TUTORIAL REVIEW

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The natural constituents of historical textile dyes

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The sources and structures of dyes used to colour Western historical textiles are described in this *tutorial review*. Most blue and purple colours were derived from indigo—obtained either from woad or from the indigo plant—though some other sources (*e.g.* shellfish and lichens) were used. Reds were often anthraquinone derivatives obtained from plants or insects. Yellows were almost always flavonoid derivatives obtained from a variety of plant species. Most other colours were produced by over-dyeing—*e.g.* greens were obtained by over-dyeing a blue with a yellow dye. Direct analysis of dyes isolated from artefacts allows comparison with the historical record.

1 Introduction

The textile dyeing industry has been in existence for more than 4,000 years. For all but the last 150 years, the dyes were obtained from natural sources.[1] Surrounded nowadays by bright, fast, inexpensive synthetic dyes and pigments, it is hard to imagine a time when a good quality dye was as valuable as gold or silver. For example, during the early Roman Empire period, only kings and priests could wear purple dyed fabrics while in the middle-ages, scarlet dyed fabrics were reserved exclusively for important members of the clergy. Dye sources were even important enough to lend their names to New World countries. Thus, the similarity between 'Brazil wood' from indigenous Indo-Asian *Caesalpinia* trees and vast numbers of a related species growing in the South American region originally called 'Terra de Vera Cruz' led Spanish explorers to rename the country 'Brazil'.[1]

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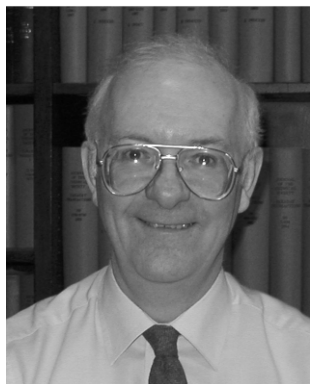
Ester Ferreira


Alison Hulme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Where did the dyes come from? Botanical sources were undoubtedly the single most important source but a wide variety of other organisms was used, including lichens, insects and shellfish. Not every shade is available directly from a natural source. The range of colour can be greatly extended, for example by over-dyeing the major components which have blue, red and yellow hues. Green colours are obtained from a yellow and a blue dyestuff in this way. Very subtle shades can also be obtained, such as the skin tones of figures in tapestries.

The ideal dye is also 'fast'—*i.e.* it is not altered by washing the fabric or by exposure to light or air. Wash-fastness is often improved by the use of 'mordants' (see section 2) but loss of colour on exposure can be a serious problem, especially with very old textiles. For example, natural yellow dyes are notoriously prone to degradation by a photo-oxidation process—which explains why the grass in historic tapestries often appears to be blue.

Our historical textile legacy is extraordinarily rich, encompassing 4,000 year-old shrouds from Egyptian tombs, prestige art objects like 16th century Flemish tapestries as well as everyday objects such as items of clothing and home furnishings.

The primary aim of this article is to detail the major natural sources of dye colours used in historical times and the chemical nature of their constituents. The discussion is based primarily, though not exclusively, from a European perspective. Although much historical information is documented, identifying dye sources in actual artefacts has only been possible with the development of micro-analytical techniques. Organic dye components in a fabric or thread sample can be solvent extracted, then separated chromatographically before spectrometric comparison with authentic references for identification. Thin layer chromatography and UV-visible spectrophotometry were applied successfully before the advent of photodiode array (PDA) high performance liquid chromatography (HPLC) which directly provides both retention time and UV-visible spectroscopic parameters. The use of PDA-HPLC now enables nanogramme quantities of dye from a single 5 mm long thread (*ca.* 0.1 mg) to be routinely identified. For unknown components, whose spectra do not match those of known authentics, analysis by LC-mass spectrometry (LC-MS) has provided further information. Many dye sources have the same major constituent so identification of this major component may not uniquely define the origin of the dye. In such cases, the presence of characteristic minor constituents can act as marker compounds to allow species identification.

Dyestuff identification also provides information on trade routes, as well as for the provenance and past restoration of a historical textile—here the analytical chemist contributes with useful evidence for the historian, archaeologist and conservator. Readers interested in research in the area of historical dyes are referred to the regular series *'Dyes in History and Archaeology'* (Archetype Books) in which the proceedings of annual conferences in the field are reported.

2 Dye classification

Natural dyes can be classified as vat dyes, mordant dyes or direct dyes according to the method by which they are applied to textiles.

Vat dyes (of which indigo and woad are the most important examples) are water-insoluble but under reducing conditions, they can be converted into a 'leuco' form (soluble in alkaline aqueous solutions), which penetrates the fibres to be dyed. By exposure to air they are oxidised to their insoluble form, and these pigment aggregates are trapped in the fibre.

Mordant dyes (the vast majority of natural dyes) require the treatment of the textile fibres with a solution of mordant (generally a metal salt). The solution is absorbed by the fibre allowing the metal ion to becomes complexed to appropriate functional groups in the structure of the fibre.[2] During the dyeing process, the dye interacts with the mordant–fibre complex to form an insoluble brightly coloured species. The mordant ensures the brightness and wash fastness of the dye and also has great influence on the final colour obtained.

Aluminium, iron, tin, chromium or copper ions are examples of mordants. Aluminium could be obtained from different species of clubmoss, such as *Diphasiastrum complanatum* L. from Finland, *Diaphasiastrum alpinium* L. and *Huperzia selago* L. from Scotland,[3] (which are biological accumulators of aluminium) and iron from surface scum or bottom sediments of bogs, as well as from mineral sources.[2] Commonly used with the mordants are the so-called dye-assistants such as cream of tartar ('winestone', potassium hydrogen tartrate) or oxalic acid. These brighten the colours, protect the fibres and/or help the absorption of the mordants.

