Unit - Chemistry of Fibres, Textiles and Garments
Dyeing of fabrics.

The following links are to wikipedia for information on traditional textile dyes.
Black walnut Bloodroot Brazilin Cochineal (Polish cochineal) Cudbear Cutch Dyewoods Fustic Henna Indigo Kermes Logwood Madder Saffron Turmeric Tyrian purple Weld Woad

Medieval dyers use long poles to stir cloth in the dye bath to produce red cloth.
From the British Library, Royal Ms 15 E. III f.269 (1482) via Wikipedia

This lecture will attempt to summarise some of the topics covered in a "Tutorial Review" of historical dyes published by Hamish McNab (University of Edinburgh) in Chem. Soc. Rev., 2004, 33, 329-336.

Throughout the world, natural dyes have been used since the most ancient times until the end of 19th century when they were largely replaced by cheaper synthetic dyes. The ancient dyestuffs were generally organic materials obtained from plants, insects, shellfish and lichens, whereas many of the earliest pigments were inorganic materials obtained from natural ores.

Where did the earliest dyes come from? See the "Worst job in history" video clips that feature Tyrian purple *(Murex brandaris)* and indigo from woad *(Isatis tinctoria)*.

Initially the method we will use for classifying the dyes will be based on their colour; blue, purple, red, yellow as well as by a description of the chemical structure and identifying the chromophore responsible.

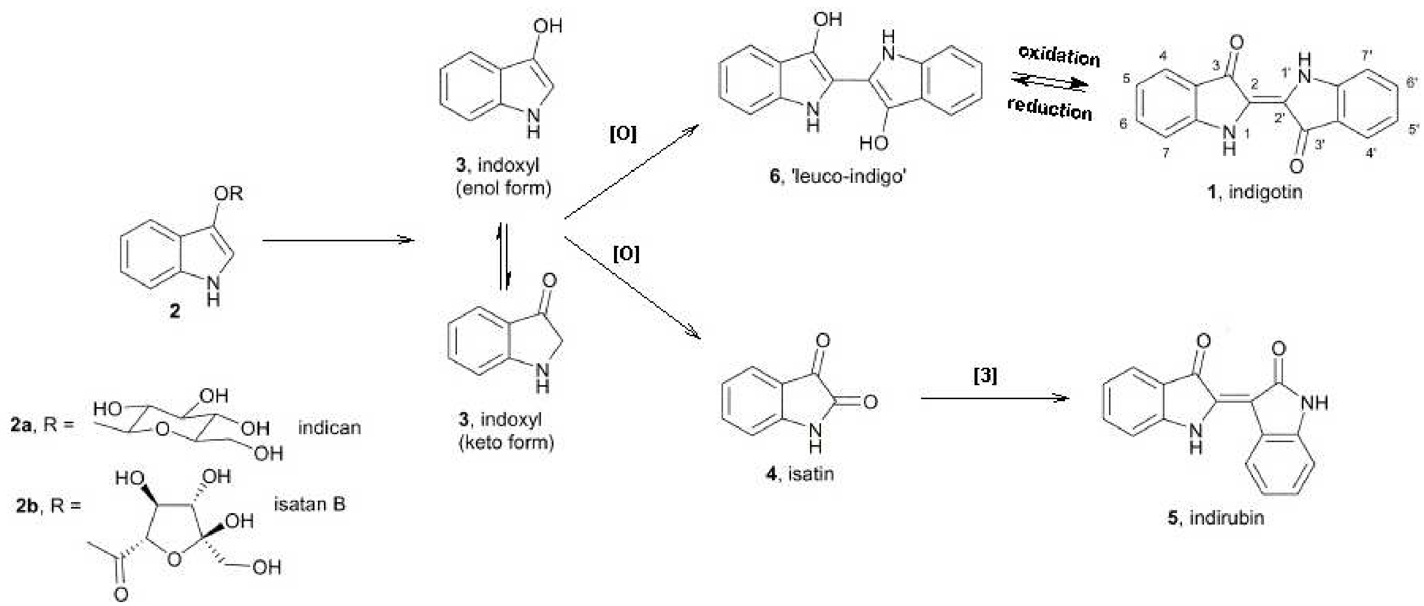
Most blue and purple colours were derivatives of indigo, obtained either from woad or from the indigo plant, though some other sources (e.g. shellfish and lichens) were used. Reds were often anthraquinone derivatives obtained from plants or insects. Yellows were almost always flavonoid derivatives obtained 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.

