regions of West Asia, where the dyestuff was sometimes sold at high prices [44]. By the middle of the century, when travelling in Armenia, Montpéreux reported that the monks of the monastery Etchmiadzin (nearby Yerevan and the mount Ararat) were using a red pigment made with Armenian cochineal to illuminate their manuscripts [45].

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[40] Garcia da Orta (1913, pp. 245, 247 and 249) mentions the common trade and applications of lac dye (*lacre*) in Asia in 1563. See also Donkin, 1977a, p. 865, Han, 2016, p. 231.
[41] Hofenk de Graaff, 2004, p. 71.
[42] Chardin, 1691, p. 351.
[43] Verhecken & Wouters, 1988, p. 228.
[44] Parrot, 1834, pp. 105-106. See also Donkin, 1977a, pp. 849 and 851.
[45] Montpéreux, 1839, pp. 461-462. See also Donkin, 1977a, p. 851.

Other sources in the 19th century not only address the use of Armenian cochineal in the region, but also the trade of a cochineal variety that would seem to be the Polish one. Indeed, perhaps even before the beginning of the century, Bukhara received from Russia shipments of cochineal "found in the root of a plant that flourishes in a marsh", although locals were not aware of how to prepare it. From Bukhara, this cochineal (*kírmes*) was also sent to Herat and Kabul (Afghanistan) and to Turkistan [46]. From Bukhara and Kabul, it was passed along to India, although here it found competition from the American variety, which was being brought in from the Indian seaports [47]. Regardless, both types of cochineal were co-existing in Indian workshops as exemplified by Moorcroft, who describes several tints used to dye crimson in a local textile centre in the province of Kashmir in North India, somewhere between 1819 and 1825: "the best kind is derived from cochineal, imported from Hindustan *[North India]*. Inferior tints are from Lacand Kirmis (Chermes), distinguished as Kirmisi, Kirmdana, and Kirmisi lac, or cochineal and lac chermes" [48]. The best kind is likely to be the American variety brought by merchants from the Indian sea ports. *Kirmisi lac* or *lac chermes* is no doubt lac dye commonly produced in India. As for *Kirmisi*, *Kirmdana* or *cochineal* it probably corresponds to the cochineal brought from Bukhara, the Russian variety [49].

This co-existence of both dyes is once more verified in Kashgar (Northwest China), as late as 1876. There, cochineal (*kershes*) imported from Russia was used exclusively to dye silk, and in local bazaars this dark purple dyestuff was valued at 16 to 18 ducats per *pood*, whereas the grey American cochineal (*grana fina*) was valued at 14 to 16 ducats per *pood* [50]. Perhaps by this time, prices for American cochineal were much lower in relation to previous decades because of higher competition from synthetic dyes, as well as increased availability of the insect in international markets, due to its widespread dissemination around the world. Indeed, in the last decades of the 19th century, American cochineal and other native insect dyes were being displaced by synthetic aniline dyes in India, while cochineal imported from

[46] Aitchison, 1874, p. 140; Burnes, 1834, pp. 429 and 434, 1842, p. 301; Prinsep, 1833, pp. 239 and 652–653; Vigne, 1840, p. 69. Turkistan encompassed regions of the present countries of Kazakhstan, Uzbekistan, Tajikistan, Kirgizstan and Turkmenistan. In 1820, Meÿendorf (1826, pp. 245 and 250-251), too, states that merchants of Bukhara were receiving cochineal from Russia, and Kabul was acquiring it there in Bukhara. Some years before, in 1815, Elphinstone (1839, pp. 384-386) had furthermore noticed cochineal as one of the imports of Kabul from Turkistan. This may as well be the same Russian variety.

[47] Burnes, 1834, p. 434,1842, p. 301; Prinsep, 1833, p. 653.

[48] Moorcroft & Trebeck, 1841, p. 175. See also Vigne, 1840, p. 22.

[49] Aitchison, 1874, p. 140.

[50] The Russian *pood* was considered to be equivalent to c. 36 lb. Kuropatkin & Gowan, 1882, p. 74.

Bukhara (likely the Russian variety) was being displaced in Tashkent (Uzbekistan) by fuchsine dyes brought from Russia [51].

Conclusions. Although not much information is available for the trade and dyeing practices of insect dyes in Asia after the 16th century, it is possible, nevertheless, to draw fruitful interpretations. For instance, it seems plausible that despite the growing availability of American cochineal in Asian markets, both lac dye and Asian cochineal species (Armenian, Russian and perhaps even other Asian varieties) kept being produced until the 19th century, either for local applications, or for export into other Asian regions, and in the case of lac dye to Europe as well. Indeed, as exemplified by one 19th-century dyeing workshop in India, local and foreign insect dyes were still being applied at this time, although dyers were aware of the disadvantages of their local materials in relation to the American dyestuff.

Although patterns of trade certainly changed in Europe and Asia after the 16th century, as verified in previous sections of this work, this is not entirely true for their centres of textile production. From the interpretations presented above, and in Chapter 6, contrary to what has been defended by contemporary researchers (and also suggested by the opening citation of this chapter), American cochineal does not seem to have completely dethroned other insect sources of red, nor was its acceptance as immediate as expected. Instead, this process seems to have been more complex, with local dyeing practices maintaining the use of native insect dyes. Indeed, it appears that the American dyestuff was clearly accepted in the major cloth-producing centres of Europe and West Asia; whereas in other parts of Europe and in Central, Southeast and East Asia, the American dyestuff found resistance, owing to long-established traditions of production, trade and dyeing of indigenous insect dyes. Indeed, as late as the 19th century, old traditional mercantile routes between Russia and Central Asia still appear to have provided some variety of Polish cochineal, which successfully competed with American cochineal. Notwithstanding, the number of historical sources available concerning the trade and dyeing applications of European and Asian insect dyes after the 16th century is limited.

In order to further understand the impact of American cochineal on local dyeing practices, as well as to confirm the historical evidence considered thus far, material analysis

[51] Balfour, 1885, p. 1004; Schuyler, 1877, p. 182.

of textile objects could offer additional information for assessing the historical propositions presented here and in previous sections. For instance, more conclusive interpretations could be established for the dissemination of the American insect in the main European and Islamic textile centres and its competition with local insect dyes. Indeed, the identification of American cochineal in textiles from the 15th to 17th centuries could provide vital results for determining the precise point at which this dyestuff became so important for European and Asian traditions in detriment to other local insect sources. Hence, chemical analysis of red dyes in a broad range of historical textiles is proposed as the next step. However, given the current limitations reported for the chemical characterization of cochineal dyes, it is fundamental to develop an analytical method that can bring more accurate results, as discussed in the next section.

CHAPTER 8

EVALUATION BETWEEN ULTRAHIGH PRESSURE LIQUID CHROMATOGRAPHY AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ANALYTICAL METHODS FOR CHARACTERIZING NATURAL DYESTUFFS

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Note for the thesis. Analytical limitations verified in the scientific literature concerning the chemical characterization of cochineal dyes, and as described in Chapter 2, require the development of an optimized analytical approach that can deliver more precise information about the source of insects used to colour historical textiles. In this way, it is possible to ascertain more conclusive historical interpretations about the acceptance of American cochineal in European and Asian dye workshops, from the 16th century onwards.

Therefore, this chapter, published as a paper in the Journal of Chromatography A, aims to develop an analytical method using ultra high-performance liquid chromatography coupled to photo-diode array detector (UHPLC-PDA), in order to bring more accurate chromatographic results than the conventional HPLC method, often applied to the analysis of natural dyes in the field of cultural heritage. Moreover, the optimization of an UHPLC-PDA method aims to identify, in one single analysis, a wide range of dye compounds with closely related and/or different physicochemical properties, belonging to natural dyestuffs, usually present in historical textiles. Thus, it is expected that improved analytical conditions can display more accurate information about dye sources present in textile objects, namely cochineal species or mixtures of these with other insect sources of red.

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Abstract

An evaluation was undertaken of ultrahigh pressure liquid chromatography (UHPLC) in comparison to high-performance liquid chromatography (HPLC) for characterizing natural dyes in cultural heritage objects. A new UHPLC method was optimized by testing several analytical parameters adapted from prior UHPLC studies developed in diverse fields of research. Different gradient elution programs were tested on seven UHPLC columns with different dimensions and stationary phase compositions by applying several mobile phases, flow rates, temperatures, and runtimes. The UHPLC method successfully provided more improved data than that achieved by the HPLC method. Indeed, even though carminic acid has shown circa 146% higher resolution with HPLC, UHPLC resulted in an increase of 41 to 61% resolution and a decrease of 91 to 422% limit of detection, depending on the dye compound. The optimized method was subsequently assigned to analyse 59 natural reference materials, in which 85 different components were ascribed with different physicochemical properties, in order to create a spectral database for future characterization of dyes in cultural heritage objects. The majority of these reference samples could be successfully distinguished with one single method through the examination of these compounds' retention times and their spectra acquired with a photodiode array detector. These results demonstrate that UHPLC analyses are extremely valuable for the acquisition of more precise chromatographic information concerning natural dyes with complex mixtures of different and/or closely related physicochemical properties, essential for distinguishing similar species of plants and animals used to colour cultural heritage objects.

Keywords: Natural dyestuffs; Flavonoids; Anthraquinones; Indigoids; Ultrahigh performance liquid chromatography (UHPLC); High-performance liquid chromatography (HPLC).

8.1. Introduction

Natural organic dyes can be found in diverse species of plants and animals associated with specific regions of the world [1-3]. The identification of these natural dyes in cultural heritage objects is essential to establish conservation and restoration treatments, solve historical questions regarding provenance, date and production of the objects, and trace the international routes of the global trade in dyestuffs [1-7]. Identification has been widely achieved using high-performance liquid chromatography (HPLC) [6-11].

Organic dyes generally comprise very complex and polar mixtures of compounds and minor compounds with low molecular weight (circa 200 - 600 Da), belonging to several chemical families, such as flavonoids, anthraquinones or indigoids [3-5, 12-13]. Historical objects are usually dyed with mixtures of natural dyes, derived from different dye sources, in order to obtain a certain hue or shade. Additionally, individual dye sources are often composed of a mixture of closely related compounds. The exact composition and ratio of these compounds can be used for identifying the specific dye source and, hence, an analytical technique is required to distinguish closely related compounds, as well as compounds with very different structures. Recently, resolution has become a major concern, and thus, more detailed information regarding natural dyes has been undertaken to improve HPLC analyses and distinguish the chemical composition of dye sources, especially those with closely related chemical compositions [1-2, 14-17]. This has been possible through the optimization of dye extractions [7, 9, 18-19], the application of additional analytical techniques such as mass spectrometry [6, 8-10, 12-13, 18, 21-22], and multivariate data analysis of chromatographic results [2, 15, 23-24].

Recent chromatographic progress resulting from ultrahigh pressure liquid chromatography (UHPLC) has led to more efficient and sensitive analyses, and demonstrated increased chromatographic resolution over HPLC. Owing to instrument improvements, this novel chromatographic technique allows the use of smaller dimension columns packed with sub-2 µm porous particles, along with the possibility of achieving extreme pressures, faster flow rates and shorter runtimes [25-31]. As a result, analyses with UHPLC lead to lower solvent consumption [31] and to faster analyses of an increasing number of samples, while maintaining a high separation efficiency [25, 29].

UHPLC has brought new possibilities and advantages to diverse areas, such as the environmental field [32-34], as well as the pharmaceutical [35-37] and food industries [38-41]. For the analysis of natural dye substances, UHPLC has furthermore demonstrated improved results for the characterization of several flavonoid compounds in the pharmaceutical [42-43] and food industries [44-46]. Although applied in such different areas, these compounds might also be found as yellow dyes in cultural heritage objects [3-6]. Recently, Taujenis and Olšauskaitė [47] developed a UHPLC method to identify dyestuffs in historical textiles, through the characterization of a mixture of nine representative dye compounds usually present in cultural heritage objects. Although the developed method allowed the separation of the majority of the compounds in a much shorter analysis than that generally provided by HPLC, it was not suitable for detecting the indigotin compound, for which a separated method had to be created.

The main objective of this study concerned the optimization of a unique UHPLC method that could permit the accurate characterization of a wide range of natural dyes in one single analysis without compromising chromatographic resolution or the detection of their compounds and minor compounds. This characterization is indispensable to determine the plant or animal dye sources originally used to colour cultural heritage objects. For instance, superior resolution is fundamental to characterize the compounds and minor compounds present in diverse species of red cochineal insects from different regions of the world. The accurate distinction of the chromatographic profiles of each of these insect species brings invaluable information concerning the historical provenance and date of production of cochineal-dyed historical textiles, and furthermore, for solving historical questions such as the impact of American cochineal in European and Asian dyeing traditions after the advent of the Iberian Expansion at the beginning of the 16th century [2]. In this study, resolution, accuracy and detection limit were major parameters to achieve a detailed chromatographic characterization of natural dyes like cochineal. For this reason, the reduction of the analysis runtime, a parameter which is often considered for UHPLC analyses [25, 30], was not considered here. Plus, a longer runtime was also preferable for further comparison with a conventional HPLC method.

The analytical parameters for the optimization of the UHPLC method were selected from previous UHPLC studies [28, 32-35, 37-39, 41-48] and using the software Acquity UPLC

Columns Calculator from Waters Corporation, conceived to transfer HPLC to UHPLC analytical conditions. The collected information was subsequently adapted to conduct the optimization process, by applying several analytical tests to seven UHPLC columns with different dimensions and stationary phase compositions. One mixture of seven standard references of natural dye compounds with different physicochemical properties, and one mixture of two insect dye extracts with similar dye compositions (Fig. 8.1), were analysed with these UHPLC columns by applying different mobile phases, gradient profiles, flow rates, column oven temperatures and runtimes. Henceforth, validation and system suitability testing (SST) were assessed to evaluate and compare the efficiency of the optimized UHPLC method in relation to a HPLC method, which has often been applied to identify natural dyes in cultural heritage objects [49]. Finally, the UHPLC optimized method was used to analyse 59 natural reference materials in order to build a spectral database for the future identification of natural dyes in cultural heritage objects.

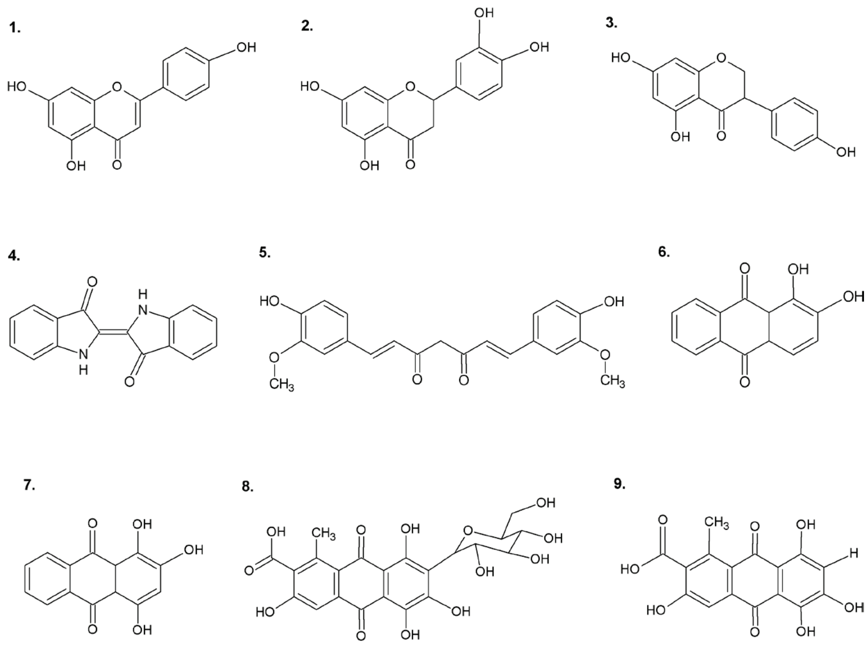

Fig. 8.1. Molecular structures of the major compounds of the mixture of dyestuff references and the mixture of insect dyes: Flavonoids - 1. apigenin (5,7,4’-trihydroxyflavone), 2. luteolin (5,7,3’,4’-tetrahydroxyflavone), 3. genistein (5,7,4’-trihydroxyisoflavone); Indigoid - 4. indigotin (2,2'-bis(2,3-dihydro-3- oxoindolyliden)); Carotenoid - 5. Curcumin ((1E,6E)-1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione); Anthraquinones - 6. alizarin (1,2-dihydroxy-9,10-anthracenedione), 7. purpurin (1,2,4-trihydroxyanthracène-9,10-dione), 8. carminic acid (7-α-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxoanthracenecarboxylic acid), and 9. kermesic acid (9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid) [3, 6].

8.2. Experimental

8.2.1. Chemicals and reagents

Nine natural dyestuffs were used to carry out optimization of the method: alizarin from Merck (Darmstadt, Germany), apigenin from Fluka (Buchs, Switzerland), cochineal Dacylopius coccus from Kremer-Pigmente (Aichstetten, Germany), turmeric (curcumin) from the Canadian Herb Distributors (Canada), genistein from the ICN Pharmaceuticals Inc. Life Sciences Group (Plainview, U.S.A.), indigo from the Technische Hogeschool (Amsterdam, The Netherlands), Kermes vermillio insects given by Dr. Andre Verhecken, luteolin from Extrasynthèse (Genay, France) and purpurin from the Doerner Institute (Munich, Germany). Using the optimized UHPLC method, a spectral database of natural dye compounds was created with the analysis of 59 natural reference materials (Table 1, Electronic Supplementary Material (ESM [in Appendix 4]) belonging to the reference collection of the Cultural Heritage Agency of the Netherlands (Amsterdam, The Netherlands).

N,N-Dimethylformamide (DMF) from Sigma-Aldrich (Germany) was used for the preparation of all the dye samples. Methanol (99.9%, HPLC gradient grade), formic acid and phosphoric acid from Sigma-Aldrich (Germany), acetonitrile (ACN, HPLC gradient grade) from Riedel-deHaën and deionised water (Millipore SimplicityTM Simpak® 2, R=18.2 MΩ.cm, U.S.A.) were used for the UHPLC and the HPLC gradient grades.

8.2.2. Analytical parameters

8.2.2.1. Samples preparation

The nine natural dyestuffs intended for the method optimization were accurately weighted (circa 0.4 - 0.5 mg), dissolved in 2 mL of DMF, and submitted to mechanical agitation and centrifugation. As curcumin, cochineal and kermes displayed a very low absorbance in the UV-visible, it was necessary to increase the amount of sample until an adequate detection of the compounds was obtained in the UHPLC system. In order to improve dye extraction, the DMF extracts of cochineal and kermes were heated to 90 ºC in a water bath for 10 min, before centrifugation.

For the analytical procedure, a mixture of seven equal parts of the dyestuff references of alizarin, apigenin, curcumin, genistein, indigo, luteolin and purpurin was prepared, as well as a mixture of the two insect dyes, cochineal and kermes. Later on, 100 mg/mL of aqueous extracts of madder and weld were analysed to assess the suitability of the optimized UHPLC method for separating the compounds of complex natural dyes. These two natural dye sources were soaked in deionized water overnight, heated for half an hour at a temperature of 80 ºC, and submitted to centrifugation and 0.45 µm filtration prior to UHPLC analysis.

8.2.2.2. Apparatus

HPLC and UHPLC analyses were performed using a Waters AcquityTM H-class UHPLC system (Waters Corporation, Milford, MA, USA) equipped with a quaternary solvent delivery system, a column oven, an autosampler and a photodiode array (PDA) detector. PDA data was recorded from 200 to 800 nm with a resolution of 1.2 nm (2 scan/s), and the analyses monitoring was settled at a detection wavelength of 254 nm. The equipment was controlled by Empower 2.0 Chromatography Data Software from Waters Corporation.

The two mixtures of dyes were analysed at a constant injection volume of 2 µL and submitted to several analytical parameters, with runtimes ranging from 15 to 45 min; flow rates between 0.1 and 0.35 mL/min; and column oven temperatures from 30 to 50 ºC. The optimization tests were carried out on seven UHPLC columns and one HPLC column, with different dimensions and stationary phase compositions. Five UHPLC columns were purchased from Waters Acquity®: one UHPLC BEH C18 1.7 µm 2.1 x 100 mm; two UHPLC BEH Shield RP18 1.7 µm of 2.1 x 100 mm and of 2.1 x 150 mm; one UHPLC HSS C18 1.8 µm 2.1 x 100 mm; and one UHPLC HSS T3 C18 1.8 µm 2.1 x 100 mm. The other two UHPLC columns and the HPLC column were obtained from Phenomenex®: one UHPLC Kinetex C18 1.7 µm 2.1 x 150 mm; one UHPLC Kinetex 1.7 µm XB-C18 2.1 x 100mm; and one HPLC Phenomenex Luna 3 µm C18 (2) 2 x 150 mm. All UHPLC columns were protected by filter unit (0.2 um), while the HPLC column was protected with a security C18 guard column (Phenomenex). Several gradient elution programmes were tested by combining three solvents in the mobile phase: A - 10% aqueous methanol (v/v) or 10% aqueous ACN (v/v); B - 100% methanol or 100% ACN; and C - 5% aqueous phosphoric acid (w/v) or 1% aqueous formic acid (v/v).

Further analyses with the optimized UHPLC method were undertaken using the BEH Shield column of 150 mm length kept at 40 ºC, using 2 µL injection volume and 0.2 mL/min flow rate. The mobile phase comprised 10% aqueous methanol (v/v) (solvent A), pure methanol (solvent B) and 1% aqueous formic acid (v/v) (solvent C) in a gradient elution program scheduled for a 40 min run: 0-1.33 min, isocratic gradient of 80A : 10B : 10C (v/v/v); 1.33-2.33, linear gradient to 74A : 16B : 10C (v/v/v); 2.33-5.33, linear gradient to 55A : 35B : 10C (v/v/v), kept in isocratic gradient until 9 min; 9-14 min, linear gradient to 30A : 60B : 10C (v/v/v); 14-25 min, linear gradient to 5A : 85B : 10C (v/v/v); 25-26 min, linear gradient to 100B, kept for 4 min; and 30-32 min, linear gradient to 80A : 10B : 10C (v/v/v), kept for 8 min. This method was subsequently assigned to build the spectral database of natural dye compounds, using an injection volume ranging from 0.1 to 4 µL.

HPLC analyses of the dye samples were carried out on Luna column, using 2 µL injection volume, 0.2 mL/min flow rate and 35 ºC column oven temperature. The mobile phase consisted of 10% aqueous methanol (v/v) (solvent A), pure methanol (solvent B) and 5% aqueous phosphoric acid (w/v) (solvent C) in a gradient elution program of 40 min run: 0-3 min, isocratic gradient of 74A : 16B : 10C (v/v/v); 3-18 min, linear gradient to 90B : 10C (v/v), kept for 2 min; 20-28 min, linear gradient to 100B, kept for 4 min; and 32-35 min, linear gradient to 74A : 16B : 10C (v/v/v), kept for 5 min.

8.2.2.3. UHPLC and HPLC methods evaluation

The optimized UHPLC method was compared with a conventional HPLC method [49], so that it would be possible to evaluate the efficiency of both chromatographic systems. Therefore, and according to the SST, both methods were used to analyse six replicates of the two mixtures of dyestuffs in one day (intra-day analyses), three replicates every day for five consecutive days (inter-day analyses), and three replicates once a week for one month (samples stability). As the precise concentration of the compounds from the mixture of insect dye extracts cannot be determined, it was only possible to perform method validation using the mixture of seven dyestuff references. Therefore, a stock solution was prepared with DMF and 209 µg/mL luteolin, 208 µg/mL genistein, 202 µg/mL alizarin, 210 µg/mL apigenin, 202 µg/mL indigotin, 2308 µg/mL curcumin and 203 µg/mL purpurin. This stock solution was subsequently diluted with the same solvent using the following dilution factors

(DF): 1.2; 1.5; 2; 3; 5; 10; 20; 50; 100; 200; 500; 1000; 2000; 5000; and 10000. The samples were analysed in triplicate with both the UHPLC and the HPLC systems using an injection volume of 2 µL.

For a qualitative evaluation of the results, chromatograms from the mixture of dyestuff references were examined at 275 nm, as the most of the dye compounds could be detected at this wavelength. Chromatograms from the mixture of insect dyes were observed at 430 nm, where both the red and orange compounds could be detected. In order to carry out the quantitative evaluation of the results, the integrated peak areas of the most representative compounds of both mixtures of dyestuffs were acquired at their optimal absorbance in the visual area: luteolin at 350 nm, genistein at 330 nm, apigenin at 430 nm, alizarin and curcumin at 430 nm, indigotin at 600 nm and purpurin, carminic acid and kermesic acid at 500 nm. The effective plate number (Neff), the peak asymmetry factor, the intra-day precision and the inter-day repeatability were determined with the average of the integrated peak areas and the retention times of the most representative dye compounds of the two mixtures of dyestuffs. The calibration curve and therefore, the linearity, the limit of detection (LOD) and the limit of quantification (LOQ) for the method validation were assessed with the concentrations and the average of the integrated peak areas from the seven most representative compounds of the mixture of dyestuff references.

8.3. Results and Discussion

8.3.1. Optimization of the UHPLC method

8.3.1.1. Gradient elution, flow rate and temperature

Dyestuffs comprise complex mixtures of compounds with variable physicochemical properties, and thus, different levels of polarity and retention times. For this reason, the analysis of these multi-compound samples was undertaken using a gradient elution program [26-27, 29, 47]. The combination of a runtime of 15 min and a flow rate of 0.35 mL/min in columns of 10 cm length, resulted in chromatograms with narrow windows of retention time, unsatisfactory separation and detection, and a swift elution of the dye compounds. Superior resolution was verified when shallower slopes of gradient elution were produced: 40 min analyses combined with a flow rate of 0.2 mL/min, resulted in larger windows of retention time and a better separation of the dye compounds. The increase of the flow rate up to 0.3 mL/min only brought about a reduction of 20% in the analytical time and an increase of 50% in solvent consumption, while presenting a similar resolution to that given by analyses carried out at a flow rate of 0.2 mL/min. As the analytical time is not considered here a major concern for the characterization of natural dyes, the flow rate of 0.2 mL/min was selected for further analytical tests. As for the gradient elution program, the variation of the slope was not sufficient to separate some closely related dye compounds, like ruberythric acid and lucidin, present in the madder dye extracts. The addition of an isocratic step into the gradient elution program could successfully separate these compounds. Results were furthermore improved by varying the temperature of the column oven. By increasing the temperature up to 40 ºC, a lower retention time and an improved separation of the dye compounds were obtained, mostly due to an increase of the mobile phase viscosity [25-27, 30, 35-36]. Temperatures above 40 ºC provided band broadening and inadequate detection, perhaps owing to sample degradation.

When the percentage of solvent B was reduced and the percentage of solvent A was proportionally increased at the beginning of the elution program, chromatograms exhibited larger windows of retention time, a higher retention and a better resolution of the dye compounds. The diminished eluent strength of the mobile phase corresponds to the growing affinity of the dye compounds with the stationary phase, and therefore, to the increase of the compounds retention time in the analytical column [26]. When the percentage of solvent B was raised at the beginning of the elution program, the percentage of solvent A was proportionally reduced as reflected by the higher eluent strength of the mobile phase. As a result, the affinity of the dye compounds with the stationary phase was reduced and chromatograms presented a poorer resolution.

8.3.1.2. Mobile phase composition

When methanol was replaced by ACN in the mobile phase, a clear reduction of the compounds retention time was observed, which explains why ACN is often preferred for UHPLC analyses [27, 34, 36-41, 44-48, 50]. This solvent has a high eluent strength that permits a rapid elution of the compounds in the analytical column, causing very short runtimes [26-27, 50]. Although ACN has previously shown a successful performance for the

UHPLC analyses of natural dyes [44], in this study, this solvent has caused diminished resolution, band broadening and an unsatisfactory detection. Aiming to improve chromatographic resolution, the percentage of ACN (solvent B) was lowered in the analytical method. However, no positive changes could be observed for the peaks separation. Therefore, and since ACN is currently a very expensive solvent, it was advisable to use more economically accessible solvents, such as methanol [50]. In spite of its lower eluent strength, methanol has shown to be suitable for achieving superior chromatographic resolution with UHPLC analyses [32, 35, 42-43] and it has been widely assigned for the HPLC study of natural dyes [2-3, 7, 15-16, 19, 22-23, 47, 49].

An additional solvent (C), which might typically be an aqueous solution of phosphates or organic acids [3, 49], is often added to control the pH of the mobile phase, by suppressing ionic interactions between the dye compounds and the stationary phase, thus resulting in lower band broadening [47-48]. As depicted in Fig. 8.2, chromatograms acquired with the HPLC Luna column using formic acid (B and D) presented a narrower window of retention time, band broadening and inadequate detection and separation of some compounds such as luteolin and genistein, in comparison to chromatograms acquired with phosphoric acid in the same analytical method (A and C). Chromatograms obtained with the UHPLC Shield column using formic acid (F and H) displayed slightly larger windows of retention time, as well as a better separation of alizarin and apigenin compounds, in relation to chromatograms achieved with phosphoric acid in the same analytical method (E and G). When comparing both UHPLC and HPLC methods, it was evident that UHPLC chromatograms acquired with formic acid displayed the most adequate resolution. This was especially noticeable for the peaks of luteolin and genistein, and the peaks of flavokermesic acid and kermesic acid. Improved chromatographic behaviour was also observed for the minor compounds of the mixture of insect dyes, the detection of which is fundamental for the identification of specific species of plants and animals as dye sources in cultural heritage objects. Moreover, formic acid possesses volatile properties that offer the advantage of combining UHPLC with MS analyses to further characterize natural dye compounds, similar to previous UHPLC-MS [38, 45] and HPLC-MS [1, 3, 7, 18, 22] studies.