Finally, direct dyes are applied directly to the fibre but usually are less wash- and light-fast than vat or mordant dyes. Examples of direct dyes include turmeric (*Curcuma longa*) and saffron (*Crocus sativus*) (Section 5.2).

3 Blue and purple dyes

3.1 Indigo

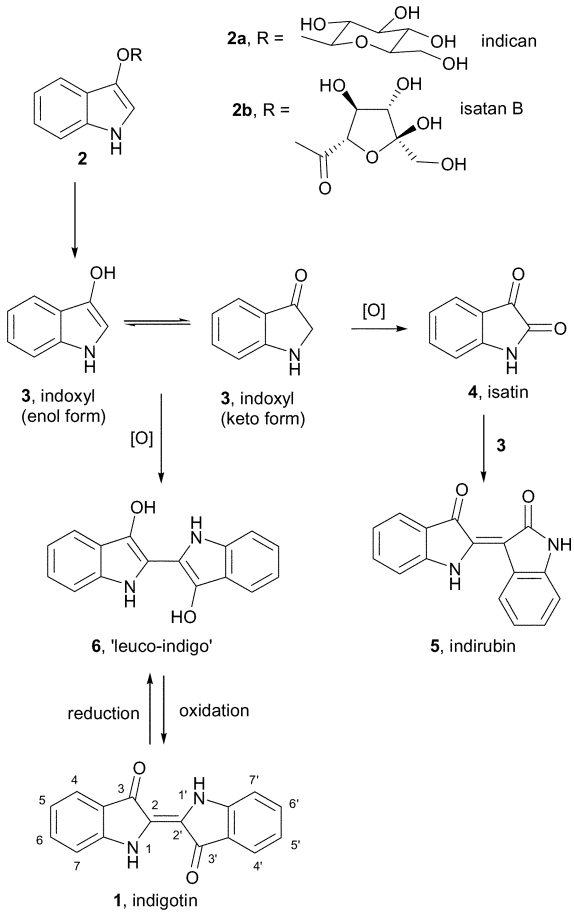
The major constituent of the indigo dye is indigotin **1**. Indigo-bearing plants can be found all over the world and the chemistry of this vat dyestuff renders it compatible with all natural fibres.[4] Evidence of the use of indigoid dyes dates back to 2000 B.C. in Egypt.

The natural products from which indigo is obtained include indican **2a**, which occurs in Indigofera species, native to tropical and subtropical countries (*e.g.* the indigo plant *Indigofera tinctoria* L., a native of tropical Asia). In temperate climates, woad (*Isatis tinctoria* L. widely available in Southern and central Europe, North Africa and West Asia) contains indican **2a** and isatan **2b**.[1,5]

Independent of the plant source the chemistry of dye extraction and preparation is similar. The pigment formation occurs through the process described in Scheme 1 after the plant has been harvested. During the fermentation stage, the indoxyl glycosides **2** are converted by enzymatic hydrolysis to indoxyl **3** (a mixture of keto and enol tautomers) which is oxidised by exposure to air to 'leuco-indigo' **6** and then to indigotin **1**. This insoluble blue pigment is then collected and used as a vat dye. As a side reaction during fermentation, indoxyl **3** is over-oxidised to isatin **4** which condenses with more **3** to provide the red pigment indirubin **5**, whose presence gives indigo dyes a purple hue. It follows that little provenance information can currently be obtained from indigo dyes because the main detectable components are common to all sources.

The history of indigo production paints a fascinating picture of the importance of dyes as trading commodities. In the Middle Ages woad was extensively cultivated in Europe and at the same time small volumes of the indigo pigment from *Indigofera* was imported from India. This trade presented little threat to the woad industry and the indigo pigment was used mainly for inks and paints. By the 16th century in Britain the cultivation of woad was so profitable that vital grain supplies were threatened. The overland trade of indigo from the East Indies was dominated, controlled and highly taxed by Middle Eastern countries and Italy. The successful circumnavigation of the Cape of Good Hope by Vasco da Gama in 1498 opened a new trade route and indigo became one of the major commodities imported. By the middle of the 17th century the development of indigo plantations in the West Indies and Americas soon outweighed the imported indigo from the East. Finally, the introduction of synthetic indigo in late 19th century brought a halt to the cultivation of the natural indigo plant sources.

Indigo, when used in combination with red, yellow and brown dyes produces purple, green and black colours.



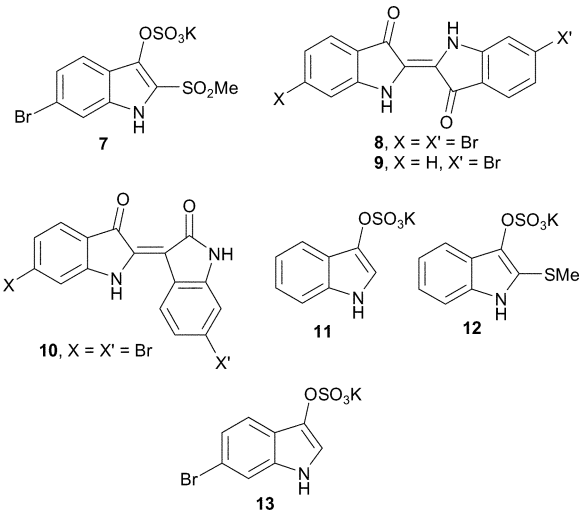
Scheme 1

3.2 Shellfish purple

The purple dyes obtained from shellfish are also derivatives of indigotin **1**. There is considerable interest in this area; a recent review cites 133 references.[6] The three main species of molluscs used in the Mediterranean region were spiny dye-murex (*Bolinus brandaris* L. or *Murex brandaris*), rock-shell (*Thais haemastoma* L. or *Purpura haemastoma*), and banded dye-murex (*Hexaplus trunculus* L. or *Murex trunculus*).[7] As in the case of indigo plant sources, the dye is not present in the live mollusc. It is generated by enzymatic hydrolysis of precursors found in the animals' hypobranchial glands (to provide derivatives of indoxyl **3**) followed by photochemical conversion to the purple pigment.[6,8] Only very small amounts of dye (often < 1 mg) can be obtained from each mollusc (enough to dye only *ca.* 1 g of wool) making these dyes very expensive commodities.

