Modern Alchemy 102: Dye molecules

It’s like the dating game, but with organic chemistry

Lucia de Moranza
luciademoranza@gmail.com

The science of colour in history

The science of colour is really a rather recent phenomenon, in the grand scheme of things. In our pre-1600 time period colour theory was primarily based on Aristotle’s belief that four colours had been sent by God through celestial rays of light. (*The Science of Color*, 2015) Leonardo da Vinci had his own theories on colour, getting up to six colours. It is not until 1666 when Isaac Newton started playing with his prism that we get the notion of spectrums, and refraction of light. At that point, colour theory started having basis in theories recognizable to modern physics. (*Color Theory | Causes of Color*, n.d.) There’s a huge jump in the science of dyes in the late 19th century, when artificial dyes get sorted out, and it’s not until the 1930s that there’s a deep understanding on exactly how dye molecules reflect colour. (“A Theory of the Color of Dyes,” 2014) Dye research is still very much an evolving field, perhaps surprisingly for something that has been going on for much of human history.

What is colour anyhow? How do we see colour?

Most who have ever played, as Newton did, with a prism are comfortable with the notion of colours being the visible spectrum of light, and confident with rhyming off the colours of the rainbow.

What is generally not even thought about is that the colour of an object is the result of the light that is being reflecting back to us. That red sweater is red only because it is rejecting the red wavelengths and reflecting them back at us for our eyes to see and say ‘yep, that’s red.’ The sweater is absorbing all of

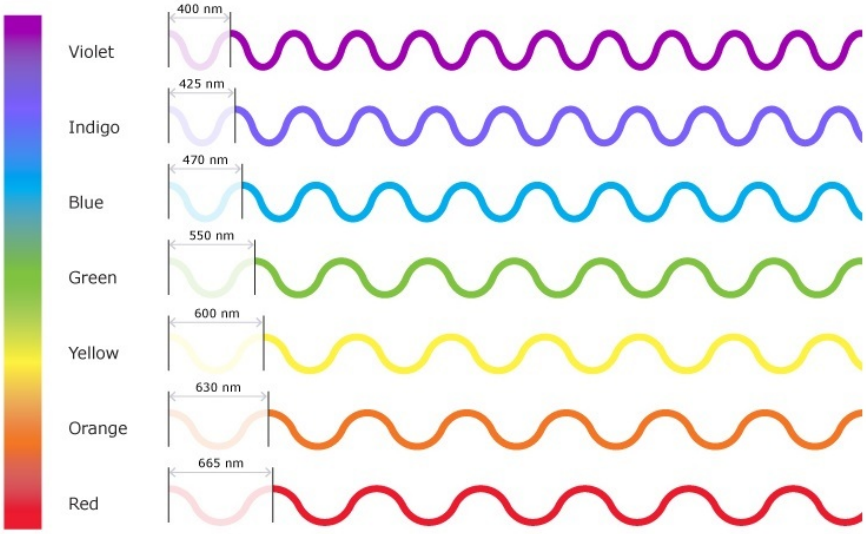


Figure 1 Wavelengths of visible light

those other colours on the spectrum other than red. White is a function of reflecting all of the colours back at us, and black is a function of reflecting none of the colours back.

Wavelength Range (nm)	Absorbed Colour	Reflected Colour
400-435	Violet	Green-yellow
435-480	Blue	Yellow
480-490	Green-blue	Orange
490-500	Blue-green	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-blue
605-750	Red	Blue-green

(Buccigross, 2006)

At the core of it, to turn your white wool red is as simple as coating your white wool in a substance that will start to absorb all the colors other than red and leave those red wavelengths to be reflected back to the eye. Simple, right?

Reality of course makes this slightly more complicated. Most dyes are not the basic reflection of one colour but a combination of colours, which makes for the rich and varied collection of colours that we have from natural dyes.

While dye molecules can vary greatly, they generally contain at least three unique chemical groups, each responsible for a particular property. They need to produce colour, those are usually the function of chromaphores. They need to make a chemical bond with fibre, which is the job of an auxochrome (also responsible for the intensity of the dye). Finally they need to dissolve in water, the job of the solubilizing group. (Epp, 1995) This is a general statement, there are coloured compounds that do not contain chromaphores or auxochromes, but it is a good place to start in the classification of dye molecules.

