T10.2 Organic colorants in ancient and contemporary art

Dyes, Dyeing and Lake Pigments – Historical Background

Jo Kirby

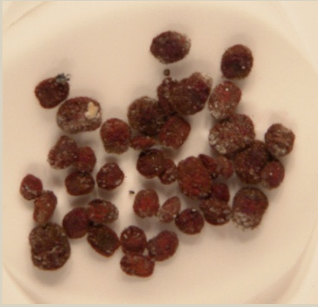
Back to the Roots – Workshop on the Preparation of Historical Lake Pigments

Doerner Institut, Munich, 23–25 March 2011

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes






- **Red**: roots of *Rubia* spp. (madder, wild madder) and *Galium* spp. (bedstraws), flowers of *Carthamus tinctoria* (safflower), heartwood of *Caesalpinia* spp. (soluble redwoods), scale insect dyes *Kermes vermilio* (kermes), *Porphyrophora* spp. (Old World cochineals), *Dactylopius coccus* (Mexican cochineal), *Kerria lacca* (lac) ...




Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

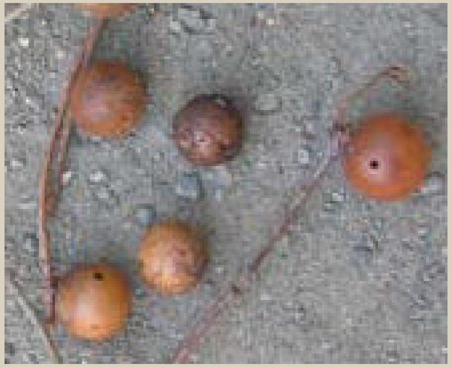

Yellow: green plant and flowers of *Reseda luteola* (weld), *Genista tinctoria* (dyer's broom or greenweed), *Serratula tinctoria* (sawwort), *Daphne gnidium* (trentanel), berries of *Rhamnus* spp. (buckthorn), wood of *Cotinus coggygria* (young fustic), *Maclura tinctoria* (old fustic), *Quercus velutina* (black oak – quercitron), stigmas of *Crocus sativus* (saffron), seeds of *Bixa orellana* (annatto), root of *Curcuma longa* (turmeric) ...

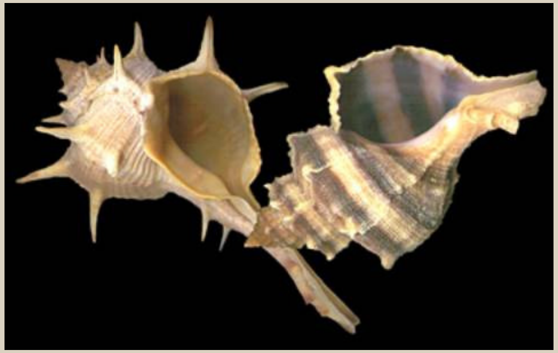


Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

- **Brown, grey, black**: galls from *Quercus* spp. (oak), bark and wood of *Castanea sativa* (chestnut), bark of *Alnus* spp. (alder), leaves of *Rhus coriaria* (Sicilian sumac), leaves and galls of *Pistacia* spp., peel of fruits of *Punica granatum* (pomegranate) ...
- **Black**: As above and *Haematoxylum campechianum* (logwood)
- **Blue**: *Indigofera* spp., *Isatis tinctoria* (woad), berries of *Vaccinium myrtillus* (bilberry) and similar
- **Purple**: *Bolinus brandaris* (spiny dye-murex), *Hexaplex trunculus* (banded dye-murex), *Stramonita haemastoma* (red-mouthed rock-shell) – shellfish purple, lichens including *Roccella tinctoria* (orchil), *Ochrolechia tartarea* (cudbear – litmus) and many others





Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

- No **green** dyes: have to dye with blue and yellow or adjust colour of yellow dye with mordant (but see below)
- Combinations of dyes were widely used to give a huge range of colours
- Some dyes were (or are) used as pigments to a greater extent than they are in dyeing:

Sap green: the juice of ripe berries of *Rhamnus* spp. (buckthorn, Persian berries, *stil de grain*) mixed with alum

Folium or tournesol, juice extracted from *Chrozophora tinctoria* onto pieces of linen, dried and stored (these are known as clothlets); the colour (bluish under alkaline conditions) can then be extracted in water for use

The juice from the petals of cornflowers, irises, poppies and other flowers is used similarly

All for use in watercolour

Detail from the Wollaton Antiphonal, East Anglian School, 15th Century, f.246. © University of Nottingham, Manuscripts and Special Collections

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

In practice, the range of dyes used for pigment making is very much smaller than that used for dyeing, although we should remember that some dyes suitable for use on a small scale, for home dyeing or for cheaper purposes would not be used on a large scale as their quality is unsuitable.

Galium verum L., lady's bedstraw, a wild plant from the madder family; the roots contain dye, but are thin and not rich in colouring matter.

The most important dyes used for pigment making are red and yellow

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

Red dyes

- kermes
- Polish cochineal, Armenian cochineal and other *Porphyrophora* spp.
- Mexican cochineal
- lac dye
- madder

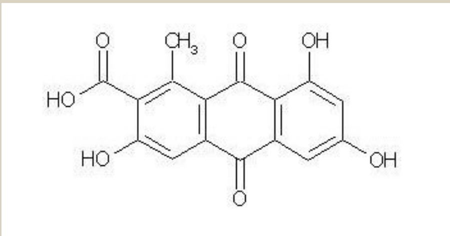
} anthraquinone dyes

- soluble redwoods (sappanwood, brazilwood) — homoisoflavonoid dye
- safflower — *C*-glucosylquinochalcone

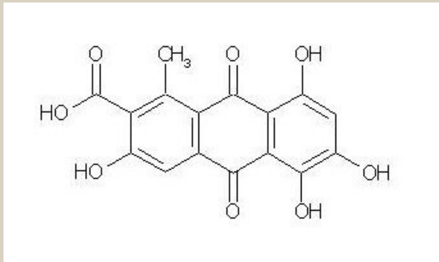
Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

