History of Natural Dyes in the Ancient Mediterranean World

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> *The colours used on textiles and artifacts, their social significance and the scope of their trade, are part and parcel of a people's overall history.*
>
> Jenny Balfour-Paul, in *Indigo*, British Museum Press, 2000

1.1 Introduction

1.1.1 Ancient Mediterranean World

The build-up of *Mare Nostrum* probably began much earlier than the 6th–5th millennium BC and there is material evidence pointing to such activity as early as the 12th–11th millennium BC [1]. *Mare Nostrum*, the Roman name for the Mediterranean Sea, was to become the home for a global market that expanded beyond its natural borders in the 1st millennium BC. The Phoenicians, the Etruscans, the Greeks and finally the Romans shaped *Mare Nostrum*, a geographic as well as a cultural domain. It was also home for the first global dye, Tyrian purple, which was traded by the ingenious and industrious Phoenicians. The purple of Tyre was famous, as were the textiles dyed and produced by the Phoenicians. It is said that the Greeks named the Phoenicians after *Phoinikes*, the ancient Greek word for 'red colour', probably as a result of their famous purple trade.

By the time of the founding of the Mediterranean civilizations, what we would consider the classical palette for natural dyes had already been established, and the most valued colours were indigo for the blues, anthraquinone-based chromophores for the reds and 6,6′-dibromoindigo for purple. These colours were traded all over the Mediterranean,

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regardless of distance to be travelled or the price to be paid. The natural sources for yellows were much more diverse, so yellows could generally be obtained locally. For dyeing, with the exception of some browns, all other colours and shades, including green and orange, could be obtained with these blue, red, purple and yellow dyes. This classical palette was preserved over centuries, if not millennia. The first adjustment resulted from the loss of Tyrian purple following the fall of Constantinople and the subsequent collapse of the Roman social and commercial web. This was followed by a new entry, cochineal red, brought by the Spanish from the New World [2]. However, even with the introduction of cochineal the chemical nature of the classical pallete was maintained, as carminic acid is still a substituted 1,2-dihydroxy anthraquinone. This classical palette was only challenged by the audacity of chemists, who created new molecules, and colours never seen before, from the mid-19th century on [3].

1.1.2 Dyes from Antiquity

Natural dyes, discovered through the ingenuity and persistence of our ancestors, can resist brightly for centuries or millennia and may be found hidden in such diverse places as the roots of a plant, a parasitic insect and the secretions of a sea snail. By contrast, the bright colours that we see in the green of a valley, the red of a poppy, the purple of mauve or the blue of cornflower are less stable. Natural dyes were used to colour a fibre or to paint. It is useful to distinguish between dyes and pigments based on their solubility in the media used to apply the colour; dyes are generally organic compounds that are soluble in a solvent, whereas pigments, used in painting, are usually inorganic compounds or minerals that are insoluble in the paint medium (oil, water, etc.) and are dispersed in the matrix. A lake pigment is a pigment formed by precipitation, namely by complexation with a metal ion, forming a dye on the surface of an inorganic substance.

Dyeing, in red, blue, purple or yellow, is a complex task that requires skill and knowledge [4]; this is true now and has been for several millennia. Colour is obtained by applying a chemical compound called a chromophore or chromogen, something that brings or creates colour. When used as a textile dye, the chromophore must also be captured as strongly as possible into the fibres; i.e. it must be resistant to washing. Dyes can bind to the surface of the fibre or be trapped within them. They are often bound to the textile with the aid of metallic ions known as mordants, which can also play an important role in the final colour obtained. Alum, as a source of the aluminium ion, is an important historical mordant and was widely used in the past. Other important mordants used in the past were iron, copper and tin ions [4,5]. Dyes, like indigo, which are trapped in the fibres due to an oxidation–reduction reaction, without the aid of a mordant, are known as vat dyes.

Natural dyes, as lake pigments, have been widely applied in painting. For example, anthraquinones and their hydroxy derivatives have been used as red dyes and pigment lakes from prehistoric times, and we can find written accounts of the use of anthraquinone reds and purples as dyes in ancient Egypt [5, 6]; anthraquinone lakes (e.g. madder red) were also very popular with Impressionist painters, including Vincent van Gogh. Lake pigments can be prepared by precipitating the dye extract with aluminium or other inorganic salts, such as alum [7]. Pure dyes such as indigo were also used as painting materials, e.g. in medieval illuminations (Figure 1.1).

Figure 1.1 *Medieval Portuguese illumination, dating from a 12–13th century, Lorvão 15, fl. 50 kept at Torre do Tombo (Lisbon). Dark blues were painted with indigo, whereas for the backgound the inorganic and precious pigment lapis-lazuli was used (See Colour Plate 1)*

These *eternal* colours will be described in more detail in the following sections, after a brief account of the analytical techniques used to reveal the secrets of these ancient materials. The natural colorants will be organized according to the colour: first the anthraquinone reds, followed by the blues and purple, where indigo and its bromo derivatives play a major role. Yellows will close this historic overview.

1.1.3 Unveiling the Secrets of Ancient Dyes with Modern Science

Identifying the dyes and dye sources used in the past has only been possible with the development, in the past two decades or so, of sensitive new microanalytical techniques [8,9]. Chromophores are extracted, then separated chromatographically and characterized by UV-Vis spectrophotometry or mass spectrometry; whenever possible comparison with authentic references is performed. Currently, the use of HPLC-DAD (high-performance liquid chromatography with diode array detection) enables dyestuff characterization from as little as 0.1 mg of thread. For unknown components, or those not characterized before, analysis by HPLC-MS (HPLC with mass spectrometric detection) may provide further information. Recently developed mild extraction methods allow more detailed chemical information to be obtained on the historical natural dyes, and as a consequence it is sometimes possible to identify the natural sources [10, 11].

Mordant analysis can also provide relevant information about the dyeing method or process used. The metal ions can be quantified by inductively coupled plasma separation with atomic emission spectrometric (ICP-AES) or mass spectrometric detection (ICP-MS) of samples (*ca.* 0.25 mg textile strands) previously digested with nitric acid solutions [12, 13]. Before the sample analysis, calibration curves must be constructed using standards. Concentration linearity in the range of ppb to ppm (or higher) can be achieved.