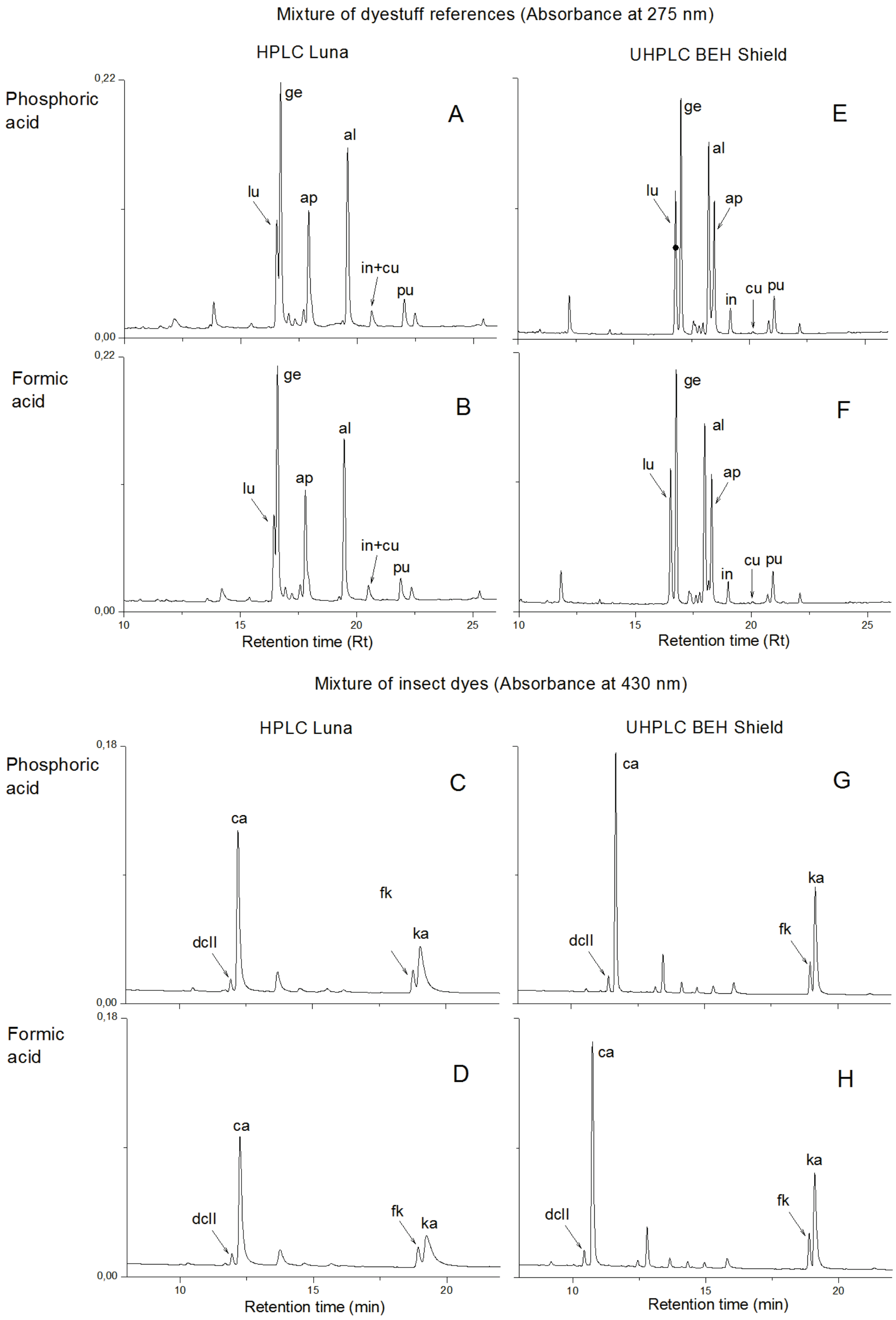

Fig. 8.2. Chromatograms obtained with the 15 cm HPLC Luna column (A-D) and the 10 cm UHPLC BEH Shield column (E-H), using aqueous phosphoric acid or aqueous formic acid in the mobile phase. The chromatographic resolution is compared for the most representative compounds (luteolin (lu), genistein (ge), alizarin (al), apigenin (ap), curcumin (cu), indigotin (in), purpurin (pu), dcII (minor compound of *Dactylopius coccus* L.), carminic acid (ca), flavokermesic acid (fk) and kermesic acid (ka)) and other minor compounds of the mixture of dyestuff references and the mixture of insect dyes. UHPLC and HPLC analyses were carried at similar gradient elution conditions with a runtime of 40 min and a flow rate of 0.2 mL/min. The column oven temperature was settled at 35 ºC for the HPLC analyses, while the UHPLC analyses were carried at 40 ºC.

8.3.1.3. UHPLC analytical columns

Different chromatographic profiles were obtained by gradually testing the analytical parameters previously discussed in sections 3.1.1 and 3.1.2 in several UHPLC columns with different dimensions and C18 reversed stationary phases.

According with Fig. 8.3, UHPLC Kinetex columns have revealed chromatograms with a very poor resolution, especially for the mixture of dyestuff references (A and B) and for the mixture of insect dyes (G and H). Indeed, luteolin and genistein were hardly separated using the Kinetex column (A), while these compounds were co-eluting when testing the Kinetex XB column (B). Furthermore, flavokermesic acid and kermesic acid compounds were not even detected with the Kinetex column (G). Owing to the high level of hydrophobic selectivity of this column, a reduced affinity is expected with hydrophilic compounds, such as the anthraquinones present in the mixture of insect dyes, whereby decreasing the chromatograms resolution. On the other hand, the higher level of hydrogen bonding with hydrophobic selectivity of Kinetex XB column should stimulate a stronger affinity with hydrophilic compounds, thus reflecting a better chromatographic resolution (H). The co-elution of the dye compounds might also be explained by the core-shell silica particles technology characteristic of both Kinetex columns, which may possess a lower percentage of carbon composition than the porous silica particles from Waters columns, hence causing reduction of the compounds diffusion path in the analytical column. Although this characteristic has been previously reported to be advantageous for the separation of large molecules [26, 29], it might not bring improvements for the separation of the small molecules present in natural dyes.

UHPLC Waters columns have generally brought improved chromatograms with variable resolution, depending upon their stationary phase. In this study, the 100 mm columns comprised either porous ethylene bridged hybrid (BEH) or high strength silica (HSS), both enclosing tri-functional silica particles bonded at a high ligand density to C18 groups. The difference between both is that HSS comprises an endcapping process of its silica particles. The HSS column brought larger windows of retention time (D, J, P and V) than those obtained with the BEH column (C, I, O and U). As the endcapped silica particles of the HSS technology yield a higher level of hydrogen bonding, a greater affinity with acidic compounds is expected. However, the HSS column also provided a reduced absorbance and a lower level of separation. This is particularly observable for flavokermesic acid and kermesic acid compounds which are co-eluting (J). With the BEH column, these compounds (I) and other minor compounds (C, O and U) were not properly separated either.

HSS T3 column includes tri-functional endcapped silica particles bonded at a very high ligand density to C18 groups that strongly increase the retention time of very acidic compounds [41]. Chromatograms acquired with this column (E, K, Q and W) displayed a higher retention time of the dye compounds and an improved detection, fundamental for the characterization of minor compounds in the dye samples. However, this column has also led to narrower windows of retention time and, as a result, the separation of some compounds and minor compounds was reduced, which is the case for luteolin and genistein (E) or the ruberythric acid and the lucidin-3-O-primeveroside (Q).

HSS T3 column has been previously reported to give a successful performance over the BEH and the BEH Shield columns for UHPLC analyses of crocin yellow dye compounds [44]. In this study, BEH Shield column has shown to provide the best results. This column comprises tri-functional silica particles with an additional hydrophilic carbamate group bonded at a high ligand density to C18 groups that increase the affinity of very acidic compounds with the stationary phase, thus resulting in a higher retention time. Chromatograms acquired with this column displayed the largest windows of retention time (F, L, R and Y), and additionally, the compounds from the mixture of dyestuff references tended to elute later (F). Although this column showed a poorer detection than the HSS T3 or the BEH columns, it provided the highest peak capacity and an improved separation, especially for the minor compounds. Indeed, the separation of the flavokermesic acid and the kermesic acid compounds was successfully achieved with this column (L), something that could not be reported with the previous columns. It is also noteworthy to emphasize that alizarin and apigenin have been reported to elute in a different order when using the BEH Shield column. This might be due to the dissimilar selectivity of the stationary phase of this column in relation to the other UHPLC columns.

In general, differences in chromatographic behavior were small between the UHPLC Waters columns, particularly for the HSS T3 and the BEH Shield. One could argue that the resolution of the mixture of dyestuff references could be improved even more for the HSS T3 column, if the gradient elution program was adapted. Nevertheless, the BEH Shield column

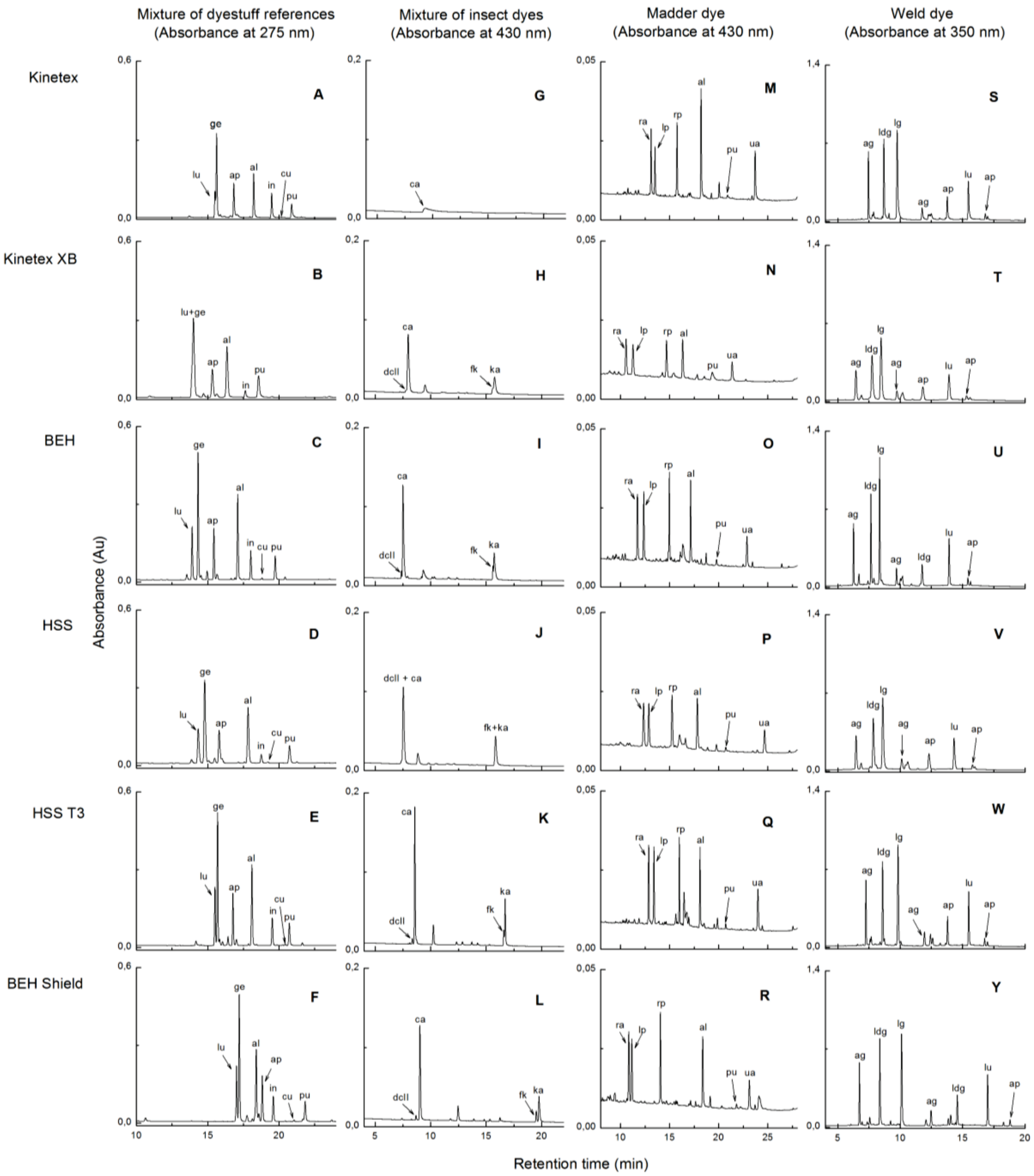

Fig. 8.3. Qualitative evaluation of the chromatograms obtained with the different UHPLC columns using the optimized method, through the comparison of the separation and the detection of the most representative compounds and minor compounds of the mixture of dyestuff references (A-F), the mixture of insect dyes (E-L), the madder dye (M-R – ruberythric acid (ra), lucidin-3-O-primeveroside (lp), rubiadin-3-O-primeveroside (rp), alizarin (al), purpurin (pu) and an unknown anthraquinone (ua)) and the weld dye (S-Y – apigenin-7-glucosyde (ag), luteolin 3’7-diglycoside (ldg), luteolin-7-O-β-D-glycoside (lg), apigenin (ap)).

was selected to carry on further analyses, as it showed superior chromatographic resolution for the mixture of insect dyes. Therefore, and in order to obtain even better resolution, the 100 mm BEH Shield column was replaced by a 150 mm column, as moreover reported in earlier researches [27-28, 30]. By maintaining the analytical conditions of the optimized method, this longer column provided chromatograms with improved detection, larger windows of retention time, higher retention time of the dye compounds, and therefore, better resolution.

8.3.2. UHPLC and HPLC methods evaluation

As UHPLC analyses have not been applied in the field of cultural heritage so far, it is of interest to compare this technique with the conventional HPLC technique to identify natural dyes in historical works of art. A conventional HPLC method along with a HPLC Phenomenex Luna C18 (2) column were selected for this study, owing to their widespread application for the identification of natural dyes in cultural heritage objects [8, 13, 22, 49, 51-52]. A qualitative interpretation of the analytical results acquired with both the optimized UHPLC and the conventional HPLC methods (Fig. 8.4) immediately shows that chromatograms achieved with HPLC (B, D, F and H) presented narrow windows of retention time and a poor separation of some compounds and minor compounds, namely between luteolin and genistein (B), or flavokermesic acid and kermesic acid (D). On the contrary, chromatograms obtained with UHPLC exhibited a superior resolution and a higher peak capacity (A, C, E and G), essential characteristics for successfully characterizing dye compounds with closely related and/or different physicochemical properties in one single analysis [28]. Such results might be explained by the different levels of selectivity of the chromatographic columns used for both methods [25, 29]. While the UHPLC column encloses a BEH Shield stationary phase of 1.7 µm silica porous particles, the HPLC Luna column includes a stationary phase of 3 µm silica porous particles bonded to C18 groups. With this larger particle size, an increase of the diffusion path of the dye compounds is expected, along with a higher retention time (D, F and H) and band broadening (D). Moreover, the BEH Shield column possesses a hydrophilic stationary phase that promotes a high affinity with acidic compounds, while the Luna column embraces a more hydrophobic stationary phase, which leads to a lower affinity with acidic compounds. For this reason, HPLC chromatograms present a lower level of separation of some closely related compounds and minor compounds (D). This difference in the selectivity of both columns also explains the different elution order of apigenin and alizarin and some other minor compounds.

A quantitative evaluation of the most representative dye compounds from the mixture of reference dyes and the mixture of insect dyes was moreover undertaken to assess the efficiency of both UHPLC and HPLC methods (Tables 8.1 and 8.2). As these comprise analytical columns with similar dimensions and different stationary phases, calculation of the effective plate number (Neff) was required to evaluate the resolution performance of both columns. According to Table 8.1, the BEH Shield column could generally provide an Neff about two times higher than the Luna column. The opposite result was only observed for carminic acid, to which values of Neff were evidently higher with the Luna column. The same compound also exhibited an improved symmetry factor with the HPLC method, although the low level of separation of the chromatograms (Fig. 8.4) precluded the calculation of the symmetry factor of luteolin, genistein, and curcumin compounds. As for the intra-day precision of both chromatographic methods, the majority of the compounds successfully provided values of relative standard deviation (% RSD) below 1 %, which demonstrates a satisfactory reproducibility of both methods. Excellent results were also achieved for the inter-day repeatability of the peaks retention time, while most of the values

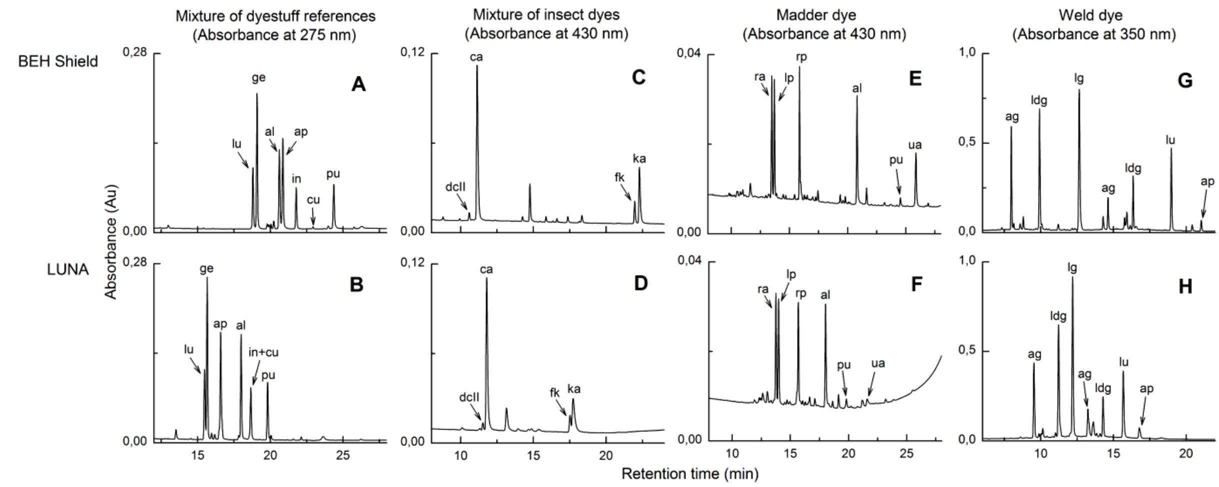

Fig. 8.4. Comparison of the analytical results for the mixture of dyestuff references (A and B), the mixture of insect dyes (C and D), and the madder (E and F) and the weld dye extracts (G and H), using the UHPLC optimized method (BEH Shield column) and the HPLC method (Luna column).

Table 8.1: Evaluation of the UHPLC and HPLC methods following the SST parameters and using the most representative compounds of the mixture of dyestuff references and the mixture of insect dyes.

	carminic acid	kermesic acid	luteolin	genistein	alizarin	apigenin	indigotin	curcumin	purpurin
Retention time (min)									
UHPLC	**11.042**	**22.087**	**18.795**	**19.065**	**20.599**	**20.838**	**21.771**	**22.934**	**24.300**
HPLC	11.577	17.292	15.792	15.970	19.898	16.898	18.991	18.814	20.167
Effective Plate number (N_{eff})									
UHPLC	**35873**	**166376**	**273702**	**283797**	**277129**	**314506**	**312580**	**383276**	**322640**
HPLC	52551	98297	113650	118421	179790	124629	175411	138223	196414
Peak asymmetry									
UHPLC	1.79	1.89	1.16	1.04	1.14	1.10	1,18	0.95	1.28
HPLC	1.57	2.04	-	-	1.34	1.86	1,48	-	1.64
Precision (% RSD)									
UHPLC	**0.23**	**0.46**	**0.35**	**0.79**	**0.40**	**0.40**	**1,04**	**0.90**	**1.15**
HPLC	0.13	0.30	1.52	0.71	0.37	0.43	0,71	0.98	0.51
Repeatability (% RSD) – A									
UHPLC	**1.66**	**1.86**	**1.40**	**0.98**	**1.35**	**1.26**	**0,36**	**0.85**	**1.54**
HPLC	1,84	1.53	1.39	1.42	1.39	1.39	0,99	2.43	1.43
Repeatability (% RSD) – R_t									
UHPLC	**0.07**	**0.03**	**0.11**	**0.10**	**0.10**	**0.10**	**0,09**	**0.08**	**0.08**
HPLC	0.10	0.05	0.18	0.18	0.16	0.16	0,16	0.13	0.13

Table 8.2. Validation tests of the UHPLC and the HPLC methods using the most representative compounds of the mixture of dyestuff references.

	luteolin	genistein	alizarin	apigenin	indigotin	curcumin	purpurin
Linearity (R^2)							
UHPLC	**0.9999**	**0.9999**	**0.9998**	**0.9999**	**0.9991**	**0.9994**	**0.9978**
HPLC	0.9998	0.9998	1.0000	0.9999	0.9998	0.9994	0.9981
LOD (ng injected)							
UHPLC	**0,047**	**0,080**	**0,303**	**0,046**	**0,296**	**8,133**	**0,179**
HPLC	0,197	0,140	0,276	0,121	0,321	9,765	0,264
LOQ (ng injected)							
UHPLC	**0,156**	**0,268**	**1,010**	**0,152**	**0,988**	**27,110**	**0,598**
HPLC	0,656	0,465	0,920	0,403	1,070	32,551	0,879

for the integrated peak areas were higher than 1 %. In general, these values were lower for the UHPLC, rather than for the HPLC chromatograms. Such variability of the results might be due to the stability of the samples, and hence, fresh samples should always be prepared prior to analysis.

Linearity, LOD and LOQ values calculated for the most representative compounds of the mixture of reference dyestuffs were generally better for the UHPLC method (Table 8.2), which had calibration curves with shallower slopes than those obtained with the HPLC method. A satisfactory linearity for indigotin was only reached for both chromatographic methods when the two most concentrated solutions (stock solution and DF 1.2 solution) were not considered for the calibration curve. This might be explained by the elevated detection of this compound in the detector, which caused its saturation at too high concentrations, and thus, presented a lower response in the resulting chromatograms. The calculation of the LOD and the LOQ was based on a range of six data values corresponding to the lowest concentrations of the calibration curve from each compound (DF 200 – DF 10000), and using the standard deviation of the integrated peak areas and the slope of the calibration curve, according with [53]. However, as a great concentration of curcumin was required to obtain an adequate detection in the PDA, the respective LOD and LOQ values for this compound increased proportionally, and therefore, the six data values used to calculate these parameters ranged between DF 50 – DF 2000. The results assessed with these calculations were subsequently verified with a visual evaluation of the chromatograms, by considering the compounds at their optimal absorbance in the visual area, through the examination of the peaks response and the respective PDA spectra. Furthermore, the compounds response was compared with that given by blank DMF samples at similar retention times. This comparison was suitable to verify that HPLC chromatograms displayed several compounds co-eluting with each other, thus leading to a higher response. On the other hand, UHPLC chromatograms have displayed an improved resolution, thereby providing a lower response of the compounds. Therefore, LOD and LOQ HPLC results for alizarin might have been influenced by interfering compounds. This evaluation was essential to conclude the legitimacy of the performed calculations and thus verify the success of UHPLC over HPLC, especially for further characterization of minor compounds in complex mixtures of natural dyes in closely related species of plants or animal dye sources with similar dye compositions.

8.3.3. UHPLC spectral database

Aiming to provide a useful tool for future studies, a spectral database was subsequently built with the UHPLC-PDA analysis of 59 natural reference materials, belonging to the reference collection of the Cultural Heritage Agency of the Netherlands. These reference materials comprise compounds and minor compounds, namely anthraquinoids, flavonoids, indigoids, carotenoids and tannins, which usually are reported in complex mixtures of similar and/or different physicochemical properties from plants and animal dye sources [3-4, 6].

From the analysis of the 59 natural reference materials, a total of 85 compounds (Table 1, ESM [in Appendix 4]) could be successfully characterized and distinguished using the UHPLC optimized method and the detailed examination of the compounds retention time and PDA spectra. This method has demonstrated that the application of a long runtime to a 15 cm UHPLC column is highly advisable for characterizing such a wide range of compounds in one single method, especially those eluting at very close retention times. A proper separation of the compounds, allied to the observation of their PDA results, thus constitutes a very significant step to swiftly identifying different dye sources in complex mixtures used to colour cultural heritage objects, and thus respond to urgent conservation and restoration issues, for example. On the other hand, when focus is given to the accurate distinction of closely related dye sources, particularly to respond to historical questions regarding the provenance and date of cultural heritage objects, the optimized UHPLC method could allow a suitable characterization of similar compounds and minor compounds eluting at similar or different retention times, while depicting very alike PDA spectra. For instance, by presenting a very analogous chemical structure, several CT compounds from safflower extracts have shown similar PDA spectra at different retention times: 16.22 min, 16.84 min, 16.99 min and 17.56 min. This has been reported as well for other dye sources, such as American cochineal (*D. coccus*), which dye extracts presented compounds with similar chemical structures, namely carminic acid and the minor compounds dcIV and dcVII, eluting at 10.94 min, 15.73 min and 16.49 min, respectively. Known as isomers, these compounds possess different stereochemical properties that enable them to absorb in the same wavelength, while eluting at different or closely related retention times [13]. In combination with improved resolution and detection, the accurate examination of the PDA spectra and the retention time of these types of compounds is essential to ascertain any minimal characteristics that permit the differentiation of the chromatographic ratio of very complex mixtures of compounds with similar physicochemical properties, and which are often present in closely related species of certain families of plants and animals dye sources. This is particularly important when regarding the characterization of minor compounds. With the developed UHPLC method, the detection of these constituents has shown to be properly assessed, as clearly indicated in Fig. 8.4. Therefore, the construction of a UHPLC spectral database should constitute a valuable approach for obtaining more conclusive interpretations regarding the origins of dye sources, and hence, for future studies in the field of cultural heritage.

8.4. Conclusions

With equivalent operation requirements as HPLC, UHPLC equipment brings the advantage of using smaller particle size columns to achieving increasingly accurate chromatographic results. Indeed, the method developed in this study has shown that testing several analytical columns, flow rates, column oven temperatures, runtimes, mobile phase compositions and gradient elution programs could bring significant improvements for the analysis of natural dye compounds. The optimized analytical method using a UHPLC BEH Shield column has generally produced chromatograms with improved resolution and peak capacity, displaying an increase of up to 61% inefficient plate number and an improvement of up to 422% for limit of detection and limit of quantification for the majority of the dye compounds, in relation to the results achieved with a conventional method, applied to a HPLC Luna column, using the same analytical equipment. Nevertheless, and although currently UHPLC columns are not as economically available as HPLC columns, both BEH Shield and Luna have indicated a high reproducibility, as well as an enduring life-span.

The UHPLC optimized method has furthermore demonstrated that the application of a long runtime to a UHPLC column with a reasonable length, followed by the construction of a spectral database, is a very suitable approach for characterizing a wide range of dye compounds with different and/or closely related physicochemical properties in one single method, as well as providing greater chromatographic information for ascribing the origin of unknown dye sources. For instance, the accurate UHPLC identification of cochineal insect species in historical textiles could greatly enhance the determination of their provenance and date, as well as assess the technological impact of American cochineal on European and Asian dyeing traditions from the 16th century onwards [2]. Hence, when regarding the application of UHPLC to this case study, or any other research concerning natural dyestuffs, the main focus should be the level of accuracy required, especially in regard to discriminating closely related species of certain families of plant and animal dye sources. In this context, the UHPLC method developed here should be considered a highly recommendable tool for achieving more detailed information regarding the identification of natural dye sources in cultural heritage objects.

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CHAPTER 9

INVESTIGATION OF CRIMSON-DYED FIBRES FOR A NEW APPROACH ON THE CHARACTERIZATION OF COCHINEAL AND KERMES DYES IN HISTORICAL TEXTILES

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Note for the thesis. By using the UHPLC-PDA conditions optimized in the previous chapter, along with mass spectrometry (MS) and image scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX), a research approach is developed in this chapter, in order to overcome the analytical limitations verified in the scientific literature concerning the chemical characterization of cochineal dyes, as described in Chapter 2.

Hence, this research approach, published as a paper in the Analytica Chimica Acta, involves the application of the above-mentioned analytical techniques to investigate the colorant behaviour of cochineal and kermes insect dyes in a large set of experimentally-dyed and artificially-aged samples of silk and wool. Through the evaluation of the colorant ratio of the insect dyes in these samples, it is possible to assess the stability of the dyestuffs and, thus, verify if it is possible to determine whether cochineal species (or mixtures of them with kermes) can be characterized in historical textiles. Since a large quantity of analytical results with very similar but variable dye compositions is obtained here, partial-least squares discriminant analysis (PLS-DA) is applied to interpret the chromatographic results and, therefore, confirm the suitability of the developed method to identify cochineal dyes, especially the American variety, in red historical textiles.

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Abstract

The colorant behaviour of cochineal and kermes insect dyes in 141 experimentally-dyed and 28 artificially-aged samples of silk and wool was investigated using ultra-high performance liquid chromatography coupled to photodiode array detector (UHPLC-PDA), liquid chromatography electrospray ionisation mass spectrometry (LC-ESI-MS) and image scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX). Partial-least squares discriminant analysis (PLS-DA) was then used to model the acquired UHPLC-PDA data and assess the possibility of discriminating cochineal insect species, as well as their correspondent dyed and aged reference fibres. The resulting models helped to characterize a set of 117 red samples from 95 historical textiles, in which UHPLC-PDA analyses have reported the presence of cochineal and kermes insect dyes.