- *Kermes vermilio* Planchon is a scale insect parasitic on *Quercus coccifera* L., an evergreen oak, found around the Mediterranean in Spain, southern France, north Africa and in the eastern Mediterranean, but now very rare. The dyestuff contains red kermesic acid and a proportion of yellow flavokermesic acid (also found in the related lac dye).



flavokermesic acid



kermesic acid

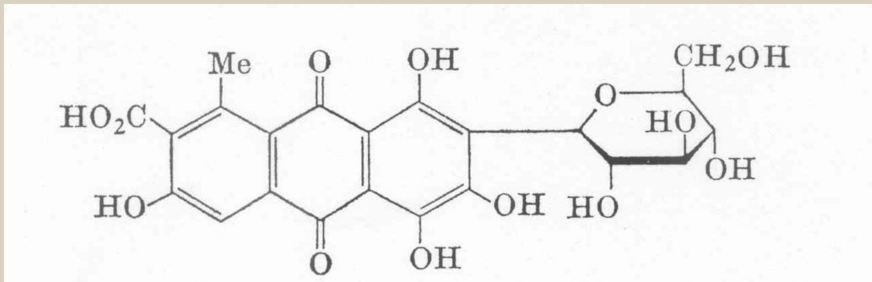
Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

- Cochineal, *Dactylopius coccus* Costa, is also a scale insect, parastic (but cultivated) on the nopal cactus in Mexico. It became available in Europe during the 16th century. Its superior dyestuff content meant that it quickly ousted kermes and also the unrelated (and incorrectly called) Old World cochineals, found in various parts of eastern Europe and Asia,
- *Porphyrophora polonica* L., Polish cochineal
- *Porphyrophora hamelii* Brandt. , Armenian or Ararat cochineal

and there are (or were) other species.

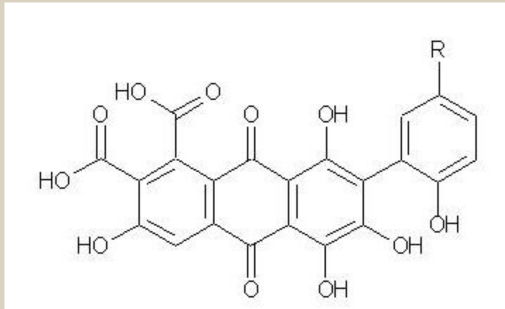
The dyestuff present is carminic acid. Polish cochineal also contains a marked proportion of kermesic acid.



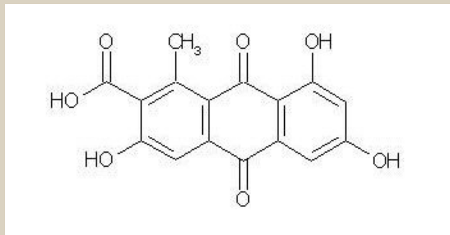
Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

- Lac dye is produced by the scale insect *Kerria lacca* Kerr, and several other species. The insect, which is parasitic on several tree species in India and the Far East, secretes a substantial protective coating that covers the twigs in a brown mass, enclosing each insect in its own cell. This is known as stick lac. The purified resin-like substance is better known as shellac, for which the insect is now 'farmed', but it was an extremely important source of dye for centuries. The colouring matter contains several water-soluble and closely similar laccaic acids, of which the most important is laccaic acid A, and some alkali-soluble constituents, including erythrolaccin. As lac lakes were made directly from sticklac, both erythrolaccin (etc.) and the shellac constituents may be found in the lake.



laccaic acids A, B, C,.E



flavokermesic acid (laccaic acid D)

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

- Madder, *Rubia tinctorum* L. (family Rubiaceae) and related species, including
- *Rubia peregrina* L., wild madder

  both of which are found widely in Europe and madder itself has been cultivated for centuries. Other species are found in India and the Far East. Some members of a widespread related group, the bedstraws, including
- *Galium verum* L., lady's bedstraw

  also contain dye with a similar range of constituents.

The dye is obtained from the root.

R. tinctorum L.

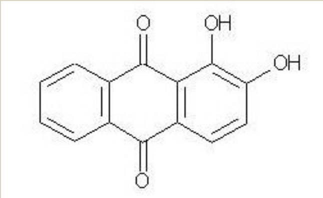
R. peregrina L.

G. verum L.

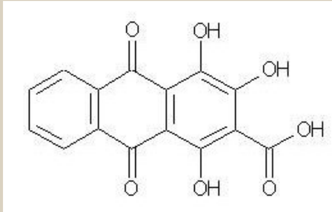
Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

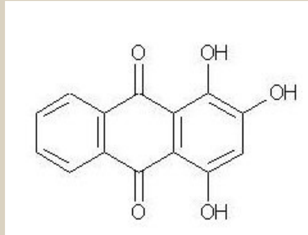
- Madder anthraquinones include



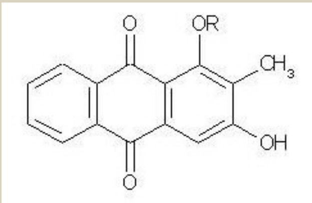
alizarin



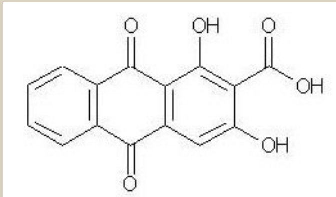
pseudopurpurin



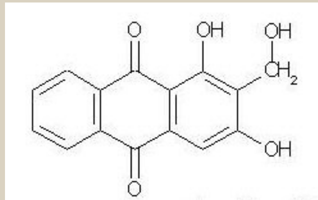
purpurin



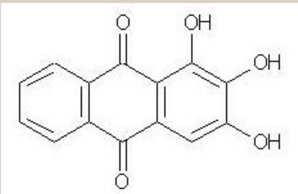
rubiadin, etc



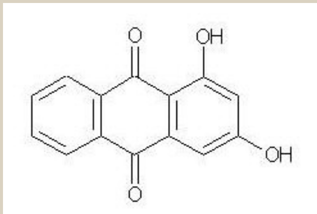
munjistin



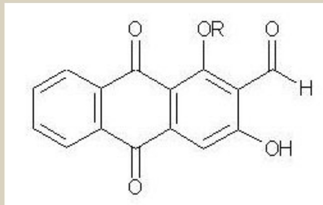
lucidin



anthragallol



xanthopurpurin



damnacanthal,
nordamnacanthal

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

Homoisoflavonoid dyes are found in the so-called soluble redwoods, loosely known as brazilwood. These closely related trees include

- *Caesalpinia sappan* L., sappanwood, found in central and southern India, Burma, Thailand, Indochina, southern China, Malaysia
- *Caesalpinia echinata* Lamarck, pernambuco wood, found in Brazil
- *Haematoxylum brasiletto* Karsten, peachwood, found in Central America

(The closely related logwood, *Haematoxylum campechianum* L., also from Central America, gives a blue-black dye.)