1.2 Ancient Reds

1.2.1 Anthraquinone Reds

The most stable reds used in antiquity are based on the 1,2-dihydroxy anthraquinone chromophore (Figure 1.2), also known as alizarin. Dyes containing anthraquinone and its derivatives are among the most resistant to light-induced fading [5]. These dyes were obtained from parasitic insects, such as the famous *Kermes vermilio*, or from the roots of plants belonging to the Rubiaceae or madder family, and were among the reds that dominated the dye markets of Europe [2, 14]. Alizarin and purpurin are the main chromophores in *Rubia tinctorum*, the most important species of the family Rubiaceae. In Persia and India, other red dyes – of animal origin – were also used. These dyes were imported, or sometimes found locally, and were considered luxury goods. Well-known examples are the reds based on the laccaic acids, kermesic acid and carminic acid (Table 1.1), from the parasite insects, lac, kermes and cochineal, respectively [2]. The female lac insect secretes a red resin, stick-lac, from which are obtained both the lac dye and the shellac resin. Common or Indian lac, *Kerria lacca* (= *Laccifer lacca*, *Carteria lacca*, *Tachardia lacca* and *Lakshadia lacca*) and *Kerria chinensis* are examples of species that have been widely exploited [5]. In both cochineal (*Dactylopius coccus*) and kermes (*Kermes vermilio*)

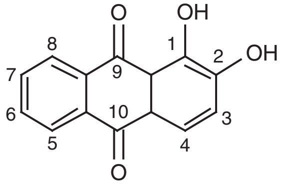
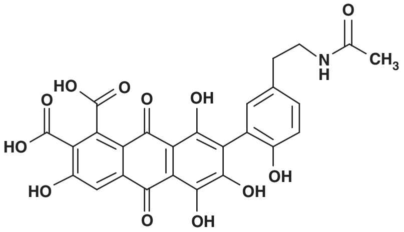
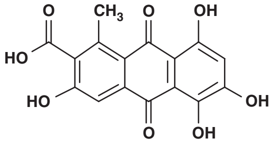
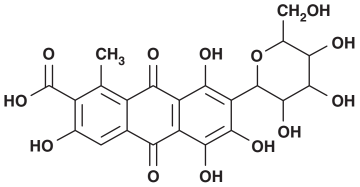


Figure 1.2 *Alizarin; 1,2-dihydroxy anthraquinone*

Table 1.1 Chemical structures for anthraquinone reds

Anthraquinone reds	
lac-dye *Kerria lacca*	
kermes *Kermes vermilio*	
cochineals *Dactylopius coccus* *Porphyrophora* sp.	

the red dye is obtained from the eggs of the female insect, and therefore there were harvest seasons that corresponded to the phase where the eggs displayed the highest dye content. It was at this stage that the impregnated female insects were cropped before depositing their eggs. *Kermes vermilio* is probably the most famous of the European insect parasites and produced a dye 'brighter than madder and faster than cochineal' [2, 7a], and was already described in the works of Theophrastus and Pliny. The word for worm in many latin languages is based on *verme-* (or *vermiculu* = small worm) and thus is the root of the word for red in several modern European languages, namely vermejo, vermelho, vermeil and vermilion in Spanish, Portuguese, French and English, respectively [15].

Other important historical insect sources of red or scarlet dyes derived from species of *Porphyrophora*, e.g. Polish cochineal (*P. polonica*) and Armenian cochineal (*P. hamelii*). In Europe, most of these sources were replaced in the 16th century by the American cochineal (*Dactylopius coccus*), which had earlier been carefully domesticated and cultivated by the indigenous peoples of the New World, and was commercialized by the Spanish empire. Although the various species of *Porphyrophora* also contain carminic acid, dried specimens of *Dactylopius coccus* have a much higher content (15–20%) of the dye [2, 5], compared with only 0.8% and 0.6% for the Armenian and Polish ones, respectively [5].

1.2.2 Redwoods

Redwoods, also known in antiquity as brasil [4, 16], were used as sources of dyes and pigment lakes [5, 7a]. It is said that the country Brasil was named after those redwoods, this possibly being the only country in the world named after a tree. The name the Portuguese had in mind was *Terra da Vera Cruz* (Land of the Holy Cross). The reds obtained from the bark of the tree are not as stable as the previously described anthraquinone reds, but they were much more affordable and were widely used for dyeing and in medieval miniature painting [17, 7a] as well as in cosmetics. In his book [16], Cennino Cennini recommends the use of a good *verzino* (brazilwood) to highlight the reddish-blue tone of purified lapis lazuli. This good *verzino* should be obtained from a young lady, who, using it for lipstick and other cosmetics, would take care that she had obtained a well-prepared product of a nice colour.

The main colorant in *Caesalpinia brasiliensis*, *C. echinata, C. sappan, C. violacea* and *Haematoxylum brasiletto* is brazilin. In *Haematoxylum campechianum* the main colorant is haematoxylum. Through oxidation, brazilin and haematoxylum are converted to the darker red compounds, brazilein and haematein, respectively (Figure 1.3) [18].

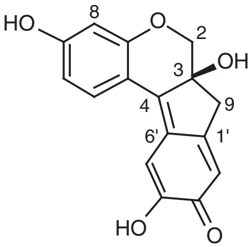


Figure 1.3 *Brazilein; haematein is 8-hydroxy brazilein*

1.2.3 Flavylium/Anthocyanin Reds

Anthocyanins are ubiquitous water-soluble colorants responsible for the impressive red and blue colours of flowers and fruits (Figure 1.4). Natural flavylium reds can be considered their aglycone ancestors. There are several references to the use of these

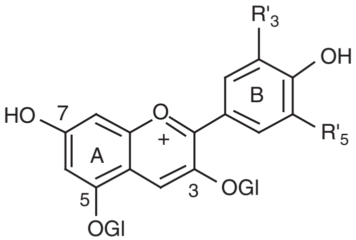
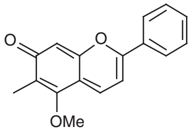
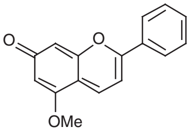
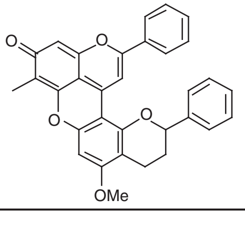
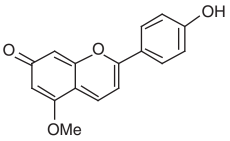


Figure 1.4 *In the basic structure of anthocyanins, a hydroxyl group is present at positions 4′ and 7, and a sugar at position 3 (monoglycoside) or positions 3 and 5 (diglycoside)*

compounds to substitute for unavailable inorganic pigments or to give special lighting effects in ancient illustrations. The use of these materials ranges from the Roman Empire (described by the famous architect Vitruvius) to paintings of the Maya civilization [19]. Their use as 'watercolours' has been described in several treatises or recipe books on illumination painting, including the Strasbourg manuscript, an 'Old Portuguese work on manuscript illumination: the book on how one makes colours of all shades' and 'De Arte Illuminandi' [20]. Anthocyanins were used to produce clothlets/watercolours [16], as described by Cennino Cennini in the 15th century, and to dye textiles [5, 21, 22]. With anthocyanins the colour domain ranges from red to blue, but with natural flavylium dyes it is limited to the yellow-red. One of the most famous examples of a natural flavylium red can be found in dragon's blood resins.