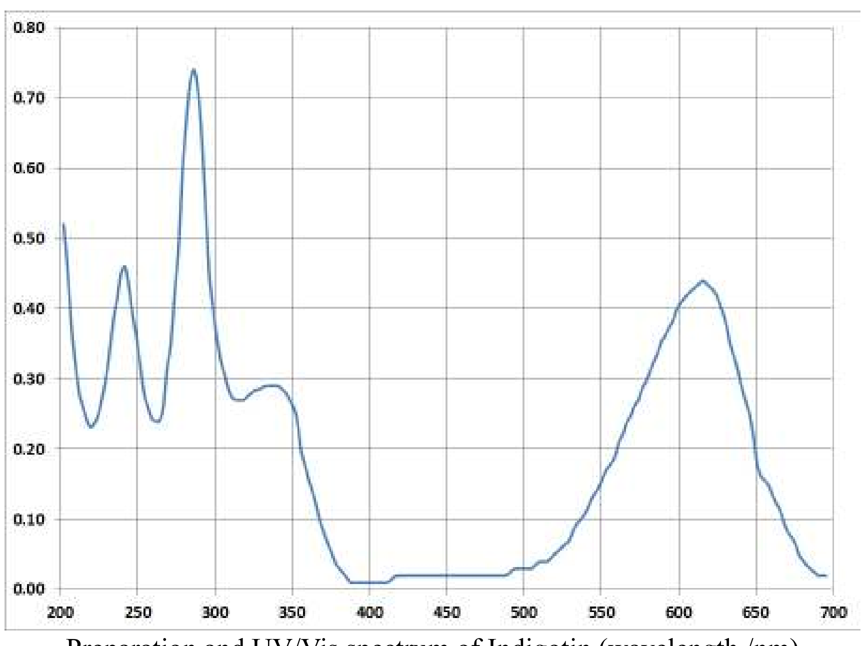
Blue dyes

Most of the naturally occurring indigo derivatives are insoluble in water but may become soluble in the presence of reducing agents. The fibres are therefore treated using a technique called vat dyeing such that whilst the dye is in solution the fibre is added to the dye bath and following its removal and exposure to air the insoluble dye is trapped inside the fibre.

The natural products from which indigo is obtained include indican (2a), which occurs in Indigofera species, e.g. the indigo plant itself *Indigofera tinctoria* L., as well as woad (*Isatis tinctoria* L. which contains both indican (2a) and isatan (2b).

Irrespective of the starting plant source the dye extraction follows the same process. The fermentation stage degrades the glycosides by enzymatic hydrolysis to indoxyl (3) (a mixture of keto-enol tautomers) which is then oxidised to 'leuco-indigo' (6) and eventually to indigotin (1). A side reaction can occur if indoxyl is converted by oxidation to the diketone, isatin (4) that can then further react with another molecule of indoxyl (3) to produce indirubin (5).





Preparation and UV/Vis spectrum of Indigotin (wavelength /nm)

The primary use for indigo today (several thousand tons each year) is as a dye for cotton yarn, which is mainly for the production of denim cloth for blue jeans. On average, a pair of blue jeans requires 3 - 12 g of indigo. Small amounts are used for dyeing wool and silk. All of the dye used is synthetically produced.

Indigo carmine, or indigotine, is an indigo derivative (sodium salt of 5,5'-indigodisulfonic acid) that is also used as a colorant. Approximately 20M kilograms are annually produced, again mainly for blue jeans. In addition it is used as a food colorant, and is listed in the USA as FD&C Blue No. 2, and in the European Union as E132.