Spiny dye-murex and rock shell contain only the precursor **7** (*ca.* 0.6 mg per gland) which provides 6,6′-dibromoindigotin **8** and a small amount of dibromoindirubin **10**.[7,9] Bromo-substituted and unsubstituted precursors **7** and **11–13** occur in banded dye-murex; in one study, average levels of 0.24, 0.54, 0.06, 0.36 mg per gland respectively were found.[8] These apparently provide dyes of varying composition whose components can include 6,6′-dibromoindigotin **8**, 6-bromoindigotin **9** and indigotin **1** as well as smaller amounts of indirubins such as **5** and **10**.[6] The presence of bromoindigotin **9** and indigotin **1** give the final dye a bluish hue when compared with the reddish purple obtained from rock-shell and spiny dye-murex. Because many of the dye precursors have sulfur-containing substituents in the 2-position of the indoxyl derivative the release of mercaptans in the final oxidation stage gives a well-documented bad odour to the dyeing process.

Different shades of purple can be obtained from these molluscs, sometimes used in combination.[10] The most important were a red purple (*argaman*, Tyrian) and a blue purple (*tekhelet*, hyacinthine). In addition the dyeing technology may influence the hue. For



example, it has been suggested that since the reduced form of 6,6′-dibromoindigotin **8** can suffer debromination when exposed to light providing some **9** and **1**,[11,12] exposure of the vat dyebath to light will give the final result a stronger blue hue.

Ancient texts describe an important Phoenician shellfish purple dye industry dating back to the 14th century B.C.[13] and evidence of a large scale industry has also been provided by archaeological findings.[14] Pliny the Elder describes the details of capture of the molluscs, the removal of a colourless gland, the preparation of these glands with salt and water, and the 10-day heating process with the addition of urine and water.[13] The purple dye industry had largely collapsed by the 7th century A.D. and mass production ceased in the 15th century.[13]

Shellfish purple dyes are not exclusive to Europe and different species of molluscs have been used all over the world to provide a direct dye. Examples include *Nucella lapidus* L. (the North Atlantic), *Purpura patula* L. (Caribbean and Florida), *Purpura patula* subsp. *pansa* L. (Mexico to Equador), *Rapana bezoar* L. and *Thais clavigera* Küster (Japan) and *Mancinella kieneri* Deshayes[1] and *Dicathais orbita* Gmelin[15] (Australia).

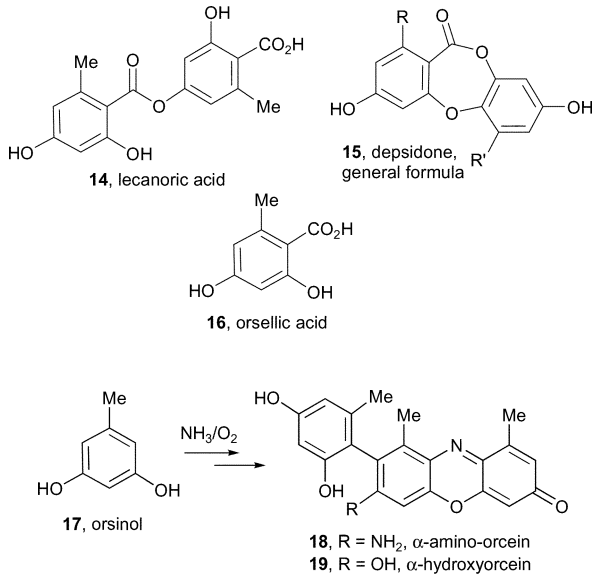
3.3 Lichen dyes

Lichen dyes were occasionally used to produce 'false shellfish purples'. Generally called orchil or archil dyes they were obtained by fermentation of extracts from lichens of different species in the presence of ammonia and air.[16] The most important lichens were *Rocella tinctoria* D.C. and *Rocella fuciformis* D.C. which can be found in the East Indies, South and Central America, Cape Verde Islands (West Coast of Africa), Madagascar and Europe. *Pertusaria dealbescens* Erichs. from France and *Orchrolechia tartarea* L. ('cudbear') from Scandinavian and Celtic countries were also used.[1,17]

The lichens were prepared by immersion in ammonia-rich aqueous solution (*e.g.* urine) and during the resulting fermentation, depside (*e.g.* **14**) or depsidone **15** components were hydrolysed to orsellic acid **16**. Decarboxylation of **16** yields orsinol **17** which reacts by a sequence of condensation reactions incorporating nitrogen from the ammonia to give various orcein derivatives of which **18** and **19** are examples (Scheme 2). Depending on the pH and the presence of mordants, these can give bright red, purple or orange dyes.[1]

3.4 An historical example

A wool textile found at the Al-Tar caves in Iraq (a site which dates from 3rd century BC to 3rd century AD) was shown, by UV and X-ray fluorescence spectroscopy, to contain Tyrian purple.[18] It is



Scheme 2

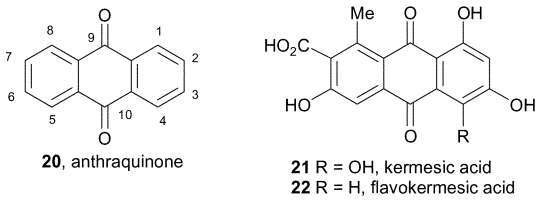
noteworthy that indigoid dyestuffs can survive on cloth for at least 2000 years.