Dragon's blood is a natural resin, having a deep, rich red colour, which is obtained from various trees, namely from *Dracaena draco* and *Dracaena cinnabari*, which belong to the Liliaceae family. The resin appears in injured areas of the plant and has been used for centuries for diverse medical and artistic purposes [23]. These resins contain not only the red chromophores but also additional flavonoids and steroids; Dragon's blood resins have been used in traditional Chinese medicine. The molecules responsible for the red colour of the resin obtained from the palm tree *Daemonorops draco* (*Calamus draco* was used in the past) have been characterized by Brockmann *et al.* and named dracorubin and dracorhodin (Table 1.2) [24]. Brockman *et al.* concluded that dracorhodin was a natural flavylium chromophore belonging to the Anthocyanin family. More recently, other natural flavylium chromophores, such as dracoflavylium, have been identified in *Dracaena draco, Dracaena cinnabari* and other Dracaenaceae [23] (Table 1.2).

Table 1.2 *Chemical structures responsible for the red colour in Dragon's blood resins. The structures correspond to the quinoid bases (A)*

Dracorhodin	*Nordracorhodin*	*Dracorubin*	*Dracoflavylium*
			

1.2.3.1 Equilibria in Solution

As stated above, dracorhodin and dracofalvylium are natural flavylium reds related to anthocyanins. Anthocyanins are characterized by a hydroxyl group in position 4′ and 7, and a sugar in position 3 (monoglycosides) or 3 and 5 (diglycosides). On the other hand, in anthocyanidins the hydroxyl groups take the positions of the glycosides, leading to unstable structures in solution. In contrast, the so-called deoxyanthocyanidins correspond to 'anthocyanidins' lacking the hydroxyl in position 3 (but bearing a hydroxyl in position 5), and are quite stable in solution [19, 25].

In the 1970s, it was firmly established by Dubois and Brouillard (anthocyanins) [26a] and McClelland (synthetic flavylium salts) [26b] that both families of compounds undergo multiple structural transformations in aqueous solution, following the same basic mechanisms [22, 27] (Figure 1.5). The flavylium cation (**AH+**) is the dominant species in very acidic solutions, but with increasing pH a series of more or less reversible chemical reactions take place: (1) proton transfer leading to the quinoidal base (**A**), (2) hydration of the flavylium cation giving rise to the colourless hemicetal (**B**), (3) a tautomerization reaction responsible for ring opening, to give the pale yellow Z-chalcone, form (**Cc**), and, finally, (4) *cis–trans* isomerization to form the pale yellow E-chalcone (**Ct**). Furthermore, at a higher pH, and depending on the number of hydroxyl groups, further deprotonated species are found, such as $\mathbf{Ct}^{n-}$ and $\mathbf{A}^{n-}$. The relevant contributers to colour are $\mathbf{AH}^+$ and the quinoid bases, **A** and $\mathbf{A}^-$. The red colour of dragon's blood resin was found to be due to the red quinoid bases of the respective yellow flavylium cations [23].

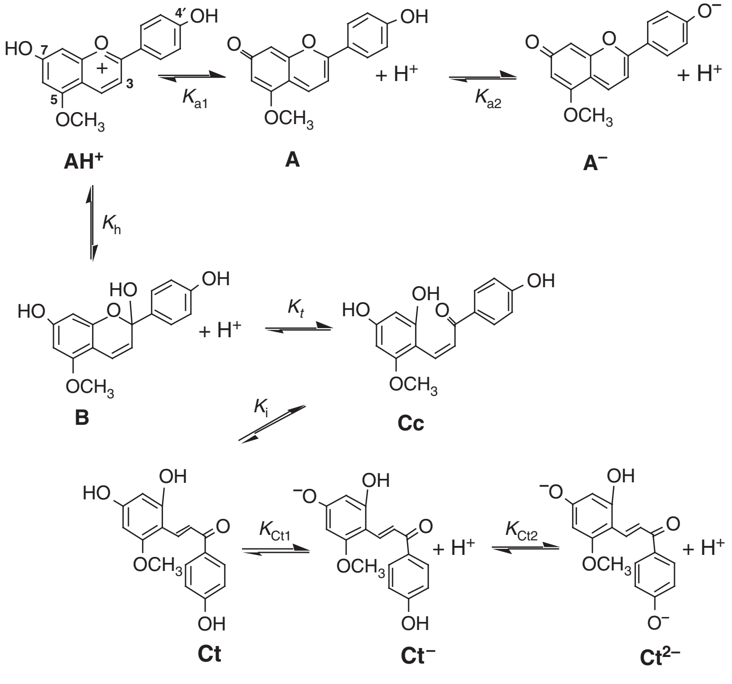


Figure 1.5 Scheme of chemical reactions for dracoflavylium. Reprinted with permission from Reference [23], Melo, M. J., et al., Chem. Eur. J., **13**, 1417–1422 (2007). © 2007, Wiley–VCH

1.3 Ancient Blues

1.3.1 Indigo Blues

Indigo blue was one of the earliest and most popular dyestuffs known to man (Figure 1.6). It is still a universally used colour, as the worldwide use of indigo-dyed blue jeans can

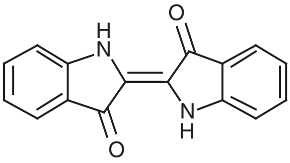


Figure 1.6 Indigo (=indigotin)

attest. Indigo, as the name implies, has its origins in ancient India. In the great civilizations of Egypt, Greece and Rome, it was prized for its quality as a dye even though transportation costs meant it was very expensive [28]. Indigo sources are found all over the world, and several plants were most probably used in antiquity. Julius Caesar, in his *De bello Gallico*, describes the warrior skin paintings of his Gaulish adversaries as being obtained from a blue juice; the warriors' faces were frightening and they believed that dyeing the skin would protect them, making them invulnerable!