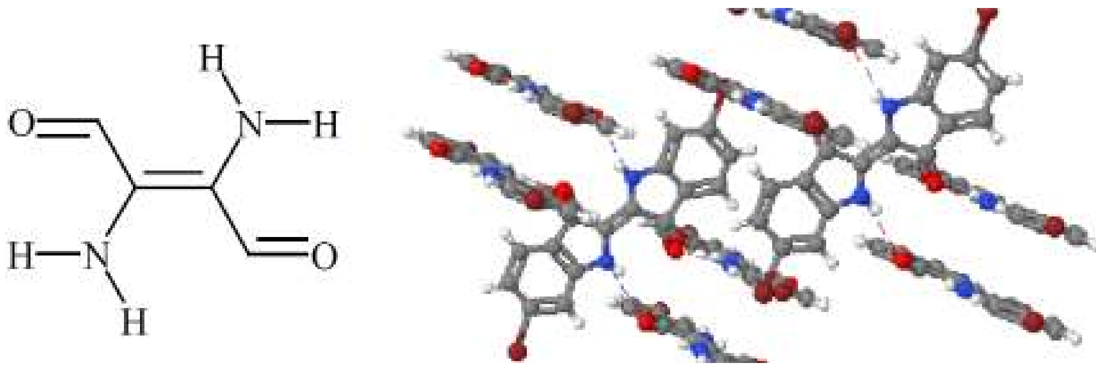
Assignment

Describe the processes that have been used for the commercial synthesis of indigotin and indigo carmine.

Shellfish purple

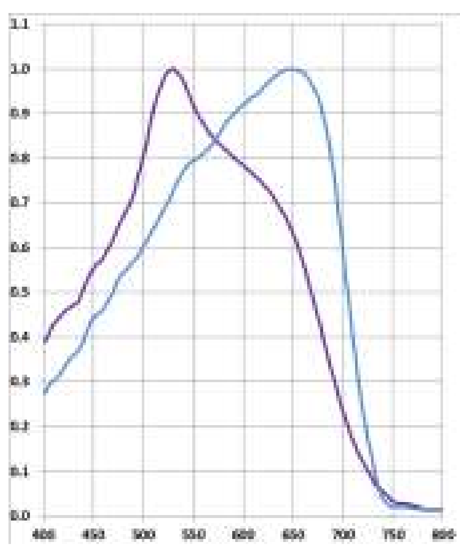
The purple dyes obtained from shellfish are bromo-derivatives of indigotin (1). Arguably, 6,6'-dibromoindigotin is the oldest known pigment, the longest lasting, the subject of the first chemical industry, the most expensive and the best known. See the Review by Chris Cooksey in Molecules 6 (9),736-769 (2001). and a bibliographic list of references related to Tyrian purple.

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*). 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. 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.



possible chromophore and crystal structure of 6,6'-dibromoindigotin

A comparison between the use of indigo or dibromoindigo as dyes can be seen from the reflectance spectra of wool samples. The absorption maximum of indigo shifts from 605 nm in solution to over 650 nm as a dye, whereas that of dibromoindigo shifts from 590 nm to 520 nm.