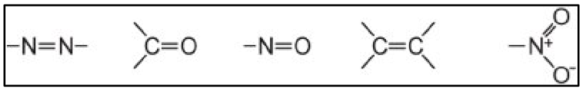


Figure 2 A selection of chromaphores


Figure 3 A selection of auxochromes

Let’s meet some dye molecules!

A lot of the time, when discussing dye molecules, we are generally dealing with individual components of the molecule in question. There are structures in organic chemistry that we know to be stable, they like to hang out together as a clique of atoms if you will, and those structures tend to move as a structure, rather than breaking up into their individual bits at the slightest provocation. By and large, looking at what components are present tends to give us some idea on what to expect from the larger molecule, right up until something surprises us. Dye chemistry, and especially natural dye chemistry is an actively evolving field of study even now in the 21st century. To some degree, it is still alchemy, even to the modern chemist.

All of the tables below have been reproduced from Coordination Chemistry of Pigments and Dyes of Historical Interest. (Kauffman, 1994) unless otherwise indicated.

Blue and Purple

Indigoid dyes. There are two main places to find indigoid dyes, and interestingly one is from plants and the other is from mollusks. Indigo and woad possess the same molecule, even if they were assumed to be different historically. In fact it was once assumed that indigo did not come from a plant. (Spoilers: it does. *Indigofera tinctoria.*) Purple as a colour in its own right, rather than a combination of blue and red, is also an indigo based compound. It is collected from a selection of Mediterranean shellfish. The most common were from the genus *Murex*, providing a dye know as Tyrian Purple (named for the city Tyre). All of the indigoid dyes start out as pigments that need to be reduced to a soluble intermediate form before they can be bonded with the fibre. They are then reacted with oxygen (oxidized) back to pigment, now attached to the fibre. (Koren, 2015) The mechanism of that reduction changes between indigo and tyrian purple, but the principle is the same.

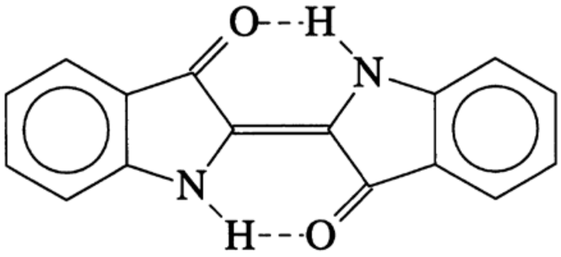


Figure 4 Indigo

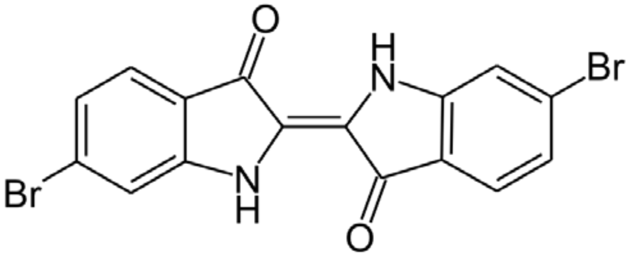


Figure 5 Tyrian Purple (source: Wikipedia)

Yellow

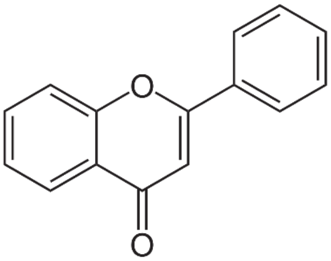


Figure 6 flavone backbone By NEUROtiker - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=3850694

Flavonoids (from the Latin word *flavus* meaning yellow) yield yellow dyes. The most common yellow dyestuff is weld which contains luteolin pigment, which we can see below. It is not prone to oxidation, which means it tends to be very stable in spite of oxygen being notorious for reacting with everything. This results in it being a very fast colour and exceptionally popular.