Isatis tintoria was grown in Europe, but it is known that indigo from *Indigofera tinctoria* was traded to Europeans, namely from Persia to Muslim Spain, and from there distributed to other European countries [29]. Species of *Indigofera* produced a high-quality indigo, which was used in medieval illuminations (Figure 1.1) [30].

Indigo is also one of the most light-stable organic dyes, a characteristic that explains not only its wide use in antiquity and the pre-modern area but also its longevity as a colorant [31]. The stability of indigo is also the reason why it was used in medieval illuminations and by some of the great masters of the 17th and 18th centuries, such as Rubens [32]. Usually, with the exception of some necessary and almost irreplaceable colour lakes, organic compounds were avoided in oil painting, as it was known that they were far less stable to light than the inorganic available pigments. Highly pure indigo was an exception.

In 1865 Bayer started his work on indigo, and some years later proposed the chemical structure as well as a possible synthesis of indigo. At the time, indigo was an important molecule due to its commercial value as a dye; synthetic indigo paved the way not only for the development of 'big' German chemical and pharmaceutical industries but also helped to end the colonial production of indigo, which until then had come from natural sources in British, French and Iberian colonies. This particularly affected the British Indian colony, which was the major producer at that time. Even at the beginning of the 21st century, indigo is still a surprisingly important dye. Inasmuch as indigo can be obtained from natural sources using microbial fermentation, its production using 'green' chemistry is of considerable interest [33].

The precursors of indigo (= indigotin) can be extracted entirely from plants. The extract, a solution of the water-soluble indoxyl glucoside, indican, is hydrolysed via fermentation to give indoxyl (Figure 1.7), which will further react with another indoxyl molecule producing indigo or with isatin resulting in indirubin, a reddish dye [5, 34]. The indigo derivatives are generally known as vat dyes and, in their oxidized forms, are insoluble in water [5].

A common characteristic of vat dyes is the presence of one or more carbonyl groups, which, when treated with a reducing agent in the presence of an alkali, form a water-soluble dye known as the leuco species. The process of dyeing a textile with these species involves

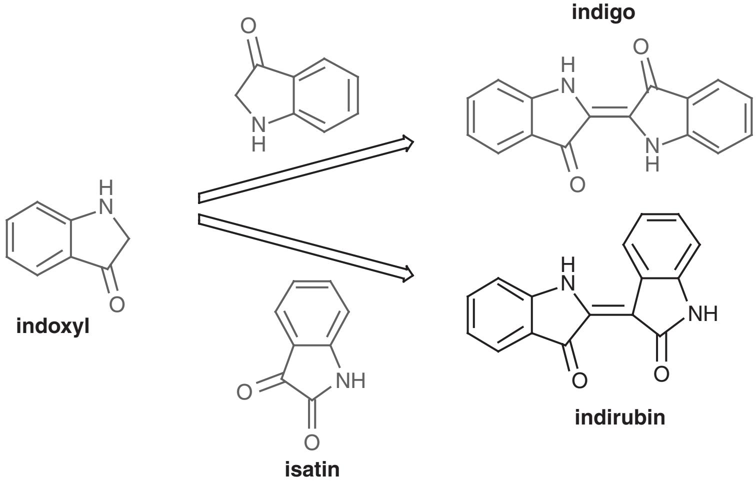


Figure 1.7 Indigo dye bath

the use of the vat dye in a reducing media, leading to its leuco form [5, 33]. The explanation of the blue colour of indigo and its derivatives has also been an intriguing and fascinating subject, and was explored with great detail and ingenuity during the 1970s and 1980s of the 20th century [35]. It has been discovered that the fundamental chromophore of the indigo dyes includes the central double bond (connecting the two rings) together with the nitrogen and carbonyl groups [35a–c]. Substitution in different ring positions of indigo is likely to promote significant shifts in both the visible long-wavelength and UV bands [35d].

Indirubin can be formed during the dyeing with indigo, namely in the interface where more oxygen is available; this is the reason why it is also known as the red shade of indigo [36]. As already mentioned, indirubin is formed through the reaction of indoxyl anion with isatin, a side reaction in the reaction of indoxyl anion with itself to give indigo (Figure 1.7). It can also be present in the Muricidae (see Section 1.4 on ancient purple). As for dragon's blood, its renaissance has been a consequence of its pharmaceutical activity [36]. Marine indirubines are contained in the purple pigment derived from marine selfish of the Muricaidae and Thaisidae families.

1.3.2 Anthocyanin Blues

As reported in Section 1.2.3, there are several ancient references to the use of anthocyanin watercolours for painting, particularly for illuminations, e.g. as described in the Strasbourg Manuscript [20a]. In the past, extracting and capturing an anthocyanin blue was not an easy task; these blues are complex, self-assembled, supramolecular structures, bound by non-covalent interactions. The overall supramolecular complex must be preserved, not just the monomeric subunits, otherwise the colour is lost. For example, to obtain a 'cornflower' blue, the supramolecular assembly must be maintained within a certain pH range. Apparently this was achieved by following the recipes described in ancient treatises such as the Strasbourg Manuscript [19, 20]. The structure of the self-assembled supramolecular pigment from the blue cornflower (*Centaurea cyanus*) was elucidated by Kondo *et al.* [37a]; the supramolecular components are succinylcyanin (Sucy), a cyanidin chromophore with a sugar in position 3, malonylflavone (Mafl), a flavone with a sugar in position 3, and the metal ions Mg^{2+} and Fe^{3+}, the exact composition being $[Sucy_6Mafl_6Fe^{3+}Mg^{2+}]$. These authors proposed that the supramolecular complex should be similar to that of commelinin (Figure 1.8). The metal centre organizes the geometry of the complex, which is held together by weak hydrophobic interactions, such as π–π stacking of the aromatic rings and hydrogen bonding through the sugar moieties [37].

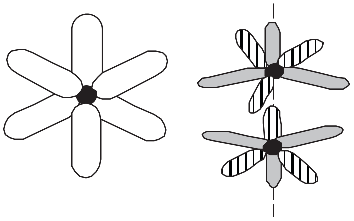


Figure 1.8 *Schematic representation of the blue supramolecular complex involving anthocyanins. The two metals (dark spheres) are at the centre of two planes; a top view of one of these planes is represented on the left. Each metal coordinates three anthocyanin chromophores (vertical lines); three flavones (grey) are intercalated with the three anthocyanins, filling the void spaces*

In both cornflower blue and commelin, the blue colour is only stable in concentrated solutions. When diluted, the solution quickly becomes colourless due to dissociation of the components of the complex.