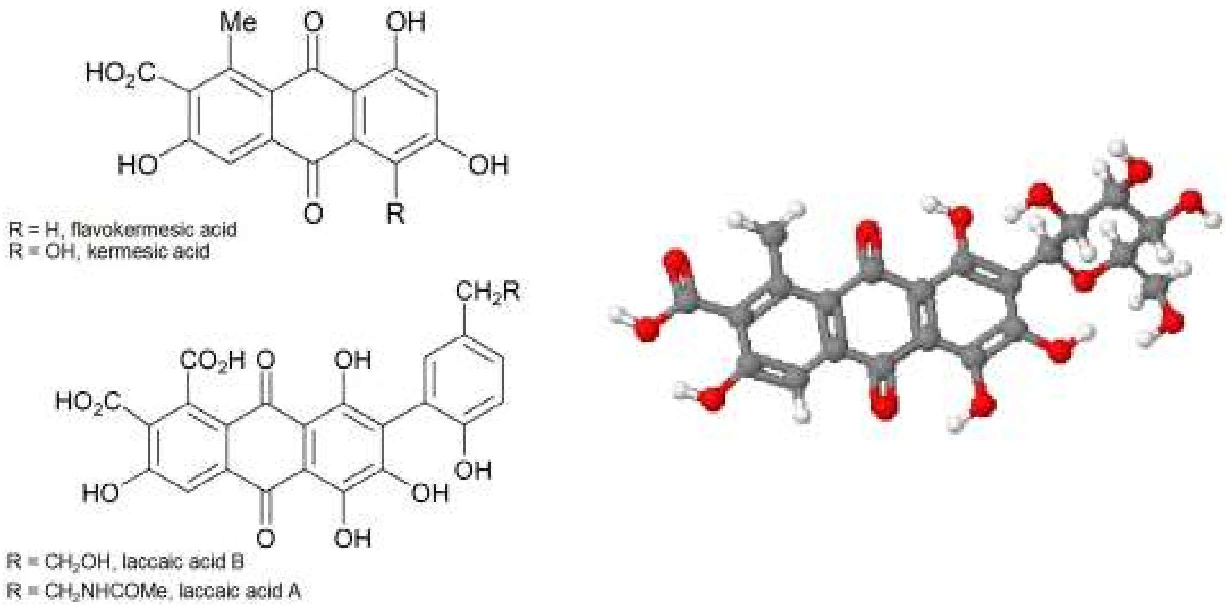
Reflectance spectra of wool samples dyed with dibromoindigo (purple) and indigo (blue).

Red dyes

Insect dyes

The main red insect dyes are from plant parasites belonging to the Coccidea family and 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 of these scale insect dyes are derivatives of anthraquinone.

In the case of cochineal the colourant (carminic acid) is extracted from the bodies of female insects just prior to egg-laying time and as such, may contain from 10 to 20% of their dry weight of the dye. The collected insects are dried and extracted with hot aqueous basic solution that may contain a samll amount of ethanol. It has estimated that about 25 million insects are required to make 14.5 kg of water-soluble extract.