C. sappan L.

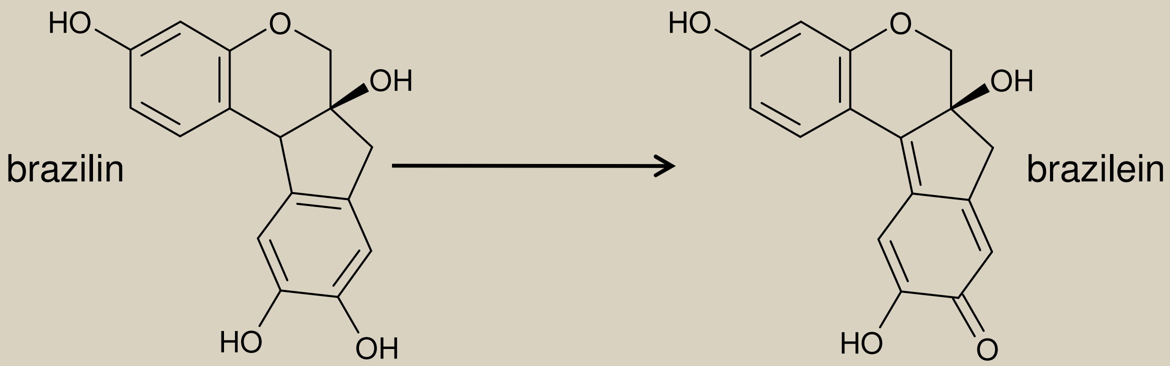
C. echinata Lamarck

H. brasiletto Karsten

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

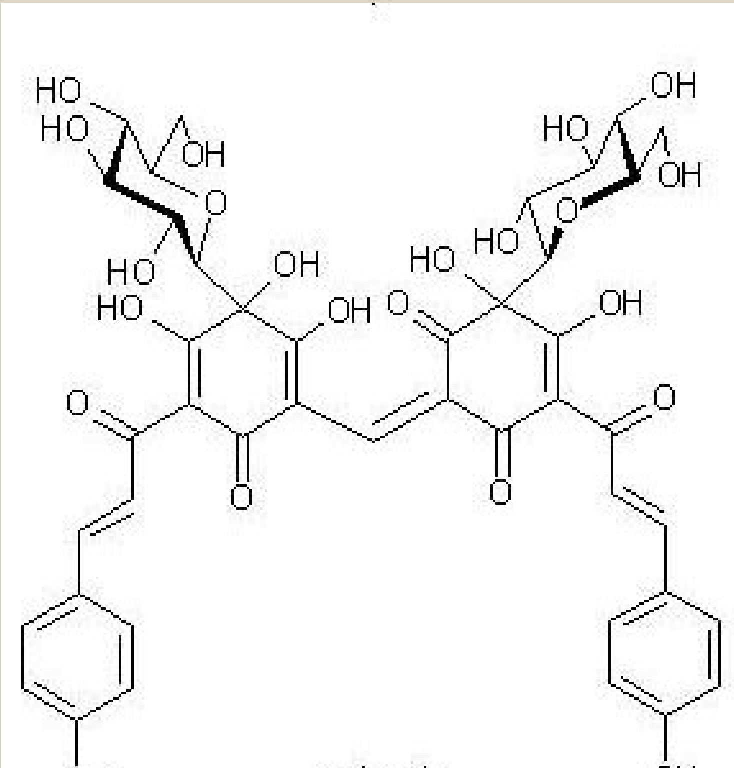
- The dye is obtained from the heartwood. The principal constituent present in the wood is the colourless brazilin; this is readily oxidised by the air (e.g., when the wood is sawn or rasped for use) to brazilein.



Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

- The flowers of safflower, *Carthamus tinctorius* L. contain two dyes, a water-soluble yellow which is usually discarded and an alkali-soluble red which can only be extracted after the yellow has been thoroughly washed out of the petals. The principal constituent of the red dye is the *C*-glucosylquinochalcone, carthamin.



Natural dyes

Yellow dyes

- weld
- dyer's broom
- sawwort
- buckthorn
- quercitron
- young fustic
- saffron

weld, dyer's broom, sawwort: dye from green parts (including flowers

buckthorn: dye from unripe berries

quercitron, young fustic: dye from wood

weld, dyer's broom, sawwort, buckthorn, quercitron, young fustic: flavonoid dyes

saffron: dye from stigmas — carotenoid

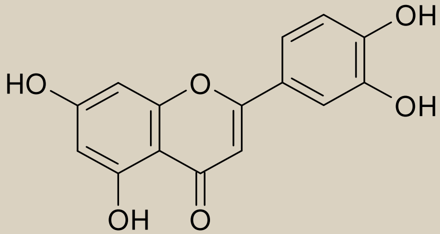
but no evidence to date that sawwort was used for pigment preparation

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

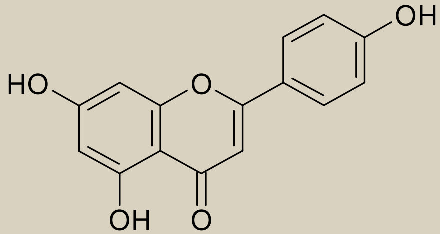
Natural dyes

Weld, *Reseda luteola* L.