1.4 Ancient Purple (Tyrian Purple)

The high status of the wearer of purple-dyed textiles in the past was never to be surpassed by any other colour, natural or synthetic. Purple has a commercial and economic history but also a cultural one, with profound political and religious impact [5, 38, 39]. Purple was a status symbol for the Roman emperors as well as, in later years, for the powerful representatives of the emergent power, the Catholic Church. It was the Persian monarchs who, as early as the 9th century BC, made purple the official mark of royalty. The kings of Israel also wore purple. Imperial or divine purple was used for powerful emotional moments, where authority was conveyed, in rituals of high visual impact. Purple was also the colour of the mantle Christ used in His sacrifice. Thus it is the symbol of His sacrifice but also of His glory, the glory He found when sacrificing Himself for mankind [38]. With it, purple achieved the status of a sacred colour. The original colour was the most expensive dye in the market, but even its imitations (as purple obtained by a combination of indigo with madder or other similar red) could maintain its status symbol [40]. In our present times, it would be hard to find an example that could convey the impact of purple in antiquity.

The first true purple dye, Tyrian purple, was obtained from Mediterranean shellfish of the genera *Purpura* (Figure 1.9) [41]. The Mediterranean purple molluscs, *Murex brandaris*, *Murex trunculus* and *Purpura haemastoma*, have recently been renamed *Bolinus brandaris*, *Hexaplex trunculus* and *Stramonita haemastoma*, respectively, with the result that *Murex* and *Purpura* have disappeared from the name, and with it the memory of their importance as historic dyes was cancelled [39]. As already mentioned in the introduction, it was one of the luxury goods traded by the Phoenicians, and hence the common name 'Tyrian purple', named after the Phoenician city of Tyre. This purple dye was produced by extraction of the secretions of the hypobranchial glands of Mediterranean gastropod molluscs, probably since the mid-2nd millennium BC. Piles of purple-yielding mollusc shells on Crete and along the Levantine coast, and elsewhere in the Mediterranean, have provided the primary archaeological evidence for the extent of this industry [41b]. Pigments from these invertebrates were used in the Akrotiri frescos, on Santorini in Greece, which date back to the 17th century BC [42].

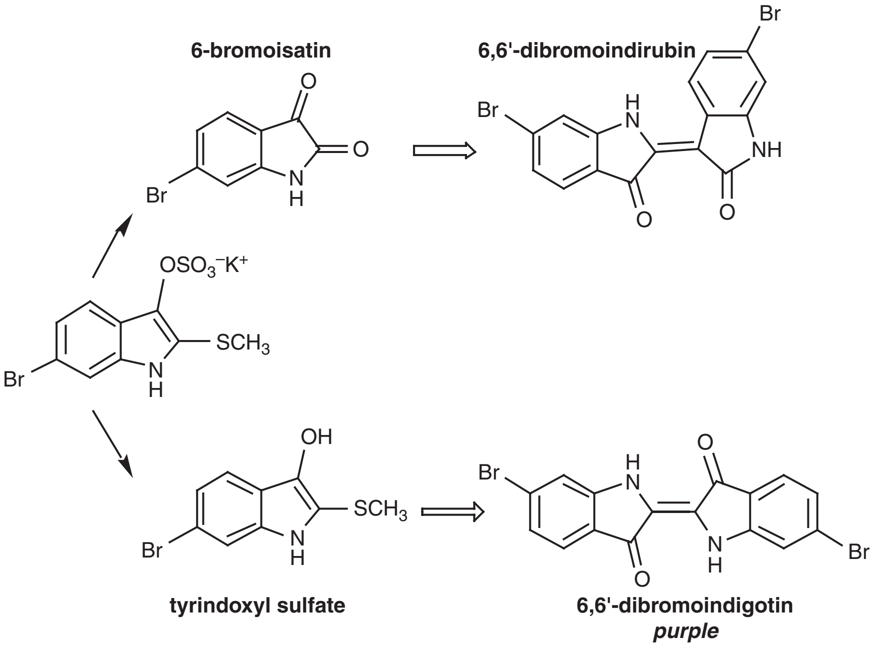


Figure 1.9 Percursors and schematic pathways for the chromophores obtained from the muricids

The percursors of Tyrian purple and derivatives such as monobromoindigo are stored in the hypobranchial glands of live muricids and can be released after death or when the mollusc is pressed and rubbed. The entire biosynthetic pathway for the production of dye precursors is yet to be elucidated, but the compounds generated in the pathway are biologically active and include choline esters, which may be employed as muscle relaxants and indole derivatives with cytotoxic (anticancer activities) and microbial properties [43]. Tyrian purple and its derivatives also occur naturally in the egg masses of the Muricidae.

In Figure 1.9 are depicted the coloured compounds that can be obtained as final products from the glandular secretions: true purple (6,6′-dibromoindigotin), the monobrominated indigo derivatives (6- and 6′-bromoindigotin), brominated indirubin derivatives (6,6′-dibromoindirubin, 6- and 6′-bromoindirubins), indirubin and indigo [44]. It is worth pointing out that indigo is blue, whereas its brominated derivatives are violet and indirubin is reddish. The shade of purple obtained depends on the species of mollusc and on the dyeing process used. McGovern and Michel report the chemical distribution of these insoluble dyes to be the following: *M. brandaris* and *P. haemastoma* produce mainly 6,6′-dibromoindigotin (purple), while *M. trunculus* gives also indigotin (blue), i.e. indigo in addition to the purple. The first steps of the synthesis are believed to involve an enzymatic process resulting in the production of tyrindoxyl sulfate (Figure 1.9), which is followed by chemical processes involving light and oxygen. Because the hypobranchial glands of the species that produces indigo, *M. trunculus*, contain a more efficient enzyme, *M. trunculus* was mixed with other species for purple vat dyeing in the Mediterranean. Hence the final colour obtained ranged between reddish purple and bluish violet [41b].

The story of purple was to be continued in the 19th century with the discovery of mauve by Perkin and the rebirth of the ancient *purple mania* as *mauve mania* [45]. The synthesis of mauveine in 1856 [46] – subsequently known as aniline purple (1857), Tyrian purple (1858) and mauve dye (from 1859) – is a story that demonstrates how a well-prepared mind can change history. The synthesis of the iconic mauveine is a major landmark in the history of science and technology, as it led to the establishment of the synthetic dye industry. In this case, the colour purple did not denote power or status, but opened a new era for chemistry.