Red dyes and the structure of carminic acid

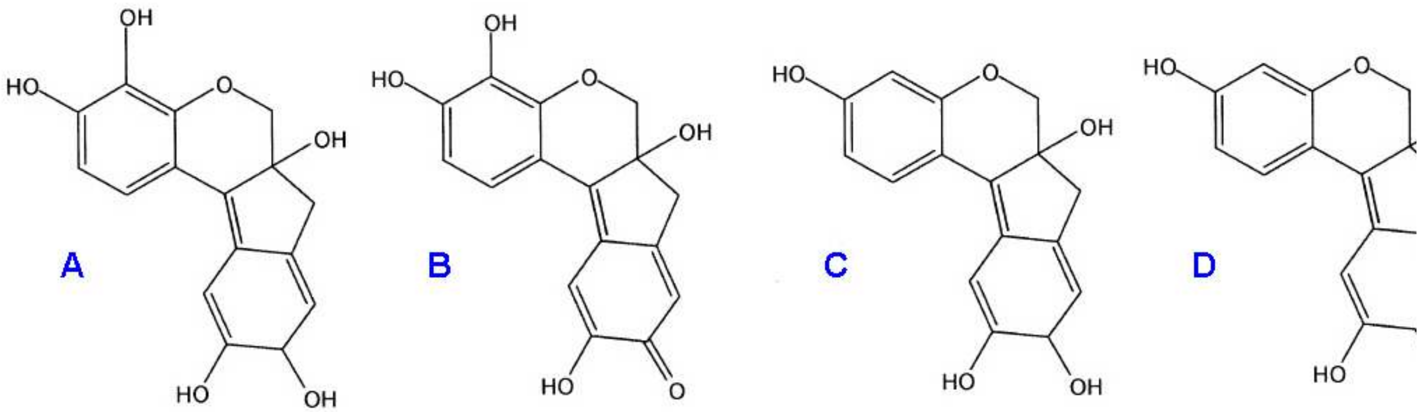
Plant anthraquinone reds

Redwoods

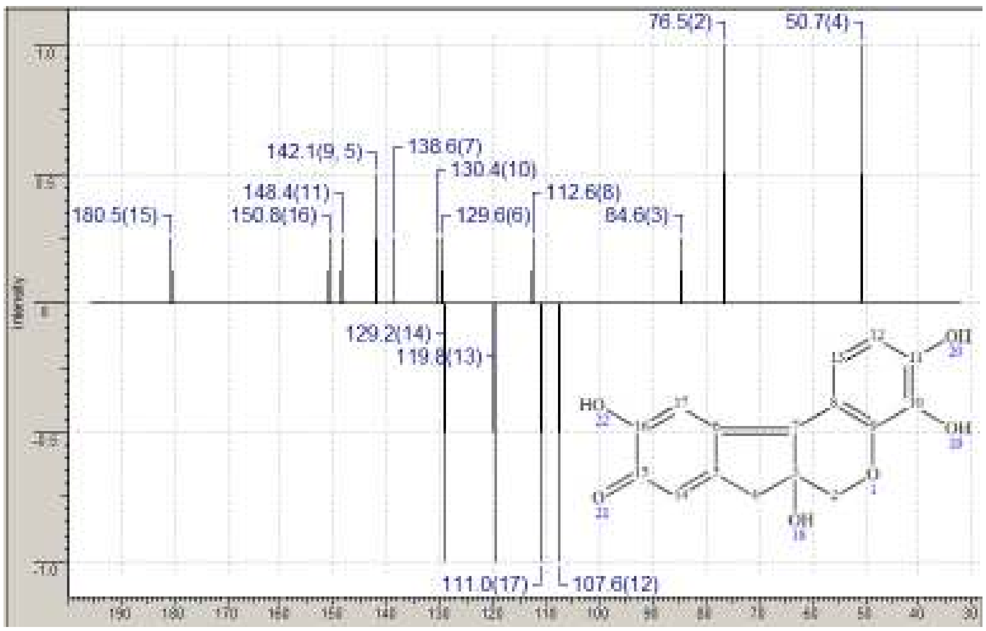
Logwood and Brazilwood

Haematoxylum campechianum (Logwood) was used for a long time as a natural source of dye, and still remains an importance source of haematoxylin, which is used in histology for staining. The bark and leaves have found use in various medical applications. In its time, logwood was considered a versatile dye, and was widely used on textiles and for paper. The dye's colour depends on the mordant used as well as the pH. Like litmus, it is red in acidic environments and blue in alkaline ones.

Caesalpinia echinata (Brazilwood) is a species of Brazilian timber tree in the pea family, Fabaceae. Common names include Brazilwood, Pau-Brasil, Pau de Pernambuco and Ibirapitanga (Tupi). This plant has a dense, orange-red heartwood that takes a high shine, and it is the premier wood used for making bows for stringed instruments. The wood yields a red dye called brazilin, which oxidizes to brazilein.



A=haematoxylin, B=haematein, C=brazilin and D=brazilein.