Analytical investigation of the experimentally-dyed and artificially-aged fibres has demonstrated that the ratio of compounds in the insects dye composition can change, depending on the dyeing conditions applied and the type of fibres used. Similarities were observed when comparing the UHPLC-MS and SEM-EDX results from the dyed and aged references with the historical samples. This was verified with PLS-DA models of the chromatographic data, facilitating the classification of the cochineal species present in the historical samples. The majority of these samples were identified to contain American cochineal, which is in agreement with historical and dye identification literature that describe the impact of this dyestuff into European and Asian dyeing practices, after the Iberian Expansion in the 16th century.

The analytical results emphasize the importance of using statistical data interpretation for the discrimination of cochineal dyes, besides qualitative and quantitative evaluation of chromatograms. Hence, the combination of UHPLC-PDA with a statistical classification method, such as PLS-DA, has been demonstrated to be an advisable approach in future investigations to assess closely related species of natural dyes in historical textile samples. This is particularly important when aiming to achieve more accurate interpretations about the history of works of art, or the application of natural dyes in old textile production.

Keywords: Insect dyes; Historical textiles; Ultra high-performance liquid chromatography; Partial-least squares discriminant analysis; Electrospray ionisation mass spectrometry; Image scanning electron microscopy - energy dispersive X-ray spectroscopy.

9.1. Introduction

In the last decades, a growing interest has been put onto the analytical characterization of natural organic dyes in cultural heritage objects, as a way of achieving more information about provenance, date and production of the objects, evaluating conservation and restoration treatments for those objects or to respond questions that historical documentation has not fully covered [1–4].

This characterization has been widely undertaken using high performance liquid chromatography (HPLC) [4–10]. Cultural heritage objects are often coloured with complex matrices of closely related species of certain families of plant and animal dye sources. These comprise similar compounds and minor compounds with variable ratios. Accurate HPLC characterization is essential to distinguish between each species, as the knowledge of their specific chromatographic profiles can help identifying them in the objects [10–16].

In this context, there has been an increasing awareness to improve resolution and detection in HPLC results, in order to obtain more detailed chromatographic information. For instance, an increasing number of dyestuff extraction methods has been developed [4, 8, 9, 17-20]: as the type of dye extraction adopted can influence the quality and the quantity of the isolated compounds, a suitable extraction method can bring more detailed information about the dye source [6]. Also, a method using ultra-high performance liquid chromatography coupled to a photodiode array detector (UHPLC-PDA) has been recently optimized for the characterization of natural dyes in cultural heritage objects, which has been shown to deliver more efficient and sensitive results than an HPLC-PDA method previously used [10].

Chromatographic information can be moreover supported by additional techniques. Mass spectrometry (MS), for instance, has become an indispensable tool for the investigation of molecular structures of unknown dye compounds detected with liquid chromatography [3-6, 8, 21-24]. In addition, multivariate statistical analysis has recently become a powerful tool for the study of natural dyestuffs, if a large amount of data displaying similar chromatographic profiles is available [11, 12, 16, 25]. For example, Serrano et al. used principal component analysis (PCA) to discriminate the HPLC results of (closely related) species of cochineal insect dyes and characterize them in historical textiles [11].

Cochineal and other insect dyes have always been among the most appreciated natural organic dyestuffs for colouring textiles. Their fame was especially owed to the brilliant and enduring shades of crimson they provided to animal fibres (silk and wool). Though, given their scarcity, laborious collection and complex dyeing process, they were inevitably expensive and, hence, principally used in the manufacturing of luxury fabrics [2, 26-29].

Until the 16th century, Asian and European manufacturers obtained their crimson from insects of lac (*Kerria lacca*), kermes (*Kermes vermillio*) and Polish and Armenian cochineal (*Porphyrophora polonica* and *Porphyrophora hamelii*, respectively). Growing in specific geographic regions, these dyestuffs were used locally or traded to the most important dyeing centres, through the main trade routes connecting both continents [2, 27, 29]. With the Iberian Expansion at the beginning of the 16th century, the Spanish started to bring from Mexico a new species of cochineal (*Dactylopius coccus*), which European dyers soon realized to be much richer in red colorant than the European and the Asian insect dyes (10-12 times more colorant than kermes, for instance). This allowed for a lesser number of American insects to be used for dyeing the fabrics, thus bringing a decrease to their final price [2, 26-31]. This economical factor would inevitably raise the demand for this dyestuff in European and Asian markets, in such way that it would become one of the most profitable Spanish imports from the Americas [28, 36, 32].

Contemporary historical publications have been systematically affirming that, within few decades after the first shipments of American dyestuff started to arrive to Europe, this was swiftly adopted by textile manufacturers, replacing all other insect sources of red, by the end of the 16th century. Some further support that a similar process occurred when the American dyestuff was traded to Asian regions [26-28, 30-36]. While the European case is reasonably well documented, historical sources confirming the use of American cochineal in Asia are rare [34]. Extensive chemical studies have attempted to identify the precise insect dye used in European and Asian historical textiles [31, 33, 34] and paintings [36], to provide important evidence for tracing the global impact of American cochineal.

The HPLC characterization of insect dyes in cultural heritage objects was firstly suggested by Wouters and Verhecken [17, 37, 38] and it is generally based on the visual examination and quantification of representative compounds detected with a UV-vis detector, Table 9.1.

Cochineal and lac dye insects comprise different compounds and minor compounds that make them easily discernible in colorant mixtures. While lac dye comprises laccaic acids, cochineal is currently well characterized by the major compound carminic acid (ca, 2-C-glucopyranoside of kermesic acid) and other minor compounds, such as dcII (2-C-glucopyranoside of flavokermesic acid), dcIV (2-C-α-glucofuranoside of kermesic acid) or dcVII (2-C-β-glucofuranoside of kermesic acid) [22]. On the other hand, kermes alone can be distinguishable from cochineal or lac, but not in mixtures with them, since they share similar compounds (flavokermesic acid (fk) and kermesic acid (ka)). As for cochineal insect species, they also share analogous compounds and, hence, their differentiation depends on the ratio of minor compounds dcII, fk and ka. Based on this ratio, Wouters & Verhecken [17] were able to determine the cochineal species present in wool and cotton historical fibres.

Table 9.1. Representative compounds in insect dye extracts and respective relative abundances, obtained with the integration of chromatograms at 275 nm [17, 38].

Insect Dyes	**Representative compounds**	**Relative abundances (%)**
Lac dye	Laccaic acids (la's), flavokermesic acid (fk), kermesic acid (ka)	La's (71-96), fk + ka (3.6-9.0)
Kermes	Fk, ka	Fk (0-25), ka (75-100)
Polish cochineal *(P. polonica)*	ppI, carminic acid (ca), dcIV, dcVII, fk, ka	Ca (62-88), fk + ka (12-38)
American cochineal (*D. coccus*)	dcII, ca, dcIV, dcVII, fk, ka	dcII (1.4-3.8), ca (94-98), fk + ka (0.4-2.2)
Armenian cochineal (*P. hamelli*)	dcII, ca, dcIV, dcVII, fk, ka	dcII (0.1-1.2), ca (95-99), fk + ka (1.0-4.2)

Recently, the same methodology was used to determine the cochineal species present in silk historical fibres. Though, a significant variation of the minor compounds was observed in the insects dye extracts, thus compromising the characterization of the precise species [11, 38]. Indeed, similar chromatographic compositions have frequently brought inconclusive results when ascribing cochineal species to cultural heritage objects [7, 8, 11, 31, 38-43]. For this reason, results are often supported by historical interpretations, and hence, studies claim to identify American cochineal in European [31, 33] and Asian textiles [34, 35, 44], dating to and after the 16th century.

Furthermore, cochineal species identification in historical samples is generally made by comparing the unknown chromatographic results with that from reference insect dyes. However, it should be considered that different dye extraction methods [11, 18], dyeing treatments [45, 46], or the natural ageing of both colorant [47-49] and fibres [49, 50], can potentially influence the chromatographic composition of the historical cochineal-dyed fibres. In fact, it has been recently reported that the amount of dcII present in silk fibres dyed with American cochineal is much smaller than that detected in wool dyed fibres or in insect dye extracts [42].

In this study, an analytical investigation was developed to fully assess the colorant behaviour of cochineal insect species, before establishing comparative interpretations with historical fibres. UHPLC-PDA analyses were undertaken on 66 samples of kermes, American, Armenian and Polish cochineal insects, 141 wool and silk fibres dyed at different dyeing conditions using these insects, and 28 artificially-aged fibres (from the total of 141). After qualitative and quantitative examination of the chromatographic results, and given the large amount of data obtained, partial-least squares discriminant analysis (PLS-DA) was applied to model the data and assess the possibility of discriminating cochineal insect dyes and their correspondent dyed and aged reference fibres. In addition, given the possibility of detecting a mixture of cochineal with kermes in historical fibres, this type of chromatographic composition was assessed here as well. A set of 117 fibres from 95 historical textiles was then analysed with UHPLC-PDA and, afterwards, the results identified with cochineal species were projected on the models constructed with the dyed and aged reference samples. Cochineal representative compounds and unknown compounds detected in artificially-aged and historical fibres were investigated with electrospray ionisation mass spectrometry (ESI-MS) coupled to the UHPLC system. Additionally, the 28 samples selected for artificial-ageing and the historical fibres were compared with image scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX), in order to compare the dyeing conditions used for both experimentally-dyed and historical samples.

9.2. Experimental

9.2.1 Materials and solvents

Methanol (99.9%, HPLC gradient grade) and formic acid 98% from Sigma–Aldrich (Steinheim, Germany), and deionised water (Millipore SimplicityTM Simpak® 2, R = 18.2 MΩ cm, U.S.A.) were used for the UHPLC gradient grade and UHPLC-MS analyses. For sample preparation, besides methanol and deionised water, dimethyl sulfoxide (DMSO) from Merck (Munich, Germany) and hydrochloric acid 37% (HCl) from Acros Organics (Geel, Belgium) were used.

About 129 experimentally-dyed samples were prepared on tussah silk and fleece wool from P&M wool craft (Hanslope, England). Given that reproducibility was an important factor when comparing experimentally-dyed samples, it was opted to use, when possible, laboratory grade materials: distilled water (pH ~5), tap water (pH ~8.2), lake water (pH ~8.5), rain water (pH ~6.2), bottled water (pH ~8), Marseilles soap, alum (potassium aluminium sulfate 99.5%) and starch from Lamers en Indemans/Interpharm b.v. ('S-Hertogenbosch, Netherlands), tin chloride and tannic acid from Riedel-de Häen (Seelze, Germany), cream of tartar (potassium hydrogen tartrate) and potash (potassium carbonate) from Merck (Darmstadt, Germany), calcium nitrate from Interchema b.v. (Oosterzee, Netherlands), calcium carbonate from Acros Organics (Geel, Belgium), sodium nitrate from Sigma–Aldrich (Steinheim, Germany), oxalic acid from Sigma–Aldrich (Steinheim, Germany), oak galls and gum Arabic from Kremer-Pigmente (Aichstetten, Germany), turmeric, copper sheets and sea salt from local stores and ashes from burnt oak wood. The 129 samples, along with other 12 experimentally-dyed samples donated for this study, were submitted to UHPLC-PDA analyses (6 replicates per sample).

A total of 66 types of insect samples of kermes and American, Armenian and Polish cochineal insect species were analysed with UHPLC-PDA (3 replicates per type of insect sample) for further comparison with the experimentally-dyed samples. American cochineal supplied by Kremer-Pigmente (Germany) was used as a standard for UHPLC-PDA and UHPLC-MS analytical conditions and for carrying out most dyeing experiments, since it is more accessible and economic. Experiments were carried out as well using kermes, Armenian and Polish cochineal.

A total of 117 red samples of silk and wool were obtained from 95 historical textiles belonging to diverse cultural heritage institutions. The majority of these samples had been previously analysed in other papers [11, 33, 38, 51] and, hence, the presence of insect dyes was expected. In addition, new samples (of unknown dye source) were obtained as well. Sample selection was principally based on the crimson shade exhibited by the respective historical textiles, but also on their date (mostly between 15th to 17th centuries), provenance (European and Asian regions), and type of fibres (silk or wool).

Additional information on the materials used for carrying out the dyeing experiments, as well as details about the provenance of the insects, the experimentally-dyed samples and the historical samples are given in Electronic Supplementary Material, ESM 1 [in Appendix 5; see also Appendix 6].

9.2.2. Dyeing experiments

Based on the revision of several contemporary studies [17, 45, 46, 52] and historical recipes dated between the 15th and 18th centuries [2, 53-57], about 129 dyeing experiments on silk and on wool were undertaken following a three-step procedure of soap, mordant and dye baths, while varying different parameters: types of mordant (alum and tin), additives (cream of tartar, tannic acid, oak galls, calcium nitrate, calcium carbonate, sodium nitrate, turmeric, gum Arabic, starch, copper sheets, wood ashes and sea salt), insect dyes (kermes and American, Armenian and Polish cochineal), water (distilled, tap, lake, rain and bottled – used in all baths, as well as for washing and rinsing the fibres), temperatures (100 ºC, 80 ºC, 40ºC and room temperature), pH (4, 7 and 10 – controlled by potash or oxalic acid) and time of exposure to both mordant or dye baths (30 min, 1h and overnight). These parameters were tested to evaluate the quality of the dyed results, as well as possible influences on the chromatographic ratio of compounds in the insects' colorant. Ultimately, the aim was to achieve a relatively close shade to that observed in crimson historical fibres, as well as comparable chromatographic results. Details on the general procedure and parameters used to carry out dyeing experiments are given in ESM 2 [in Appendix 5; see also Appendix 7]. Colour coordinates (CIE L* a* b*) measurements were performed in all 129 samples (three times per sample), using a Minolta spectrophotometer CM-2600D (Konica Minolta Sensing, inc., Japan).

9.2.3. Artificial ageing

A selection of 28 experimentally-dyed samples was made, based on the most representative dyeing parameters applied. These were submitted to artificial light ageing conditions, using a Xenotest, Alpha High Energy (Atlas®) equipment, with a filtered Xenon-Arc-lamp (Xenochrome type 320 (nm)). Samples were exposed for a total period of 160 hours, with a test chamber temperature of 50±5 ºC, relative humidity (RH) of 40±5% and an illuminance of 105 Klux. Colour coordinates measurements and UHPLC-PDA and UHPLC-MS analyses were performed on the aged samples to investigate the photo-oxidation damage, depending on the quality of the fibres (silk or wool) and the dyeing conditions.

9.2.4. UHPLC-PDA and UHPLS-MS

9.2.4.1. Sample preparation

In order to accurately characterize both insect dyes and textile samples in this study, it was important that acquired chromatograms displayed high reproducibility and resolution.

Insect samples were grinded and accurately weighted (circa 0.2–0.3 mg). They were then dissolved in 100 µL of DMSO, subjected to mechanical agitation and heated up to 80 ºC in a water bath for 10 min. To American cochineal samples which were often too concentrated, 100 µL of DMSO was added. Samples were centrifuged for 10 min at 2000 rpm and part of the resulting supernatants was transferred to new vails. These vails were centrifuged once more prior analyses.

Because the colorant in cochineal-dyed fibres is mainly in mordant form, an acidic extraction solution of HCl 37%: MeOH: H_2O (2:1:1, v/v/v) [17] was used. This provided efficient and reproducible chromatograms, essential to compare quantitatively both insect dyes and textile samples. Then, a two-step extraction method was adapted [58], using DMSO prior to hydrochloric acid. In this way, information on the potential presence of additional dyestuffs (especially in unknown historical samples) can still be obtained, as DMSO is able to extract vat and direct dyes: 1) DMSO was added to the fibres and heated up to 80 °C in a water bath for 10 min, after which, the extract was transferred to another vial; 2) acidic extraction solution was added to the fibres and heated up to 100 °C in a water bath for 10 min. After the extraction, the dye extracts were evaporated to dryness under gentle nitrogen flow, and the resulting dry residues were reconstituted with the DMSO extracts, thus combining the two steps. These were then subjected to mechanical agitation and centrifugation twice, as performed for the insect samples, before analyses. For the dyed and aged reference samples, a relatively large sample size (1 mg), along with 100 µL DMSO and 100 µL acidic solution, was adopted, in order to determine the chromatographic behaviour of the colorant. For historical samples, however, a smaller sample size was used (0.1-0.3 mg), along with 50 µL DMSO and 50 µL acidic solution.

9.2.4.2. Apparatus

UHPLC-PDA analyses were performed using a Waters Acquity™ H-class UHPLC system (Waters Corporation, Milford, MA, U.S.A.) equipped with a quaternary solvent delivery system, a column oven, an autosampler and a PDA detector. PDA data was recorded from 200 to 800 nm with a resolution of 1.2 nm (2 scan/s), and the analyses monitoring was settled at a detection wavelength of 254 nm. The equipment was controlled by Empower 2.0 Chromatography Data Software from Waters Corporation.

Separation was performed using a method published earlier by Serrano et al. [10], which has demonstrated to deliver suitable chromatographic detection and resolution for the analysis of mixtures of insect dyes. Thereby, analytical conditions were carried out using in a Waters Acquity® UHPLC BEH Shield RP18 1.7 µm of 2.1 x 150 mm column, protected by a filter unit (0.2 µm), with 2 µL injection volume, a flow rate of 0.2 ml min^{-1} and a constant temperature of 40 °C. The mobile phase comprised 10% aqueous methanol (v/v) (solvent A), pure methanol (solvent B) and 1% aqueous formic acid (v/v) (solvent C) in a gradient elution program scheduled for a 40 min run: 0–1.33 min, isocratic gradient of 80A:10B:10C (v/v/v); 1.33–2.33, linear gradient to 74A:16B:10C (v/v/v); 2.33–5.33, linear gradient to 55A:35B:10C (v/v/v), kept in isocratic gradient until 9 min; 9–14 min, linear gradient to 30A:60B:10C (v/v/v); 14–25 min, linear gradient to 5A:85B:10C (v/v/v); 25–26 min, linear gradient to 100B, kept for 4 min; and 30–32 min, linear gradient to 80A:10B:10C (v/v/v), kept for 8 min.

ESI-MS Micromass Q-tof-2 was coupled to UHPLC to assess the minor compounds in the cochineal standard and dyed fibres (silk and wool), as well as photo-oxidation products present in one aged extract from the cochineal standard and in extracts of artificially-aged and historical samples (silk and wool). A flow split of 1/5 (v/v) was set between the MS and the PDA, respectively. MS detection was undertaken in the negative ionisation mode, which gives higher sensitivity for anthraquinones [11, 38], a collision energy of about 8-10 eV for single MS mode, a capillary voltage of 3.2 kV, a cone voltage of 40 V and a source temperature of 80 °C. The nitrogen gas flow rate had a desolvation temperature at 150 °C, and was set for 120 L h^{-1} for cone gas, 90 L/h for nebulizer gas and 120 L h^{-1} for desolvation gas. The scan range for m/z was set for 0-800.

9.2.5. Data treatment

9.2.5.1. Compounds evaluation

For the qualitative interpretation of the chromatographic results, and further evaluation of the integrated peak areas [11, 17, 38], chromatograms were always examined at 275 nm, as the major and minor compounds from the insect dyes, as well as the photo-degradation products, could be detected at this wavelength. Hence, characterization of the compounds and minor compounds in cochineal insects, dyed-fibres and historical samples was undertaken based on the integrated peak areas at which the respective PDA spectra could still be recognized. This step was essential to recognize whether minor compounds should be considered noise, something that is particularly helpful when characterizing species of cochineal in unknown historical samples. Given the relatively high amount of ca compound in cochineal extracts, it was expected that this would be always detected in “real” samples, along with the minor compounds. Indeed, if the response of ca would be too small, the minor compounds should not be detected and, for this reason, such chromatographic results could not be considered.

9.2.5.2 Multivariate statistical analyses

Given the considerable number and the variation of data acquired with UHPLC-PDA, a supervised classification method, partial-least squares discriminant analysis (PLS-DA), was used to model and, furthermore, assess the possibility of discriminating the chromatographic profiles between cochineal species, as well as their corresponding experimentally-dyed and artificially-aged samples. The chromatographic data region considered (absorbance at 275 nm) was between 14.5–17.5 and 20.5–24 min (retention time), because this includes relevant dye compounds (dcIV, dcVII and/or fk and ka). Models were built with samples of known identity (insect dyes and artificially aged and non-aged silk and wool fibres experimentally-dyed with them), grouped into classes of insect dye species (American cochineal, Armenian cochineal, Polish cochineal and a mixture of American cochineal and kermes). Historical samples characterized by UHPLC-PDA with the presence of cochineal or, possibly, a mixture with kermes, were projected onto these models to reveal their identity. For this, the PLS Toolbox 7.9.3 (Eigenvector Research, Manson, WA, USA) in Matlab R2014a (Mathworks, Natick, MA, USA) was used. Details on the models construction are given in ESM 3 [in Appendix 5].

9.2.6. SEM-EDX

Few fibres, from the 28 selected experimentally-dyed samples (prior to ageing) and from the historical samples, were fixed on carbon adhesive over aluminium stubs for SEM-EDX analyses. Samples were observed with a SEM, JSM5910LV from JEOL, to assess possible contaminating particles on the textile fibres, using 20 kV accelerating voltage, 11 mm working distance, 48 spotsize, and backscattered signal (BES) at 40 Pa. EDX analyses were undertaken using a SDD detector from Thermo Fisher scientific and a NSS software. Analyses were undertaken on regions free of contaminating particles to evaluate the presence of mordants and additives, using 80 seconds live time and pulse processor with projected maximum throughput of 71400 cps. Owing to the non-uniform surface and variable thickness of the fibres, EDX analyses were performed three times for each sample, to obtain a qualitative assessment of the elements present.

9.3. Results and Discussion

9.3.1. Experimentally-dyed samples

The characteristic compounds of cochineal and kermes dyes could be properly characterized in the insects and textile samples analysed with UHPLC-PDA and UHPLC-MS, as displayed in ESM 4 [in Appendix 5]. An additional compound, DCOFK (3-O-glucoside of flavokermesic acid, with 475 $[M\text{-}H]^-$) recently characterized by Stathopolou et al. [22], was detected as well in the insect extracts and in the dyed wool samples. Other compounds identified in this publication were not found, which can be explained by the fact that different extraction and analytical conditions were used.

The best crimson shades are obtained when cochineal and kermes dyes are applied to animal fibres. UHPLC-PDA results for silk and wool cochineal or kermes-dyed fibres obtained in this study can be explained by three types of reactions that can occur depending on the dyeing parameters used: complex reactions that produce stable and insoluble chelate complexes of dye–aluminium cation–fibre; direct reactions between polar groups of both colorant and fibres; and acid reactions, through the ionic linkage of carboxylic groups from the colorant and the fibres amino groups [45, 59, 60].

In general, skipping the soap bath, using other water than distilled or rain, or using calcium carbonate or sodium nitrate has brought light, uneven dyed silk fibres. Indeed, these can trigger side reactions creating insoluble compounds that attach to the fibres or precipitate the colorant, and thus, the yield of colorant interacting with the fibres diminishes [45, 46]. For this reason, historical recipes recommend to use water or alum as much pure as possible [46, 55, 56].

To avoid side reactions, historical recipes often suggest the use of additives, such as cream of tartar and oak galls [46, 53-57]. These contain acidic compounds that produce complex reactions with contaminants, freeing the mordant and the colorant to interact with the silk fibres [46, 55]. Cream of tartar, applied in both mordant and dye baths, has revealed to have a greater influence than tannic acid (or oak galls), as lower concentrations are required [46].

The above-mentioned parameters had a small effect on wool. This generally has a higher dye adsorption than silk, and this is clearly observed when comparing their chromatographic profiles, Fig. 9.1. Indeed, it was observed that the ratio and response of dye compounds in dyed wool are similar to those of insect extracts, and they are not prone to alterations as much as silk. This might be related to the fibres structural composition: wool principally comprises amorphously arranged amino acid chains with functional side groups, connected by disulphide cross-linked bonds, and readily available for interactions with alum and cochineal; silk, on the other hand, mainly comprises very crystalline regions with chains of small organized amino acids with side hydroxyl groups that make silk very difficult to interact with outside compounds [61].

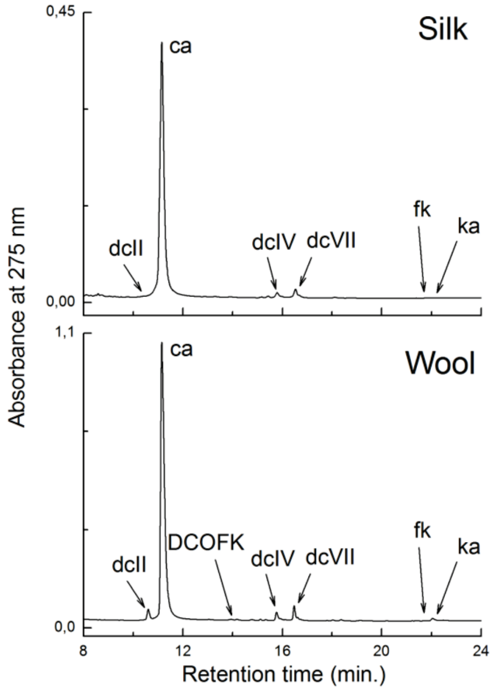


Figure 9.1. Chromatograms obtained for silk and wool samples dyed with American cochineal at optimal conditions.

On the other hand, it is possible that dye compounds react differently to both mordant and fibres because of their molecular structures (ESM 4 [in Appendix 5]), as previously reported for alizarin and purpurin, when dyeing with madder [62]. At optimal dyeing conditions, the neighbouring carbonyl and hydroxyl groups in cochineal compounds create stable complex reactions with aluminium cations, which are partly connected to the hydroxyl groups of silk amino acids [59, 60]. Since complex reactions occur on both sides of the ca, dcIV, dcVII and ka molecules (double-sided), stable cross-linking chains should form with alum and silk, besides less stable direct and acid reactions. On the other hand, dcII, DCOFK and fk compounds have one less hydroxyl group (single-sided) and, hence, they can only engage in complex reactions with one side of the molecule. Therefore, stable cross-linked chains cannot be formed, which might explain why silk samples dyed at optimal conditions have shown a decreased response/absence of dcII and fk (and no DCOFK at all). On the contrary, if dyeing conditions are not propitious, the rate of mordant reactions decreases and, consequently, the amount of double-sided compounds. In this case, it is likely that direct and acid reactions play a more important role in the binding mechanism, thus increasing the rate of single-sided compounds. This was furthermore verified when the colorant was easily extracted from the fibres, using DMSO.

Given the amorphous composition of wool, it is expected that a balance of mordant, direct and acid reactions would occur with the dye compounds. The same could be applied for tin chloride-mordanted silk fibres (mordant and dye baths at low pH and no additives), since tin seems to interact stronger than alum on silk, thus creating a stable ground to receive the dyestuff.

Optimal conditions to dye crimson with alum were obtained using cream of tartar in the mordant and dye baths (pH 7); mordant for 1h at 80 ºC, followed by 24 h at room temperature; dyestuff extraction for 1h at 100 ºC; and dye bath for 1h, kept at 80 ºC [45, 46]. At these conditions, UHPLC-PDA results were highly reproducible, indicating high yields of colorant and with silk fibres displaying a lower response of dcII and fk. When altering the dyeing parameters, opposite results were obtained.

In order to achieve shades closer to crimson historical samples, calcium nitrate was added to the mordant bath. In old dyeing practices, calcium would have been added through wood ashes, alum rocks or diluted in water [45]. Indeed, EDX analyses performed in this study on historical fibres have systematically displayed the presence of this cation, as also reported elsewhere [63]. In addition, by following a historical recipe [52], results on wool were similar to those achieved before but, on silk, very similar results to those of historical textiles were obtained. Although further research is required to assess the individual role of the ingredients added in the dyeing process (copper sheets, sea salt, turmeric or gum Arabic), it is evident that their presence is fundamental, not only to enhance the final colour, but to protect silk from abrasion as well [2, 56, 61].

When testing the colorant behaviour for other insect dyes (kermes, Polish and Armenian cochineal), dyeing conditions applied were similar to those optimized for American cochineal, although it was soon observed that lighter shades were obtained with these insects on silk. Further research would be required to assess the best approach for obtaining crimson with these insects, although their availability is quite limited [29]. Nevertheless, deeper shades were achieved on wool, with kermes displaying orange red shades, rather than crimson. This is probably related with the insects' colorant composition: kermes-dyed fibres comprise a mixture of (red) ka and (orange yellow) fk, whereas the pinkish red cochineal-dyed fibres, mainly contain (more bluish red) ca [60]. This might explain why turmeric (yellow colorant) is mentioned in post-16th-century historical recipes to achieve orange red shades with American cochineal, while recipes with kermes are not.

UHPLC-PDA results for silk dyed with Armenian cochineal have demonstrated colorant behaviour similar to that reported for American cochineal-dyed silk, with a decrease/absence of dcII and fk response. The same was observed for a mixture of American cochineal and kermes, which chromatographic profile becomes similar to that of silk dyed with Polish cochineal (fk and ka compounds from kermes amount for c. 20% relative abundance) [17, 37].

Due to this alteration, compounds quantification [17, 37] can be compromised. As previously demonstrated by Serrano et al. [11], Fig. 9.2 shows that this method is not sufficient for dyed fibres, especially when dcII and fk are too small. Indeed, scores for American and Armenian insects and dyed samples show dispersion; fall outside the zones of highest probability; and overlap each other zones.