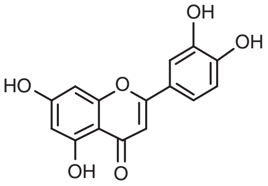
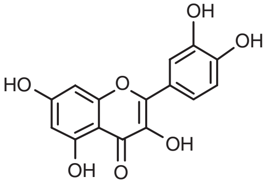
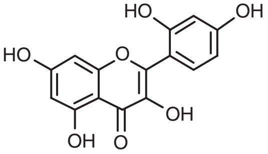
1.5 Ancient Yellows

1.5.1 Flavonoid Yellows

Contrary to the situation for the reds, the sources for yellow dyes is enormous, as indicated in Table 1.3. Knowledge of many of these natural sources for yellow and how to dye with them has been lost, and therefore many of these species are not described or well documented in the literature. In addition, the yellow dyes are considerably less resistant to fading [8, 47, 48] than the reddish or bluish colours, and therefore it may be expected that the actual yellow colours observed today are different from the originals. Also, the reason why many old tapestries look blue (and red) is that all the yellows have faded, leaving only indigo blue (and some anthraquinone reds). The yellow chromophores based on the flavone chromophore can be divided in two large groups, those with and those without a hydroxyl group in the 3 position (Figure 1.10 and Table 1.3) [8, 49].

To the first group belong important chromophores such as apigenin and luteolin. These appear in the plant as glycosides, i.e. with sugar residues attached to one or more of the hydroxyl positions shown in Figure 1.10. Luteolin and its sugar derivatives are considered to be among the most stable yellows, and thus were widely used for dyeing. Perhaps the most used plant source for luteolin derivatives was weld, *Reseda luteola* (*lírio-dos-tintureiros* in Portuguese, *arzica* in Italian and *gaude* in French) (Table 1.3) [7a].

Table 1.3 Chemical structures for flavone and flavonol yellows

Flavones and flavonol yellows	
Weld *Reseda luteola*	 Luteolin 5, 7, 3', 4'-OH-flavone
Persian berries *Rhamnus* spp.	 Quercitin 3, 5, 7, 3', 4'-OH-flavone
Old fustic *Chlorophora tinctoria*	 Morin 3, 5, 7, 2', 4'-OH-flavone

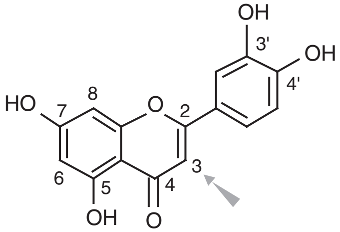


Figure 1.10 Luteolin (flavone)

The second group, the flavonols (3-hydroxy flavones), contains flavonoids, widely known for their antioxidant properties, e.g. quercetin, kaemferol and rhamnetin, and also morin, myrecetin and fisetin, just to name a few. These yellows are found in a variety of plants, including Persian berries (*Rhamnus* spp.), young fustic (*Cotinus coggygria*), old fustic (*Chlorophora tinctoria*) and yellow wood (*Solidago virgaurea*). Other sources are onion skins (*Allium cepa*), sawwort (*Serratula tinctoria*), dyer's greenweed (*Genista tinctoria*), marigold (*Chrysanthemum* spp.), dyer's chamomile (*Anthemis tinctoria*), flax-leaved daphne (*Daphne gnidium*), etc. [5].

1.5.2 Carotenoid Yellows

Carotenoids are present in our everyday diet, in the red of a tomato, in the orange of a carrot or, less frequently, in the golden yellow of 'Riso alla Milanese'. The traditional yellow used in this Italian receipe for rice is obtained from the stigmas of saffron, *Crocus sativus*, a beautiful flower, 10 cm high, and has been used for dyeing since antiquity. The main chromophore is the aglycone, crocetin, which can be found in the form of the glycoside, crocin (Figure 1.11) or with other substituted glycoside patterns. Other carotenoid yellows were used in the past, but the most famous was the golden saffron yellow.

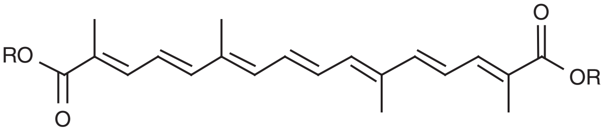


Figure 1.11 Crocetin, R=H, and crocin, R=β-D-gentiobiosyl (a diglycoside), are all-trans carotenoids found in saffron

1.5.3 Chalcone and Aurone Yellows

Like saffron, these chromophores absorb light at longer wavelengths and have more golden/orange hues. Chalcone yellows have been recently identified in ancient Andean textiles, as marein and other glycosides of okanin (2′,3′,4′,3′,4-pentahydroxychalcone), possibly obtained from a *Coreopsis* species (Figure 1.12) [50, 51].

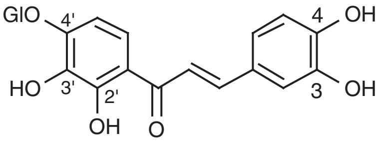


Figure 1.12 Marein, okanin 4′-O-glucoside (chalcone)

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References

1. F. Braudel, *The Mediterranean in the Ancient World*, Penguin Books, 2002.
2. (a) R. A. Donkin, Spanish red. An ethnogeographical study of cochineal and the Opuntia cactus, *Transactions of the American Philosophical Society,* New Series, **67**(5), 1–84 (1977). (b) R. A. Donkin, The insect dyes of western and west-central Asia, *Anthropos*, **72**, 647–680 (1977).
3. P. Ball, *Bright Earth: Art and the Invention of Color*, Farrar, Straus and Giroux, New York, 2002.