Table I. Some Important Yellow Dyes

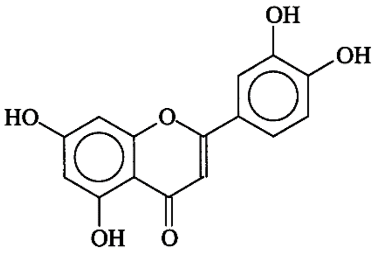
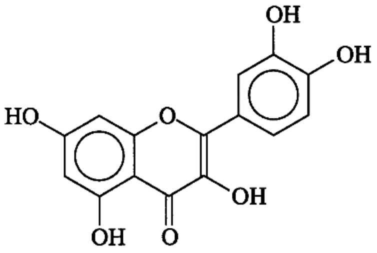
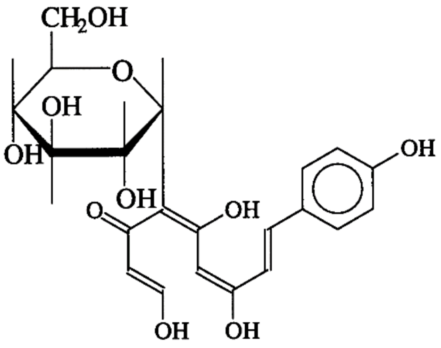
Dye	*Chemical Compound*	*Source*	*Structure*
Weld	Luteolin	Flavone dye extracted from the seeds, stems, and leaves of *Reseda luteola L.* (Dyer's Rocket)	
Quercitron	Quercetin	Flavonol dye from the bark of the North American oak, *Quercus tinctoria nigra*	
Safflower	Carthamin	Chalcone dye from dried petals of *Carthamus tinctorius* (Dyer's Thistle)	

Figure 7 Yellow Dye structures

Brazilwood (*Caesalpinia echinate*) has a structure that is closely related to flavones, and we can also put Logwood (*Haematoxylon campechianum*) in this category as well.

Brazilwood contains the flavonoid compound brazilin which looks yellow, but in a beautiful illustration of how chemical reactions change things, once it has reacted with oxygen to become brazilein it looks red. (Dapson & Bain, 2015) It is an almost identical compound to the one found in logwood (haematoxylin), which generally dyes purple. Exceptions abound!

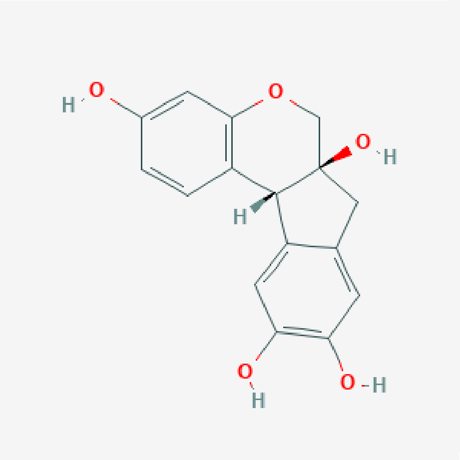


Figure 8 Brazilin National Center for Biotechnology Information (2021). PubChem Compound Summary for CID 73384, Brazilin. Retrieved February 19, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Brazilin

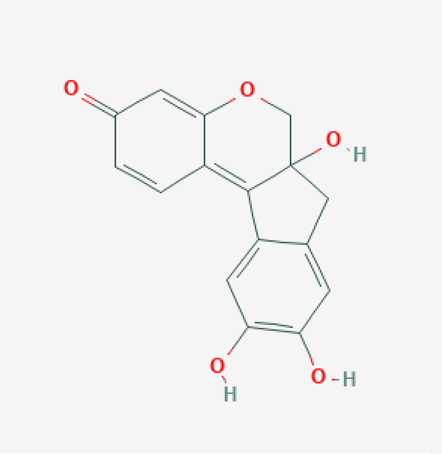


Figure 9 Brazilein National Center for Biotechnology Information (2021). PubChem Compound Summary for CID 6453902, Brazilein. Retrieved February 19, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Brazilein

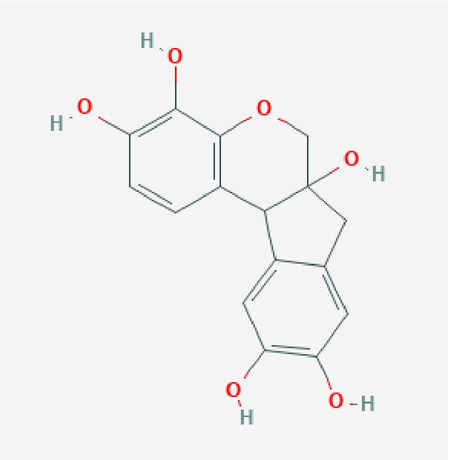


Figure 10 Hematoxylin National Center for Biotechnology Information (2021). PubChem Compound Summary for CID 10603, Hematoxylin. Retrieved February 19, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/Hematoxylin.