PLS-DA models were built to discriminate cochineal species, using chromatographic regions which had relevant common compounds - dcIV, dcVII, fk and ka. Regions including ca or dcII compounds were not considered, because they substantially vary between samples of the same class. Given the dissimilar chromatographic profiles exhibited by dyed-wool and silk, more accurate discriminations were obtained when considering the two types of fibres in separate models, Figs. 9.3 and 9.4.

In both figures, the first two LV's depict a higher degree of separation between cochineal species (American, Armenian, Polish and mixture of American with kermes), in comparison with Fig. 9.2. For instance, American cochineal insects and respective dyed fibres are well distinguished from other dyestuffs, generally displaying negative scores in LV1 (higher amount of dcIV and dcVII). The majority of these scores show high congregation, indicating a low variability in the examined chromatographic region. American cochineal samples displaying positive LV1 mostly correspond to fibres dyed at unsatisfactory conditions (lower dcIV and dcVII). On the other hand, Armenian and Polish cochineal samples show higher within-class variation. Although they show some separation in relation to other classes, there is some overlap with the region of American cochineal samples (on the first 2 LV's).

However, cross-validation has demonstrated that a higher number of LV's is optimal to classify both sets of samples. When using 5 LV's for the silk model and 9 LV's for the wool model, approximately 5.2 % (silk) and 4.1 % (wool) of samples were wrongly predicted (confusion matrices in ESM 3 [in Appendix 5]).

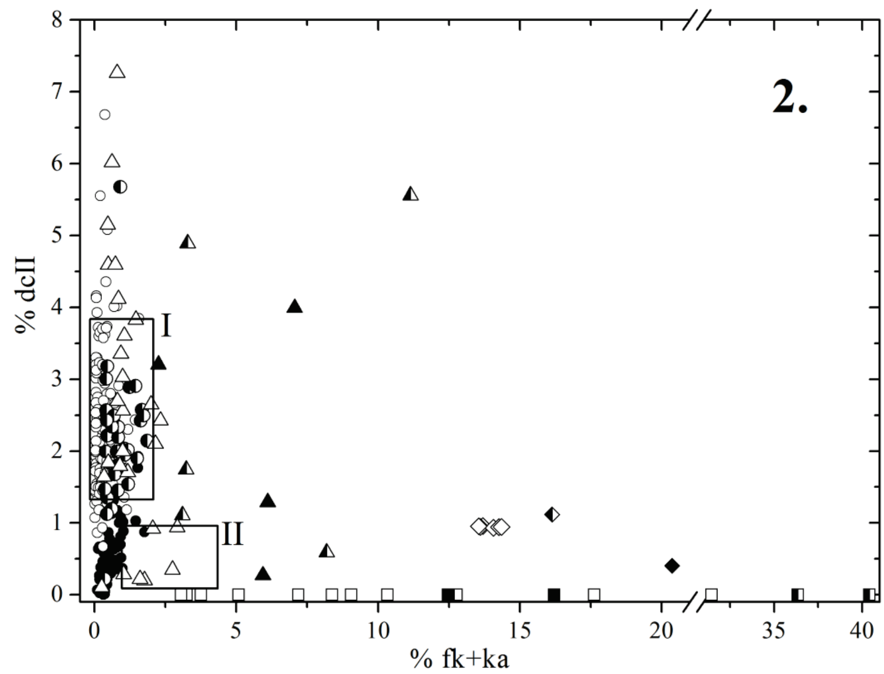
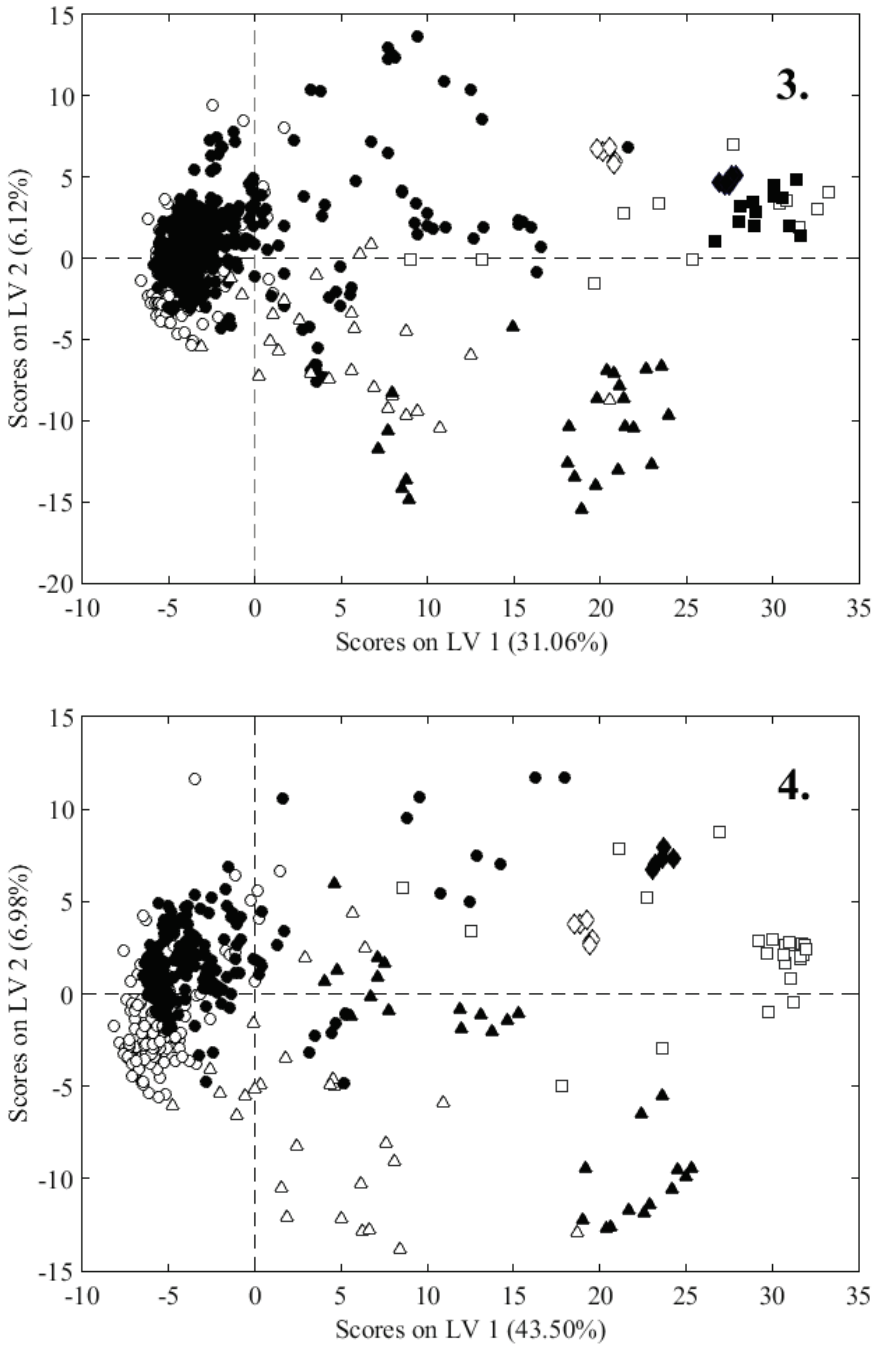


Fig. 9.2. Graphical system based on the relative percentages of minor compounds dcII and fk+ka, with rectangular areas representing the zones of higher probability (I. American cochineal, and II. Armenian cochineal), according to [17, 38]: American cochineal (circles); Armenian cochineal (triangles); Polish cochineal (squares); mixture American cochineal and kermes (diamonds) / insects (white shapes), silk fibres (black shapes), wool fibres (left black shapes).



Figs. 9.3 (Silk) and 9.4 (Wool). Scores on the first 2 LV's of a PLS-DA model of insect dyes and their respective dyed fibres: American cochineal (circles); Armenian cochineal (triangles); Polish cochineal (squares); mixture American cochineal and kermes (diamonds) / insects (white shapes), silk or wool fibres (black shapes).

9.3.2. Artificially-aged samples

As historical textiles are expected to have been through photo-degradation during their lifetime, induced ageing of the experimentally-dyed samples was carried out. This was important to ascertain possible changes in the chromatographic ratio of the colorant, which could influence the insect dyestuffs discrimination and possibly give comparable results to those of historical samples.

After submitted to artificial ageing, samples were compared with their non-aged correspondents, using colour measurements. In Table 9.2 [and Appendix 8] it is noticeable that the rate of fading can vary between samples, depending on the quality of the dyeing and the type of fibre. In all of them, ΔL^* values are always positive, which means that all samples have suffered fading (became lighter). Wool dyed with American cochineal became slightly redder (positive Δa^*), while most wool samples dyed with other insects and all silk samples tended to become less red. Additionally, more than half of the samples tended to become more yellow (positive Δb^*).

"Yellowing" of samples is expected to occur during photo-oxidation of the fibres, as UV radiation interacts with the keratin of wool and fibroin of silk. These interactions occur with their side groups, principally tyrosine in silk, and cysteine, tryptophan and tyrosine in wool. By absorbing UV radiation, they are reduced into new groups, such as aspartic, glutamic and cysteine acids in wool. These new groups are responsible for the yellow shade exhibited by fibres [48-50, 61], especially those prepared with tannic acid.

Although no significant photo-degradation had been previously observed in aged cochineal-dyed fibres [49], here UHPLC-PDA results have generally shown lower amounts of chromophore compounds in relation to the non-aged ones. Absolute amounts of colorant registered with UHPLC-PDA before and after ageing are given in Table 9.2. Here, it is observable that the percentage of colorant loss in wool is reported to be smaller than in silk [50]. Moreover, fibres most severely faded are those prepared at unsatisfactory dyeing conditions. This demonstrates that the occurrence of stable complex reactions (fibre-alum-colorant) at optimal conditions brings more resistant and light-fast colours, preserving the fibres protein matrix [45, 49, 50, 59].

Table 9.2. Differences in colour registered with colour measurements and UHPLC-PDA analyses, between the aged and non-aged experimentally-dyed samples [Appendix 8].

	[Exp.] Fibre	ΔL*	Δa*	Δb*	Δcolorant (%) [1]
No additives	[14] Silk	20.41	-28.01	14.65	44.96
Dye extract 100 ºC + low pH (dye bath)	[11] Silk	15.96	-21.85	9.08	65.09
Cream of tartar + low pH (dye bath)	[3] Silk	10.80	-20.24	2.54	79.14
	[25] Wool	1.59	2.00	2.73	30.63
Tannic acid + low pH (dye bath)	[13] Silk	16.82	-26.61	18.27	86.33
	[26] Wool	3.74	3.28	6.53	54.14
Cream of tartar + $Ca(NO_3)_2$)	[32] Silk	11.93	-21.86	1.32	64.58
	[33] Wool	10.21	10.01	17.61	55.91
Tannic acid + $Ca(NO_3)_2$)	[36] Silk	7.87	-16.74	11.39	66.84
	[37] Wool	9.09	7.87	15.67	62.04
Tap water	[38] Silk	10.87	-18.74	6.59	60.17
	[39] Wool	12.86	0.48	-9.06	53.26
Lake water	[40] Silk	15.90	-23.41	5.69	74.93
	[41] Wool	9.70	6.26	-5.16	49.94
Rain water	[42] Silk	11.99	-16.05	-1.52	58.77
	[43] Wool	3.61	4.17	6.22	42.31
Historical recipe adapted	[95] Silk	5.03	-9.07	-1.10	24.27
Tin chloride	[73] Silk	8.62	-17.02	-10.06	62.04
	[74] Wool	5.86	1.04	10.06	53.35
Kermes (no additives)	[62] Wool	6.48	4.47	11.18	7.15
Kermes (cream of tartar + $Ca(NO_3)_2$)	[86] Silk	9.50	-13.76	5.97	45.14
	[87] Wool	13.56	-11.89	-0.26	60.73
Armenian cochineal (low pH)	[82] Silk	7.58	-14.28	7.85	71.44
	[83] Wool	6.95	-3.50	-7.64	54.50
Polish cochineal (no additives)	[59] Silk	12.07	-14.67	10.32	73.34
	[60] Wool	7.86	-7.38	-8.46	32.35
American cochineal + kermes	[63] Silk	5.22	-14.04	-1.71	42.67
	[64] Wool	3.18	2.69	5.44	45.81

[1] Difference calculated with the sum of absolute amounts (integrated peak areas) for the representative dye compounds detected with UHPLC-PDA (dcII, ca, dcIV, dcVII, fk and ka) in the aged and non-aged (100%) experimentally-dyed samples.

Chromatograms for artificially-aged and historical samples also revealed the occurrence of similar photo-degradation compounds, in agreement with Degano et al. [49]. In general, these compounds have shown a higher response in aged silk, than in aged wool samples. These were found as well in the extract of an old cochineal standard, prepared about one year before and kept at room temperature and UV light exposure. Non-aged fibres or fresh insect extracts either did not contain these compounds, or their response was very small.

The first two compounds eluted at an early retention time and were colourless according to their UV-vis spectra (ESM 5 [in Appendix 5]). This loss of colour and early retention time can be related to a strong increase in polarity, due to degradation mechanisms. MS analyses indicated that the first compound (λmax=255 nm) has a molecular mass of 452 ($[M-H]^-$ 451; very small response). This can probably be a by-product of splitting bonds in the conjugated system of anthraquinone molecules or a ring opening reaction, possibly followed by a reduction process of adjacent molecules. Due to its small response in the MS detector, the molecular mass of the second compound (λmax=280 nm) could not be characterized. This could perhaps correspond to hydroxybenzoic acid, which has been suggested to be a by-product of the photo-degradation of tyrosine and tryptophan in protein fibres [47, 50], as well as flavonoids present in aged textile samples [47, 48].

Two more photo-degradation compounds were detected as well, displaying spectra in the visible area. The third compound (λmax=498) was found in aged samples (experimentally-aged and historical fibres and insect extract), but its molecular mass could not be ascertained because of its small response in the MS detector. Though, owing to its UV spectrum, close to that of red anthraquinones (ESM 5 [in Appendix 5]), it could be a photo-degradation by-product of small induced changes occurring in these molecules. The fourth compound (λmax=340) was reported to be an isomer of dcII ($[M-H]^-$ 475), and it only occurred in the cochineal insect extract. Further research on the characterization of these compounds would be necessary to understand their photo-degradation path, although this falls outside the scope of the current study.

3.3. Historical Samples

The red samples from a large group of 95 European and Asian historical textiles were analysed with UHPLC-PDA to determine the cochineal species present. This not only confirmed the methodology developed in this study, but also the impact of American cochineal into local dyeing practices. About 50% of these textiles are of Italian origin, but other exemplars are from Spanish, Dutch, Turkish, Iranian, Indian and other regions. They are dated before and after the documented arrival of this dyestuff in Spain in 1521, Italy (and the Ottoman Empire) in 1543, Iran before 1618, and India in 1612 [28-30]. For details about these textiles and their chromatographic results, see ESM 6 [in Appendix 5; see also Appendix 2].

In a first phase, UHPLC-PDA results were visually examined and the presence of cochineal and/or kermes dyes was detected. In some samples, compounds from other dyestuffs were reported as well, such as indigotin, type C component, alizarin or luteolin. These compounds were often recognized as cross-contaminations from adjacent fibres in the textiles weaving structure, although, in specific cases, they were considered part of the colorant mixture as well. Gallic acid (ga) and/or ellagic acid (ea) compounds were detected in about 65% of the samples, which indicates the importance of tannins, such as gallnuts, in crimson dyeing recipes. This ingredient would be added to improve the strength of the fibres [41], while protecting them from contaminations [46]. Also, it would make them advantageously heavier, as silk was sold by weight [2, 40, 60, 61].

From the total of 117 samples, 13 samples from Italian and Spanish textiles, and dated before the 16th century, were characterized with the presence of kermes dyes. From these, one sample (MT33357, pile) was characterized with a mixture of kermes and Polish cochineal; and two samples (MT22864), with a small amount of ca compound, along with kermes compounds. Compounds quantification of UHPLC-PDA chromatograms was often undertaken to ascribe the cochineal species used but, in this case, the small amount of ca compound and the absence of cochineal minor markers made this task impossible. Indeed, when minor compounds dcII, fk and ka were not detected, quantification was not achievable and, for this reason, species characterization for 21 of the samples was based on the chromatograms visual examination.

If at least one of the compounds was detected, quantified results were plotted in Fig. 9.5. Given the alteration of minor compounds in dyed silk fibres reported in section “3.2. Experimentally-dyed samples”, it was opted to not include the results for the insect dyes. Hence, for more accurate results interpretation, the unknown historical samples were compared with the reference experimentally-dyed and aged samples. Though, it is worthwhile noticing that, despite their low response, minor compounds in the reference samples were still considered, because the respective cochineal species were known *a priori*. However, and as previously reported in Fig. 9.2, the overlap of American and Armenian cochineal reference samples compromises the proper characterization of these species and, therefore, their identification in historical textiles. As for unknown samples distanced from this region and showing an absence of dcII, this graphical system can be more clearer about the presence of Polish cochineal, or a mixture with kermes.

PLS-DA models for silk and for wool were made with the experimentally-dyed and the aged samples of cochineal species and the mixture of American cochineal and kermes. Since insects have shown variation in relation to the respective dyed fibres in Figs. 9.3 and 9.4, it was opted to not consider them. In this way, a more accurate classification of the insect sources in unknown historical samples could be obtained. Furthermore, outliers were removed, based on the 95% confidence intervals of the Hotelling T^2 and the Q-statistic: it was found that 3.9% silk and 4.3% wool experimentally-dyed samples were above both limits, and they correspond to very unsatisfactory dyeing conditions. As a result, cross-validation has shown a decrease of optimal number of LV's (3 LV's), as well as fewer

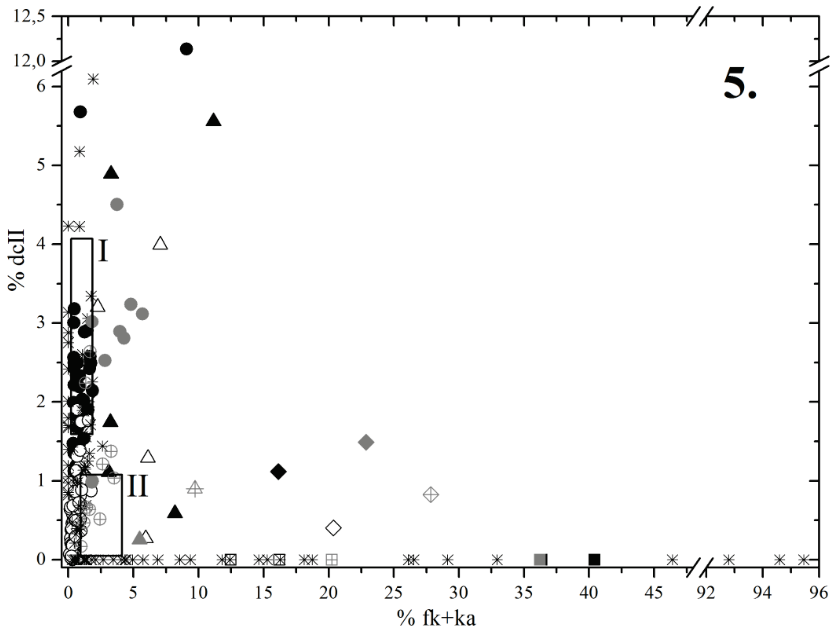
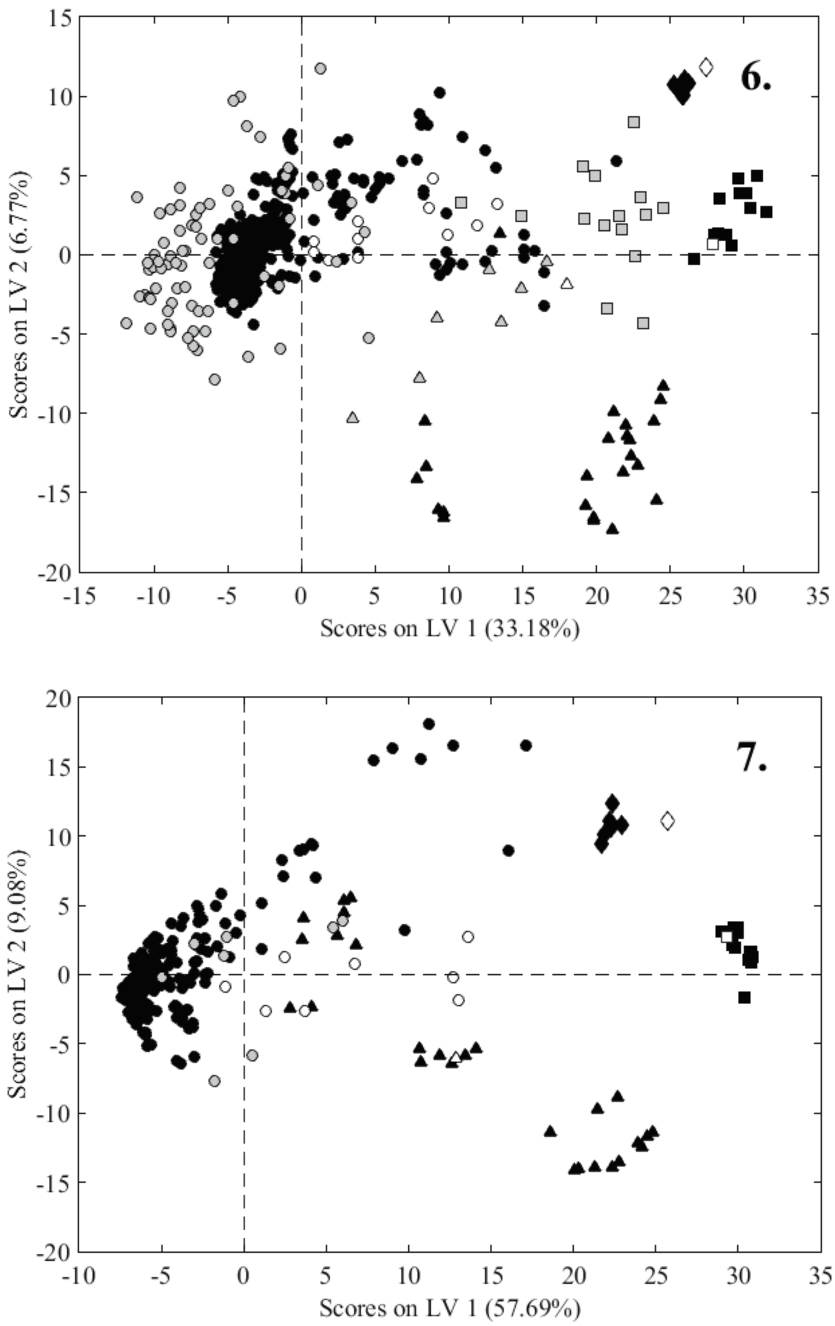


Fig. 9.5. Graphical system based on the markers relative percentages as described in Fig. 9.2, with rectangular areas representing the zones of higher probability (I. American cochineal, and II. Armenian cochineal): American cochineal (circles); Armenian cochineal (triangles); Polish cochineal (squares); mixture American cochineal and kermes (diamonds) / silk fibres (white shapes); wool fibres (black shapes); aged silk fibres (grey crossed shapes); aged wool fibres (grey shapes); historical fibres (asterisks).



Figs. 9.6 (Silk) and 9.7 (Wool). Projection of historical samples over PLS-DA models (2 LV's) of aged and non-aged dyed fibres: American cochineal (circles); Armenian cochineal (triangles); Polish cochineal (squares); mixture American cochineal and kermes (diamonds) / non-aged silk and wool fibres (black shapes); aged silk and wool fibres (white shapes); historical fibres (grey shapes).

misclassifications, with 0.4 % of the silk reference samples and 3.3 % of the wool reference samples predicted wrongly (confusion matrices in ESM 3 [in Appendix 5]). This means that almost 100% of the reference samples were classified correctly.

Cochineal-dyed historical samples (97 silk and 8 wool fibres) were projected on these models. These samples did not include the two samples characterized with a small amount of ca compound (MT22864), neither a sample (AS4921), in which a complex mixture of dyestuffs was detected along with cochineal compounds. In these cases, the chromatographic regions analysed are too different from those in the reference samples and, therefore, results may not be accurate.

Classification of cochineal species in historical samples was based on strict predictions (a sample being classified in precisely one class), and when this was not available, classification was based on most probable predictions, and on visual inspection of Figs. 9.6 and 9.7 (2 LV's). These results were then verified with those already obtained with the qualitative and quantitative interpretation of the chromatographic results, as well as the textiles date and provenance. For instance, for sample SGL1907/114, the most probable prediction was American cochineal (99% of highest probability), and the respective plot corresponded to that region in Fig. 9.6. This was furthermore in agreement with the chromatogram's qualitative and quantitative interpretations, and the textile's date and provenance. On the other hand, for sample MNAA1616, American cochineal was the most probable prediction (though, only 30% of highest probability) and the respective plot was relatively close to the region of Polish cochineal in Fig. 9.6. When comparing with the qualitative and quantitative results and the textile's date and provenance, Polish cochineal was a more reasonable attribution.

From the total of 105 historical samples projected onto the PLS-DA models, almost 80% of the samples were classified based on strict predictions. The results achieved have successfully shown agreement with the textiles date and the provenance (ESM 6 [in Appendix 5]), except for six samples that were strictly predicted with American cochineal, although they belong to 15th-century textiles. In these cases, the date of the textiles should probably be reconsidered.

It is possible that a higher percentage of strict predictions would be obtained if the number of reference samples for Polish and Armenian would be increased. Moreover, it is important to emphasize that reference samples can never be complete reproductions of the historical samples and, for this reason, PLS-DA classifications are not as accurate as the cross-validation results on the experimentally dyed and aged samples. Figs. 9.6 and 9.7 show that historical samples have a lower score on LV1 (higher amount of dcIV and dcVII) than experimentally-dyed and the aged samples.

These results indicate that historical samples are well conserved, and this is supported by the very small response of photo-degradation compounds reported in the respective UHPLC-MS results. Also, these results point out that historical fibres possess more colorant than the experimentally-dyed ones, probably due to the efficiency of the dyeing recipe, but also due to the type of fibres. Indeed, SEM analyses revealed that historical fibres are somewhat thicker, which could perhaps provide a wider surface for more reactions to occur with the colorant, thus increasing the colorant yield.

Furthermore, some historical fibres presented many dirt particles under SEM observation, and this was translated in high EDX peaks of aluminium, magnesium, potassium, silicium, calcium, sodium or chloride. Smaller peaks of these elements in historical fibres that were apparently clean, could be an indication of diluted cations in water used for dyeing, or due to additives. The presence of potassium could be related to the use of wood ashes or from the alum, while peaks of sodium and chloride might indicate the use of salt, by contamination or additives. On the other hand, the presence of phosphorus could indicate possible use of phosphate-containing detergents used in conservation treatments [61].

From a historical point of view, the majority of the samples (70%), dating to and after the 16th century and produced in both European and Asian regions, were characterized with the presence of American cochineal. Textiles dated before the 16th century were classified as containing Armenian and Polish cochineal. Interestingly, only one sample was reported with a mixture of kermes and Polish cochineal, while none of the samples was characterized with a mixture of kermes and American cochineal, as suggested by Pearson [56]. These are very important interpretations, as they bring more accurate knowledge of the use of cochineal insects in historical textiles, while establishing invaluable connections with historical and dye identification literature, concerning the impact of American cochineal in local dyeing practices [26-28, 30-34].

On the other hand, it is worthwhile noticing that these results contradict those obtained by Serrano et al. [11]. In the previous study, not only insects were mainly used as references, but also a non-classification method, PCA, was adopted. In this case, unknown historical samples were predicted according to the dominant class in the region of the principal components space, where the samples were projected on. While PCA has often been used for discrimination, this is not a particularly reliable approach and more suitable methods exist, such as PLS-DA [64]. PLS-DA is a classification method that performs discriminant analysis on scores on latent variables, which are designed to capture information in the data that is most useful for predicting the class [65]. Thus separation between classes is improved, and the use of discriminant analysis allows estimation of the accuracy of the models (ESM 3 [in Appendix 5]). For this reason, PLS-DA analyses, along with the qualitative and quantitative interpretation of chromatographic results, constitutes a recommendable approach for future studies about cochineal and kermes dyes identification in historical textiles.

However, in such studies, researchers would need to prepare their own reference dyed-fibres, although Armenian and Polish cochineal are very hard to obtain nowadays, since they are near extinction [29]. In addition, researchers in the field of dye identification in cultural heritage do not often have the knowledge to carry out multivariate statistical analyses. As a future perspective, a possible solution would encompass the creation of an international online database that could include the PLS-DA models developed here. Researchers analysing unknown textile samples at similar analytical conditions, would be able to plot their results onto these models and, hence, ascertain the identity of their samples. This could be developed in such way that researchers could even add their own reference samples and the results for their historical samples, thus expanding the database for future studies. The potential success of such platform could be even prolonged to other applications, such as the identification of cochineal dyes in historical paintings.