4. F. Brunello, *L'Arte della tintura nella Storia dell'Aumanità*, Neri Pozza, Vicenza, 1968.
5. (a) D. Cardon, *Le Monde des Teintures Naturelles*, Éditions Belin, Paris, 2003. (b) D. Cardon, *Natural Dyes. Sources, Tradition, Technology and Science*, Archetype Publications, 2007.
6. R. Halleux (ed.), *Les Alchimistes Grecs: Papyrus de Leyde, Papyrus de Stockholm, Recettes*, Les Belles Lettres, Paris, 2002.
7. (a) J. Kirby, Paints, pigments, dyes, in T. Glick, S. J. Livesey and F. Wallis (eds), *Medieval Science, Technology, and Medicine – an Encyclopedia*, Routledge, 2005. (b) A. Burnstock, I. Lanfear, K. J. van der Berg, L. Carlyle, M. Clarke, E. Hendriks and J. Kirby, Comparison of the fading and surface deterioration of red lake pigments in six paintings by Vincent van Gogh with artificially aged paint reconstructions, in Preprints of the 14th Triennial Meeting of the ICOM Committee for Conservation, Vol. 1, 2005, pp. 459–466.
8. E. Ferreira, A. Hulme, H. McNab and A. Quye, The natural constituents of historical textile dyes, *Chem. Soc. Rev.*, **33**, 329–336 (2004).
9. (a) J. Wouters and A. Verhecken, The coccid insect dyes: HPLC and computerized diode-array analysis of dyed yarns, *Studies in Conservation*, **34**, 189–200 (1989). (b) J. Wouters and A. Verhecken, The scale insect dyes (*Homoptera*: Coccoidea). Species recognition by HPLC and dyode-array analysis of the dyestuffs, *Annales de la Société Entomologique de France*, **25**(4), 393–410 (1989).
10. X. Zhang and R. A. Laursen, Development of mild extraction methods for the analysis of natural dyes in textiles of historical interest using LC-diode array detector-MS, *Anal. Chem.*, **77**(7), 2022–2025 (2005).
11. P. Guinot and C. Andary, Molecules involved in the dyeing process with flavonoids, in 25th Meeting on *Dyes in History and Archaeology*, Suceava, Romania, 21–22 September 2006 (forthcoming in *Archetype*).
12. D. A. Peggie, *The Development and Application of Analytical Methods for the Identification of Dyes on Historical Textiles*, PhD Dissertation, The University of Edinburgh, 2006.
13. M. J. Melo, A. Aguiar-Ricardo and P. Cruz, A green approach to antique textile cleaning, in Preprints of the 14th Triennial Meeting of the ICOM Committee for Conservation, Vol. 2, 2005, pp. 944–954, James & James, 2005.
14. R. Chenciner, *Madder Red. A History of Luxury and Trade*, Curzon Press, 2000.
15. H. Schweppe and H. Roosen-Runge, Carmine-cochineal carmine and kermes carmine, in Robert L. Feller (ed.), *Artists' Pigments – A Handbook of Their History and Characteristics*, Vol. 1, Cambridge University Press, Cambridge, 1986.
16. (a) Cennino Cennini, in F. Brunello (ed.), *Il Libbro dell'Arte,* Neri Pozza Editore, Vicenza, 1997. (b) Clothlets, translated from the Italian *pezzuole*; small pieces of cloth imbibed with the dye, that would be applied as a watercolour.
17. P. Roger, I. Villela-Petit and S. Vandroy, Les laques de brésil dans l'enluminure médiévale: reconstituition à partir de recettes anciennes, *Stud. Conserv*., **48**, 155–170 (2003).
18. D. Cardon with C. Higgitt, Appendix: Chemical structures of the dyestuff groups, in Reference [5b].
19. M. J. Melo, Missal blue: anthocyanins in nature and art, in 21st Meeting on *Dyes in History and Archaeology*, Avignon, France, 10–12 October 2002 (forthcoming in *Archetype*).
20. (a) V. and R. Borradaile, *The Strasburg Manuscript – A Medieval Painters' Handbook*, Transatlantic Arts, New York, 1966. (b) S. Blondheim, An old Portuguese work on manuscript illumination, *JQR*, **XIX**, 97–135 (1928).
21. F. Brunello, *De Arte Illuminandi e altri Trattati sulla Miniatura Medievale*, Neri Pozza Editore, Vicenza, 1992.
22. A. Roquero, *Tintes y Tintoreros de America*, Ministerio de Cultura, Madrid, 2006.
23. M. J. Melo, M. Sousa, A. J. Parola, J. S. Seixas de Melo, F. Catarino, J. Marçalo and F. Pina, Identification of 7,4′-dihydroxy-5-methoxyflavylium in 'Dragon's blood'. To be or not to be an anthocyanin, *Chem. Eur. J.*, **13**, 1417–1422 (2007).
24. (a) H. Brockmann and H. Junge, Die Konstitution des Dracorhodins, eines neuen Farbstoffes aus dem 'Drachenblut', *Ber. Dtsch. Chem. Ges. B*, **76**, 751–763 (1943) (b) forenames>H. Brockmann and R. Haase, Über Dracorubin, den roten Farbstoff des 'Drachenblutes', *Ber.*, **69**, 1950–1954 (1936).