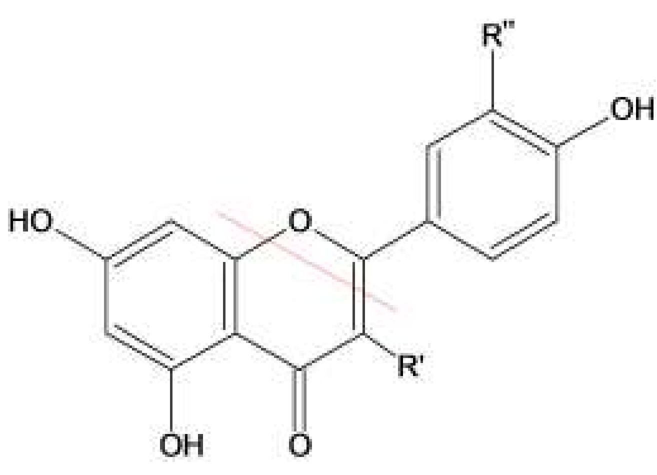


Simulation of C-NMR of B=Haematein

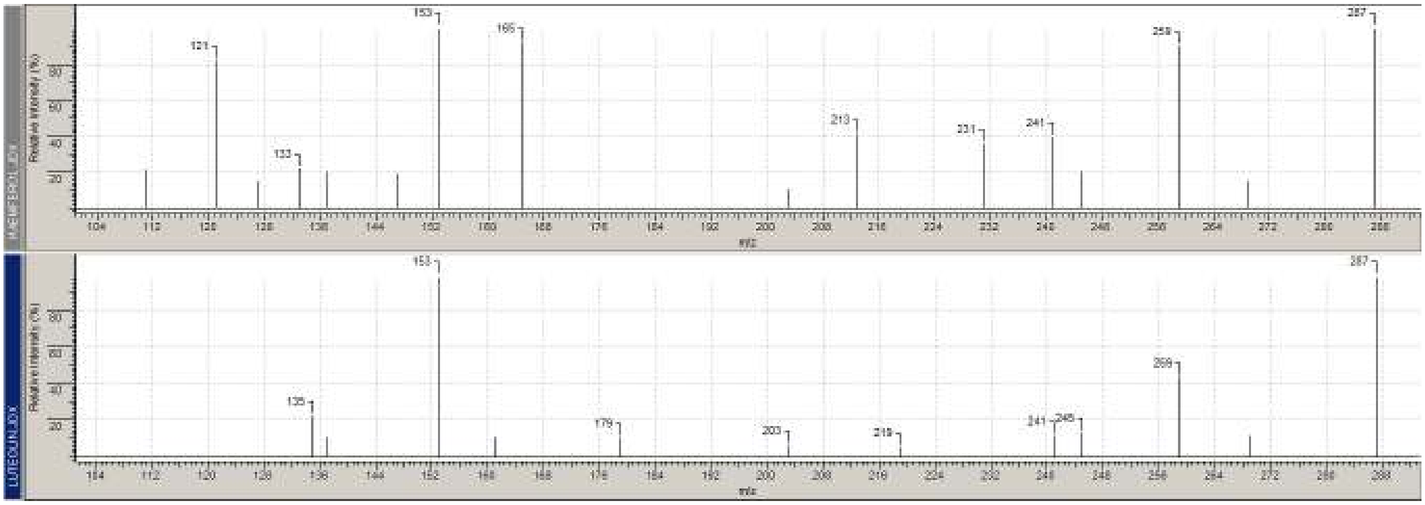
Yellow dyes

Flavonoids and flavones

Flavonoids are the most important plant pigments for flower colouration producing yellow or red/blue pigmentation in petals designed to attract pollinator animals.



R'= H, R"=H apigenin; R'= H, R"=OH luteolin; R'= OH, R"=H kaempferol



MS of luteolin and kaempferol

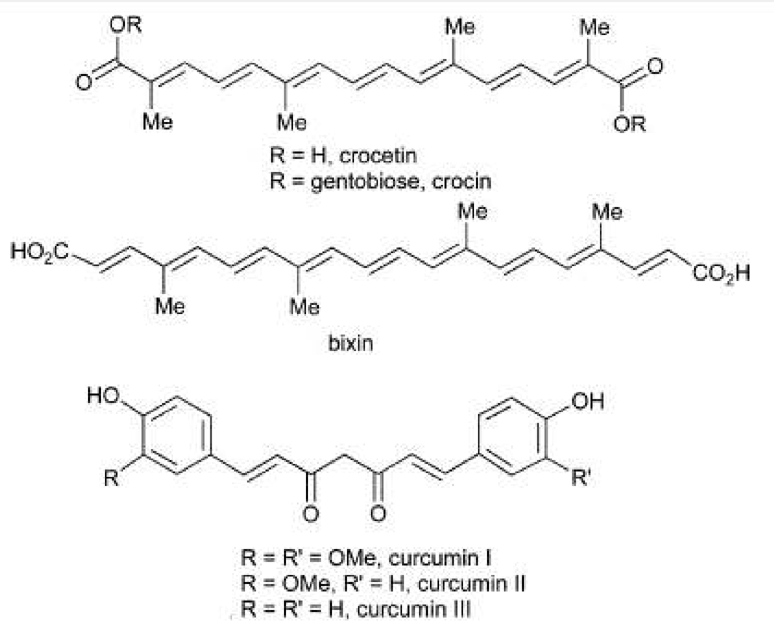
Although both luteolin and kaemferol have the same RMM and show a peak at 287 they can be readily distinguished by the intense peak at 165 for kaempferol that comes about by the cleavage shown by the red dotted line above. This leaves the left hand benzene ring intact and is stabilised by the R' hydroxy group (not present in luteolin).