Red

Almost all the red natural dyes are based on the anthraquinoid structure. The most common examples are madder, lacs, kermes, and cochineal. There is one clarification I wish to make on the table of red colourants, (Figure 9). It lists madder (*Rubia tinctorum*) as having only alizarin, which is an oversimplification. Madder also contains another anthraquinone compound called purpurin which I have included in that figure, and some munjistin (see below). Madder can also be used to refer to *Rubia cordifolia*, also referred to as Indian madder, which has a somewhat different collection of molecules as shown below. (Yusuf et al., 2013) No matter which madder, everything involved is still based on that anthraquinone structure.

Table II. Anthraquinone-Based Red Colorants

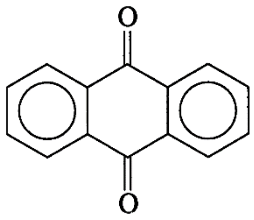
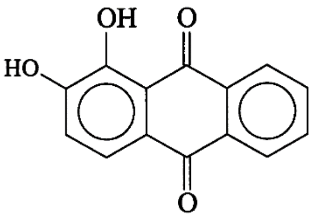
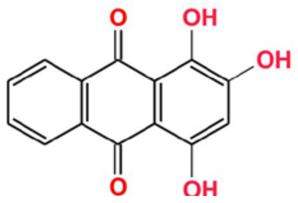
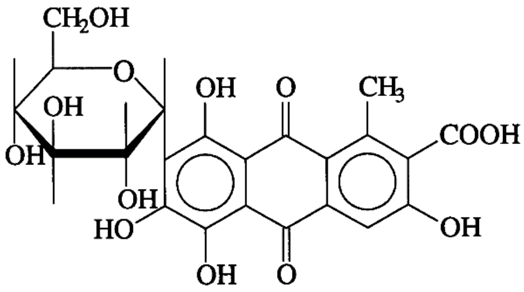
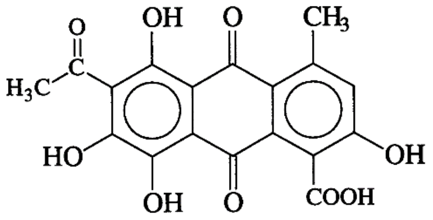
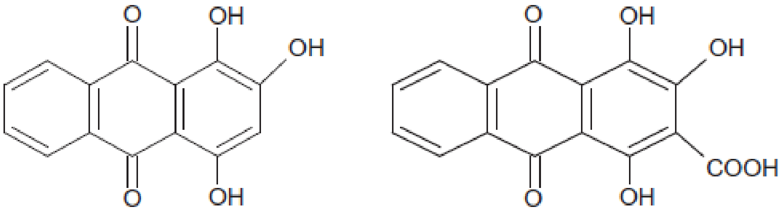
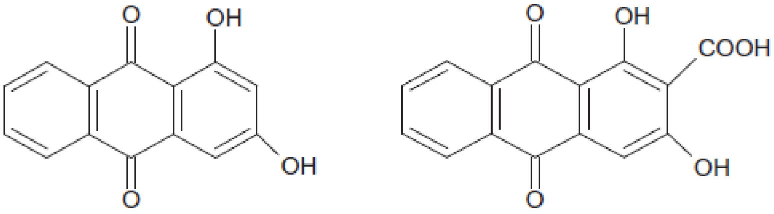
Dye	*Structure*
Anthraquinone	
Madder or Alizarin. Roots of the *Rubia tinctorum* plant. Roots were known as "alizari," hence alizarin	  Purpurin
Cochineal (Carminic Acid). Female insect, *Coccus cacti*, which lives on Prickly Pear cactus, found in Mexico. 200,000 insects yield 1 kg. of dye	
Kermes (Kermesic Acid). Female scale insects, *Coccus ilicis*, which infect the Kermes oak	