25. M. J. Melo, M. Moncada and F. Pina, On the red colour of raspberry (*Rubus idaeus*), *Tetrahedron Lett.*, **41**, 1987–1991 (2000).
26. (a) J. R. Brouillard and J. E. Dubois, Mechanism of structural transformations of anthocyanins in acidic media, *J. Am. Chem. Soc.*, **99**, 1359 (1977). (b) R. A. McClelland and S. Gedge, Hydration of the flavylium ion, *J. Am. Chem. Soc.*, **102**, 5838–5848 (1980).
27. (a) F. Pina, Thermodynamics and kinetics of flavylium salts – malvin revisited, *Chem. Soc., Faraday Trans.*, **94**, 2109–2116 (1998). (b) F. Pina, M. Maestri and V. Balzani, in H. S. Nalwa (ed.), *Handbook of Photochemistry and Photobiology*, Vol. 3, *Supramolecular Photochemistry*, American Scientific Publishers, 2003.
28. J. Balfour-Paul, *Indigo*, British Museum Press, 2000.
29. O. R. Constable, *Trade and Traders in Muslim Spain*, Cambridge University Press, Cambridge, 2003.
30. M. Clarke, Anglo-Saxon manuscript pigments, *Stud. Conserv.*, **49**, 231–244 (2004).
31. (a) J. Seixas de Melo, A. P. Moura and M. J. Melo, Photophysical and spectroscopic studies of indigo derivatives in their keto and leuco forms, *J. Phys. Chem. A*, **108**, 6975–6981 (2004). (b) Micaela M. Sousa, Catarina Miguel, Isa Rodrigues, A. Jorge Parola, Fernando Pina, J. Sérgio Seixas de Melo and Maria J. Melo, A photochemical study on the blue dye indigo: from solution to ancient Andean textiles, *Phtochem. Photobiol. Sci.*, **7**, 1353–1359 (2008).
32. M. van Eikema Hommes, *Discoloration in Renaissance and Baroque Oil Paintings*, Archetype Publications, 2004.
33. (a) A. Berry, T. C. Dodge, M. Pepsin and W. Weyler, Application of metabolic engineering to improve both the production and use of biotech indigo, *J. Ind. Microbiol. Biotech.*, **28**, 127–133 (2002). (b) A. N. Padden, V. M. Dillon, P. John, J. Edmonds, M. D. Collins and N. Alvarez, Clostridium *used in mediaeval dyeing,* Nature, **396**, 225–225 (1998).
34. (a) R. J. H. Clark, C. J. Cooksey, M. A. M. Daniels and R. Withnall, Indigo-red, white and blue, *Educ. Chem.*, 16–19 (1996). (b) C. J. Cooksey, Tyrian purple: 6, 6′-dibromoindigo and related compunds, *Molecules*, **6**, 736 (2001).
35. (a) M. Klessinger, Captodative substituent effects and the chromophoric system of indigo, *Angew. Chem. Int. Ed. Engl.*, **19**, 908–909 (1980). (b) E. Wille and W. Lüttke, 4,4,4′,4′-Tetramethyl-δ2,2′-bipyrrolidine-3,3′-dione, a compound having the basic chromophore system of indigo, *Angew. Chem. Int. Ed. Engl.*, **10**, 803–804 (1971). (c) G. Pfeifer, W. Otting and H. Bauer, Octahydroindigo, Angew. Chem. Int. Ed. Engl., 15, 52 (1976). (d) P. W. Sadler, Absorption spectra of indigoid dyes, *J. Org. Chem.*, **21**, 316–319 (1956). (e) G. M. Wyman, Reminiscences of an accidental photochemist, *EPA Newsletter*, **50**, 9–13 (1994).
36. L. Meijer, N. Guyard, L. A. Skaltsounis and G. Eisenbrand (eds), *Indirubin, the Red Shade of Indigo*, Life in Progress, Roscoff, France, 2006.
37. (a) T. Kondo, M. Ueda, M. Isobe and T. Goto, A new molecular mechanism of blue color development with protocyanin, a supramolecular pigment from cornflower, Centaurea cyanus, Tetrahedron Lett., **39**, 8307–8310 (1998). (b) T. Kondo, K. Yoshida, A. Nakagawa, T. Kawai, H. Tamura and T. Goto, Structural basis of a blue-colour development in flower petals from Commelina communis, Nature, **358**, 515–518 (1992). (c) T. Goto and T. Kondo, Structure and molecular stacking of anthocyanins – flower color variation, *Angewandte Chemie Int. Ed. Engl.*, **30**(1), 17–33 (1991).
38. Guglielmo Cavallo, La porpora tra scienze e culture. Una introduzione, in Oddone Longo (ed.), *La Porpora, Realtà e Immaginario di un Colore Simbolico*, Istituto Veneto di Scienze, Lettere ed Arti, Venezia, 1998.
39. R. Haubrichs, Natural history and iconography of purple shells, in Reference [36].
40. D. Cardon (ed.), *Teintures Précieuses de la Méditerranée: Poupre, Kermès, Pastel*, Musée des Beaux-Arts de Carcassonne – Centre de Documentació I Museu Tèxtil de Terrassa, Carcassonne, 1999.
41. (a) P. E. McGovern and R. H. Michel, Royal purple dye: the chemical reconstruction of the ancient Mediterranean industry, *Acc. Chem. Res.*, **23**, 152–158 (1990). (b) P. E. McGovern and R. H. Michel, Royal purple and the pre-Phoenician dye industry of Lebanon, *Masca Journal*, **3**, 67–70 (1984).
42. S. Sotiropolou and I. Karapanagiotis, Conchlian purple investigation in prehistoric wall paintings of the Aegean area, in Reference [36].

43. C. B. Westley, K. L. Vine and K. Benkendorff, A proposed functional role for indole derivatives in reproduction and defense Muricidae (Neogastropoda: Mollusca), in Reference [36].
44. (a) Z. C. Koren, High-performance liquid-chromatographic analysis of an ancient tyrian-purple dyeing vat from Israel, *Is. J. Chem.*, **35**, 117–124 (1995). (b) Zvi C. Koren, Historico-chemical analysis of plant dyestuffs used in textiles from ancient Israel, inM. V. Orna (ed.), *Archaeological Chemistry: Organic, Inorganic and Biochemistry Analysis*, ACS Symposium Series 625, 1996.
45. (a) A. S. Travis, *The Rainbow Makers – The Origins of the Synthetic Dyestuffs Industry in Western Europe*, Lehigh University Press, Bethlehem, Pennsylvania, 1993. (b) S. Garfield, *MAUVE. How One Man Invented a Color That Changed the World*, W. W. Norton & Company, 2002.
46. J. Seixas de Melo, S. Takato, M. Sousa, M. J. Melo and A. J. Parola, Revisiting Perkin's dye(s): the spectroscopy and photophysics of two new mauveine compounds (B2 and C), *Chem. Commun.*, 2624–2626 (2007).
47. (a) M. Heitor, M. Sousa, M. J. Melo, J. Hallett and M. C. Oliveira, The colours of the carpets, in T. Pacheco Pereira and J. Hallett (eds), *The Oriental Carpet in Portugal. Carpets and Paintings, 15th–18th Centuries*, Museu Nacional de Arte Antiga, 2007. (b) J. S. de Melo, M. J. Melo and A. Claro, As moléculas da cor na arte e na natureza, *Química-Boletim da Sociedade Portuguesa de Química*, **101**, 44–55 (2006).
48. H. Böhmer, *Koekboya, Natural Dyes and Textiles: a Colour Journey from Turkey to India and Beyond*, Remhob-Verlag, Ganderkesee, 2002.
49. (a) E. Haslam, *Practical Polyphenols. From Structure to Molecular Recognition and Physiological Action*, Cambridge University Press, Cambridge, 1998. (b) J. B. Harbone, *The Flavonoids – Advances in Research since 1986*, Chapman & Hall, London, 1994.
50. X. Zhang, R. Boytner, J. Cabrera and R. Laursen, Identification of yellow dye types in pre-Columbian Andean textiles, *Anal. Chem.*, **79**, 1575–1582 (2007).
51. M. J. Melo, I. Rodrigues, A. Claro, M. Montague and R. Newman, The color of Andean textiles from the MFA-Boston collection, in 26th Meeting on *Dyes in History and Archaeology*, Vienna, Austria, 7–10 November 2007 (forthcoming in *Archetype*).