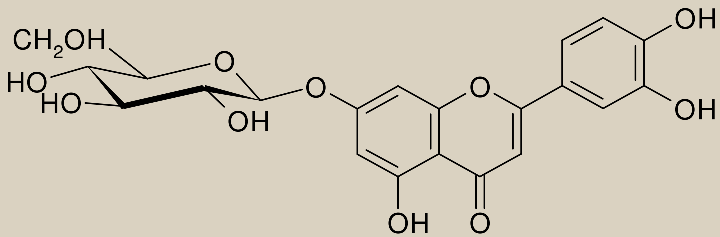
Dye constituents include:



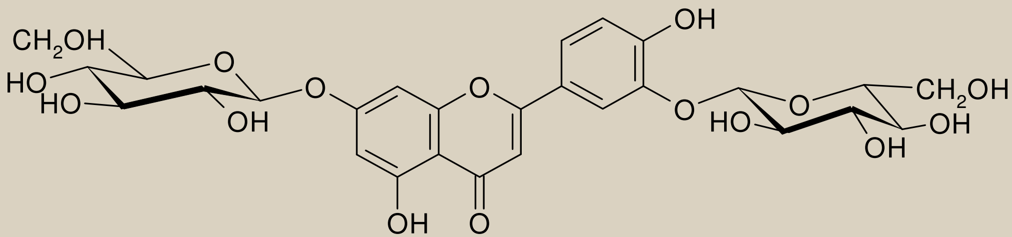
luteolin



apigenin



luteolin-7-glycoside



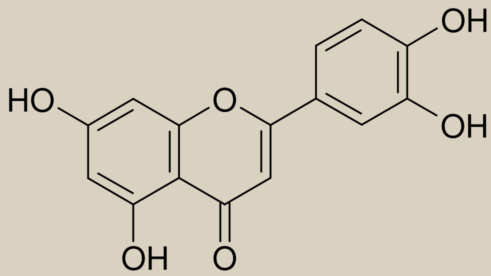
luteolin-3',7-diglycoside

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

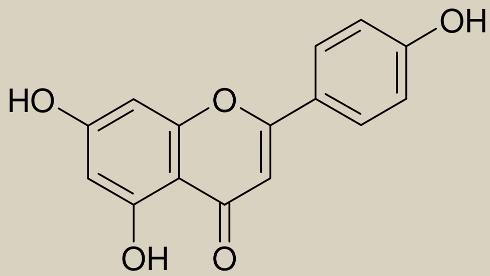
Natural dyes

Dyer's broom, *Genista tinctoria* L.

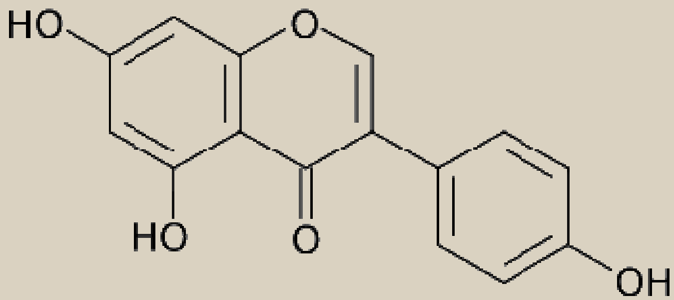
Dye constituents include:



luteolin



apigenin



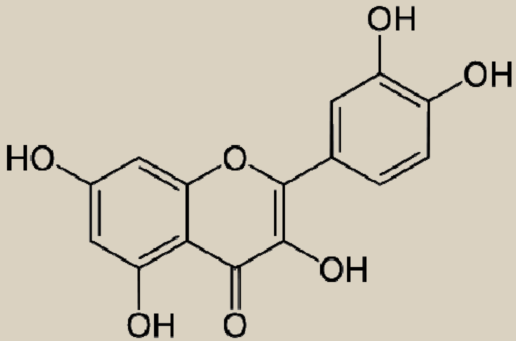
genistein

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

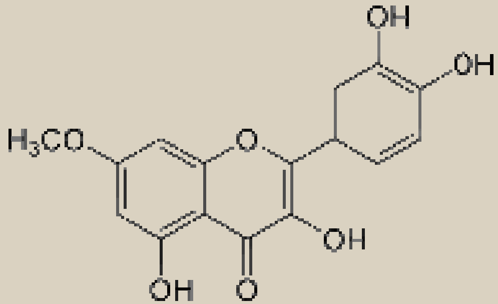
Natural dyes

Buckthorn, *Rhamnus catharticus* L. and other species. Dye is obtained from unripe berries

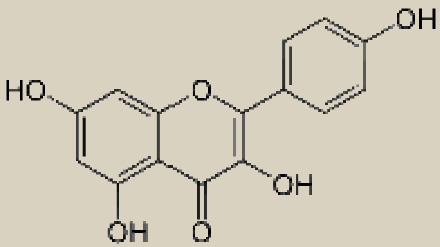
Dye constituents include:



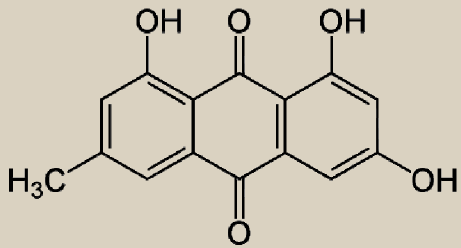
quercetin



rhamnetin



kaempferol



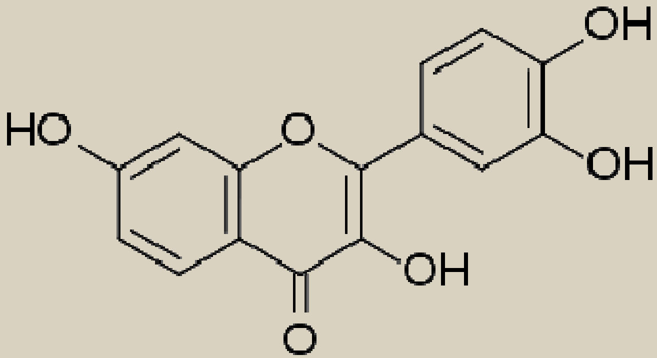
emodin

Quercitron dye, from the American black oak, also contains quercetin

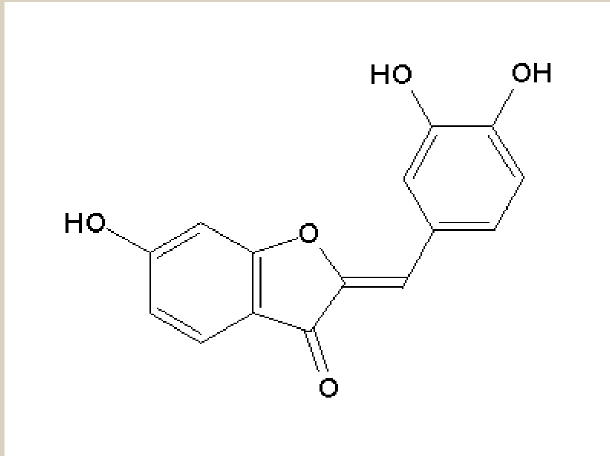
Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Natural dyes