4 Red dyes

4.1 Insect reds

Scale insect red dyes are historically very important. The main dye sources, all of which are plant parasites from the Coccidea family, are extracted from American cochineal (*Dactylopius coccus* Costa), kermes (*Kermes vermilio* Planchon), Polish cochineal (*Porphyrophora polonica* L.), Armenian cochineal (*Porphyrophora hamelii* Brandt) and lac (*Kerria lacca* Kerr). The chromophores in all scale insect dyes are derivatives of anthraquinone **20**; they were mainly used as mordant dyes with the carbonyl and the adjacent phenol groups participating in the fibre–mordant–dye complex.

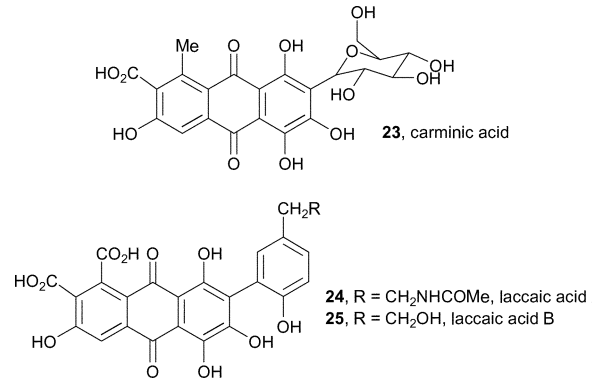
Kermes has been used in Europe since Roman times or before. It is obtained from the dried egg-filled female insects which grow on the prickly evergreen Mediterranean oak *Quercus coccifera* L. This tree was widespread in the Mediterranean but the parasite is now threatened by extinction.[19] The main components of the kermes dye are kermesic acid **21** (> 75%) and flavokermesic acid (laccaic acid D) **22**. It was the main insect red dye in Europe and in Asia, and when the shellfish purple dyeing declined it took its place in the garments worn by high clergymen. It was widely replaced by American cochineal in the 16th century.



The major constituent of all cochineals is carminic acid **23** but the various species have characteristic fingerprints of anthraquinone minor components (including the laccaic acids **24–25**) which allows them to be distinguished in historical samples.[20,21]

Armenian cochineal contains the highest proportion of carminic acid **23** (> 95%) and is obtained from the cysts of the females of *Porphyrophora hamelii* Brandt collected from the base of its hosts *Aeluropus littoralis* Gouan or *Phragmites communis* Trin. It occurred in Armenia, Turkey and Iran. Evidence of its use dates to the 8th century B.C.[1]

Polish cochineal is obtained from the cysts of females of *Porphyrophora polonica* L. collected from the roots of its plant host *Scleranthus perennis* L. It contains up to 30% kermesic acid **21** as



well as the ubiquitous carminic acid **23**.[20,21] Employed from the 6th century AD, and possibly before, this dyestuff was used in central and northern Europe especially when kermes was difficult to obtain, as in periods of military conflict.[1] Its use declined with the introduction of the American cochineal.

American cochineal was introduced to Europe by the Spaniards late in the 16th century, though it had been used in South and Central America long before.[22] It is obtained from the egg-filled female insects of *Dactylopius coccus* Costa (a parasite of the cactus of the *Opuntia* family) dried under the sun or in ovens. Like Armenian cochineal, this product consists predominantly of carminic acid **23** (> 95%) with traces of flavokermesic acid **22** and kermesic acid **21** also present. In the period between 1758 and 1858, 27,000 tons of cochineal were exported from Mexico into Europe. This was one of the largest sources of income for the country, second only to the export of silver. This high demand in Europe was due to the fact that the American cochineal had a higher content of colouring principles than the other scale insect dyes available.[1] Several attempts were made to breed cochineal in Europe, particularly in the Canary Islands, and this was successful for the first time only a few years before Mexico gained its independence in 1836. The Canary Islands eventually became one of the main cochineal suppliers in Europe.

Around 1630, it was discovered that American cochineal produced brighter reds than related plant dyes when a tin mordant was used. Prior to that date, plant and scale insect dyes produced colours of similar quality with the available mordants.

Lac was obtained from the female insects of the species, and was used in India and the Far East for hundreds of years before it was introduced to Europe in the late 18th century.[23] The major constituents are laccaic acid A **24** (> 70%) and laccaic acid B **25** (< 20%).[20,21]

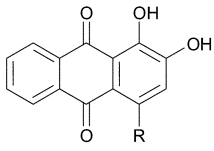
4.2 Plant anthraquinone reds

Historically, the most important red dye structures obtained from plants are again based on the anthraquinone ring system **20**. The dyes were obtained from the roots of different species of the Rubiaceae family including madder (*Rubia tinctorum* L.), wild madder (*Rubia peregrina* L.), munjeet (*Rubia cordifolia* L.), ladies' bedstraw (*Galium verum* L.) and several species of *Relbunium* native of South America. Unlike the insect-derived anthraquinones, those isolated from plants are substituted in only one of the rings.