9.4. Conclusions

A combination of UHPLC-PDA, UHPLC-MS, SEM and multivariate statistical analysis for the study of cochineal dyes in experimentally-dyed and aged samples has brought fruitful insights for the characterization of historical textiles. The methodology developed demonstrated that it is possible to obtain consistent information about dyed samples and their composition, depending on the experimental parameters and the textile substrate used. Furthermore, it has been demonstrated that compounds ratio in the colorant composition are directly related to the type of fibres (especially silk) used and the dyeing parameters applied to them, because of different types of reactions occurring between the fibres and the insects' colorants. For this reason, minor compounds quantification alone cannot be considered for characterizing cochineal species in silk historical textiles. On the other hand, comparison between experimentally-dyed and aged samples has revealed, for the first time, the occurrence of photo-degradation compounds in cochineal and kermes dyestuff composition and the fibres matrix, especially in silk fibres. This was reported in historical fibres as well. Research on the chemical nature of these photo-degradation compounds is advisable in future studies.

Considering the experimentally-dyed and aged samples as references for the identification of the cochineal dye source in historical textiles, it has been possible to obtain more conclusive classifications, rather than with direct comparison with reference insect dye extracts. Hence, by combining PLS-DA analyses, with the qualitative and quantitative interpretation of chromatographic results, it became possible to obtain accurate classifications of cochineal species present in historical textiles. Further historical interpretation of these results has come to support historical and dye identification literature, which defend a strong impact of American cochineal into European and Asian dyeing traditions, from the 16th century onwards. These successful results are proof of the powerful combination of UHPLC-PDA with a statistical classification method, to accomplish more accurate interpretations about closely related dyestuffs. Therefore, it is highly recommended for future studies on natural dyes identification in historical textile objects.

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CHAPTER 10

THE RED ROAD OF THE IBERIAN EXPANSION:

A Multidisciplinary Study

"The whole spectrum of colours can be obtained
from a multitude of plants, animals and fungi, to dye
clothes, textiles and artefacts" Dominique Cardon [1]

Historical textile objects and their dye materials represent important sources of information for answering historical questions concerning where, when and how they were produced. In this thesis, this information is used to assess the wider historical picture of the impact of American cochineal in Europe and Asia, thus demonstrating that the study of textile objects can bring important evidence to historical discussions.

Based on this premise, this chapter focuses on the study of dyestuffs (particularly insects) present in a large group of textile objects, by undertaking a multidisciplinary discussion that combines the historical and chemical studies, developed earlier in this thesis. Hence, this discussion aims to assess the historical significance of the chemical results obtained with dye analysis, not only through the characterization of "Old World" insect dyes in relation to American cochineal, but also by looking at other dyestuffs present in the textiles. Hence, it is expected that correlations attained here can help us to better evaluate those accomplished so far in the historical parts of this work (Chapters 1-2, 4-7).

This chapter begins with an assessment of how the multidisciplinary analysis of the samples was carried out, before undertaking a geographical discussion, beginning with the analysis of the results for the European textiles, and then, for the Asian ones. This division reflects the fact that, although both regions display some similarities between their dyeing traditions, they also show preferences for different and specific dyestuffs. Each section begins with an analysis of local and imported red insect dyes, and then looks at the presence of other dyestuffs (plants, fungus and lichens), and ends with a discussion summarizing the

[1] Cardon, 2010, p. 1.

relationships observed between foreign and local dyes. Given the complexity of this chapter, a full appreciation of it requires consultation of additional materials, availed in Appendix 2 and in ESM 6 in Appendix 5.

10.1. Multidisciplinary Analysis

By interweaving the arguments achieved through the revision of the historical literature with the results obtained from the chemical analysis of a sizeable number of historical textiles, it is hoped that more detailed historical conclusions can be drawn about: 1) the widespread adoption of American cochineal in the main European and West Asian dyeing centres; 2) the possibility of verifying and/or completing the uneven historical evidence available for peripheral European regions, as well as for East and Southeast Asian manufacturing centres; and 3) confirming whether European and Asian insect dyes continued to be employed, or were completely overthrown by the American dyestuff, once it entered into local dyeing practices. In other words, it is proposed here to further elucidate the arguments made in the historical chapters about how American cochineal came to shape new patterns of trade, and what its impact was on long-standing European and Asian dyeing traditions.

As described in Chapter 3, the group of textiles selected for this multidisciplinary study follows specific requisites, namely the type of textile and fibre (elaborate silk objects); potential presence of cochineal dyes (red crimson shades); provenance (Europe and Asia); and date (15th to 17th centuries). Based on these criteria, a total of 287 samples, from 115 European and Asian historical textiles, and one Peruvian example, were investigated (Appendix 2). These were analysed using the analytical UHPLC-PDA conditions described in the Chemistry chapters.

After performing UHPLC-PDA analyses, 117 red samples from 95 historical textiles were reported with the presence of cochineal and kermes dyes. The accurate characterization of the cochineal species (American, Polish or Armenian) present in the textiles is assessed in Chapter 9, through evaluation of the dyestuffs' compositions and statistical comparison with reference fibres dyed with insect dyes (ESM 6 in Appendix 5).

As for the other samples, in which compounds from cochineal or kermes were not detected, respective analytical results were interpreted based on examination of the dyestuffs' characteristic compounds, with the help of the UHPLC-PDA reference library developed in Chapter 8 (Appendix 4). When unknown compounds were not available in the reference library, interpretations were based on scientific literature.

Additionally, it is important to emphasize that a full or complete interpretation of the results was sometimes hindered. Indeed, often the presence of compounds from different dyestuffs was reported in the same chromatogram. These could indicate cross-contaminations from adjacent threads in the packed weaving structure of the textiles, or simply, a mixture of several dyestuffs. When suspicion of a cross-contamination might have occurred, the results were carefully compared with other coloured fibres present in the textiles, where the samples were taken. In some cases, the interpretation of the results could not bring an accurate attribution of the dyestuff used, either because the chromatographic response was too small (possible photo-degradation of compounds in light-sensitive dyes), or because the detected compounds could not be matched with those of the reference library (Appendix 9). This was especially verified for yellow fibres and, hence, the term "yellow dye plant" was applied.

Finally, it must be acknowledged at the outset that, in a small number of cases, the dates attributed to the textiles by their respective museums were either quite general (i.e., time range) or did not coincide with the scientific results. Hence, these dates were sometimes revised. For example, if a historical textile was dated to the "15th century" or to the "15th/16th century", and dye investigation revealed the use of American cochineal, then the most recent plausible date, i.e., 16th century, was considered. However, if a Eurasian cochineal species was detected in a "15th/16th century" textile, the date was then re-evaluated in relation to the objects iconography and the textile literature. If there was any doubt, the latest date (i.e. 16th century) was used. In this context, it is important to remember that the dating of textiles is a complex subject and secure dates are rare. Nevertheless, as we shall see, scientific data can sometimes offer valuable evidence to narrow the time range of attributed dates.

10.2. The Red Road to European Dye Workshops

When American cochineal started arriving from the Americas in the 16th century, European textile manufacturing centres gradually started assimilating it in their dyeing practices, as demonstrated by the historical evidence presented in Chapters 6 and 7. Along with other imported and locally available dyestuffs, American cochineal was soon part of the construction of intricate, expensive textiles, which examples are found today in cultural heritage institutions.

From the total number of 116 historical textiles investigated in this thesis, 77 are of European origin. These principally date to the 16th century (c. 44%) and to the 15th century (c. 35%), although examples from the 17th century (c. 19%) are considered as well. These are, therefore, suitably representative of the period under study, given the expectation that traditional dyestuffs existed in 15th-century European dye workshops, and were gradually replaced by overseas dyestuffs (especially American cochineal), during the 16th and 17th centuries.

Due to the international popularity of Italian workshops for their production of rich silk fabrics, it comes as no surprise that the majority of the European textiles investigated here are attributed to that region (c. 65%). By combining luxurious materials with complex weaving structures, high-quality Italian textiles were extensively exported to other parts of Europe and to Asia, and were even portrayed in paintings by many European masters [2]. The Italian textiles examined in this work are mainly dated to the 15th and 16th centuries, whereas very few examples are dated to the 17th century. A smaller number of 15th- and 16th-century silk textiles are attributed to other European regions, namely the Low Countries (Belgium and the Netherlands), Spain, France, Germany and Sweden. The few woollen textiles investigated here (mainly tapestries) are attributed to Switzerland and to the Low Countries, especially in the 17th century to North Low Countries.

These proportions of textiles seem to be in agreement with the historical interpretations achieved earlier in Chapter 6, namely a noticeable downturn in Italian production of luxurious silk fabrics for international markets after the 16th century and, by contrast, the expansion and increasing international recognition of northern European

[2] Monnas, 2008, p. 19.

production centres. Although it would be useful for a larger number of European examples dated to this period should be investigated to undertake further interpretations on this matter.

Since many studies on dye identification have been dedicated to the dyes in European textiles, not many non-red samples were considered for this study, as little information would be added. Hence, from the total of 152 samples from European textiles examined here, almost 80% comprise red, pink or orange-dyed fibres, whereas most of the remaining 20% are yellow-dyed fibres. The former were mainly coloured with insect dyes, brazilwood and/or roots of madder; and the latter, with weld, young fustic or dyer's broom. Additional ingredients, like tannins and indigo or woad were detected as well.

Red Insect Dyes. Among all the samples obtained from European textiles, 91 were characterized with the presence of insect dyes. The majority of those that have been characterized with cochineal species (American, Polish or Armenian) show agreement with the date attributed by the respective textiles' host institutions (Fig. 10.1; see also ESM 6 in Appendix 5).

Indeed, thirteen silk samples from ten textiles of Italian (and one of Spanish) origin and dating up to the 16th century, were characterized with the presence of kermes dyes. From these, one sample (MT33357, pile) was identified with a mixture of kermes and Polish cochineal (Appendix 9); and two samples (MT22864) with a small amount of carminic acid (ca) compound, along with kermes compounds. This corroborates the common practice of mixing cochineal and kermes, or giving a final bath of cochineal to fabrics dyed with kermes [3]. Polish cochineal was classified in fourteen silk samples, and lac dye in four silk samples [4], both of which belonging to thirteen Italian (and two Dutch) textiles, dated to the 15th and the 16th centuries. Moreover, Armenian cochineal was classified in five silk samples from four Italian textiles, dating from the 15th century.

[3] Molà, 2000, p. 114; Gargiolli, 1868, pp. 35-37.

[4] Interestingly, lac dye components were frequently reported along with kermes components in the chromatographic results of the same sample. Analyses to lac dye insects in this study (Fig. 2.2 of Chapter 2) and by Santos et al. (2015, p. 133) did not report kermesic nor flavokermesic acids in the matrix composition of the insects' colourant. Although one could argue that both dyestuffs may have been combined in the same dye bath, this hypothesis becomes improbable when regarding the results for Asian textiles, as shall be further discussed in this chapter.

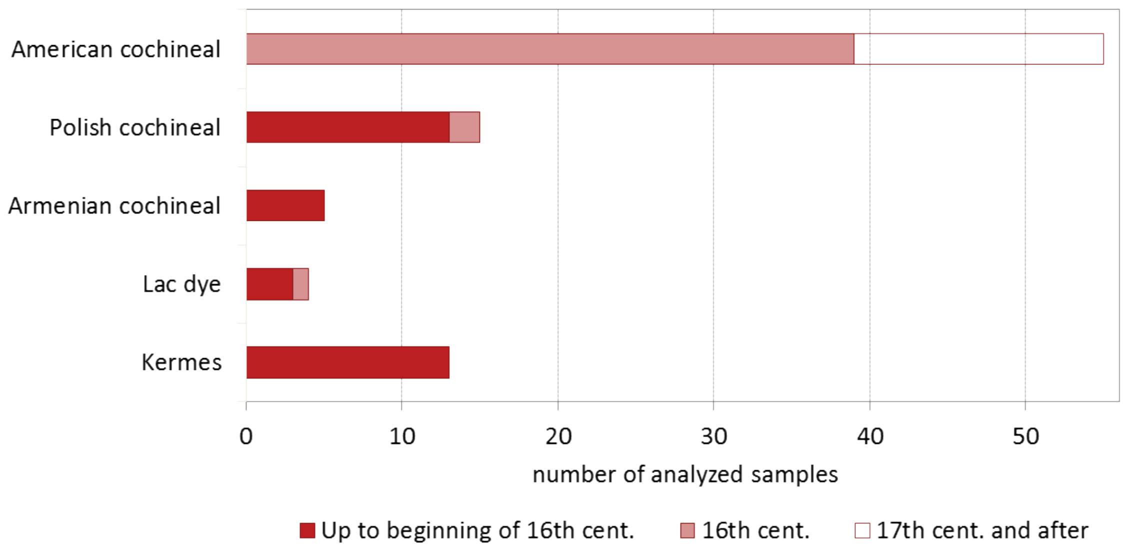

Fig 10.1. Diagram of the sum of samples from European historical textiles, in which insect dyes were characterized - organized by the respective date of the historical textiles.

These results corroborate the traditional use of European and Asian insect dyes in complex silk textiles until the 16th century, while also reaffirming the leading role of Italy in this period. Although this study only represents a small fraction of extant European textiles coloured with insect dyes held by worldwide collections today, it is nevertheless interesting to note:

1) The proportion of silk textiles in which kermes and Polish cochineal were identified is equivalent. This indicates that kermes was regularly applied on silk and not only on wool (especially in Spain, where the dyestuff was abundant), as also demonstrated by 15th- and 16th-century dyeing recipes [5] (discussed in Chapter 1) and scientific publications on dye identification [6].

2) The number of textiles identified with the presence of Armenian cochineal and lac dye demonstrates that these insects were less often applied than kermes and Polish cochineal. This is consistent with historical information attained earlier in Chapter 1, where it is emphasized that Armenian cochineal and lac dye imported from Asia had to compete with

[5] Gargiolli, 1868, pp. 35-37 and 49-51; Rosetti, 1969, pp. 133-136 and 144-145.
[6] Bommel & Joosten, 2009, p. 168; Hofenk de Graaff & Roelofs, 1972, pp. 11-23.

local European dyestuffs, because they required additional dyeing expertise and the colorant yield especially of Armenian cochineal is much lower than for the Polish variety.

3) The results clearly suggest that European and Asian insect dyes were commonly applied up to the 16th century, although they seem to completely vanish afterwards, in detriment to the growing popularity of American cochineal. As witnessed in Chapter 7, while Armenian cochineal and lac dye practically disappear from the majority of European markets after the 16th century, Polish cochineal and kermes keep being produced (although, at a slower pace) to respond to the demand of European cloth-making centres, until the 19th century - particularly in regions nearby the areas of exploitation of these insect dyes.

Investigation into a larger number of European historical textiles dated to this period is required to undertake further interpretations concerning whether these insect dyes continued to be applied in European centres of textile production after the 16th century. Even so, it seems reasonable to advocate that, given the economic attractiveness of American cochineal, this was a suitable dyestuff to colour silk fabrics meant for the consumption of an insatiable market. By contrast, the use of local insect dyes may have become, more than ever at this time, restricted to the most sumptuous and expensive silk cloths probably intended for or even commissioned by a very restricted elite.

American cochineal was classified in 38 silk samples from 26 textiles, largely of Italian, but also of Spanish, French, Swedish and Flemish origin, dating from the 16th century. For the 17th century, ten silk samples chiefly from Italian textiles and, to a lesser extent, from Spanish, Swiss, Flemish and Polish textiles, were characterized as well by the presence of the American dyestuff. In this context, it is worth emphasizing that the Polish textile was dyed with the American dyestuff, rather than with the locally available Polish cochineal.

Interestingly, American cochineal was the only insect dye to be classified in woollen samples - one sample from a 16th-century Swiss tapestry, and six samples from Dutch 17th-century tapestries. This indicates that, by the 17th century, American cochineal was well integrated into European dyeing practices, as corroborated by the increasing volumes brought from the Americas at this time.

In addition to bringing important historical interpretations about the dye applications of insect dyes in European textiles, the accurate classification of cochineal species has brought additional evidence for the history of specific textiles. While cochineal species have been conclusively attributed to the great majority of the analysed fibres (in agreement with the date and provenance for the textiles, given by their respective institutions), six silk samples were classified with the presence of American cochineal, although they belong to four Italian items and one Dutch, dated to the 15th century (ESM 6 in Appendix 5). In this case, the date ought to be reconsidered, since the presence of American cochineal indicates that these textiles may have been produced at a later period.

In addition, important conclusions were obtained about composite textiles, i.e., objects comprising several textile components:

- MAKT8473 is a liturgical chasuble dated by its host institution to the beginning of the 16th century, and which has a red pile dyed with Polish cochineal. A buckle accompanies this garment and is dated by the museum to a later age, probably the 18th century. The red fibres of this buckle were determined to have been dyed with American cochineal, which indicates a later date for this object than for the chasuble.

- The red fibres from the velvet of an Italian dalmatic (PVV3102), attributed by its host museum to the 15th century, were shown to have been dyed with Polish cochineal, while the red fibres from the lining, by contrast, with American cochineal. This demonstrates that the lining was added later to the dalmatic, perhaps even during a more-recent contemporary restoration [7].

- For the MAKF221 liturgical cape (Fig. 10.2; see also Appendix 2), UHPLC-PDA

Fig. 10.2. Detail of MAKF221, with enhanced division of the panels of fabric from where samples a1, a2 and b (panel 1) and samples c, d1 and e (panel 2) were collected. Photograph kindly provided by the MAK.

[7] Personal correspondence with curator Maria de Jesus Monge (Palácio de Vila Viçosa, Portugal).

chromatograms from samples a1, a2 and b (panel 1) have shown slightly different profiles in relation to samples c, d1 and e (panel 2). Although these profiles clearly suggest the presence of a cochineal dye, it appears that different batches of dyed yarns were used. In fact, further statistical analyses on the chromatographic results have shown that samples from panel 2 had a higher correspondence with American cochineal than samples from panel 1. Even so, samples of panel 1 were still classified by PLS-DA with American cochineal (ESM 6 in Appendix 5). Moreover, the stylistic designs of the two panels do not match, even if they seem to be part of the same (or a very similar) fabric. Hence, it is likely that the same cochineal species was used but in two distinct dye baths to colour the yarns of these panels, thus creating the subtle differences observed.

The determination of the precise species of cochineal used in these textile objects not only offers invaluable information about production, but also demands the revision of attributed dates. These are usually attributed on the basis of art historical methodologies, namely the examination of the stylistic, technical and/or iconographic characteristics, as well as through the comparison with historical sources, such as archival documentation or paintings [8]. In this context, the interpretations achieved here based on chemical and statistical evaluations constitute important contributions for the history of these textiles (and related examples) in future Art History examinations and Conservation and Restoration assessments.

Italian Selvedges and Insect Dyes. Art History, in combination with the chemical attribution of insect dyes, can provide further historical interpretations, through the appraisal of the selvedges found in some Italian fabrics.

Selvedges and seals were commonly applied in some Italian centres of textile production in the 15th and 16th centuries. In Venice, for instance, the finest silk textiles (*parangon*) generally held a seal with a crown, as they were intended for the local aristocracy. Moreover, merchants were obliged to mark the selvedges of fabrics they were selling with their own seals. Manufacturers too, left their marks on their products to distinguish them, not only in terms of their origin, but also to indicate which dyestuffs were

[8] Folsach & Bernsted, 1993, pp. 26-27, 31 and 39-44; Monnas, 2008, pp. 17 and 19.

used. This was a very important addition, since the type of dyestuff used could highly influence the final price of the textile. Therefore, selvedges were striped with different colours depending on the quality of the red dye applied (as indicated in Table 10.1), while strict regulations often attempted to prohibit mixtures of insect dyes - or these with brazilwood, madder or orchil -, especially if they were meant for *parangon* textiles (luxurious products commissioned for aristocratic costumers, for instance). Moreover, representative colours for each type of dyestuff could change among Italian centres [9].

Table 10.1. Colours for Italian selvedges in silk textiles, according to the literature [10].

Dyestuff	Selvedge colour
Kermes	Venice: white
Lac dye	Venice: yellow
(Polish/Armenian) cochineal	Venice (15th cent.): green with gold stripe in the middle Venice (16th cent.): green with yellow stripe or half black and half yellow Florence: stripes with two gold threads on each side Genoa: yellow
(Polish/Armenian) cochineal and lac	Venice (15th cent.): black strip thread in the middle of yellow borders
(Polish/Armenian) cochineal and kermes	Venice (15th cent.): half-green and half-white
American cochineal	Green with silver thread or thread of white silk
Brazilwood type	Venice (15th cent.): turquoise Venice (16th cent.): half turquoise/half *pelo di lione* (beige) Florence: half-yellow/half-black Genoa: white, green and red

If the fabrics were meant for international markets, they were not subject to very strict regulations. This was precisely because textiles produced for export were manufactured on a large scale and intended for a broader and less-demanding clientele. They were, for this reason, more profitable for the local centres of textile production and, obviously, for the dyers, who could sometimes adopt more economic solutions that decreased production costs, such as mixing dyestuffs (or using the more advantageous

[9] Atasoy et al., 2001, p. 183; Bensi, 2009, p. 40; Buss, 2009, p. 46; Molà, 2000, pp. 112-115 and 117; Monnas, 2008, pp. 17 and 319, 2012, p. 25; Phipps, 2010b, pp. 80-81.

[10] Buss, 2009, p. 46; Massa, 1970, p. 123; Molà, 2000, pp. 115-117 and 129; Monnas, 2008, pp. 17 and 319, 2012, p. 25.

American cochineal) to achieve the fashionable colours demanded by international customers [11].

Some of the Italian textiles, examined in this study, present selvedges that seem to match the insect-dye attributions determined by chemical analysis (cf. Table 10.1). For instance, damasks V&A1016-1888, dated to the second half of the 16th century, and DTM01982 (Fig. 10.3), dated to the 16th century, exhibit green plain selvedges, and both of their red fibres show the presence of American cochineal. Damask SGL1907/106, dated to the second half of the 16th century, displays a green selvedge with a central stripe of white and pink threads (Fig. 10.4), and the red fibres from this textile were also dyed with American cochineal. The same classification was obtained for the red fibres of the velvet brocade MAKT9236 (Fig. 10.5), which depicts a similar selvedge. The original date attributed was the second half of the 15th century, but it seems clear that it was produced at a later time, according to the chemical identification. As for the 16th-century Italian *brocatelle* SZT268, its selvedge depicts a thin green stripe, accompanied by another stripe made in golden thread (Fig. 10.6). The red fibres of this textile were classified, by contrast, with the presence of Polish cochineal. The white selvedge from one textile dated to the 15th century (DTM00059, Fig. 10.7) also seems to be in agreement with Table 10.1, since the red fibres were characterized with the presence of kermes.

In addition, another 15th century textile (DTM00185), exhibiting a green selvedge with a white outer edge (Fig. 10.8), was shown to have been dyed with kermes, something that is not in agreement with Table 10.1. This contradiction may be connected with possible fraud and counterfeiting schemes, as manufacturers (in complicity with merchants) were always looking for the best profits. For example, they could mix cheap dyestuffs with more expensive ones, or produce their own selvedges, while contradicting the guidelines fixed by the guilds of their city [12]. Thus, it is plausible that DTM00185 was initially dyed with kermes and later sold at more expensive prices, as if it had been dyed with Polish cochineal [13]. On the other hand, as selvedge colours representative of each type of dyestuff could differ between Italian centres, it is possible that the historical information depicted in Table 10.1 is

[11] Bensi, 2009, p. 40; Jacoby, 2004, pp. 239-240; Molà, 2000, pp. 115-116 and 118-119.

[12] Buss, 2009, pp. 46 and 49; Monnas, 2012, pp. 25-26.

[13] As discussed earlier in Chapter 1, the final price of clothes dyed with cochineal dyes was at least twice as more expensive than dyeing with kermes (Molà, 2000, p. 359; Gargiolli, 1868, p. 78).

incomplete or incorrect and does not reflect the entire picture. For this reason, visual characterization of selvedges in Italian textiles should always be corroborated by chemical analyses of the textiles' red dyestuffs, so that conclusive interpretations can be achieved.

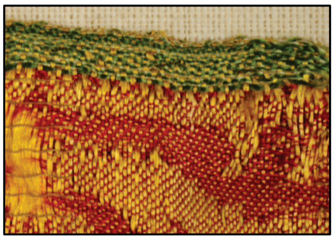

Fig. 10.3. Detail of selvedge from 16th century Italian damask DTM01982 [14].

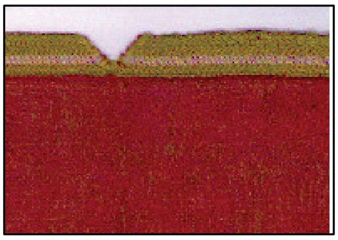

Fig. 10.4. Detail of selvedge from Italian damask SGL1907/106, dated to the second half of the 16th century [14].

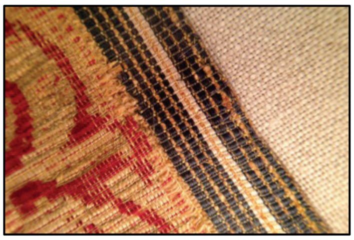

Fig. 10.5. Detail of selvedge from Italian velvet brocade MAKT9236, originally dated to the 15th century [14].

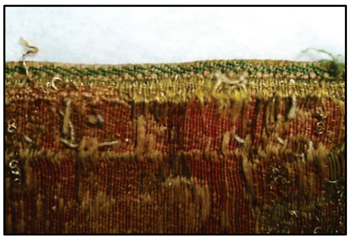

Fig. 10.6. Detail of selvedge from 16th-century Italian brocatelle SZT268 [14].

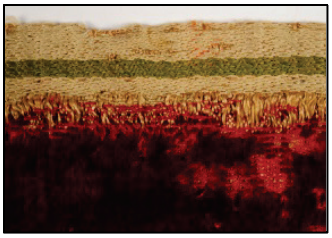

Fig. 10.7. Detail of selvedge from 15th century Italian velvet DTM00059 [14].

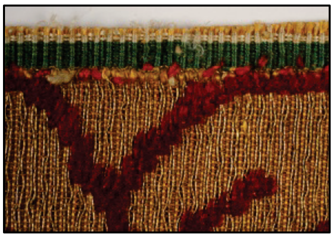

Fig. 10.8. Detail of selvedge from 15th century Italian velvet brocade DTM00185 [14].

Mixtures of Vegetable and Insect Dyes. Mixtures of different dyestuffs in Italian fabrics were a common procedure to obtain the fashionable colours demanded by international markets. This was the case of the fashionable dried-rose crimson (*rosasecca di cremisi*) or the flesh-like crimson (*incarnate di cremisi*) shades of the beginning of the 16th century, which required the mixture of cochineal with other dyes, such as orchil. Red shades could also be obtained by mixing insect dyes with vegetable red dyes, such as madder or brazilwood, as exemplified by sample DTM00059, which has a mixture of kermes and brazilwood, or sample DTM0982, with a mixture of American cochineal and brazilwood (although this could reflect cross-contamination from adjacent fibres).

[14] Picture kindly provided by the cultural heritage institution that hosts the textile.

Red shades could furthermore be improved by adding small amounts of yellow plant dyes to obtain orange-red shades – however, except for cross-contaminations of weld compounds from adjacent yellow yarns in the red fibres of textiles DTM01982 and SGL19667/7, no yellow compounds were detected in insect-dyed fibres analysed in this study. Furthermore, deep violet crimson colours, or *paonazzo,* could be acquired with cochineal or kermes (or sometimes with madder or brazilwood), on a fabric previously dyed with orchil, indigo or woad [15]. For scarlet-dyed wool, a blue dye also served as a ground colour for further dyeing with kermes to obtain a red-purple colour and, later on, also with American cochineal [16].

Indeed, the presence of indigotin was identified in 22 samples in which compounds from insect dyes, madder or brazilwood were ascribed as well. These samples did not only belong to Italian silk textiles, but also to Dutch (including wool samples), Polish, Flemish and Spanish textiles. Even so, in some cases indigotin may be a cross-contamination from adjacent blue fibres, which seems to be the case of samples from some Dutch woollen tapestries.

The exact source of indigotin present in these fibres cannot be ascribed, because indigo and woad cannot be chemically discriminated, as they share the same characteristic compounds [17]. However, it is worth noticing that the use of indigo is clearly suggested in 15th- and 16th-century Italian recipes for dyeing silk, whereas woad is often suggested for dyeing woollen fabrics. This could have happened in Italy, but in France, Low Countries, England or Germany, woad was an important crop for local economies, as discussed in Chapter 5. Thus, textiles produced in these places were probably dyed with woad, rather than with indigo, until the end of the 16th century [18].

Orchil obtained from several types of lichens, was not detected in any of the European historical samples. It is possible that, given its high fading rates, this violet dyestuff

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[15] Bensi, 2009, pp. 37-38 and 39-41, 2012, pp. 32 and 35; Gargiolli, 1868, pp. 48-51; Rebora, 1970, pp. 74-78; Molà, 2000, pp. 115-116 and 118-119; Rosetti, 1969, pp. xvi-xvii, 114, 127, 150, 152 and 154-155; Verhecken & Wouters, 1988, pp. 217 and 227.

[16] Munro, 1983, pp. 54-55 and 57.

[17] The main compounds of indigo and woad are indigotin and indirubin. Cardon, 2007, p. 339; Hartl et al., 2015, pp. 20-21; Hofenk de Graaff, 2004, pp. 244, 251 and 257, 2006, p. 39.

[18] Bensi, 2009, p. 40; Hofenk de Graaff, 2004, pp. 326; Rebora, 1970, pp. 66-67 and 83-96.

is no longer detectable in the fibres, or it was simply not used [19]. Nevertheless, orchil compounds were detected in one Turkish example, as later discussed in this chapter.