Young fustic, *Cotinus coggygria* Scop.



fisetin



sulfuretin

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Dyes and pigments

- A colorant used to dye textile, leather, wood or other material is in **liquid** form; it may or may not require a chemical adjunct – a mordant – to enable it to bond with this material
- A pigment needs to be in **solid** form in order for it to be mixed with a suitable binding medium to form the paint. Some dyes (e.g. indigo, shellfish purple) are solid and can be used directly; most need to be converted to a solid form. A few (e.g. saffron, tournesole, etc.) are used directly as liquids in watercolour

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Definition of a lake pigment

... and a lake is a pigment made by precipitating (or adsorbing) a dye onto an insoluble, relatively inert substrate. The traditional definition gives the substrate as hydrated alumina – in practice this is too restrictive.

The pigment thus has two parts, the coloured dye and the substrate, and characteristics such as opacity and working properties are determined by the substrate.

The mordant of a textile dye is of similar importance

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Dyeing and mordants

Considering dyes as textile colorants first, dyes may be described as

- Direct : soak or boil dye in water or other liquid; soak textile in bath (e.g. saffron, lichens)
- Vat: indigo and shellfish purple – reduce insoluble dye to soluble yellowish form under alkaline conditions; allow textile to absorb dye; expose to air to oxidise
- Mordant: most others. The mordant may have an important influence on the dye, its colour and its stability, quite apart from its function of attaching the dye firmly to the textile by complex-formation

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Dyeing and mordants

Some salts used as dyeing mordants are also used in lake pigment making

- Aluminium: identified on textiles from c. 1000BC. From potash alum, $KAl(SO_4)_2 \cdot 12H_2O$, also alunogen, ammonium alum, etc; the most important and widely used variety; obtained from Egypt, Greece and, in the 15th century, Tolfa north of Rome. From the end of the 16th century, exploitation of shales found across Europe : alumina content converted to aluminium sulphate or ammonium alum. Brightens colours
- Tin: developed in the 17th century by Cornelis Drebbel who observed the effect of a solution of tin in nitric acid on cochineal; process developed by his sons-in-law, the Kuffler brothers, in Stratford; now usually tin(II) chloride, $SnCl_2$. Brightens colours considerably; particularly associated with cochineal but used with other reds and yellows

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Dyeing and mordants

Iron, copper and chromium salts, all of which darken colours, are rarely found in lake pigments (occasionally from the 19th century)

- Iron: the earliest identified variety (Egypt 1500–1300BC), recipes using iron salts occur in the Leyden and Stockholm papyrus (early 4thC AD); darkens colours and used for browns, greys, particularly black with galls and other tannins, also logwood. From iron(II) sulphate, $FeSO_4{\cdot}7H_2O$; also iron rust with vinegar, chalcopyrite (double sulphate of iron and copper), etc.
- Copper: from copper sulphate, $CuSO_4{\cdot}5H_2O$, or acetate (verdigris); associated with iron mordants from Antiquity (due to impurity of salts) and also darken colours; particularly used with yellows to give an olive or bronze green and verdigris is mentioned for this purpose in the Stockholm papyrus
- Chromium: used from the 19th century, e.g. for blacks with logwood, in the form of potassium dichromate, $K_2Cr_2O_7$
- Tannins: also contribute to preparation of cellulosic fibres for dyeing (usually galls used); contribute to the mordanting of fibres if present; used to weight silk after degumming

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Dyeing

Not all dyes were considered suitable for use on all textiles: in important dyeing centres in Italy and France and other parts of Europe a distinction was made between dyes deemed to be high in quality and sufficiently fast for use on high-quality textiles such as silk and the finest wool. These included the scale insect dyes, kermes and the Old and New World cochineals, used on the very highest quality textiles, and madder. The use of lac, very important in pigment making in 14th- and 15th-century Italy (and elsewhere), for example, was very restricted in Italian textile dyeing. In 17th-century France, the distinction between the dyes of *grand* and *petit teint* was defined in statutes by Colbert in the 1670s; *petit teint* items included things like ribbons, aprons, items that were being redyed. It was well known that the dye extracted from sappanwood or brazilwood was not light-fast and there were many regulations against its use (it was a *petit teint* dye). To some extent, similar distinctions are found in the contemporary red lake pigments.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Dyeing

Four important developments in dyeing are also significant for lake pigment making:

- The discovery in the 1640s of the use of tin as a mordant salt with cochineal to give a brilliant scarlet red, closer to that of kermes
- The introduction of dyes from the Americas into Europe. These included the red dyes Mexican cochineal and brazilwood (Pernambuco wood) and the brown/ yellows old fustic and quercitron (from the black oak, a 19th-century import). Of these, by far the most significant was the introduction of cochineal during the 16th century. Cochineal contains carminic acid, like the Old World *Porphyrophora* spp. (kermes contains a different but related dyestuff), but as the quantity of dye present in the insect was far greater (about 10 times that of kermes and each cochineal insect contains about 20% dyestuff by weight!) it was far more efficient in use. The Old World insects could not compete and gradually their use decreased. Brazilwood was imported from *c*. 1500 (largely taking over from the long-used south-east Asian sappanwood).