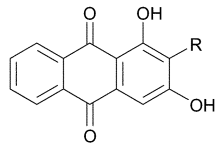
Madder in particular was a very important red dye.[24] It originated in India but during the period when it was in high demand it was widely cultivated in Europe and the Middle East. Although madder has less tinctorial power than the scale insects it has the advantage of producing shades from pinks to blacks, purples and reds with different mordants. For example, Turkey red, a very bright red dye, can be obtained from madder by a very complex method particularly suited to cotton. This method was introduced in Britain in the 18th century and large specialised dyeworks were constructed.[25]

The chemical investigation of madder dates back to 1826. The identification of alizarin **26** as the main chromophore, and the synthetic routes discovered by Graebe and Liebermann, and by Perkin in 1869 that led to the industrial production of alizarin dye (even before the exact chemical structure was known), is one of the classics of organic chemistry.[26] By 1871 synthetic alizarin was available at a fraction of the price of madder and this was said to be the origin of the expansion of the chemical industry in Germany.

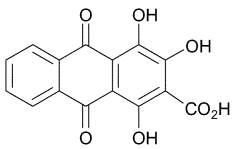
The extensive work of R. H. Thomson in the 1960s on naturally occurring quinones has shed light on the structures of the most important anthraquinone dye constituents of the Rubiaceae family.[23] The anthraquinone contents of madder roots are complex and vary with the age of the plant. For example, nineteen different anthraquinones (2% by weight of the root) have been isolated from mature plants,[27] whereas < 0.1% (by weight of the root) of a much more simple mixture of anthraquinones (alizarin **26**, purpurin **27**, pseudopurpurin **28** and rubiadin **30**) were isolated from one year old plants.[27]



26 R = H, alizarin
27 R = OH, purpurin



29 R = H, xanthopurpurin
30 R = Me, rubiadin
31 R = CH_2OH, lucidin
32 R = CO_2H, munjistin



28, pseudopurpurin

Munjistin **32**, pseudopurpurin **28**, purpurin **27** and xanthopurpurin **29** are also found in the roots of other species of the Rubiaceae family such as munjeet (*Rubia cordifolia* L.), wild madder (*Rubia peregrina* L.), and the Himalayan species (*Rubia sikkimensis* Kurz).[23]

The roots of different *Galium* spp. (also species of the Rubiaceae family) have also been used as anthraquinone dye sources. In particular the analysis of extracts from the roots of ladies' bedstraw (*Galium verum* L.) showed that alizarin **26** and purpurin **27** were the main anthraquinones present (*ca.* 70% and 15% of the total weight of anthraquinones extracted, respectively).[28] Although these two compounds were detected in an extract of a textile sample dyed with ladies' bedstraw, surprisingly rubiadin **30** was the major component.[29] It is possible that the anthraquinone content in the roots of this plant may vary with the age of the plant as reported for madder.

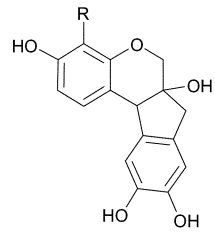
The roots of the *Relbunium* spp., which originate from South America and are also members of the Rubiaceae family, were used as red dyes. Munjistin **32**, purpurin **27**, pseudopurpurin **28**, xanthopurpurin **29** and alizarin methyl ethers have been isolated from species in this group.[19] In an extensive study of 21 *Relbunium* species pseudopurpurin **28** was found to be the main anthraquinone extracted, although munjistin **32** and purpurin **27** were also detected.[30]

4.3 Redwoods

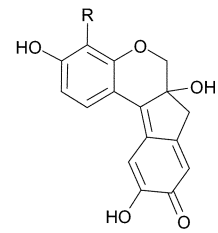
Redwood dyes have been known for nearly 700 years. They can be classified into two groups: soluble redwoods (principal colouring components are neoflavonoids), and insoluble redwoods (principal colouring components are condensed biflavonoids).

Soluble redwood dyes are extracted from various species of the genus *Caesalpinia*. The principal varieties are Brazilwood, Peachwood, Sappanwood, Limawood and Pernambuco wood, though they are frequently collectively known as Brazilwood. They are termed "soluble redwoods" because the colouring principles are readily soluble in water and they are normally used as mordant dyes.

Sappanwood (*Caesalpinia sappan* L.), native to India and Malaysia, had been imported into Europe since the Middle ages under the name of 'Brazil', derived from the Portuguese word *braza* (of Arabic origin) suggesting 'red'.[29] Brazilwood (*Caesalpinia brasiliensis* L.) originates from South America and it is due to its abundance on the Brazilian coasts that this country is so called. Pernambuco or Fernambuco wood (*Caesalpinia crista* L.), considered to be one of the best redwoods, was imported into Europe from Brazil and Jamaica. Peach or Nicaragua wood (Pau-Brasil) (*Caesalpinia echinata* L.) was once abundant on the coasts of Brazil, Nicaragua and Mexico. In all these species brazilin **33** has been isolated which by oxidation gives brazilein **35**, the chromophore in brazilwoods. Soluble redwoods were considered to be lesser dyes than madder or cochineal because they have poor fastness properties and therefore were usually used in combination with other dyes.[31]



33 R = H, brazilin
34 R = OH, haematoxylin



35 R = H, brazilein
36 R = OH, haematein

Logwood or campeachy wood (*Haematoxylon campechianum* L.), a native of Central America, also achieved commercial importance. Haematoxylin aglycone **34** results from the hydrolysis of its glycoside which exists in the fresh wood[17] and through oxidation haematein **36** is formed which is a strong chromophore. Even though the dye itself is red, it gives a range of colours when used with different mordants. These include black (copper and/or iron or chrome mordants), grey (iron mordant), blue (alum and tin mordants) and purple (alum and tin mondants) dyes which had good fastness properties and were widely used.[1]