Mixtures between insect dyes were allowed, as long as the selvedges indicated the respective mixture, as exemplified by Table 10.1. These could comprise kermes and lac dye, kermes and Polish cochineal or even Armenian and Polish cochineal [20]. Additionally, Italian historical recipes often suggest the addition of an ingredient named *pococco* (also known as *popo*, *poppo*, *oppopo*, *populo* or *dopo*), which could be used when dyeing crimson with cochineal or kermes [21]. Its meaning, however, is not clear to researchers nowadays. Edelstein & Borghetti describe it as a "finely ground and extra strong" type of kermes [22]. In agreement with this, Verhecken & Wouters suggest that this might correspond to *pastel d'écarlatte*, a type of kermes that had been freed of impurities and processed into a pulp or paste with vinegar. This was four times more expensive and provided less yellowish shades of red than the separated dried insects [23]. However, *poccoco* could also be a higher quality variety of Polish cochineal [24], prepared in a similar way as kermes and sold at higher prices than the separated dried insects [25].

Despite these arguments, Cardon gives a very different meaning to *poccoco* by affirming that it was a polypore fungus. This was profusely used in French dyeing practices from the 17th century, and knowledge of its French origins helped her to establish correspondences with the Italian *poccoco.* In Italy, the species used could have been tinder polypore (*Fomes fomentarius*) or mulberry polypore (*Polyporus mori*) [26]. Rich in tannins, the function of these fungus in the dyeing process was to help exhaust the colour in the dye bath, by promoting fermentation through the conversion of the glycosides into acids [27]. However, because they can give a yellow colour as well, they were added in small quantities.

[19] Bensi, 2009, pp. 37 and 40; Hofenk de Graaff, 2004, pp. 275 and 278.
[20] Bensi, 2009, p. 40; Gargiolli, 1868, pp. 35-37, 48-50; Molà, 2000, p. 116.
[21] Cardon, 2007, p. 525; Rebora, 1970, pp. 77-78, 110, 126 and 149–150; Rosetti, 1969, pp. 136, 139 and 146; Verhecken & Wouters, 1988, p. 216.
[22] Rosetti, 1969, p. 194.
[23] Cardon, 2007, p. 613; Verhecken & Wouters, 1988, p. 216.
[24] Bensi, 2009, p. 38; Gargiolli, 1868, p. 134.
[25] Cardon, 2007, p. 641; Hellot, 1750, pp. 366-367.
[26] Cardon, 2007, pp. 528, 530 and 642.
[27] Other ingredients suggested by historical dyeing recipes had a similar function to these fungus, namely bran, white starch, sour beer, other types of mushrooms, wheat flour, bean meal, sugar, sour cheese and arsenic. Bensi, 2009, p. 40; Cardon, 2007, pp. 528 and 530; Hofenk de Graaff, 2004, pp. 56-58 and 77-79; Verhecken & Wouters, 1988, pp. 216-217 and 227.

Indeed, Gargiolli mentions that Polish cochineal does not provide the beautiful shades of those of the Armenian variety, and hence, he suggests that a small amount of *pococco* should be added to the dye bath to enhance the final colour when dyeing with the Polish variety [28]. For this reason, Polish cochineal must not be a suitable attribution for *pococco,* as defended by contemporary researchers.

However, no additional colorant compounds were detected in chromatographic data obtained in this work that could indicate the presence of polypore fungus. Either these were not present in the samples, or they cannot be detected with the present UHPLC-PDA analytical conditions. Even so, polypore funguses are rich in tannins and, in fact, gallic and/or ellagic acid (colourless) compounds were mainly detected in about 68% of the samples that were characterized with the presence of kermes and cochineal dyes.

Unfortunately, it is not possible to ascertain if these tannin compounds are an indication of polypore funguses or any other tannin-based plants, such as gallnuts (*Quercus* species), which were also profusely applied in crimson dyeing recipes [29]. On the one hand, gallnuts were chiefly added to make the silk more heavy, since previous degumming treatments would decrease its weight; and the fabric was sold by weight. On the other hand, preparing the silk with tannins also improved the strength of the fibres, while protecting them from contaminations and promoting fermentation of the colorant in the dye bath [30].

Given these results, further investigation should be carried out on these sources of tannins, as well as on the *pastel d'écarlatte* of kermes, in order to achieve more conclusive interpretations about the origins of *pococco.* But if *pococco* is in fact *pastel d'écarlatte*, then its investigation could raise problems, since its addition to a cochineal bath would result in a mixture of insect dyes, and kermes and cochineal share the same dye compounds.

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[28] Cardon, 2007, pp. 528 and 530; Gargiolli, 1868, p. 33.

[29] Currently available analytical techniques do not allow the precise identification of the tannin source used. Regardless, based on historical studies, it is possible to know that other tannin-based plants like the bark of alders (*Alnus* species) or sumac (*Rhus* species) were added when dyeing black or brown colours, through the combination with iron sulphate. Gallnuts were more adequate to lighter colours, usually using an alum mordant, because they did not influence the final colour (they are colourless). These are spherical excrescences formed on the twigs of oak trees, caused by oak gall wasps which puncture the twigs to deposit their eggs. Bensi, 2009, p. 37, 2012, p. 34; Bommel & Joosten, 2009, p. 169; Cardon, 2007, pp. 410, 415, 422-427 and 431-433; Degano et al., 2009, p. 376; Hofenk de Graaff, 2004, pp. 286-287 and 336; Kirby et al., 2014, pp. 20-22.

[30] Degumming the silk was a necessary procedure to remove the sericin, the glue that binds the silk fibres. This had to be removed, because it made silk hard, brittle and difficult to dye. Bensi, 2009, p. 37; Bommel & Joosten, 2009, p. 169; Cardon, 2007, pp. 409; Golikov, 2001, pp. 23 and 31-32; Hofenk de Graaff, 2004, pp. 286-287, 289, 325 and 336; Kirby et al., 2014, p. 22; Tímar-Balázsy & Eastop, 1998, p. 45.

Perhaps this could be overcome by following the same analytical methodology as developed in Chapter 9, by combining UHPLC-PDA with statistical analyses to evaluate possible changes in the colorant composition, and therefore, in the ratio of compounds present in mixtures of dyestuffs. Even so, such investigation might be hindered for the same reason that impeded further experiments of mixtures of kermes with Polish and Armenian cochineal in this study: the fact that the availability of these insects in their natural habitat is currently limited and even rare, which makes their exploitation extremely difficult.

Dyeing procedures with American cochineal. Given that reproducibility was an important factor when comparing reference samples dyed with cochineal with samples from textile objects, it was opted to use, whenever possible, laboratory grade materials, as indicated in Chapter 9. Although considering this for the majority of the dyed samples, in one additional experiment, the parameters from one historical recipe were followed, by using non-laboratory grade ingredients, such as copper sheets, sea salt, turmeric and gum Arabic (Appendices 5 and 7) [31].

By applying this dyeing procedure on silk, very similar visual results and chromatographic profiles were observed in relation to those of silk samples from historical textiles (Exp. 95 in Appendix 7), as also discussed in Chapter 9. This denotes that the application of non-laboratory ingredients has an essential role in obtaining closely related results to those from historical fibres; although further research on historical reproductions is required to assess the individual role of these ingredients added to the dyeing process.

EDX analyses performed on all the historical samples reported with the presence of cochineal and kermes revealed that the main mordant used was alum, while tin was not encountered in any of the samples. Tin chloride became part of European dyeing practices from the 17th century onwards, to achieve the Dutch shade of scarlet (*ecarlatte de cochenille ou façon de Hollande*, according to Colbert [32]) on silk or wool with American cochineal [33].

[31] Hacke, 2006, p. 38.
[32] Colbert, 1672, pp. 23-25.
[33] Beckmann, 1846, pp. 402-403; Férnandez, 1778, pp. 147-149; Hofenk de Graaff, 2004, pp. 79-80; Hellot, 1750, pp. 276-277; Pearson, 1705, pp. 59-64 and 160-162.

In comparison with the traditional pinkish red, or crimson, fibres prepared with alum, the brilliant orange red, or scarlet, fibres were mordanted with tin at acidic conditions (Appendix 7). This dyeing procedure may have been invented by Cornelius Drebbel at his dye workshop in England. However, it was only after his death in 1634 that his two sons-in-law and business partners, Sibertus and Abraham Kuffelaar, promoted and introduced it to the European dyeing industry, where it would spread and thrive throughout the second half of the century, especially in the French Gobelin textile manufactures and the English Bow Dyeworks [34]. In this study, the investigated 17th-century European textiles are mainly dated to the first half of the century. This probably explains why tin was not reported in any of them.

Warps, Wefts And Piles. Rich crimson textiles were often manufactured with yarns that were dyed with expensive insect dyes, but also with yarns dyed with other dyes. Although weavers were obliged to use yarns dyed with the same colorant for both warp and weft in one fabric, this rule was often circumvented. Red fabrics were frequently produced with a weft dyed with insect dyes and a warp dyed with a cheaper dyestuff, usually a red vegetable dyestuff. In the case of velvets, the pile warp was dyed with cochineal and the bottom warp and weft could be dyed with a cheaper dyestuff (Figs. 10.9 and 10.10). This was mainly due to the fact that the warp would be hiding under the weft, or in the case of velvets, both warp and weft were completely covered by the pile. Also, different shades of colour could visually enhance and deepen the final colour of the textile: for instance, the red orange from brazilwood, or the yellow from weld, applied to the warp and/or the weft, could provide a more orange-red ground to the crimson pile [35].

[34] Brunello, 1973, pp. 200-202; Beckmann, 1846, pp. 402-403; Born, 1938, pp. 220-221; Hofenk de Graaff, 2004, p. 330; Kirby et al., 2014, p. 22; Lee, 1951, pp. 222-223; Marichal, 2014, p. 213; Sandberg, 1997, pp. 52-53.

[35] The silk pile is created from secondary warp threads that, at intervals in the weaving, are carried over thin rods to create loops which are cut when the rods are removed. Buss, 2009, p. 49; Folsach & Bernsted, 1993, p. 81; Kirby et al., 2014, p. 6; Molà, 2000, pp. 119-120; Monnas, 2008, p. 24, 2012, p. 21; Phipps, 2010b, p. 80.

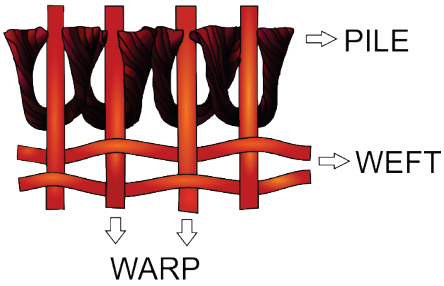

Fig. 10.9. Schematic representation of a velvet weave.

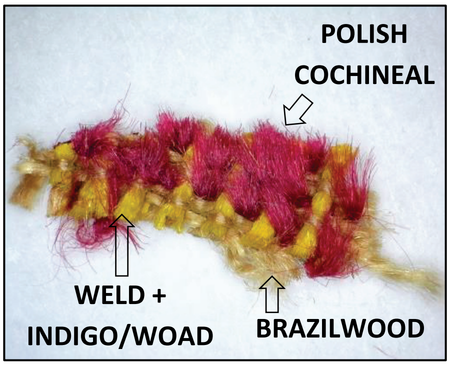

Fig. 10.10. Velvet sample from 15th-century chasuble. The pile velvet has been identified with Polish cochineal and tannins; the warp, with a mixture of weld and indigo or woad; and the weft, with brazilwood (now faded).

Brazilwood. About 22% of the fibres from the European textiles examined here were reported with the typical presence of type C component, which is a (colourless) compound present in brazilwood dyes and the identity of which remains unknown [36]. Additional characteristic compounds, such as type A compound and brasilin, were detected in samples from textiles KLS31450, KLS9358, SZT295 and SGL1966/32b. Brasilein, produced by the oxidation of brasilin, was not reported in any of the samples. An unknown yellow dye compound was often reported as well (Appendix 9).

In agreement with the previous section and preceding work on dye identification [37], the majority of the samples in which brazilwood compounds were reported belong to the warp threads of 21 textiles and to the weft threads of six (velvet) textiles. Brazilwood was furthermore identified in a mixture with madder in the pile of one Italian silk velvet (MAKT4572), dated to the 15th and 16th centuries.

Nearly half of these samples in which brazilwood was found, belong to textiles dated to the 15th century. Italian dyeing recipes dating from this period and to the first half of the 16th century denote the frequent use of brazilwood. This is a clear indication of the well-established European trade with Asia at this time and, later, with the Americas [38].

[36] Type C component was first labelled by Nowik (2001, pp. 132 and 134-136). Peggie (2006, pp. 155, 157 and 195) labels it as Bwd2 compound, which was testified by the author to be more lightfast than other compounds present in brazilwood dyes.
[37] Bommel & Joosten, 2009, pp. 168-169.
[38] Gargiolli, 1868, pp. 50-53, 62 and 150-151; Rebora, 1970, pp. 127-132; Rosetti, 1969, pp. 110, 114, 126-127, 140, 151 and 154-156. By the middle of the 16th century, brazilwood had become an important red dyestuff, along with kermes and madder. Indeed, “this extensive use [of brazilwood] in commercial dyeing could only have come about because of its new availability at a very low price, for its properties were exceedingly poor”. In the same way, “the greater availability of indigo from India resulted in a blue of lower cost, of equal fastness, and of greater brilliance than woad” (Rosetti, 1969, p. xviii). See also Bensi, 2009, p. 40; Molà, 2000, p. 130.

However, brazilwood species (*C. echinata*, *C. sappan*, *C. violacea* or *H. brasiletto,* as described in Chapter 5) cannot be easily discriminated because they share the same characteristic compounds. Moreover, the compounds' ratio can vary substantially, not only because of possible variations according to the species diversity, but also to the poor lightfastness of the compounds in historical fibres [39]. Nevertheless, it is possible to suggest that brazilwood identified in samples from 15th-century European historical textiles, is likely to be the *C. sappan* species. The other species would not reach Europe before the final years of the century - the Spanish, led by Cristóbal Colón, reached Hispaniola in the Caribbean in 1492, whereas the Portuguese, led by Pedro Álvares Cabral, reached Brazil in 1500 [40]. After this date, more precise information cannot be obtained about the species of brazilwood present in historical textiles.

Yellow Dyes. Besides brazilwood, yellow warp and weft threads from several insect-dyed textile objects were characterized with the presence of compounds from yellow dyestuffs, which are interesting for characterizing the history of the textiles and European dyeing applications. The yellow warps (and one weft) of SGL1966/7 and of MNAA1616tec (Fig. 10.10) were identified with weld alone, and a mixture of weld and indigo/woad, respectively. Weld was identified through the detection of its representative flavone compounds, luteolin-3',7-diglucoside, luteolin-7-O-ß-D-glycoside, apigenin-7-glycoside, luteolin and apigenin. The yellow weft of MNAA1925tec was identified with a mixture of dyer's broom and young fustic. Whereas the former was identified by the detection of flavones genistin and genistein (in addition to the compounds also found in weld), the latter was characterized by the presence of fisetin and sulfuretin [41].

These yellow dyes were moreover found in non-yellow fibres. For instance, two light brownish orange yellow warp fibres from textiles PVV3102 and MT30935 were identified with the presence of brazilwood, mixed with dyer's broom and young fustic, respectively.

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[39] The fading of brazilwood is very characteristic, since the original red orange shades tend to fade into a lighter shade or even turn to a brownish yellow colour, as seen in Fig. 10.10 and in many of the samples identified with the presence of brazilwood in Appendix 2. Degano et al., 2011, p. 207; Hofenk de Graaff, 2004, p. 147, 2006, p. 46; Nowik, 2001, pp. 135 and 142; Monnas, 2012, p. 25; Peggie, 2006, p. 195.

[40] Cardon, 2007, pp. 286-287; Phillips, 1990, pp. 45-46 and 74-75.

[41] Cardon, 2007, pp. 171, 180 and 192; Hofenk de Graaff, 2004, pp. 176, 214-216, 219 and 222; Kirby et al., 2014, p. 16; Troalen et al., 2014, p. 8919; Valianou et al., 2009, p. 881.

Given the presence of brazilwood, it is likely that these fibres must have originally depicted a strong orange shade. In the green fibres from SGL1907/208 and ABMt02194.53, weld was found mixed with the compounds of indigo/woad. In the case of ABMt02194.53, it is likely that the blue dyestuff used was woad, since it was made in Germany, in the 15th century.

In dye workshops from Europe and West Asia, the flowers and leaves of weld (*Reseda luteola* L.) were a particularly elected source of yellow, given their relatively fast properties (predominant presence of luteolin) when applied on fibres prepared with a mordant, such as alum. Weld was often used to achieve yellow or green colours [42]. Dyer's broom was extracted from the flowers and roots of *Genista tinctoria* L., which grew all over Europe. As indicated by historical recipes, this was often applied on mordanted fibres in combination with other dyes, because it was considered to be inferior to weld - genistein has a lower lightfastness than luteolin [43]. The bushes of young fustic or Venetian sumac (*Cotinus coggyria* Scop.) were native to Europe and to West Asia. With its heartwood, orange or orange yellow shades could be obtained but, due to its low lightfast properties (fisetin is a flavonol), this dyestuff was often forbidden. Nevertheless, it was often mixed with other dyes on mordanted fibres [44].

Madder. This plant dyestuff was identified in about 15% of the samples, belonging to textiles in which insect dyes were generally not found, and hence, an indicator that reinforces the absence of kermes, lac and cochineal. These textiles comprise seven 15th- to 17th-century woollen tapestries, from Switzerland and Low Countries (north and south), as well as six 15th-century silk textiles, produced in the Low Countries (north and south), Germany, Spain and Italy. Although this constitutes a small group of samples, and further investigation is required, results seem to indicate that madder, in contrast to brazilwood, may not have been used commonly for the ground yarns of rich insect-dyed textiles. Indeed,

[42] Brunello, 1973, p. 143; Cardon, 1994, pp. 59-60 and 69-70, 2007, pp. 168, 170-171 and 176; Hofenk de Graaff, 2004, pp. 214-216 and 327; Kirby et al., 2014, p. 16; Peggie, 2006, p. 135.
[43] Bensi, 2012, p. 33; Brunello, 1973, pp. 158; Cardon, 1994, pp. 60 and 69-70; Hofenk de Graaff, 2004, pp. 220 and 223-224; Troalen et al., 2014, p. 8915.
[44] Due to their considerably higher content of tannins, the leaves and twigs of the tree could be used to obtain brown and black colours. They could be additionally used to weight silk, in a similar way to gallnuts. Bensi, 2012, pp. 33 and 35; Bommel & Joosten, 2009, p. 169; Böhmer, 1997, p. 158; Brunello, 1973, pp. 139 and 144; Cardon, 1994, pp. 60 and 69, 2007, pp. 191-192 and 195; Hofenk de Graaff, 2004, pp. 175-177; Kirby et al., 2014, p. 17; Peggie, 2006, pp. 80 and 187-190.

madder was more expensive than brazilwood, but cheaper than insect dyes. For this reason, it seems to have been a more common option to achieve orange-red or brown shades in woollen textiles; whereas insect dyes were generally reserved for the more expensive silks or high-quality woollen cloths (and if a cheaper dye was required for the warps and wefts, then the more-economical brazilwood was applied) [45].

Madder dyes can be obtained from the roots of several species of plants from the Rubiaceae family spread throughout the globe. In Europe and Asia, madder dyes were traditionally obtained from the roots of the *Rubia tinctorum* L., which gave relatively fast and inexpensive shades of red orange. Though, its growing conditions (type of soil, climate or roots size when collected), the treatment of the roots (drying method or storage) or the dyeing procedure (type of mordant, concentration, pH or temperature) could greatly influence the colour of the dyestuff. For this reason, different qualities were available in the European markets, the best coming from the north of the Low Countries [46].

In this study, fibres dyed with madder were generally reported with the presence of the two main compounds, alizarin and purpurin, besides other minor compounds - ruberythric acid (alizarin primeveroside), lucidin-3-O-primeveroside, xanthopurpurin, pseudo-purpurin, nordamnacanthal and rubiadin. It was observed that the ratio between alizarin and purpurin can change substantially, and this is directly related to the above-mentioned conditions. Indeed, dark orange-red and brown fibres from textiles ABMt02013, ABMt02194.53, MAKT8211, RMANM1999 and RMA16495A have generally been shown to possess a comparable or higher peak of purpurin in relation to alizarin. This could mean that an inferior quality of madder was used (thin and/or young roots), or the dyeing conditions were manipulated to obtain darker red shades – purpurin absorbs in the red zone of the visible area, while alizarin, in the yellow (Appendix 4). On the contrary, if a superior grade of madder was used (thick and matured roots), this corresponds to a predominant peak of alizarin, as reported for the orange red fibres from textiles ABMt02011 and SZT276 [47]. This

[45] In some parts of Italy, the dyeing of silk with madder was even forbidden. Bensi, 2009, p. 40; Bommel & Joosten, 2009, p. 169; Cardon, 2007, pp. 114; Hofenk de Graaff, 1972, p. 26, 2004, p. 94; Monnas, 2008, pp. 25 and 341; Mouri & Laursen, 2012, p. 105.

[46] Cardon, 2007, pp. 108-111 and 114; Hofenk de Graaff, 2004, pp. 92-94 and 98, 2006, p. 44; Greenfield, 2006, p. 45; Kirby et al., 2014, p. 13; Mouri & Laursen, 2012, p. 110.

[47] If much greater amounts of purpurin would have been reported, in relation to a very small response of alizarin, this would probably mean that other European Rubiaceae plants, such as *Rubia peregrina* L. (wild madder) or *Galium* and *Asperula* species (bedstraws and woodruffs) were used – perhaps during times of short

demonstrates that madder can be a very versatile dyestuff, as different shades between orange, red and brown can be obtained, by considering diverse types of roots or dye recipes.

Local Dyes vs. Foreign Ones. Interestingly, for all the 15th-century silk German textiles analysed here, madder was the only red dyestuff detected (no insect dyes or brazilwood). These results clearly exhibit a preference for local or home dyes, rather than imported ones. Even so, it is noteworthy that by the middle of the 16th century, Cologne (where the textiles were produced) had a well-developed textile industry that made extensive use not only of local dyestuffs (like madder), but also of imported ones, like brazilwood, coming from Antwerp, in agreement with the historical information provided in Chapter 6 [48].

As for the north of the Low Countries, previous interpretations from Hofenk de Graaff (2004) excluded the presence of insect dyes in detriment to madder, in local dyeing traditions for woollen fabrics up until the end of the 16th century [49]. However, insect dyes were found in 15th-century silk textiles manufactured in this region, thus corroborating the idea that insect dyes were considered more suitable for silk, rather than for wool. Moreover, although a larger group of textiles requires examination, it seems that, after the 16th century, given the economic advantages of American cochineal, it may have gradually been accepted for dyeing wool, rather than madder, as indicated earlier in Chapter 6, and demonstrated by the results attained here for 17th-century tapestries produced in north of the Low Countries.

The early preference for home dyes in Germany or in the north Low Countries is in agreement with previous arguments achieved earlier in Chapter 6 for peripheral European territories, where textile production was not as evolved as in the great cities of Italy, France or the south Low Countries. Indeed, in smaller European centres of textile production, it seems that preference for local dyes and fibres could match the small demand of local populations. Moreover, technological expertise to handle the production of intricate fabrics

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supply for traditional madder. This type of chromatographic profile was not reported in any of the fibres analysed in this study. Cardon, 2007, pp. 112-113, 122-127; Hofenk de Graaff, 2004, pp. 92, 98, 107, 110, 125; Mouri & Laursen, 2012, pp. 105 and 107-112.

[48] Vermeylen, 2010, p. 361.

[49] Hofenk de Graaff, 2004, pp. 331-332.

and imported expensive dyestuffs may have been limited. Therefore, it is likely that local aristocrats acquired their rich crimson silks and woollen tapestries from abroad, rather than from their home manufacturers. In this context, it comes as no surprise that the majority of the textiles investigated in this study are recurrently ascribed to the same textile-producing regions.

Nonetheless, peripheral European regions were not completely without rich textile produces. In fact, imported dyestuffs, such as American cochineal or brazilwood, have been reported in 16th- and 17th-century textiles made in Switzerland, Poland and Sweden. This shows that knowledge on dyeing with insect dyes was not solely restricted to the main European hubs of textile manufacturing. In addition, previous studies on dye identification have shown the use of expensive and/or imported insect dyestuffs in regions like Hungary, Romania or Greece [50], which were neighbours and even for some time part of the Ottoman Empire. In this political context, these regions extensively received artistic influences from the main Turkish dyeing centres, while their main ports were in constant communication through trade with products and ideas coming from other parts of Europe, as demonstrated in Chapter 1.

Conclusions. Over half of the European textiles examined in this chapter were produced in Italy in the 15th and 16th centuries, with the remaining being made in other parts of Europe as well, namely in the Low Countries (north and south), Spain or France. The emphasis on textiles with Italian provenance reflects the general composition of museum collections, as Italy was the most significant manufacturer of rich silk fabrics at this time.

However, after the 16th century, Italian production for international markets decreased, while north European centres of textile production started gaining recognition, especially for their lighter and cheaper textiles in comparison to those of Italy, as previously discussed in Chapter 6. This seems to be somewhat suggested also by the study of textile objects, given the comparatively small number of Italian examples available for examination

[50] Hofenk de Graaff, 2004, pp. 106; Karapanagiotis et al., 2008, pp. 480-481; Karapanagiotis & Karadag, 2015, p. 7; Petroviciu et al., 2012, pp. 91-92 and 96. By using the analytical conditions developed here, knowledge about the exact species of cochineal present in the textiles analysed by these studies could bring important interpretations about the extension of the acceptance of American cochineal in relation to local dye sources and to Turkish dyeing traditions.

for this period; although further investigation is required on a larger group of textiles to acquire more conclusive interpretations.

The preeminent use of insect dyes for the finest and most prestigious silk textiles, as reported in Chapter 1, was confirmed by the dye results. Indeed, in objects dated to up until the beginning of the 16th century, kermes, Polish cochineal and, to a lesser extent, Armenian cochineal and lac dye were used. However, a striking change is observed in 16th- and 17th-century textiles, in which American cochineal was the main insect dye identified.

Based on these results, it is easy to subscribe to the idea that, after its arrival in European markets, American cochineal was immediately accepted in local dyeing practices, overthrowing other insect sources of red. Indeed, these results are in agreement with those achieved by preceding studies on dye identification [51]. Moreover, as verified in Chapters 4 and 6, high volumes of the American insect were being shipped from the Americas to the European ports, during the 16th and the 17th centuries.

However, the historical evidence presented in Chapter 7 also showed that, despite the adoption of American cochineal in local dyeing practices, European insects kept being traded and applied as dyestuffs in European dye workshops, especially in regions nearby their zones of exploitation. Indeed, occasional historical references mention the trade of kermes and Polish cochineal to Italy and to the Low Countries in the 17th century, as well as their application in Venetian dye workshops, as late as the 18th century. Yet, these insect dyes were not reported in any of the post-16th-century textiles examined here. This disagreement between the analytical results and historical data perhaps indicates that small quantities of these red insect dyes were being traded to respond a restricted demand.

As American cochineal greatly lowered production costs, it may have been adapted more easily and swiftly for colouring large quantities of textiles intended to meet, for example, wide international demand. By contrast, European insects might have been preferred for cultural reasons when dyeing prestigious local textiles (*parangon* textiles, for instance) as they had long been part of a distinctive local tradition and therefore intrinsic, adding special kudos. Hence, examination of a larger group of historical textiles, such as Venetian ones, could shed further light on this hypothesis.

[51] Hofenk de Graaff & Roelofs, 1972; Phipps, 2010a.

Furthermore, analytical results have shown that insect dyes were often applied along with other dyestuffs, depending on the colour in fashion. For instance, a source of indigo (from Asia or the Americas), or woad, was often part of the dyeing process to achieve a more purplish crimson shade. Mixtures between insect dyes or insects and vegetable red dyes (brazilwood or madder) were also reported in samples investigated here. These mixtures may include as well the mysterious *poccoco*, mentioned in Italian dyeing recipes, and which researchers either identify as a superior type of kermes, or a fungus rich in tannins, like the gallnuts often used in the treatment of silk. Either way, analytical results undoubtedly indicate the recurring presence of tannins in insect-dyed fibres, even though their source cannot be ascribed.

Moreover, rich crimson textiles not only comprised yarns dyed with insect dyes. Analytical results revealed that a cheaper red dye like brazilwood (from Asia or the Americas) was often found in the warp or weft threads of European velvet structures, while the more expensive insect dyes were used for the pile threads, which are more visible. This practice was undoubtedly followed for economic reasons, but it could also serve to enhance the fabric's final colour, with warps and wefts being dyed with yellow dyestuffs, as verified for some of Italian textiles examined here. Analytical results for these and other yellow and green yarns indicated the use of weld, dyer's broom and young fustic, being these the most common sources of yellow used in European dyeing centres. While weld was reported alone (or mixed with a blue dye to achieve green), the others were often found in mixtures together, or with brazilwood to obtain orange.

As for madder, this plant dye was generally characterized in wool samples, although it was detected as well in some silk examples. The application of madder on silk may have particularly occurred in regions where this dye plant was widely exploited. For example, it was the only red dyestuff detected in all of the 15th-century silk German textiles examined here. Despite a preference for home dyes, it seems that peripheral European regions also had contact with American cochineal, as suggested by the historical evidence presented in Chapter 6. This evidence is further supported here by the characterization of the American insect in textiles from territories like Switzerland, Poland or Sweden.