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacitieselucidation ' Programme GA No. FP7-228330

Dyeing

- The third development was the research into madder during the late 18th and 19th centuries, particularly in France, resulting not only in the discovery of Turkey red dyeing, but also in the research that led to the isolation and identification of alizarin by Robiquet and Colin in 1826, improvements in the extraction of the dye and the huge growth in the madder industry, until the elucidation of the molecular structure and synthesis of alizarin by Graebe and Liebermann brought this industry to a halt.
- Research into chemical structures and synthetic chemistry in the 19th century led to the development of synthetic dyes: William Henry Perkin was apparently actually trying to synthesise the anti-malaria drug quinine when he produced mauveine in 1857, the first of many synthetic dyes, some of which were used in pigment manufacture.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacitieselucidation ' Programme GA No. FP7-

Lake pigments

- We have already seen that the range of dyes used is smaller and, as insoluble pigments like indigo can be used directly, red and yellow colorants are used for pigment making (remember that there is also a wide range of mineral pigments available for use)
- As with dyeing, the introduction of Mexican cochineal was of major importance
- Mixtures of dyes in one pigment are not common before the 17th century; there are some examples thereafter, notably in yellows
- There is a significant change in the making of red lake pigments from kermes, cochineal and madder dyes at some point, perhaps during the 14th century (or earlier?) and another some time around the end of the 17th. Between these dates, these pigments were almost always made from textile shearings, not from the raw material itself

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Names for red lake pigments

There is an interesting feature about the names for the pigments

- *Lacca* – Latin, Italian, etc.
- *Lack* – German, Dutch
- Lake – English
- *Laque* – French
- *Cynople*, *senaper*, *synoper/sinoper*, *sinopre* (Latin *sinoplum*) – English, French
- *Parißrot* German, Dutch
- *Roset*, *rose*, *roseto*, *rösel* – rose pink pigments made from redwood dyestuff.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Names for yellow lake pigments

- *Ancorca* – Spanish
- *Arzica*, *giallo santo* – Italian
- *Beergael*, etc. – German
- *Pincke*, *pynck* – English
- *Scheijtgeel*, etc. – Dutch
- *Schütt Gelb*, etc. – German
- *Stil de grain*, etc. – French

do not relate to a common root!

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Lake pigment substrates

The substrate of a lake is

- insoluble in the paint binding medium
- usually, but not always, inorganic (i.e. a mineral substance of some sort)
- usually translucent (depending on the binding medium)
- inert with respect to other materials present in the paint
- NB The physical properties of the substrate dictate the handling properties of the pigment and thus, when bound in the medium, the paint.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Lake pigment substrates

Varieties of substrate:

- Usually a form of hydrated alumina
- Can be made from other white or translucent material: calcium-containing natural earth, ground egg shells, marble, lead white, flour ...
- Often made from Al and Ca salts, giving a mixture
- Sometimes, generally from the 19th century, may find coloured earth pigments of one sort or another
- Sometimes very little in the way of a conventional substrate, although some Al salt may be present (carmines, those made from dyed wool, yellows used for ‘stained cloths’ in 14th-century England consisting of deposited weld or broom dye with alum)

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Hydrated alumina substrates

- The most commonly found in red lakes, apart from those made using soluble redwood (brazilwood) dyes
- In general formed by the reaction between potash alum (potassium aluminium sulphate, $AlK(SO_4)_2 \cdot 12H_2O$) and an alkali; white amorphous hydrated alumina precipitates. The reaction usually took place in the dyestuff solution, thus precipitating the dye with the substrate – the lake
- The form of hydrated alumina produced is influenced by the order of addition of potash alum and alkali, i.e. the recipe followed. This gives essentially two types

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7-

Hydrated alumina substrates

- Type 1: Amorphous hydrated alumina

Up to the 18th century, most red lakes (apart from brazilwood lakes) were made by extracting the dyestuff using alkali; alum was then added to precipitate the pigment. This includes those where the dye is extracted from textile. The substrate formed (containing Al and O) is best described as amorphous hydrated alumina.

- Type 2: Light alumina hydrate

If alkali is added to a solution of alum, however, sulphate anions become incorporated into the substrate as it precipitates. This type of substrate is more typical of 19th-century lakes (although it is found earlier) and has been described as light alumina hydrate.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Hydrated alumina substrates

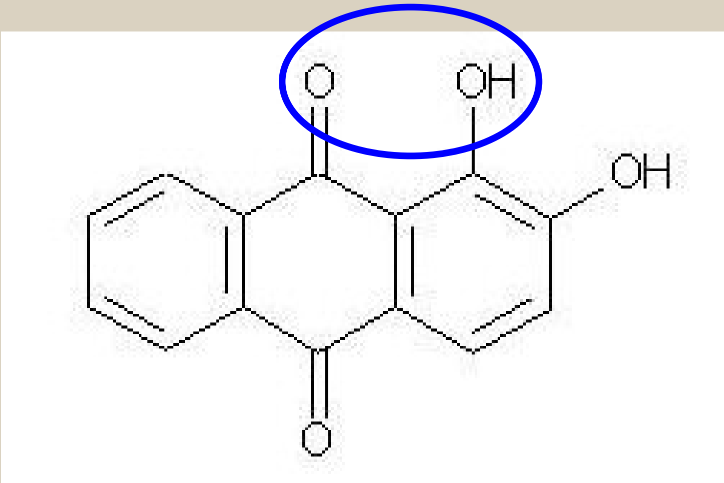
- From the 18th century onwards, lakes could be made by adding the dyestuff solution to a slurry of freshly-made alumina hydrate substrate: e.g. some cochineal lakes and, much later, modern pigments like alizarin crimson and some made from synthetic dyes.

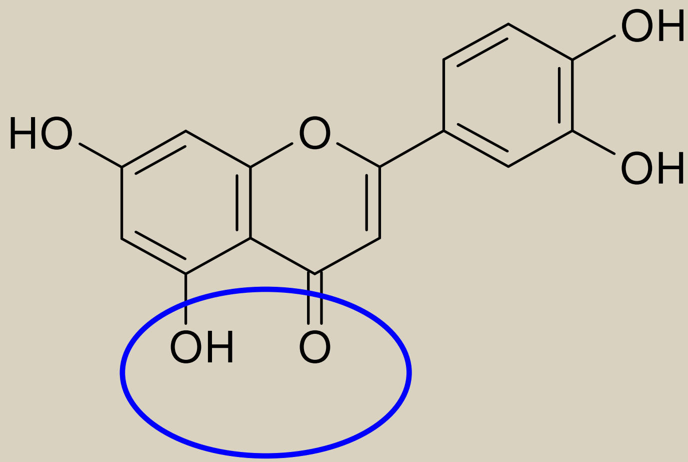
Left, cochineal lake; right, eosin lake, both on freshly made hydrated alumina substrates