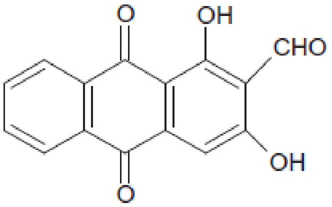
Figure 4 Red dye structures



purpurin munjistin



xanthopurpurin pseudopurpurin



nordamncanthal

Figure 5 Components of madder (Rubia cordifolia) root

Tannins

While not a colour in an of itself, the natural dye world (and the brewing world!) talks about tannins all the time without ever having a solid understanding on what exactly it is talking about. Tannins are water soluble polyphenol based compounds of many phenol groups, and vary widely depending on the plant species that has produced them. They are generally large molecules that happily bind to all sorts of things, including cellulose, to become both insoluble and very stable. Because of this they are often used as a pre-mordant to encourage alum to bind to cellulose fibres. (*Tannins*, n.d.) There are some

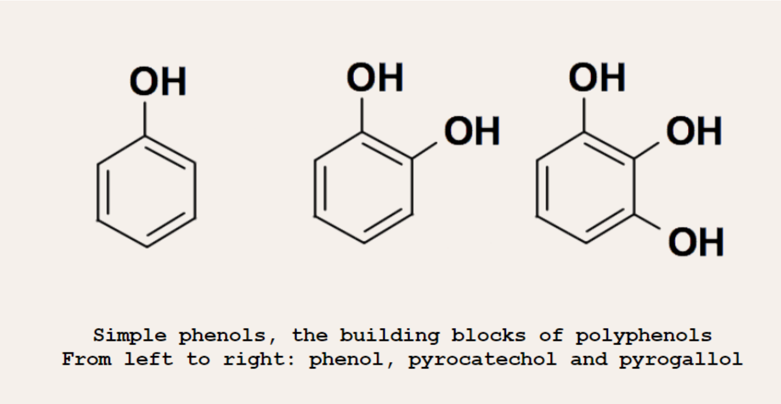
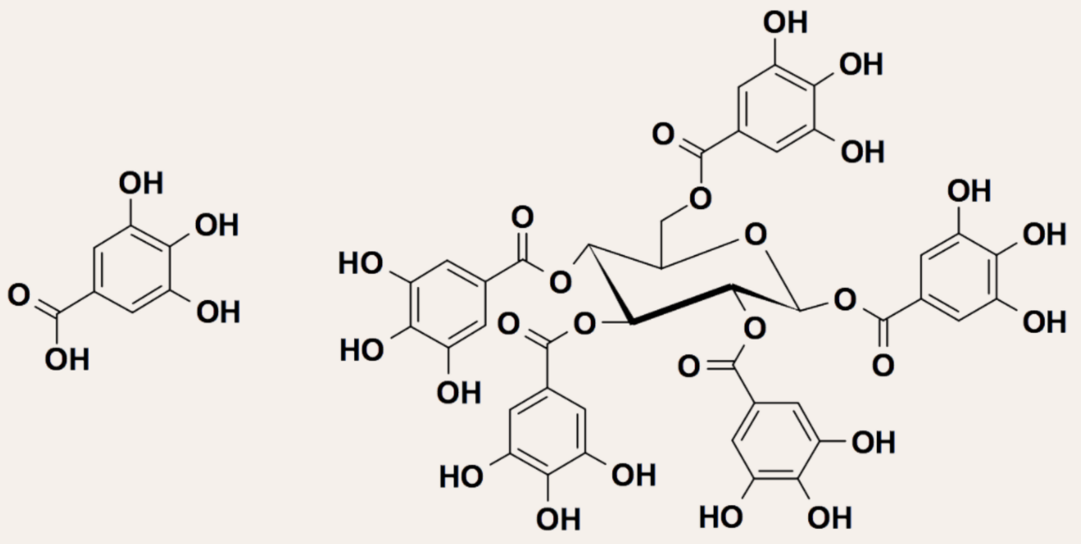


Figure 6

generalities that we can use to make some guesses on what colour to expect from various tannins, which is important to consider when using it as a pre-mordant. Maiwa very conveniently lays it out on their page: https://naturaldyes.ca/tannins.