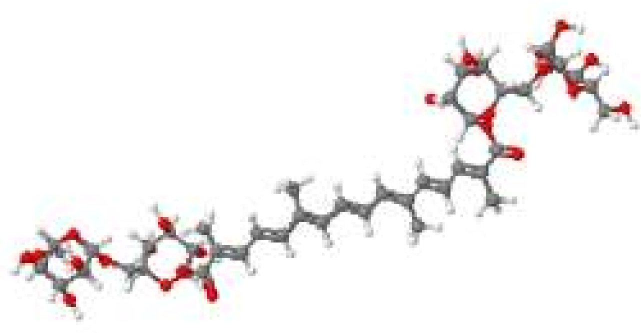
The plant species *Reseda luteola* was the most widely used source of the natural dye known as weld. The plant is rich in luteolin, a flavonoid which produces a bright yellow dye. The yellow could be mixed with the indigo blue from woad (Isatis tinctoria) to produce greens, such as Lincoln green. The dye was in use by the first millennium BC, and perhaps earlier than either woad or madder. Use of this dye came to an end at the beginning of the twentieth century, when cheaper synthetic yellow dyes came into use.

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 dating back to Egyptian times. It was very popular in Persia in Classical times. 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.

Saffron contains more than 150 volatile and aroma-yielding compounds. In addition it has many nonvolatile active components, many of which are carotenoids, including zeaxanthin, lycopene, and various α- and β-carotenes. However, saffron's golden yellow-orange colour is primarily the result of α-crocin, a glucoside of crocetin, a polyunsaturated diacid.





Yellow dyes and the structure of crocin

Turmeric (Curcuma longa) is a rhizomatous herbaceous perennial plant of the ginger family, Zingiberaceae.

If the rhizomes are boiled for several hours and then dried in hot ovens, They can then be ground into a deep orange-yellow powder commonly used as a spice in curries and other South Asian and Middle Eastern cuisine, for dyeing, and to impart color to mustard condiments. Its active ingredient is curcumin and it has a distinctly earthy, slightly bitter, slightly hot peppery flavor and a mustardy smell.

In medieval Europe, turmeric became known as Indian saffron, since it was widely used as an alternative to the far more expensive saffron spice.

See Wikipedia for a description of traditional dyes of the Scottish Highlands to see what colours were available for Scottish kilts?

Synthetic Dyes

William Perkins, who in 1856 (aged 18) discovered the first aniline dye.

The dye process

Apart from the colour they produce, dyes may be characterised by the method of their application to the fabric. For example:

- Acid dyes - anionic dyes applied under acidic conditions
- Basic dyes - usually water soluble cationic dyes
- Azo dyes - addition of the 2 components to make the azo dye
- Direct dyes - applied to cellulosic fibres in aqueous solution containing NaCl
- Vat dyes - normally insoluble but made soluble by addition of base. This includes many of the dyes mentioned earlier like indigo.
- Disperse dyes - insoluble so they are applied from an aqueous dispersion
- Mordant dyes - mordant, often chromium, is added to the textile then the dye

The 5 most widely used dyes (1996).

Dye	t/year
Indigo	15,000
Disperse blue 79	15,000
Sulphur black 1	10,000
Reactive dye black 5	8,000
Acid black 194	7,000

References

JAIC 1992, Volume 31, Number 2, Article 7 (pp. 237 to 255)
World Records in Chemistry, H-J. Quadbeck-Seeger (ed), Wiley-VCH, 1999, Weinheim, Germany

Acknowledgements.
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