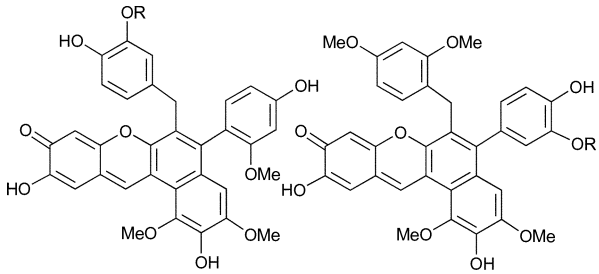
The main insoluble redwoods are sandalwood or saunderswood (*Pterocarpus santalinus* L.), indigenous to south India; narrawood (*Pterocarpus indicus* Willd.), which grows in the forests of Burma and the Philippines; barwood (*Pterocarpus soyauxii* and *Pterocarpus erinaceus*); and camwood (*Baphia nitida*), which are West Africa species. They yield much faster colours than the soluble class but the colouring matter is very sparingly soluble in water, as the name suggests. They are mainly used in combination with other dyes to obtain dark red and brown colours.

Although many natural products have been isolated from insoluble redwoods, the major colouring matters are santalins (*e.g.* **37** and **38**) (first isolated in a crude form in 1833) and santarubins (*e.g.* **39** and **40**), which are condensed biflavonoids.[32] Santalins occur in sandalwood, barwood and camwood, but santarubins are present only in the latter two species.

4.4 Other plant reds

Safflower (*Carthamus tinctorius* L.) contains a red dye that, although not light fast, has been used frequently because of the beautiful pink shades it produces as a direct dye on silk. Deriving from a species indigenous to Turkey, safflower has been cultivated since antiquity in Egypt and South East Asia and later in Europe. It is still cultivated[1] but for the oil rich seeds rather than as a source of dye.

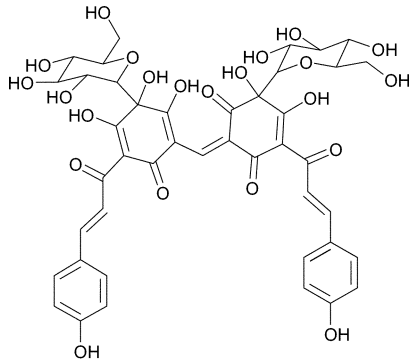
Safflower red is used as a direct dye and is suitable for most fibres. During the dyebath preparation, the petals of safflower are washed several times in water to remove yellow pigments also



37, R = H, santalin A
38, R = Me, santalin B
39, R = Me, santarubin A
40, R = H, santarubin B

present in the plant. The red pigment is water insoluble at neutral pH but can be brought into solution under alkaline conditions. The fibres are then introduced and the dyebath acidified so that the pigment precipitates in them.

The red pigment carthamin **43** was first isolated by Perkin and Kametaka in 1910,[33] but its structure (and those of the two components of safflor yellow) were not determined until the 1980s.[34,35] Carthamin is present in powdered flower petals to the extent of 0.03% (by weight), and the two yellow colouring matters in 0.1% and 0.05% (by weight) respectively.[36]



43, carthamin

4.5 An historical example

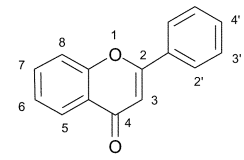
In a study of red threads taken from 18th and 19th century 'quality' Scottish tartans, the scale insect dyes, especially lac and Mexican cochineal, were identified in 84 of the 86 samples.[37] There was no evidence for the use of native dyes such as ladies' bedstraw, even for textiles made in perceptively remote locations such as the Outer Hebrides. Historical records clearly show that insect dyes were sought due to their superior colour. This is also consistent with Gaelic oral tradition which suggests that bright, not muted, colours were preferred.[37]

5 Yellow dyes

5.1 Flavonoids

Flavones **44** and flavonols (3-hydroxyflavones) are the main chromophores in flavonoid natural yellow dyes. Many occur in the plant as sugar derivatives (commonly glycosides) which are hydrolysed in the dyebath to the parent flavonoid. They are mordant dyes and bind to the metal *via* the carbonyl group and the adjacent phenol moiety. Because many plants are rich in flavonoids, no one dye source ever achieved dominance. As a consequence local sources of yellow dyes retained their importance and useful textile provenance information can often be obtained from yellow dye identification. Flavonols are more subject to degradation by photo-oxidation than flavones and so plants containing the latter were generally the more popular dye sources.

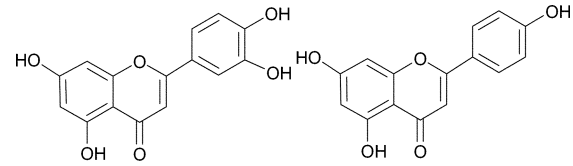
From a European perspective the main flavonoid yellow dye sources mentioned in traditional recipes are weld (*Reseda luteola*



44, flavone general structure

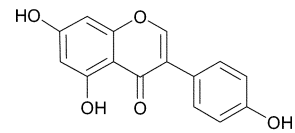
L.), young fustic (*Cotinus coggygria* Scop.), dyer's greenweed (*Genista tinctoria* L.), sawwort (*Serratula tinctoria* L. Gaud.) and dyer's camomile (*Anthemis tinctoria* L.).[38] The fruits of the different species of the *Rhamnus* spp. were also used. Later, old fustic [*Chlorophora tinctoria* (L.) Gaud.] was successfully introduced from the West Indies, and at the end of the 18th century quercitron bark (*Quercus velutina* L.) was imported from North America. Because of their good dye content these imported dyes were widely used. On the other hand, examples of locally available yellow sources which include, in the case of the north of Britain, bog myrtle (*Myrica gale* L.) and silver birch (*Betula pendula* L.), were never commercialised owing to their seasonal nature and low dye content.