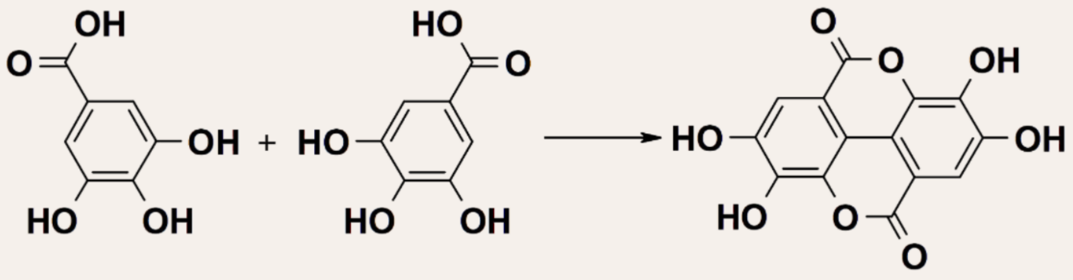
Gallic tannins are based off gallic acid as shown in the figure below and are considered to be clear or only faintly yellow. They are found in oak galls and some sumacs.



Gallic acid, left, and the simplest gallotannin, β-pentagalloyl glucose, right (Chemical diagrams courtesy of Professor Anne Hagerman, Miami University, Ohio)

Figure 7

Ellegic tannins are based off ellagic acid (which is conveniently based off gallic acid) but are generally stable. Ellagic acid is a creamy or yellow colour and is found in pomegranate, black oak and fustic.

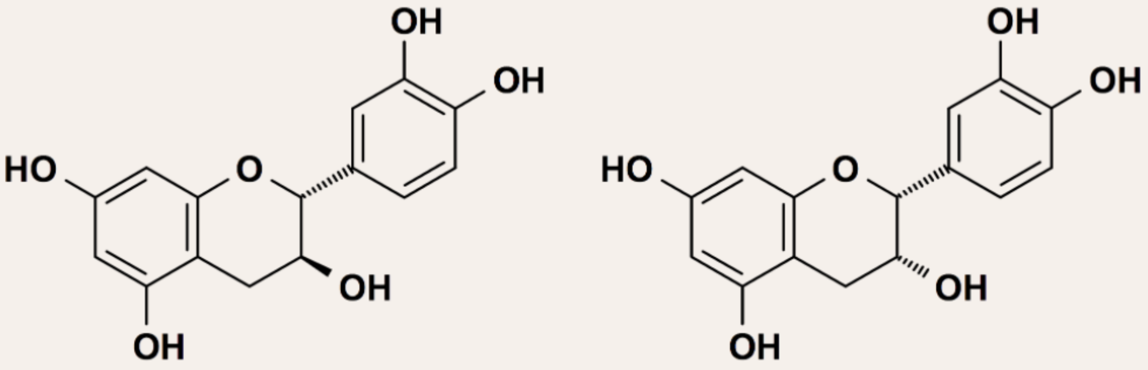


Two gallic acid molecules combine to form ellagic acid (Chemical diagrams courtesy of Professor Hagerman)

Figure 8

Gallic and elegiac tannins are both examples that fall into the hydrolysable tannin group, which is a fancy word for saying that they tend to split back down into their acid components when heated with acid. Both these tannins bind strongly with cellulose, so are very important in cotton mordanting.

The last general category of tannins that dyers are interested in are the catechic tannins. These are based on catechin and epicatechin. They can be found in cutch, tea leaves and some sumacs. They are part of a group of tannins called the condensed tannins, due to their more condensed structure compared to the hydrolysable group, and they tend to be reddish brown in colour.



Catechin, left, and epicatechin, right
(Chemical diagrams courtesy of Professor Hagerman)

Figure 9

All pictures in this section have come from this excellent webpage:
http://www.asiantextilestudies.com/brown.html

This is not a comprehensive list of dye molecules, there are absolutely others, but these are the most commonly used in western Europe during the bulk of the SCA period. My hope is that it did not scare anyone away from dye work, but instead provides some of the fascination that I enjoy in the understanding of how some of the various dyes are interconnected on a molecular level. Also? Chemistry is weird.

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