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Bonding between dye constituent and aluminium

Positions for co-ordination with aluminium in the formation of a lake on an Al (or Al/Ca) -containing substrate, taking alizarin as an example:



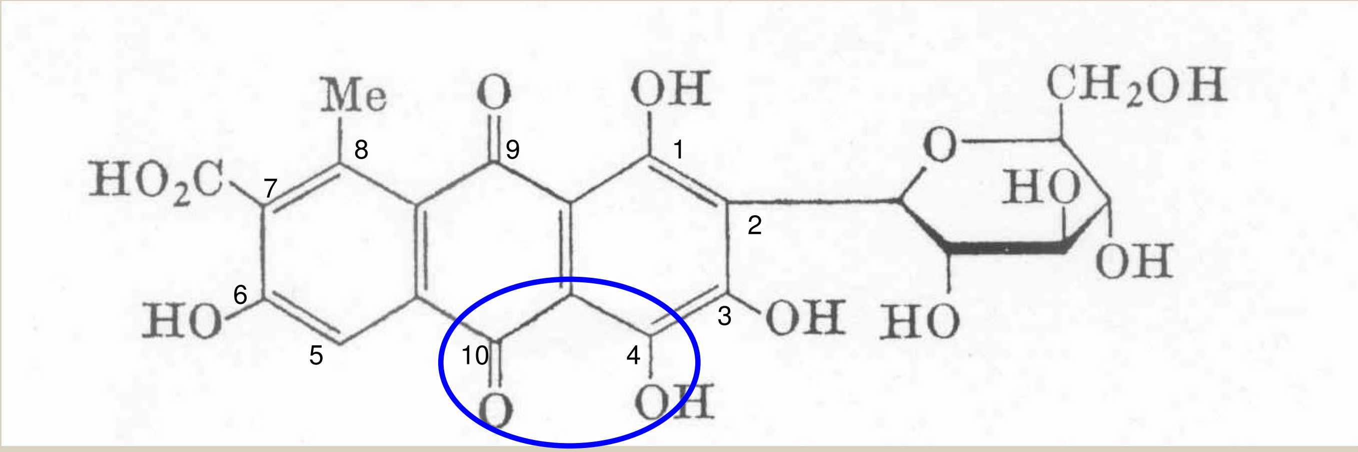


and similarly in luteolin

Sanyova, J. (2000/1) 'Contribution à l'étude de la structure et des propriétés des laques de garance', PhD thesis, Université libre de Bruxelles.

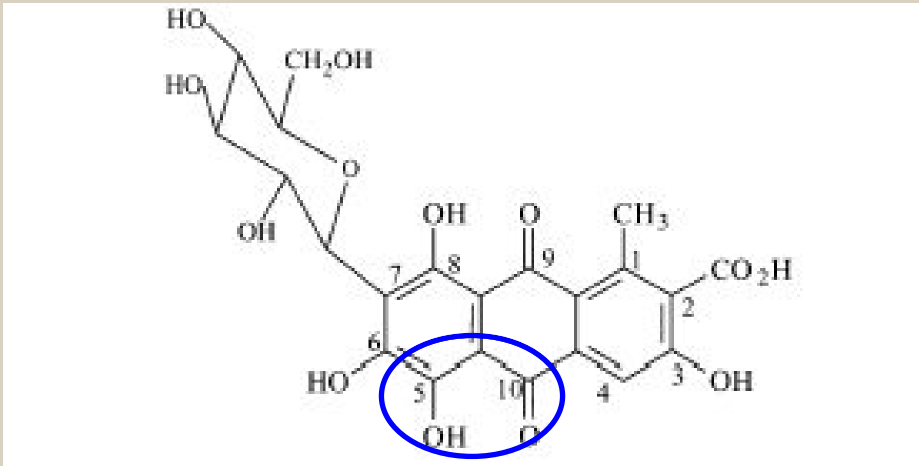
Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Bonding in modern carmine and cochineal pigments



R.H. Thomson, *Naturally Occurring Quinones*, 2nd edn, London 1971

Positions for co-ordination with aluminium in the formation of Al (or Al/Ca) -containing carmine



G. Favaro, C. Miliani, A. Romani and M. Vagnini, 'Role of photolytic interactions in photo-aging processes of carminic acid and carminic lake in solution and painted layers', *J.Chem. Soc., Perkin Trans. 2*, 2002, 192–7

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Al/Ca-containing substrates

- Pigments made by adding a calcium salt such as calcium carbonate ($CaCO_3$) to dyestuff solution containing potash alum have a substrate which may contain a little hydrated alumina and calcium sulphate ($CaSO_4$) produced by the reaction, with unreacted calcium carbonate: e.g. brazilwood lakes of the *roset* type. These are found particularly often in the yellow lakes

Left, weld lake on Al/Ca substrate filtering; right, *roset* from sapanwood

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

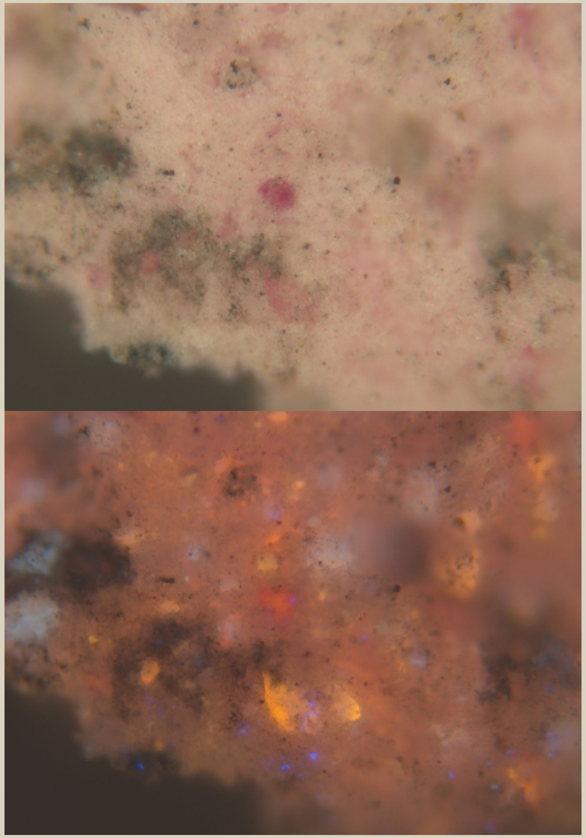
Al/Ca-containing substrates

- Translucent, but because there is a calcium or similar substance present frequently, they are not generally used in glazing in the conventional way that alumina-containing ones are used
- Yellow lakes are widely used in mixtures to give translucency and particularly in green mixtures, notably in landscape.
- In aqueous medium those yellows containing a calcium salt (or similar substrate) are a brighter yellow than the alumina hydrate ones. They were manufactured in large quantities and probably widely used as decorators' colours.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Recipes