Possibly, American cochineal reached other European territories as well; although a broader study would be required to find insect-dyed textiles from these regions. Even so, it is reasonable to suppose that such regions could have had easy access to the foreign dyestuff through long-established trade routes. In fact, this is particularly verified when looking farther afield to Asia.

10.3. Farther Afield to the Asian Dyeing Traditions

The number of scientific publications dedicated to the chemical characterization of dyestuffs in Asian historical textiles has been slowly increasing over the past few decades [52]. Concerning the assessment of American cochineal in historical objects, the recent works of Phipps (2010a,b) and Shibayama et al. (2015) have brought very important insights, although difficulties in discriminating American and Armenian cochineal have limited the authors' conclusions. Moreover, the historical information analysed for Asia in Chapters 6 and 7 requires further evidence to achieve more conclusive interpretations about the dynamics of the American dyestuff in this region. Therefore, in this chapter, the identification of insect dyes in 16th- to 17th-century Asian textiles aims to establish a clearer picture of the impact of the global circulation of American cochineal, in detriment of other Asian insect sources of red.

A total of 134 samples from 38 Asian historical textiles were characterized in this study with UHPLC-PDA analyses. The textiles are predominantly dated to the 16th century (c. 40%) and the 17th century (c. 55%), while only two textiles are dated to before the 16th century. They mainly come from three territories: Turkey (c. 47%), Iran (c. 26%), India (c. 21%) and, additionally, China (two textiles, 5%). Turkey, Iran and India are historically connected throughout the period under study, and they share a similar high esteem for the textile arts, which achieved their highest expression in court-sponsored production and consumption. Indeed, textiles were a reflection of the authority and prosperity of the Ottoman, Safavid and Mughal dynasties, and were often offered as diplomatic gifts [53].

Given the fact that not many studies on dye identification are available for these regions and this timeframe, other fibres dyed with non-red, pink or orange dyestuffs present in the textiles selected for this study are considered. Information about them provides

[52] Atasoy et al., 2001; Böhmer, 1997; Enez, 1993; Hofenk de Graaff & Roelofs, 2006; Han, 2015, 2016; Heitor, 2007; Karadag et al., 2010; Phipps, 2010b; Santos, 2010; Shibayama et al., 2015.
[53] Baker, 1995, p. 15; Atasoy et al., 2001, pp. 17, 21 and 33.

helpful insights into characterizing the history of the textiles , as well as dyeing applications of different Asian regions. Hence, from a total of 134 samples, about 47% comprised red, pink or orange-dyed fibres, 27% were yellow fibres, 8% were green, 11% were blue, 3% were brown or black and almost 4% were undyed or (possibly) completely faded fibres.

Insect dyes. From all 134 samples, about 46 were characterized with the presence of insect dyes (Fig. 10.11). In Europe, it was observed that the presence of insect dyes, other than American cochineal, declined in European textiles dated to during and after the 16th century. For Asia, possibly owing to the date of the majority of the textiles analysed (posterior to the 15th century), Polish cochineal and kermes were not identified, and only one red sample from a Turkish textile was classified with the presence of Armenian cochineal (SZT292 (pile), dated to the 15th century). Moreover, from a total of 18 Turkish textiles, c. 70% were classified with the presence of American cochineal, which shows a strong indication that this insect dye became well integrated into Turkish centres of textile production [54].

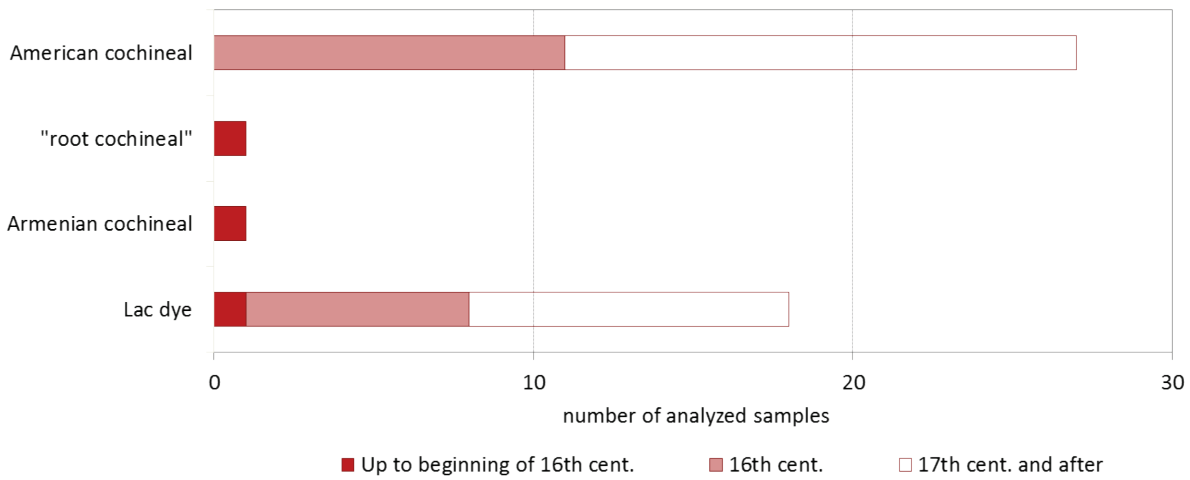

Fig. 10.11. Diagram of the sum of samples from Asian historical textiles, in which insect dyes were characterized, organized by the respective historical textiles' date.

[54] Atasoy et al., 2001, p. 196; Carboni, 2007, pp. 196 and 202; Karadag et al. 2010, pp. 7047-7048; Karapanagiotis & Karadag, 2015, p. 7; Phipps, 2010b, pp. 81.

As argued earlier in Chapter 6, the adoption of American cochineal in 16th-century Ottoman dyeing traditions must be related to its mercantile and artistic connections with Italy (especially Venice). Given this relationship, it is possible to suggest that, shortly after the Italian dyeing centres started dyeing with the insect dye in the early 1540's and increasing volumes of this commodity began flowing into the main Italian ports, the red dyestuff also flowed out of these same ports towards Turkey. There, it must have been adopted to respond to the high demand for fashionable textiles (especially velvets), highly prized among the Ottoman court and also in European markets – particularly those in Central and Eastern Europe [55]. Furthermore, owing to its geographical location, Turkey not only received American cochineal from European merchants, but lac dye coming from South Asia. In this study, this dyestuff was identified in samples from three Turkish velvets dated to the 16th century and, preceding dye identification studies confirm that it was widely used in 15th- and 16th-century Ottoman historical textiles (e.g., velvets and carpets) [56].

Despite the preference for foreign insect dyes, it is worthwhile mentioning that kermes and Polish and Armenian cochineal could still be exploited for dyeing practices or other applications, within the boundaries of the extensive Ottoman Empire, which reached as far as Hungary and Ukraine in the 16th century. Besides occupying part of Europe, the Turkish extensively traded with Poland, from where the native insect dye continued to be exported, as mentioned in Chapter 7. Therefore, similarly to the case of European textiles, it is possible that "Old World" insects continued being employed in Turkish workshops after the 16th century; and possibly also witnessed a shift in application towards colouring a specific range of fabrics, which were not meant for a wide clientele, but rather for a particular local demand [57]. Hence, the examination of a larger group of historical textiles dated to this period (and to the 15th century) could bring further insights into the application of these local insect dyes in the region.

In the ten Iranian textiles examined in this work, American cochineal was classified in the samples from seven silk textiles, mainly dated to the 16th century. These not only

[55] Atasoy et al., 2001, pp. 57, 165 and 176-182 and 196; Monnas, 2012, pp. 12-13; Sardar, 2013, p. 73.
[56] Atasoy et al., 2001, pp. 163 and 195; Böhmer, 1997, p. 156; Carboni, 2007, pp. 196 and 202; Cardon, 2007, p. 664; Monnas, 2012, p. 23.
[57] Polish cochineal has been detected in a 15th-century kaftan, attributed to Sultan Mehmed II (r. 1444-1446 and 1451-1481) (Atasoy et al., 2001, pp. 176-182 and 195). As for kermes, this widely occurs in Turkey, but it has not been reported so far in rich silk Turkish textiles (Böhmer, 1997, p. 156; Atasoy et al., 2001, p. 195).

comprised rich velvets, satins and brocades, but also a pile carpet (“small silk Kashan”, CGMT100). Even though historical evidence mentioned in Chapter 6 affirms that American cochineal was first reported in Iran during the early years of the 17th century, analytical results obtained here indicate that the American dyestuff may had already been adopted in Safavid dyeing centres several decades before. This suggestion seems reasonable, when considering that commercial transactions were frequently taking place between merchants from Iran and Turkey, at a time when American cochineal was already well established in the Ottoman dyeing traditions and thus circulating through its imperial trade routes.

Lac dye compounds were identified in a sample from an Iranian silk carpet (V&AT438-1976) and in the samples of two woollen fragments of Iranian carpets (V&AT369B-1966 and V&AT131-1926) all dated to the 17th century. In relation to the results obtained for the silk textiles, these results suggest that Iranian manufacturers may have reserved cochineal for their luxury silks, whereas lac dye was maintained for intricate wool carpets and other rich woollen cloths. This is in agreement with previous publications, in which lac dye has been identified as a regular component in the reds of Iranian carpets [58].

As for the eight Indian textiles, results seem to indicate a later adoption of American cochineal here than occurred in Iran or Turkey: the locally available lac dye was identified in seven samples of four textiles dated to the 16th and 17th centuries, while the presence of American cochineal was classified in six samples of four 17th-century textiles. These textiles comprise not only silk velvets, but also embroidered silk weaves and lampas, which suggest that for rich Indian fabrics, local insect dyes might have long been the preferred source of red.

Somewhat different interpretations have been attained by Shibayama (2015), who has recently investigated a large group of Safavid and Mughal velvet textiles, dated to the same period as that assessed in the current study. According to her results, cochineal was predominantly ascribed as the main insect source in the pile of Iranian velvets, whereas lac dye predominates in the pile of Indian velvets [59]. These interpretations correspond to those obtained for silks from Iran analysed in this study, but not to those from India. In fact, conclusions drawn by Shibayama and other earlier publications concerning lac dye

[58] Armindo et al., 2008, p. 963; Böhmer, 1997, p. 156; Enez, 1993, pp. 202-204; Heitor, 2007, pp. 26-32; Santos, 2010, pp. 13 and 19; Shibayama et al., 2015, p. 2.
[59] See also Phipps, 2010b, p. 82.

identification in 16th- and 17th-century Indian textiles emphasize engrained dyeing traditions, in relation to American cochineal [60].

By comparing with the historical evidence presented in Chapter 6, it is worthwhile remembering that, during the first decades of the 17th century, American cochineal brought by the English to India, via the maritime circuits, was not much in demand in local markets. This is probably not only because there was a lack of knowledge about the potentialities of the American insect in some Indian textiles centres, but also because of competition from the same type of cochineal coming down the land routes from Iran. Even so, analytical results achieved here show that, somewhere in the 17th century, Mughal dyers eventually disrupted old dyeing traditions by adopting American cochineal. This is likely to have happened in manufacturing centres that had contact with major trade routes connecting them with foreign markets and, thus, access to the American dyestuff. However, somewhere in the reign of the Mughal Emperor Aurangzeb (r. 1658-1707), the use of American cochineal was forbidden in Indian dye workshops. Hence, further investigation into a larger number of textiles should be able to bring more conclusive interpretations about the time of adoption of the foreign cochineal, in relation to the native lac dye.

In China and Japan, traditional dyeing practices were maintained for even longer. Since early times, lac dye was a highly prized and (probably) the only insect dye used in Chinese textile centres. This is clear when considering the number of textiles in which dye identification publications report the presence of lac dye [61]. In this study, lac dye was identified as well in the samples of one 17th-century Chinese silk fabric. By the 19th century, when American cochineal was commonly available in Asian markets, it finally began to be applied in Chinese and Japanese dyeing centres, as also mentioned in Chapter 6 [62].

In other Asian regions, such as Indonesia, early contacts with European merchants (chiefly the Dutch VOC) imply an early arrival of American cochineal to the region, perhaps already at the beginning of the 17th century [63]. However, in the markets of the interior provinces of Central Asia, such as present-day Kazakhstan, Uzbekistan, Tajikistan, Kirgizstan

[60] Böhmer, 1997, p. 156; Cardon, 2007, p. 663; Hofenk de Graaff, 2006, p. 46; Karadag et al., 1997, pp. 160-161.
[61] Cardon, 2007, p. 663; Phipps, 2010a, pp. 40-41 and 46, 2010b, p. 84.
[62] Donkin, 1977, pp. 39-40; Phipps, 2010a, pp. 40-41 and 46, 2010b, p. 84; Han, 2016, pp. 231 and 296, and personal correspondence with Jing Han (Centre for Textile Conservation and Technical Art History, History of Art, University of Glasgow, Scotland).
[63] Donkin, 1977, p. 39; Phipps, 2010a, p. 41, 2010b, p. 84.

or Turkmenistan, American cochineal seems to have been reported only from the 18th century onwards, according to Chapter 6. However, it is possible that the routes of the Silk Road could have disseminated the American dyestuff into the region at an earlier date. Even so, there, as in northern India and western China, American cochineal may have faced competition from other cochineal varieties, either locally available or coming from Russia and Ukraine.

In Ukraine, this cochineal variety could have been either *Porphyrophora minuta*, a smaller insect than Polish cochineal prevalent in Crimea, or *P. kiritshenkoi* found in the lands nearby Odessa [64]. In Russia and Siberia, species like *P. uvae-ursi* or *P. fragariae* could have been exploited for local and commercial purposes as well [65]. Another species, *P. sophorae*, growing in certain parts of Uzbekistan and Kazakhstan, has been pointed out as a very suitable match for the red cochineal dye reported in archaeological textile fragments found in that region and in western China [66]. From these species, only *P. fragariae* and *P. sophorae* are mentioned in a recent entomologic study of existing *Porphyrophora* species [67]; though it is possible that the other species were also identified, but under different designations.

P. sophorae or another *Porphyrophora* species native to this part of the continent could have been used to dye the red silk fibres of a textile from southwest China, and dated between the 8th or 9th centuries (AS4921). These fibres were characterized here with a mixture of dyestuffs, including compounds from cochineal, lac dye, brazilwood, madder and indigo or woad. Given the complexity of this mixture, the respective chromatogram could not be submitted to statistical comparison with reference cochineal fibres, to ascribe the species of cochineal present - the regions analysed are too different from those in the reference samples. However, due to the attributed provenance and date of this textile, a *Porphyrophora* cochineal species must had been used, and for this reason, the designation "root" cochineal is adopted here to refer to any possible *Porphyrophora* species breeding on the roots of grassland plants [68].

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[64] Cardon, 2007, p. 636, 2014, p. 590.
[65] Born, 1938, p. 209; Hofenk de Graaff, 2004, p. 65; Verhecken & Wouters, 1988, p. 222.
[66] In the same way, *P. hirsutissima* in Egypt or the currently extinct *P. tritici* in Anatolia, Turkey (Cardon, 2007, pp. 636 and 653-655, 2014, pp. 590 and 630-633). See also Han, 2016, p. 228.
[67] Vahedi & Hodgson (2007, pp. 99 and 110) mention *P. fragariae* as *P. ussuriensis* B..
[68] Hofmann-de Keijzer et al. 2007, p. 215.

Although very little importance has been given so far to this subject, it seems that Russian, Ukrainian or Central Asian *Porphyrophora* species were frequently used and traded by Asian populations. Further chemical investigation of *Porphyrophora* species - other than *P. polonica* (Polish cochineal) and *P. hamelii* (Armenian cochineal) - should be carried out to ascertain their colorant composition and, thus, possible applications in old dyeing traditions in Asian cultures, especially in remote Asian regions.

Chemical Note on Lac Dye. Either of European or Asian origin, samples analysed here, and attributed with the presence of lac dye, systematically depict one unknown red compound, along with kermes compounds, i.e., kermesic and flavokermesic acids (Appendix 9) [69]. In European textiles in which kermes dyes were often ascribed, it is possible to assume that this dyestuff was mixed with lac in the same dye bath. However, kermes alone was not reported in any red samples from Asian textiles analysed in this or in other preceding studies. Moreover, it seems highly unlikely that the Mediterranean insect would have been imported in vast quantities to India or China only to be used in mixtures with lac dye.

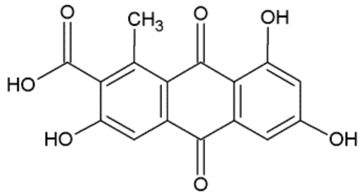
Although kermes compounds have not been reported in the matrix composition of the insects' colorant [70], Hofenk de Graaff was able to detect them in the chromatographic profile of a lac dye powder [71]. Hence, one may hypothesize that such compounds (and the unknown compound as well) might be present in specific species of lac dye or, alternatively, they might form during the dyestuff treatment or the dyeing process, through the conversion of the laccaic acid compounds (Fig. 10.12). For instance, this could happen during the extraction of the colorant using an alkali solution, which separates it from the insects' resins [72]. Further investigation on dye reproductions with this dyestuff are required to achieve more conclusive interpretations.

[69] These compounds have been reported not only in fibres dyed with lac dye (Santos, 2010, pp. 19 and 57; personal correspondence with Raquel Santos, CHAM, FCSH-UNL & UAç, Lisbon, Portugal), but also in lake pigments. In fact, due to the constant presence of flavokermesic acid in lac dye samples, this compound has been labelled as laccaic acid D (Kirby, 2008, pp. 92-93; personal correspondence with Jo Kirby-Atkinson, independent researcher, London, England).

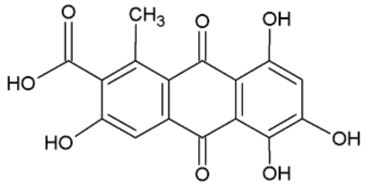
[70] In this study (Fig. 2.2 of Chapter 2) and by Santos et al., 2015, p. 133.

[71] Hofenk de Graaff, 2006, p. 88.

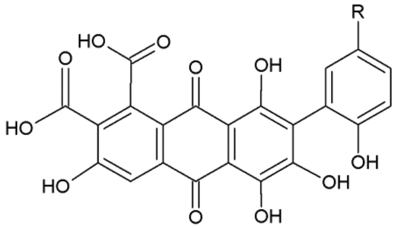
[72] Santos, 2010, p. 19; Kirby, 2008, p. 91; personal correspondence with Jo Kirby-Atkinson.



FLAVOKERMESIC ACID



KERMESIC ACID



LACCAIC ACIDS
A: R = $CH_2CH_2NHCOCH_3$
B: R = CH_2CH_2OH
C: R = $CH_2CH(NH_2) – COOH$
E: R = $CH_2CH_2NH_2$

Fig 10.12. Molecular structures of flavokermesic and kermesic acids from kermes, and of laccaic acids from lac dye [73].

Dyeing Procedures & Mixtures of Dyes and Insects. Crimson samples from Asian textiles revealed to have common characteristics to those from European textiles, suggesting similar dyeing procedures. For instance, EDX analyses revealed that alum was used to mordant all red fibres, while gallic and/or ellagic acid compounds were detected in 71% of the fibres dyed with cochineal species [74]. This signifies that a tannin-based source was used during dyeing, probably for the same reason gallnuts were used in Europe. Gallnuts might have been used as well in Asian traditions, although other local sources, like pomegranates (*Punica granatum* L.) or pistachio nuts (*Pistachia vera* L.), should not be excluded for dyeing crimson. Besides these, the addition of melon and tartrate may have had a similar effect [75].

About 28% of the total number of Asian crimson fibres dyed with cochineal dyes were characterized with the presence of indigotin compound. This points to the initial application of indigo or woad in a vat dye, before passing the textile to a bath of cochineal to obtain a purplish crimson shade, similarly to that observed in European practices.

[73] Cardon, 2007, p. 710.
[74] The presence of tannins in cochineal-dyed fibres from Asian textiles, is moreover attested by Shibayama et al. (2015, p. 3).
[75] These and other tannin-based plants could have been applied with an iron sulphate to achieve the black silk and wool samples from textiles V&ACIRC152-1920, V&AIS365-1992, V&A34-1903 and MET52.20.11. Cardon, 2007, pp. 207, 415, 419, 421 and 482; Hofenk de Graaff, 2004, pp. 286-287; Karadag et al., 2010, p. 7054; Kirby et al., 2014, p. 20; Shibayama et al. 2015, p. 14; Verhecken & Wouters, 1988, pp. 211-212 and 231.

Also, orcein compound was detected in a 17th-century Turkish fabric (CGM188B), thus suggesting that a lichen species was used to enhance the violet shade obtained with the combination of cochineal and indigo or woad. The most well-known variety of lichens used for dyeing was *Roccella tinctoria* DC., which grows on the coast of subtropical or tropical regions around the world, including the Mediterranean region. It is likely that this dyestuff may have been used when dyeing other crimson fibres examined here but, due to its low fastness to light and washing, orcein compounds can no longer be detected [76].

Interestingly, dye analysis of the crimson fibres from V&A101-1878 – a very similar textile to CGM188B in terms of iconographic composition, with a red floral pattern of a multi-petalled rosette, surrounded by tulips and rose buds, as well as a six-lappet border with rose buds (Appendix 2) – did not reveal the presence of indigotin or orcein. Probably, both examples were produced by the same manufacturer, but using different yarns.

Indigo and Woad. Indigotin was moreover detected in blue, green and some yellow fibres (c. 29% from the total Asian textiles samples). At times, a small peak of indirubin was detected as well, a typical minor compound of indigo and woad [77]. Since indigo and woad cannot be chemically discriminated, it is not possible to determine which of these blue dye sources were used in every textile. However, the area of distribution of *Isatis* species (woad) in Asia roughly comprises West and Central Asia, but not including South Asia. Hence, it is conceivable that the blue source in Indian fabrics would be one *Indigofera* species (indigo), rather than *Isatis* [78]. In Asian territories north to India, as previously observed for Europe, indigo could be used alone or in combination with woad, even though, there was a clear preference for the former [79].

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[76] Cardon, 2007, pp. 487 and 497; Bensi, 2009, p. 37; Hofenk de Graaff, 2004, pp. 274-276; Kirby et al., 2014, p. 20.

[77] The ratio between indigotin and indirubin might be affected by the dyestuff treatment and the dyeing process used. The blue fibres analysed in this study often presented a relatively low concentration of indigotin and, in the most of the times, the concentration of indirubin was so small that it was probably below LOD. Higher concentrations of indirubin would translate in more purplish fibres, but these were not verified in this work. Cardon, 2007, p. 339; Hartl et al., 2015, pp. 22-23, 25, 27-28 and 30; Hofenk de Graaff, 2004, p. 181.

[78] Cardon, 2007, pp. 339 and 353-354; Hofenk de Graaff, 2004, pp. 244-245, 251 and 257.

[79] Baker, 1995, p. 29; Shibayama et al. 2015, p. 11.

Madder. In European velvets, brazilwood was often used in the foundation warp and weft threads, hiding below the more visible pile threads which were dyed with insect dyes. In two 15th- and 16th-century Turkish velvets (SZT292 and SZT276, respectively), the typical compounds from madder were detected in the orange-red silk warp and weft silk threads, rather than brazilwood. The warp of SZT276 was even dyed with indigo or woad to enhance the final colour of the textile. Although the provenance of SZT276 was originally uncertain (Turkish or Italian), the use of madder might indicate that this textile is of Turkish origin [80].

Madder was furthermore characterized in the orange-red silk yarns of an embroidered 17th-century Turkish linen (V&ACIRC92-1953). Curiously, the design of the embroidery intends to impersonate that found in the rich silk fabrics produced in the grand Ottoman textile industries. Plus, the option for madder corroborates that this cloth was likely to have been produced in a small textile centre, or even in a domestic environment.

The roots of the vegetable dye were used as well in the red and orange knots of three 17th-century Turkish and Iranian wool carpet fragments (V&ACIRC152-1920, V&AT369B-1966 and V&AT131-1926). In these fragments, deep-red knots dyed with lac dye were present as well, while madder was either used alone to obtain orange-red, or with yellow dyes, such as weld, for more orange or orange-yellow shades.

As discussed earlier in this chapter, the colour presented by madder-dyed fibres can depend on growing conditions, treatment and dyeing procedures. This can influence the ratio of alizarin and purpurin and, thus, the final colour of the yarns. In all fibres belonging to Turkish and Iranian textiles analysed here, the peak of alizarin was at all times higher than purpurin, indicating that a superior quality was used (thick and matured roots).

In the case of one orange-yellow knot from the Iranian fragment V&AT131-1926, the only characteristic compound from madder detected was alizarin, besides those of weld (if any other madder compounds were present, they were below LOD). Alizarin alone was moreover detected in the 8th/9th-century Chinese weave (AS4921). The sole detection of alizarin could suggest that *Oldenlandia umbellata* L. (chay root) was used. This Rubiaceae species grows in India and other parts of South Asia, such as Burma, Cambodia or Indonesia.

[80] According to Monnas (2012, p. 23), madder is not mentioned in 16th-century and “contemporary silk-weaving legislation, and it is rarely encountered on surviving Italian velvets, whereas it is found on Ottoman ones”. Madder dyes have also been ascribed in the red foundation threads of Indian velvets investigated by Shibayama et al. (2015, p. 3).

Given its high colouring power in relation to that of traditional *R. tinctorum*, it is possible that Iranian textile centres imported this type of dyestuff to dye the orange yarns of the carpet fragment V&AT131-1926 [81].

Brazilwood. According to the characterisation undertaken earlier in this chapter for European textiles, brazilwood's type C component was also detected in Asian brownish-yellow fibres, which had once been orange-red. For instance, analytical results for the fibres from the Iranian silk carpet V&AT.438-1976, indicate that brazilwood was mixed with young fustic and a yellow dye source. Hence, the silk knots of this carpet may have initially varied between orange-red and yellowish-orange (now they are brownish yellow).

For the embroidered Indian velvet V&A850-1873, brazilwood was identified not only in the warp threads of the textile, but also in the pile of a section of the middle panel (Fig. 10.13) – the textile comprises three panels of velvet attached to each other. This section of brownish-yellow fibres appears to be a continuation of the rest of the middle panel, in which the red pile was characterized as having been dyed with American cochineal. During the weaving process of this panel, both cochineal-dyed and brazilwood-dyed threads may have exhibited very similar shades and hence been used together. When the red colour of the brazilwood-dyed threads started to fade, a difference between both sections in the panel became strikingly evident.

Fig. 10.13. Detail of V&A850-1873, with enhanced division of the brownish yellow section, which pile was dyed with brazilwood (1). The red pile of the rest of the fabric was dyed with American cochineal (2).

Safflower. This dyestuff (*Carthamus tinctorius* L.), while not found in any of the European examples [82], was identified in ten silk samples belonging to three 16th- and 17th-

[81] Cardon, 2007, p. 139; Hofenk de Graaff, 2004, pp. 108 and 117, 2006, p. 44.
[82] Although safflower has rarely been detected in European fabrics dated to the period in study, Degano et al. (2011, p. 208) have recently reported the presence of this dyestuff in a 16th-century Italian silk tapestry.

century Iranian textiles, and two 17th-century Indian silk textiles. This was widely produced throughout Asia, reaching North Africa and Europe. A range of shades between pink and red could be obtained with it, but an enormous quantity of flowers was required to obtain deep colours. Moreover, safflower generally has small lightfastness properties. In China and in Japan, however, dyers added specific yellow dye plants that increased the fastness of the safflower dye and the intensity of its colour [83].

The main red compound present in safflower dyes is carthamin, which is insoluble in water. Other compounds can be present as well, such as the water-soluble safflower yellow, which is very light-fugitive. To enhance the red of carthamin, the yellow compounds were often removed by rinsing the flowers in a water bath. The red carthamin was applied directly onto the fabric in an alkaline bath. However, since direct reactions took place between the dyestuff and the fabric, this contributed towards rapid fading of the colours [84].

In the samples from the textiles investigated here, the representative compounds from safflower were detected: carthamin, CT components, apigenin and kaempferol [85]. Interestingly, safflower yellow was reported as well in the yellow fibres from the 16th-century Iranian silk textile V&A832A-1898, which suggests that common rinsing procedures of the flowers were not applied here, or were not carried out carefully. In addition, in the 17th-century Indian silk carpet CGMT100, the possible presence of carthamon (red oxidative product from carthamin) was considered, based on the literature [86]. Safflower-dyed fibres analysed here have also shown combinations with lac dye, young fustic and/or a yellow dye plant, to obtain different shades of red, pink or orange.

Yellow dyes. In relation to yellow and green fibres, weld was identified as the main source of dye in 16th- and 17th-century silk and woollen Turkish examples. As mentioned earlier in this chapter, the connections between Italy and the Ottoman Empire, may have led to the conventional application of similar dyes. Therefore, and as reported with American cochineal, the application of weld in Ottoman dyeing traditions shows clear parallelism with Italian production. Moreover, it is noteworthy that weld, in addition to growing in Turkish

[83] Cardon, 2007, pp. 53-54, 57-58 and 667; Hofenk de Graaff, 2004, p. 159; Wouters et al., 2010, p. 187.
[84] Cardon, 2007, pp. 55-56; Hofenk de Graaff, 2004, p. 159; Han, 2015, p. 234; Wouters et al., 2010, p. 187.
[85] Wouters et al., 2010, pp. 195-196.
[86] Tímar-Balázsy, 1998, p. 79.

territory, also possesses relatively fast properties in relation to other yellow dyestuffs, which may be the reason why it was widely employed. Indeed, this has been previously detected in silk and wool samples from Turkish textiles dated to this period [87].