Weld (*Reseda luteola* L) grows wild in most of Europe but was also cultivated. More plant material is required than for most other yellow dyes but it is mentioned in many textile dyeing recipes, suggesting that it was quite popular. When used with alum as a mordant it produces bright and fast yellow colours[17] owing to the presence of the flavones luteolin **45** and apigenin **46** as the major constituents.[1] Sugar derivatives are also present,[39] but *O*-glycosides are usually hydrolysed to the parent flavonoid in the dyebath. The flavonoid content of weld was shown to average 2% by weight.[40] Weld was also frequently used with woad or indigo to give fast green dyes.



45, luteolin **46**, apigenin

Dyer's greenweed (*Genista tinctoria* L.) is found growing wild throughout Central and Southern Europe, across Russian Asia and northward to Sweden.[41] The flavone luteolin **45** (0.3% by weight of plant material), and the isoflavone genistein **47**,[41] are the major components. Genistein 4′-methyl ether is also present.[42]

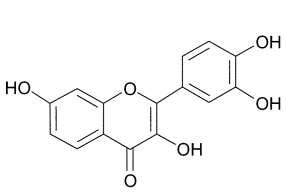


47, genistein

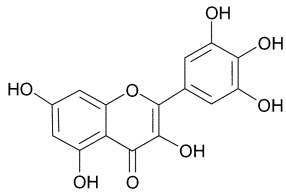
Young Fustic is the yellow wood obtained from *Cotinus coggyria* L.. This shrub was originally found in Italy, the Near East, Eastern Europe as well as France and Spain. Young fustic has been used since the Middle ages for dyeing dark shades of yellow; used as a mordant dye it produces orange-yellow to strong red-brown colours. The main colorants are two flavonols, fisetin **48** and myricetin **49** together with the aurone sulfuretin **56**.[1] It was considered to be a dye of low quality due to its low lightfastness.[17]

Sawwort (*Serratula tinctoria* L.) is a perennial plant used until the 19th century as a yellow dye.[31] Like weld, the main flavonoids found in the leaves of this plant are luteolin **45** and apigenin **46** (*c.f.* Section 5.3).[43]

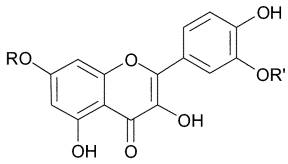
Persian berries (*Rhamnus* spp.) contain a large number of flavonoids. As well as the common flavanols such as quercetin **50** and kaempferol **53** derivatives specific to this family include rhamnetin **51**, rhamnazin **52**, rhamnocitrin **54** together with xanthorhamnin, a 3-*O*-glycoside of rhamnazin. There are also non-



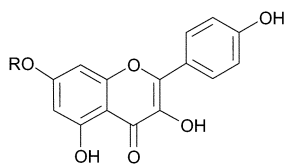
48, fisetin



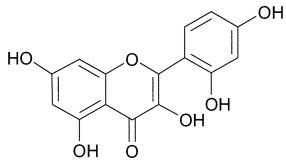
49, myricetin



50, R = R' = H, quercetin
51, R = Me, R' = H, rhamnetin
52, R = R' = Me, rhamnazin



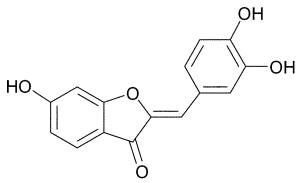
53, R = H, kaempferol
54, R = Me, rhamnocitrin



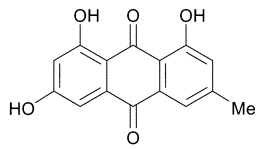
55, morin

flavonoid colouring compounds such as the anthraquinone emodin **57**.[44]

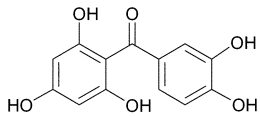
In Europe, the dye properties of dyer's chamomile (*Anthemis tinctoria* L.) were less highly considered than those of weld, but it was popular in Turkey for the manufacture of tapestries.[1] In the flowers of this yellow dye source the glycosides of luteolin **45** and apigenin **46** can be found[1] as well as quercetagetin (6-hydroxyquercetin) and patuletin (6-methoxyquercetin 7-*O*-glucoside.[42]



56, sulfuretin



57, emodin



58, maclurin

Old fustic [*Chlorophora tinctoria* (L.) Gaud.] is a large tree found in Cuba, Jamaica, Puerto Rico and other West Indian Islands. This dyestuff was first introduced into Europe in the 16th century[31] and was soon widely used as a yellow mordant dye. Although old fustic can yield bright yellows, its high content of tannins makes it difficult to control the final colour obtained. The main chromophores in this source are the flavonols morin **55** with small amounts of kaempferol **53** and the benzophenone maclurin **58**.

Quercitron bark is the inner bark of a species of North American oak, *Quercus velutina* Lamk. (or *Quercus tinctoria* L.) and has been used as a dye since the late 18th century. It grew abundantly in Pennsylvania, Georgia and the Carolinas. The bark was removed from the tree, dried and sold as a mixture of woody fibre and fine powder. Flavin is the name given to the fine brownish powder extracted from quercitron bark.[17] "It is very much stronger and yields brighter shades than the original bark".[17] The main flavonoids in this dye are quercetin **50**, quercitrin (quercetin 3-*O*-rhamnoside) and kaempferol **53**.