- The earliest pigments seem to have been made by mixing a solution of the dye with a white material (chalk; some other white earth) perhaps with some alum added (mentioned in Pliny but not clearly described)
- Often yellow lakes continued to be made in a rather similar way, with alum and chalk as ingredients, into the 18th century and at this time the darker coloured, more transparent, alumina-containing yellows become more common – the same recipes appear again and again.



Fragment of painted stucco foot, Uruk, S. Iraq, 150BC – AD 250, BM 1856,0903.1168 x 40 (top, refl. light; bottom, UV)

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Recipes

- Red lakes were also made from alum and an alkali (stale urine, potash, potash mixed with lime to give potassium hydroxide) from quite early on (probably around the 8th or 9th century AD). This was the preferred method for all but redwood (before 1500 sappanwood), where the chalk-containing pigments were also made for cheaper purposes or for use in watercolour. However, red lakes show marked technological changes over time
- Red lakes were also among the most expensive pigments, particularly those made (indirectly) from kermes or Old or New World cochineal

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Recipes

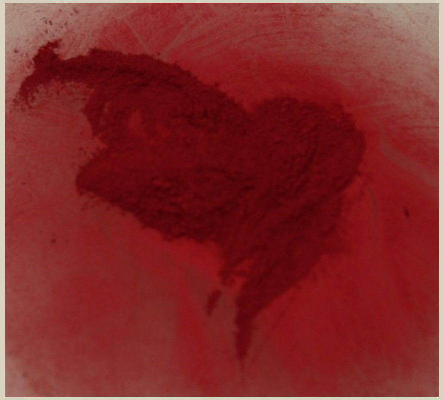
- If we take the period from the late 14th to the 17th century approximately, there is a difference in the method of treatment of lac and soluble redwood dyes, on the one hand, and kermes, the Old and New World cochineals and madder on the other: dyestuff is extracted directly from the raw material in the former cases and primarily indirectly from textile shearings in the latter. This is demonstrated by the recipes and can often be confirmed by analysis of paint samples.




Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Recipes

- The introduction of cochineal during the 16th century was as important for pigment making as for dyeing, more particularly in the 18th century. The use of tin[IV] chloride solution to precipitate a scarlet cochineal carmine pigment perhaps derives from dyeing practice, date of the method unknown but before 1750. Various 18th-century authors discussing the use of tin mordants in dyeing mention the fact that the tin can come out of solution and bring the dyestuff with it as a sort of lake.
- An extremely strong colour, essentially precipitated carminic acid with very little ‘substrate’ or extender, quite different in use to the conventional lake pigments



Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Cross-section of paint of background, top right. Red lake on tin-containing substrate with starch extender in pink layer.

Hilaire-Germaine-Edgar Degas, *Princess Pauline de Metternich* (NG 3337), *c.* 1865. Oil on canvas, 41 x 29 cm.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Recipes

- Innovations in the preparation of madder lakes directly from the root largely date from the 18th century and continue to benefit from the work done on efficiency of extraction during the 19th century, leading to the preparation of different madder preparations like garancine and Kopp's purpurin (after the identification of alizarin and purpurin, but before the synthesis of alizarin, which effectively put an end to th madder industry in France.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Claude-Oscar Monet, *Irises*, 1914-17.
London, The National Gallery (NG 6383).
Oil on canvas.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Recipes

- The recipes for the workshop thus chosen to demonstrate those most typical for each dyestuff and the range used
- For the yellow lakes, we have a typical 18th-century recipe for a pigment on a hydrated alumina substrate and two (from the 15th and 16th centuries) very widely copied recipes for pigments also containing calcium salts
- For the soluble redwood (brazilwood) dye, three 15th-century recipes: one for a rose-coloured pigment made using chalk and two made using potash alum and alkali, but varying as to which is added to the dyestuff first
- For lac, a typical 15th-century recipe extracting the dye into alkali and precipitating with alum, but note that this is very likely to dissolve some of the alkali-soluble dye constituents in the shellac as well.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Recipes

- For madder, an example of a 15th-century recipe extracting the dye from wool shearings (dyed fleece, in our case) using strong alkali, but also examples of late 18th- or 19th-century recipes extracting the dye from the root, either adding the alum before the alkali or extracting with alum
- For cochineal, a typical 15th-century recipe extracting the dye from shearings, in this case of silk, in alkali, comparing this with a pigment made by extracting the dye from the insects, based on a 17th-century recipe; both these are used for kermes as well. Unlike the Old World insects, cochineal is so rich in dye that the colouring matter could be precipitated directly using a little potash alum or tin salts and used as a pigment – cochineal carmine; we are trying a 19th-century recipe.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330

Recipes

- For the CHARISMA project we needed to make laboratory versions of the recipes to
  - obtain a clear, simple version of the recipe
  - estimate which parameters might influence the result – temperature of extraction or of carrying out the reaction, order of addition of reagents – and investigate these
  - The laboratory recipes are based on historical recipes, but modified, therefore, to investigate one or other parameter. You will have the original recipes as well, however, so you can try these yourself.
  - Some factors are difficult to control in a laboratory situation. These include the effect of scaling the recipe up or down; the dilution; the size and shape of the vessel; the speed of adding the reagents; the amount of stirring; the need to allow things time to work; the temperature; any after-treatment not stated in the recipe. All these things affect particle size, speed of precipitation and other properties of the final pigment, not least its colour.

Project co-funded by the European Commission within the action 'Research Infrastructures' of the 'Capacities' Programme GA No. FP7- 228330