In addition, weld, which was probably imported, was used in the yellow fibres of a fragment from a 17th-century Iranian carpet (V&AT131-1926). The colours depicted by this fragment, as well as its dyestuff attributions – lac dye for red and pink; weld for yellow and green; or weld and madder for orange – show very close similarities with those from other previously examined Iranian carpets [88].

Turmeric was reported to be the main yellow dye source in Indian velvets analysed by Shibayama et al [89]. In this study, curcumin and related compounds (Appendix 9), representative of turmeric (*Curcuma longa* L.), could only be identified in one yellow thread, taken from the back of a 17th-century silk Indian floorspread (V&A320A-1898). Analytical results for two other light yellow and green fibres obtained from this object did not provide sufficient chromatographic response to undertake further interpretations about their yellow dye source; they were obtained from the front edges of the object, which had been exposed to light, as strikingly evidenced in Appendix 2. Turmeric is likely to be native to the south of India, but it came to be produced in other territories of South Asia as well. This dyestuff has a high colourant yield and produces deep golden yellow shades but, because it is applied directly on fibres (direct dye), it is very light-sensitive [90]. Hence, it is possible that the fibres sampled from the front of V&A320A-1898 were originally coloured with this dyestuff.

Besides curcumin compounds, fisetin and sulfuretin from young fustic were encountered in the same yarn of V&A320A-1898. These young fustic compounds were found, moreover, alone or in combination with other dyestuffs (e.g. weld or brazilwood) in fibres from seven Turkish and Iranian silk textiles [91]. It is likely that this dyestuff was added to provide orange-yellow shades but, owing to its low lightfast properties [92], the fibres may

[87] Atasoy et al., 2001, p. 196; Carboni, 2007, pp. 202-203; Cardon, 2007, p. 176; Karapanagiotis & Karadag, 2015, p. 7; Shibayama et al., 2015, p. 6.
[88] Heitor, 2007, pp. 26-32; Santos, 2010, pp. 13, 19 and 22-23 and 30.
[89] Shibayama et al., 2015, pp. 8 and 11.
[90] Cardon, 2007, pp. 318-320; Hofenk de Graaff, 2004, pp. 208-209; Kirby et al., 2014, p. 15; Shibayama et al., 2015, p. 11.
[91] According to a preceding work, this dyestuff was only second to weld for dyeing yellow in Ottoman dyeing centres (Atasoy et al., 2001, p. 196).
[92] Böhmer, 1997, p. 158; Kirby et al., 2014, p. 17; Peggie, 2006, pp. 80 and 187-190.

have lost their original colour. In fact, in the samples of two Iranian (V&A438-1976 and V&A832A-1898) and two Turkish (V&A964-1898 and V&A145-191) examples, fisetin was no longer detected and dyestuff attribution was based only on the presence of sulfuretin. However, the threads from the Turkish textiles were sampled from the back of the objects, which means that a significant degree of photo-degradation should not have occurred. In this case, it is possible that another dye source, only yielding sulfuretin, was employed [93].

Another example of faded fibres is given by a 16th-century Turkish silk kaftan (V&A758-1884), made for the grave of a child, an Ottoman prince. The threads present a brownish-white colour that may be the result of the tomb's conditions. Chromatographic results for these threads only indicated a small response for indigotin, although it is possible that less resistant dyestuffs may have once been present as well.

Unknown "Yellow Dye Plants". Other yellow dyes were found in Asian textiles, although the source could not always be ascertained. In this case, the term "yellow dye plant" was used. This attribution was given to 19% of the total samples from Asian textiles, all of which belong to Iranian and Indian examples (regions where the more resistant weld was not available). Unknown yellow dye plants were often used alone, but also in mixtures with indigo or woad, brazilwood, safflower and/or madder.

Generally, the "yellow dye plant" term was attributed to samples in which chromatographic results the presence of flavonol compounds was detected: rutin (quercetin-3-O-rutinoside), isoquercetin (quercetin-3-O-glucoside) or hyperoside (quercetin-3-O-galactoside, the same retention time of isoquercetin), quercitrin (quercetin-3-rhamnoside), quercetin, isorhamnetin, rhamnetin and kaempferol. These compounds (3-hydroxyflavones) occur in many types of plants, which have been used as yellow dye sources all around the world and throughout the centuries. If compared with flavone compounds, such as luteolin present in weld or dyer's broom, flavonols are much more prone to photo-oxidation, thus fading at a faster rate and giving a darker shade to the dyed fibres. This is especially verified when the compounds are in aglycone form. For this reason, specialized

[93] Alternatively, other type of degradation may have occurred; or a different dyeing process could have been applied (Valianou, 2009, p. 881). This type of chemical composition has been reported as well by Han (2016, p. 148)

dyers carried out specific dyeing procedures to obtain relatively more stable yellows, by preventing the deglycosylation of the compounds glycosides [94].

The presence of flavonol glycosides in the yellow-dyed fibres investigated here could provide possible interpretations concerning which plant dye was used. However, given the promptness of these compounds for photo-degradation reactions, degradation products may be part of the chromatographic profiles of historical textile fibres. Moreover, there is a wide variety of plants in which these compounds occur and they all possess a closely related dye composition. Therefore, the identification of the exact source of plant used to colour the historical textiles can be hindered [95].

Nevertheless, there are specific flavonol-producing dye plants that have been reported in old dyeing practices, and some of them have recently been characterized by Mouri et al. (2014). This work is a very important contribution for future assessments of flavonol glycosides in historical textiles but, because different analytical conditions and sample preparation were used in the current thesis, the results obtained in this chapter cannot be directly compared with those of Mouri et al. Through a similar approach as that developed in Chapter 9 (examination of reference plants, dyeing reproductions with them, artificial ageing of the dyed fibres and examination with UHPLC-PDA and MS), it may be possible to assess in future studies possible differences between these dye plants, and thus, allow their discrimination in historical dyed fibres.

The majority of the samples, in which flavonols were detected, have typically shown a composition in which isoquercetin or hyperoside and quercitrin were the predominant compounds, accompanied at times of smaller peaks of isorhamnetin, rutin and/or kaempferol. Many dye plants could have been the source for this dye composition but, in specific cases, potential dye plants can be suggested, based on the literature and the date and provenance of the textiles.

For instance, chromatographic results from one yellow sample belonging to the 17th-century embroidered Indian velvet V&A850-1873 revealed the presence of 3-O-glycosides from quercetin (isoquercetin or hyperoside and quercitrin) along with isorhamnetin and kaempferol. This composition could possibly suggest the use of *Delphinium semibarbatum*

[94] Cardon, 2007, p. 678; Degano et al., 2009, p. 371; Mouri et al., 2014, pp. 135 and 137.
[95] Degano et al., 2009, p. 371;

Bien. ex Boiss. (yellow larkspur). This plant is native to several West and Central Asian regions, namely Iran, Afghanistan and northern India, and the dried flowers and flowering stems were widely applied to obtain yellow dyes, using a mordant, on silk and wool [96]. Yellow larkspur was one of the main sources of yellow in local centres of textile production, and in fact, has been often ascribed as the main source of yellow, in yellow and green fibres from Iranian and Indian textiles [97].

In a more darkened yellow sample from the same Indian textile, the main compound detected was rutin, although smaller peaks of quercitrin, isoquercetin or hyperoside, quercetin, isorhamnetin and kaempferol were detected as well. Due to the prominence of rutin in relation to the other compounds, the dye source could hypothetically be the flower buds of *Sophora japonica* L. (pagoda tree). This tree is native to East Asia and was extensively applied in China for dyeing silk with a mordant [98]. In this case, it seems reasonable to assume that this dyestuff was traded to India, where it was used in local dyeing practices.

In the chromatographic results for the green fibres from a 17th-century Iranian carpet (V&AT.369B-1966), quercitrin, isoquercetin or hyperoside, rhamnetin and kaempferol were reported. Due to the presence of rhamnetin, the fibres were possibly dyed with a *Rhamnus* species from Rhamnaceae family (buckthorn or Persian berries). The number of *Rhamnus* species available for dyeing is quite extensive, but in the Islamic world, the most commonly used might have been the ripe dried berries from *R. saxatilis* Jacq., *R. lycioides* L., *R. amygdalina* Desf. or *R. petiolaris* L. [99].

Despite these possibilbilities, it is important to bear in mind that many other dye plants could have been integrated into Asian dyeing practices. Indeed, besides these, other flavonol-containing plants might have been potential suitors for these results as well – for

[96] Böhmer, 1997, p. 158; Cardon, 2007, pp. 207-208; Enez, 1993, p. 196; Hofenk de Graaff, 2004, pp. 195-196; Mouri et al., 2014, p. 138; Shibayama et al., 2015, p. 6; Whiting, 1978, pp. 7-8.

[97] Enez, 1993, pp. 196, 198 and 203-204; Hofenk de Graaff, 2004, pp. 195-196; Shibayama et al., 2015, pp. 3 and 11.

[98] Cardon, 2007, pp. 210-212; Han, 2015, pp. 235-236, 2016, pp. 86 and 142; Mouri et al., 2014, p. 139; Whiting, 1978, pp. 7-8; Wouters et al., 2011, p. 239; Zhang & Laursen, 2005, p. 2024.

[99] Cardon, 2007, pp. 186-188; Hofenk de Graaff, 2004, pp. 194-195 and 198; Mouri et al., 2014, p. 139.

example, *Prangos ferulacea* L. (jashir), *Vitis vinifera* L. (leaves of grape), *Datisca cannabina* L. (bastard hemp) or *Fagopyrum esculentum* Moench (buckwheat) [100].

Additionally, in the yellow threads from two 16th-century Indian textiles (V&AIS.365-1992 and V&AIS.35-1991), a series of compounds were detected (Appendix 9), but their respective UV spectra did not show any match with other dye compounds comprising the UHPLC-PDA reference library, nor with published works on dye identification.

Given these results, the accurate characterization of the markers of Asian yellow dye plants, which could have potentially been used for dyeing, should be investigated. In this context, dyeing reproductions with them, along with artificial ageing, constitute an essential step in future studies for the investigation of yellow dyes in Asian historical textiles. Precise knowledge about them contributes invaluable evidence for narrowing or even confirming the provenance of historical textiles, as well as for the historical contextualization of local dyeing practices [101].

Conclusions. Global trade in due course brought American cochineal to Asia. Given its connections with Italy and Eastern Europe, the main textile centres of Turkey soon adopted the American insect, as supported by the analytical results carried out in this thesis on 16th-century silk luxurious textiles. Furthermore, land routes commercially connected Turkey with other parts of West and South Asia, while maritime itineraries permitted Europeans to reach the Asian markets. Through these communications, the foreign red eventually reached the major dye workshops of Iran and India. In Iran, the classification of American cochineal in 16th-century textiles suggests that the dyestuff arrived in the region decades earlier than what has been assumed by historical evidence. In Indian textiles, lac dye was often found in 16th-century silks, whereas American cochineal was only reported in textiles dated to the 17th century. Although a larger group of textiles requires further examination to achieve more conclusive interpretations, these results nevertheless suggest a later adoption of American cochineal in Indian dye workshops, which continued to give priority to engrained dyeing traditions, in agreement with the historical information presented in Chapter 6.

[100] Baker, 1995, p. 31; Cardon, 2007, pp. 208 and 211; Mouri et al., 2014, pp. 139-141.
[101] Mouri et al., 2014, p. 140.

As suggested by the historical evidence, kermes and Polish and Armenian cochineal, despite being overtaken by the American type, may have continued to be traded and applied in the dyeing spheres of the Ottoman Empire. This was likely to have been most frequent in regions nearby the insects' areas of exploitation, or through specific requests made to main centres of textile manufacturing. In addition, Armenian cochineal could have been collected in Iranian regions for dyeing purposes. The examination of a larger group of historical textiles should bring further interpretations about the application of local insect dyes in these regions.

Of the Eurasian insects, the only that may have continued to secure a place in the dyer's vats was lac dye. Indeed, this dyestuff was often reported in Turkish, Iranian and Indian textile objects (especially rich carpets), dated to the 16th and the 17th centuries. This insect dye was also reported in one Chinese textile, in agreement with previous studies.

Furthermore, it is worth noting that cochineal species, other than the most popular ones studied in this thesis, could also have had important roles in local dyeing practices carried out in Central Asia. These *Porphyrophora* insects may have been locally collected or imported from Russia and Ukraine and, according to Chapter 7, may even have represented some competition to American cochineal. Hence, future studies concerning the history of *Porhyrophora* applications in Asia should be undertaken to establish their presence in historical objects, to better understand their relationship with the foreign American cochineal.

As in the European case, cochineal-dyed samples from Asian objects were often ascribed with the presence of indigo or woad (and lichens, in the case of one Turkish velvet), as well as with tannins. Besides insect dyes, red, pink or orange fibres in Asian textile objects were ascribed with brazilwood, safflower or madder. Depending on the level of photo-degradation, safflower and brazilwood were detected also in faded yellowish fibres. Madder was particularly reported as a source of orange in Turkish and Iranian wool carpets, whereas lac dye was used as a source of red. At all times, blue shades were obtained with indigo or woad. For green, these were mixed with yellow dye sources.

As in the main European cloth-producing centres, the use of weld was widespread in Turkey, but in Iran and in India – with the exception of one yarn detected with turmeric – young fustic and flavonol-based yellow dyes, such as yellow larkspur or buckthorn, were used. In some cases, the yellow dye sources could not be accurately characterized, because compounds were too degraded, or they comprised unknown compositions. In these cases, the term “yellow dye plant” was adopted. Further research on these flavonol-based yellow dyes in Asian textile objects is necessary to develop a more conclusive picture of their historical applications, according to the regions of their occurrence.

The results obtained in this study for the selected group of European and Asian textile objects, not only provided more assertive interpretations about their origins, but also very significant information about the dyeing applications of different regions. Comparing these results with the historiography demonstrates that the adoption of American cochineal in East and South Asia may have been slower and more diffuse than has been verified in the major textile manufacturing industries of Europe and West Asia. In this context, the continued use of Eurasian insect dyes should not be dismissed, especially if these were locally collected and were part of long-established traditions.

This multidisciplinary study brings a wider, richer and more nuanced perspective of insect dyeing traditions in European and Asian societies. It demonstrates that new work on dye identification is still required to fully understand the many implications involved by the expansive circulation of American cochineal with the advent of the Iberian Expansion. This is especially important when considering its adoption in European and Asian regions, where there were long-established dyeing traditions, which were sometimes overtaken by the new dyestuff, and others that represented competition to it.

FINAL REMARKS

In this study, economic history, textile objects and analytical chemistry are combined in an innovative interdisciplinary approach, in order to achieve a more comprehensive understanding of the impact of American cochineal as a commercial product in the global circulation of dyestuffs, and its importance as a red dye source in the main centres of textile production in Europe and Asia, with the advent of the Iberian Expansion.

The first phase of research involved a comprehensive revision of historical evidence regarding cochineal's annual volumes of trade and prices in the Spanish transatlantic communications; its relationship with the Iberian transatlantic trade of American indigo, brazilwood and logwood; its impact on markets and dyeing traditions in Europe and Asia; and its local acceptance in these regions in relation to "Old World" insect dyes, namely lac dye, kermes and Armenian or Polish cochineal.

A revision of trends in volumes (and prices) for the Spanish trade in American cochineal indicate an exponential increase in its production to satisfy international demand during the colonial period. Furthermore, the data reported demonstrates that this dyestuff achieved wide popularity and commercial value outside Mexico. However, this revision also reveals that historical publications related to the Spanish trade are not always able to provide sufficient figures for proper analysis of some specific chronological periods, especially for several decades of the 17th century. These periods are often marked by commercial interruptions due to wars and conflicts or intensification of privateering assaults, as well as increased levels of smuggling owing to excessive taxation on cochineal in official trade. Nevertheless, when looking at the global picture, beyond the Spanish trade in cochineal, it is possible to see that its international significance continued, even when it was not part of the Spanish transatlantic shipments.

With regard to the comparative study between American cochineal and other dyestuffs (indigo, brazilwood and logwood) brought from the Americas by the Spanish and the Portuguese, very important historical relationships could be established between the commercial volumes and prices observed for cochineal and the other American dyestuffs. Thus, through this comparative study, it was possible to assess how sizeable was the value of cochineal in relation to other dyestuffs. Indeed, while the Spanish monopoly on cochineal allowed merchants to keep its cost high at all times, indigo and brazilwood always faced competition with other American or Asian varieties. Hence, cochineal valued at least the double of indigo, and at least 17 times more than brazilwood. Moreover, it was possible to demonstrate here that, in contrast to the case for cochineal, commercial transatlantic records for indigo and dyewoods for the 17th century are available. This validates the idea that Spanish trade with the Americas was not completely interrupted at this time, as proposed by some scholars, and that cochineal was likely entering Europe through alternative routes (e.g. contraband or privateering).

Furthermore, it was demonstrated that the political and economic conjuncture of European markets to where the American dyestuff was traded influenced its prices (due to war conflicts, for instance). These prices were also closely related to those practiced by the Spanish, which were highly dependent on Mexican production, international demand, transport and commercial interruptions, owing to wars, privateering or smuggling. For example, in the end of the 16th century, English privateers ransacked great amounts of cochineal from Spanish fleets and were selling it at low prices. As a result, prices dropped in the main European markets, in order to keep up with the competition. It was also verified that cochineal was entering European territories during the 17th century (particularly the north of the Low Countries and England), probably through privateering and smuggling, even though its trade was supposed to be strictly controlled by a Spanish monopoly. In addition, it was possible to attest that the reception and adoption of American cochineal may have not occurred as swiftly as implied by the literature. Instead, the diffusion process of cochineal in Europe and Asia in terms of trade and dyeing practices seems to have happened gradually, depending on the political and economic circumstances of each region.

This was particularly clear when evaluating the adoption of the American dyestuff in relation to other red insect dyes. Despite the growing importance of American cochineal, it was verified here that other insect dyes continued to be used in European and Asian dyeing practices. This was predominantly reported in territories where production and dye applications of local dyestuffs continued to represent significant contributions to the local economy. Therefore, and contrary to what has been systematically affirmed in the literature, American cochineal's adoption does not seem to have completely dethroned the importance of other insect sources of red.

In order to verify these historical interpretations, and to provide additional information that could bolster the meagre historical evidence available for some Asian and European regions, scientific analysis of textiles was introduced to compliment the historical approach. A large group of rich European and Asian historical silk (and some wool) objects, dated between the 15th and 17th centuries, were selected for analysis. By chemically assessing the precise sources of insect dyes used to colour their red yarns, it was hoped it would be possible to further evaluate the historical picture presented for the European case, and to track the impact of American cochineal in Asia.

However, in order to accomplish this goal, it was fundamental to establish a method that could lead to more accurate chemical results for discriminating between the various cochineal species, than previously reported in the scientific literature. Hence, a UHPLC-PDA analytical method was optimized, which demonstrated improved peak capacity and resolution in relation to a conventional HPLC method and, moreover, allowed for the characterization, in one single analysis, of a wide range of natural dye compounds with different and/or closely related physicochemical properties. This advance was fundamental to obtain more chromatographic information about the origin of unknown dyes in historical textiles, especially when discriminating closely related species of cochineal.

The combination of this UHPLC-PDA method with UHPLC-MS, SEM-EDX and, in particular, multivariate statistical analysis, was essential to create a thorough investigation of cochineal dyes in experimentally-dyed, artificially-aged and historical crimson fibres. In this context, an experimental dyeing without precedent was undertaken on an extensive set of samples of silk and wool using cochineal and kermes insects. The respective UHPLC chromatograms have brought reliable interpretations about changes in the dyestuffs' colorant composition, depending on the experimental dyeing parameters and the textile substrate used. Furthermore, it was revealed, for the first time, the occurrence of photo-degradation compounds in the colorant composition of artificially-aged and historical fibres, which had originally been dyed with cochineal and kermes. Research on the chemical nature of these photo-degradation compounds is advisable in future studies. Even so, it is now clear that further characterizations of cochineal dyes in historical textiles should always be carried out using experimentally-dyed and artificially-aged reference samples, since the colorant behaviour of insect extracts tends to change during the dyeing procedure (especially for silk).

After collecting a large number of chromatograms from reference fibres dyed with several cochineal species, and given their similar profiles with small chromatographic variations, a statistical technique like PLS-DA was required to achieve accurate discriminations between insect species. This technique, in combination with the conventional qualitative and quantitative interpretation of chromatographic results, proved to be fundamental to obtain precise classifications of unknown cochineal species present in the red fibres from investigated historical textiles.

This powerful combination of UHPLC-PDA with a statistical method, allowed for the accurate attribution of cochineal species present in the group of historical textiles selected for this study. With this approach, the achieved results brought complimentary information to support the interpretations made in the historical studies of European and Asian insect dyes and, in particular, American cochineal.

Indeed, following the analytical results, it was possible to observe that, in Europe, until the 16th century, kermes, Polish cochineal and, to a lesser extent, Armenian cochineal and lac dye were used. However, during the 16th century there was a marked widespread adoption of American cochineal in the dyeing practices of the main European textile manufacturing centres of Italy, the Low Countries, France and England. This is in agreement with the registered rise of transatlantic shipments of this dyestuff, demonstrated by the historical research undertaken in this thesis.

Interestingly, more than half of the 15th- and 16th-century European silk textiles examined here were produced in Italy, while for the 17th century few examples from this region were obtained. Although a wider number of museum collections ought to be investigated, these proportions appear to support the evidence from historical sources, indicating intense Italian production of sumptuous red clothing until the 16th century and then a decline thereafter; and by contrast, an expansion of manufacturing in northern European production centres, namely the north of the Low Countries and England, in the 17th century.

For West Asia, the analytical results moreover indicated a similar process to that occurring in Europe concerning the adoption of American cochineal, thus also confirming the propositions of the historical studies of this region. In fact, the identification of this insect dye in 16th-century Iranian textiles demonstrated that its dissemination in local dyeing practices occurred decades earlier than what was perceived from the available historical sources, which only report its presence in the region in the early years of the 17th century.

For East and Southeast Asia, the results demonstrated that the impact of American cochineal in local dyeing practices occurred at a slower pace due to engrained dyeing traditions, also in agreement with the historical information. Indeed, in 16th- and 17th-century Indian textiles analysed here, the major source of insect dye ascribed was lac dye, while only 17th-century examples were reported with American cochineal. Moreover, it is worth noting that lac dye was often reported in Turkish and Iranian textile objects (especially rich carpets), dated to the 16th and the 17th centuries. It was also identified in one Chinese textile in this study, in agreement with previous studies on dye identification. Hence, these results clearly show that lac dye continued to have had a secured place among Asian dye workshops, even after American cochineal was adopted, as also verified by the historical research carried out here. Therefore, the analytical results obtained here confirm that textile objects can represent a viable source of information to obtain more assertive historical conclusions.

However, occasional historical references to the continued shipment of kermes and Polish cochineal to Italy in the 17th century (and to the Low Countries), as well as their use in Venice as late as the 18th century is not confirmed by the scientific results. To the contrary, not a single 17th-century textile was found to have the presence of these “Old World” dyestuffs. This discrepancy could reflect the small quantities of these dyestuffs being traded, as the references only mention their inclusion in trade, not specifics about their volumes or prices. In this respect, it would be worth focusing on the analysis of Venetian textiles, for instance, to confirm the extent of the continuation of these “old” dyeing practices.

The UHPLC-PDA analysis of other dyestuffs present in the textile objects also brought important contributions as well. For instance, in European luxurious textiles, particularly velvets, results revealed that, for economic reasons, a cheaper red dye like brazilwood was often used in the warp or weft threads of the textiles' structures, while the more expensive insect dyes were used for the pile threads, which were more visible in the finished textile.

Also, knowledge about the presence of other dyes and/or certain insect species resulted in new and significant interpretations about provenance, date and history of production of the textiles. For instance, the identification of madder as the only red dye applied in the 15th-century German textiles examined here demonstrates a clear preference for native dye sources, despite the wide availability of insect dyes in nearby Italian and Flemish workshops. Moreover, these results showed a glimpse of the variety of natural dye ingredients (particularly yellow dye sources), as well as mixtures of dyestuffs applied to obtain specific colours, which are characteristic of different European and Asian textile producing centres. In this context, it is interesting to note that the results obtained here show that use of the yellow dye weld was widespread in European and Turkish centres of textile production, but not in Iranian and Indian ones. Instead, the results indicate that other locally-available (flavonol-based) Asian "yellow dye plants" were used, which deserve future study to resolve their precise characterization.

Ultimately, the interweaving of two distant fields like History and Chemistry has accomplished more accurate insights about the dynamics of American cochineal in the international markets and the local dyeing centres of Europe and Asia. Additionally, the development of a UHPLC-PDA analytical technique that can be applied widely to characterize a large number of natural dyes in one single analysis comprises an outstanding approach for skimming all the colorant information given by a single historical yarn, without wasting valuable amounts of historical samples and time. Furthermore, the development of a new analytical method, which combines UHPLC-PDA with statistical analyses for the chemical investigation of cochineal-dyed fibres, has shown the possibility of overcoming the limits of current analytical methodologies. This method was decisive for supporting the historical interpretations about the penetration of American cochineal into European and Asian dyeing traditions.

Even so, the results of this research should not be considered the end of the line. Instead, they should offer positive encouragement to the development of new perspectives and assessments regarding the historical and chemical studies of cochineal insects.

FUTURE PERSPECTIVES

This study has opened a window onto the wide world of dye technology, by bringing more conclusive insights about dyeing traditions and trade routes concerning cochineal dyes. Nevertheless, it is important to emphasize that further historical research on this subject, either by considering archival documentation or textile objects, should be carried out. Indeed, a more extensive dye investigation and a larger range of examined textiles, ideally with specific or narrow dates, could provide a clearer picture of the use of dyestuffs – particularly "Old World" insect dyes, in relation to American cochineal – in the dyeing practices of major European and Asian centres of production, and in more remote (and isolated) regions. For example, Venice still received Polish cochineal and kermes during the 18th century. In this case, further research on the history of textile production in this region could help understanding local dyeing practices with insect dyes, as well as in relation to other Italian regions and around the world.

Further research on dye reproductions, following historical recipes with insect dyes and mixtures of them (when possible, including non-laboratory ingredients), could help to understand if these can be discriminated in historical textiles manufactured in the main centres of textile production in Europe and Asia. This research is of particular interest for *Porphyrophora* and wild *Dactylopius* species (other than *P. polonica*, *P. hamelii* or *D. coccus*), because their chemical differentiation could be used to answer entomological questions regarding their origins, for instance, and ascertain their use in local dyeing or painting practices in European, Asian or American cultures, during certain periods, and for which historical evidence is often scarce. Furthermore, it should be remembered that, in the main European and Asian textile centres, these marginal species could have been applied as well, and not only the more famous insect dyes [1].

The analytical approach developed in this study, which combined a UHPLC-PDA optimized method with statistical analysis, constitutes a recommendable approach for

[1] In France, dyers used to mix a wild variety of *Dactylopius* species with madder (Colbert, 1672, p. 8; Pearson, 1705, pp. 160 and 280). Also, Phipps (2010a, b) has reported the presence of American cochineal (*D. coccus*) in American textiles, although it is not specified the hypothesis of using a wild *Dactylopius* species. So far, only one study has been able to discriminate some of the *Dactylopius* insects (Serrano et al., 2013), but an extensive study about their characterization in dyed textiles still remains to be undertaken.

future investigations about insect dyes in historical textiles. However, Armenian and Polish cochineal, as well as some *Porphyrophora* species are currently very hard to come by, as they are near extinction. Even so, new projects are currently creating suitable conditions to stimulate the controlled growth of these insects for research applications [2].

In addition, researchers in the field of dye identification in cultural heritage often do not have the knowledge to carry out multivariate statistical analyses. A possible solution would encompass the creation of an international online database that could include PLS-DA models based on those developed in this study. The potential success of such a platform could be extended to other applications, such as the possibility of discriminating closely-related plant species (e.g. flavonol-based plants) in historical textiles, and even lake pigments in historical paintings and sculptures.

Particularly, lake pigments from insect dyes should be assessed to understand their colorant behaviour and reproducibility, depending on the lakes' preparation and natural ageing. Based on this, it might be possible to discriminate cochineal species in lake pigments and, moreover, compare them with dyed fibres. This may be particularly interesting when considering red lakes in paintings dated to between the 14th and 17th centuries. These were frequently made from the red dye extract obtained by immersing the shearings (or shreds) of old or waste red insect-dyed fabrics in alkali solutions [3].

Finally, the extensive assessment of insect dyes in textile objects, paintings or sculptures, and the integration of this data into an online platform, would help historians looking closer to textiles produced in certain regions, compare them with archival sources and, ultimately, understand how local production fits in the global context of the history of insect dyes. Hence, this platform may constitute a significant contribution for the preservation, authentication and historical characterization of works of art, especially with regard to provenance, date or technological production. Moreover, it constitutes an important step towards acquiring more accurate knowledge about historical practices and habits and, in the long term, more trustworthy methods of preserving cultural heritage.

[2] Personal correspondence with Katarzyna Golan (Department of Entomology, University of Life Sciences, Lublin, Poland) and Hassan-Ali Vahedi (College of Agriculture, Razi University, Kermanshah, Iran).

[3] Present studies in painting conservation can accurately distinguish lakes made with direct insect sources and those made from waste textile shearings, through the microscopic observation of the paintings cross-sections. However, the characterization of the exact cochineal species or the possible mixtures of insect dyes still constitute a challenging task (Anderson, 2015, pp. 358-359; Kirby & White, 1996, pp. 67-68 and 70-73).

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