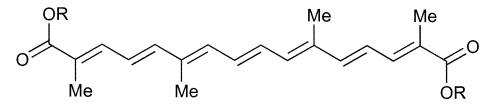
Silver birch (*Betula pendula* L.) is not a widely used dye source but it nevertheless produces bright yellow colours when used as a mordant dye. It is believed to have been used traditionally in Scotland and in Scandinavian countries.[2] The flavonoid glycosides found in the leaves of this plant are a 3-*O*-galactoside of myricetin **49** and five different *O*-glycosides of quercetin **50**.[45]

Bog myrtle (*Myrica gale* L.) is a small shrub growing extensively in the wet and boggy parts of Scotland. Several sources suggest that the leaves (either fresh or dried) were widely used in Scotland as a yellow mordant dye and is considered to be, along with heather (*Calluna vulgaris* L.), one of the finest Scottish native yellow dyes.[2] The main flavonoids extracted from the leaves of bog myrtle are *O*-glycosides of kaempferol **53**, myricetin **49**[42] and quercetin **50**.[1]

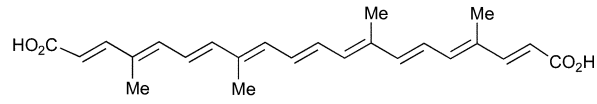
5.2 Saffron, turmeric and other yellows

Saffron is obtained from the stigmatas of the flowers of *Crocus sativus* L. and has a long history of use as a direct dye. Evidence of its use dates back to Egyptian times; it was very popular in Persia in Classical times.[31] It was later replaced by cheaper dyes, like weld, with better fastness properties. When used as a direct dye, it gives a beautiful orange yellow colour and it can also be used with alum mordant.[31] The main chromophore is crocin **60**, a glucoside of crocetin **59**, a polyunsaturated diacid.

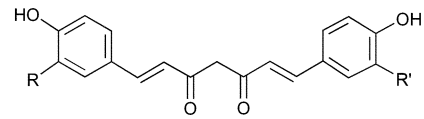
Another dye of similar chemical characteristics is annatto or orellana, extracted from the fruit of *Bixa orellana* L., a shrub indigenous to central America. The colouring principle bixin **61** is also a polyunsaturated diacid which is used as a direct dye for cotton, wool or silk.[17] Used by the Mayas and Aztecs in Mexico and the Incas in Peru, it was introduced to Europe in the 16th century but never became commercially important.



59, R = H, crocetin
60, R = gentobiose, crocin



61, bixin



62, R = R' = OMe, curcumin I
63, R = OMe, R' = H, curcumin II
64, R = R' = H, curcumin III

Turmeric or curcuma, also known as Indian saffron, is obtained from the ground roots of *Curcuma domestica* Valet. (or *Curcuma longa* L.) a plant growing abundantly in the East Indies and China.[17] It was used as a direct dye on cotton, wool or silk, mainly in combination with other dyes. The main colouring matter is a mixture of curcumin I, II and III **62–64**.

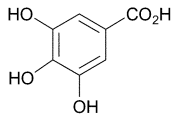
5.3 An historical example

It became apparent during conservation of an early 18th century herald's tabard (NMS 1888.303) that the stitching on the right and left sleeves was different, perhaps indicative of having been made in different workshops.[46] HPLC analysis of samples extracted from a yellow fibre taken from each sleeve of the tabard both showed the presence of luteolin **45**, apigenin **46** and a trace of a methyl ether of luteolin (3% of dyestuff). Although present in small amount, this ether is found in authentic samples of weld, but not in other common dyestuffs of which luteolin **45** and apigenin **46** are major components. The analysis therefore showed that weld was used to dye the threads used in both sleeves but evidence for place(s) of manufacture proved inconclusive.[46]

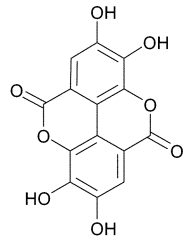
6 Brown and black dyes – tannins

Brown and black dyes absorb light over a wide wavelength range and hence their constitution is often difficult to define chemically. Oak galls and sumac are well known mordant dyes for brown and black. The colouring principles are derived from hydrolysable tannins which yield gallic acid **65** and glucose under acid hydrolysis conditions. Oak galls became very important sources of brown and black dyes due to their high tannin content (containing up to 70% by weight). The galls are formed as a reaction of *Quercus infectoria* L. buds to the egg of an insect (*Cynips* spp.).[1] The buds are collected before the insect emerges and ground to produce a light-fast black dye when used with an iron mordant. This was used very commonly in black inks. *Quercus infectoria* L. can be found in the Eastern Mediterranean and Asia Minor.

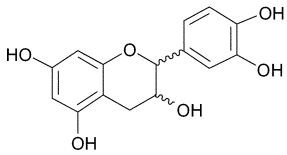
Different sumac species (*Rhus* spp.) have high levels of tannins in their leaves and there are species indigenous to Europe, India, China, Japan, North Africa and America. This dye was known and used in Egyptian, Greek and Roman times. References are also frequently made to the use of sumac in the leather tanning trade. There are other hydrolysable tannins such as those derived from ellagic acid **66**, found in the bark of oak species and chestnut tree.



65, gallic acid



66, ellagic acid



67, catechin, epicatechin

Another important group are the condensed tannins which are polymers of catechin and epicatechin molecules **67**. They are present in the bark of oak species such as *Quercus robur* L.[1]

7 Conclusions

Whilst a wide variety of plant and animal sources were used to dye textiles in historical times, the chemical classes of most blue, red and yellow dyes involved are surprisingly limited. In many cases it is now possible to determine experimentally the biological source used to dye a specific textile many hundreds of years ago, allowing chemical correlation with the archival historical record. In addition, knowledge of the fastness properties of the individual dyes provides information on the least damaging display conditions for preserving coloured historical textiles.

Acknowledgements

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