

The origin of pigment colours

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1. When the colour diversity of butterflies is explained at the nanoscopic scale of electrons and photons



Figure 1. A diversity of butterflies, colours and pigments. [Source: from © Wikimedia/Adolphe Philippe Millot in Larousse for all [1907-1910], Public domain]

Every molecule interacts with **electromagnetic radiation**, i.e. light (which ranges from the very energetic gamma and X-rays to the very low energies of radio waves). But not every molecule is coloured because we only perceive with our eyes wavelengths in the visible range (between 400 and 700 nm). In the living world, organic molecules preferentially absorb wavelengths in the far ultraviolet (between 100 and 300 nm) and appear transparent to us for the vast majority; This general property also explains why molecules in living organisms are likely to be degraded by these relatively energetic wavelengths (which can lead to mutations in the case of DNA).

Yet, the **colours** are ubiquitous in the world as we perceive it (as evidenced by the beautiful colours of the butterflies drawn in the Figure 1), which raises the question of how some molecules are able to absorb at higher (and therefore less energetic) wavelengths than average.

These molecules, with their intriguing absorption properties, are called **pigments** [1]. To understand where their originality comes from, we need to explain the phenomenon of interaction of matter with light in wavelengths between 200 and 1,000 nm (from ultraviolet to near-infrared, including visible).

2. The interplay of photons and electrons

Light is made up of particles called photons, which possess a certain energy (which also defines the wavelength, which is inversely proportional to it). Matter is made up of molecules, themselves the result of interaction between atoms, themselves composed of a nucleus and electrons. It is these negatively-charged particles that are capable of interacting with photons in the wavelength range of interest.

This is because electrons have their own energy at rest, and are capable of moving to a small number of higher energy levels if, and only if, they absorb the amount of energy exactly equal to the difference between the energy of their initial and final states. It's clear, then, that not every photon can excite every electron: an electron can only absorb a photon if the latter provides not only sufficient, but also exactly the right amount of energy to move to a higher energy state.

To make an analogy, electrons function like radio antennas, whose properties only allow them to listen to certain frequencies, since only a small fraction of them interact with the antenna. In the case of a DNA molecule, its electrons can only be excited by energies corresponding to photons located in the ultraviolet. Any other photon further away in the light spectrum, particularly in the visible range, passes through the DNA molecule as if nothing had happened.

It's clear, then, that for a molecule to be coloured, it must have electrons capable of either starting at higher-than-average energy levels, or moving to lower-than-average energy levels, since photons in the visible range carry less energy than those in the ultraviolet. However, nothing is more like an electron than another electron, and so, taken in isolation, the electrons in pigments are the same as those in DNA. In fact, it's their chemical environment that modifies their energy levels.

3. Pigments, molecules unlike any others

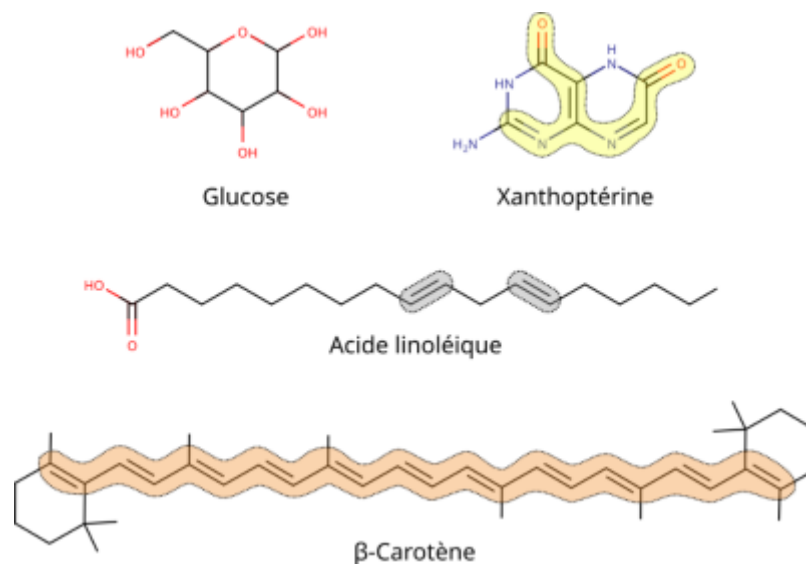


Figure 2. The chemical structure of pigments is at the heart of their colour production. This chemical structure is not fundamentally different from that of other organic molecules, but the alternation of single and double bonds (symbolized by solid colours) reduces the energy required to excite certain electrons, and therefore increases the absorption wavelength. So, although glucose and linoleic acid (found in grapeseed oil, for example) have oxygens, rings or double bonds like xanthopterin and β-carotene, their electrons still have excitation energies too high to absorb in the visible.

When pigment structures are compared with those of other transparent organic molecules (Figure 2), it becomes clear that a number of configurations between atoms are responsible for changes in their electron properties (it's important to note that the following parameters are neither necessary, exclusive, exhaustive nor even sufficient:

- a sufficiently extensive alternation of single and double bonds, known as **conjugate bonds**;
- the presence of **aromatic rings** with conjugated bonds;
- the presence and positioning of **heteroatoms** (nitrogen, oxygen, sulphur, etc.) directly linked to conjugate bonds/aromatic rings;
- **interaction** with other compounds such as proteins, metals, etc.

4. The electronic origin of pigment colour diversity

The same properties that enable pigments to be coloured are also responsible for their different hues. Indeed, any variation in one of the above parameters can lead to the electrons in a pigment absorbing at different wavelengths. The colour we perceive in a pigment is the complementary colour of the one absorbed, which means that a violet-absorbing xanthopterin (yellow bands on Wasps) appears different from a blue-absorbing erythropterin (orange spot on an Aurora; Figure 3).

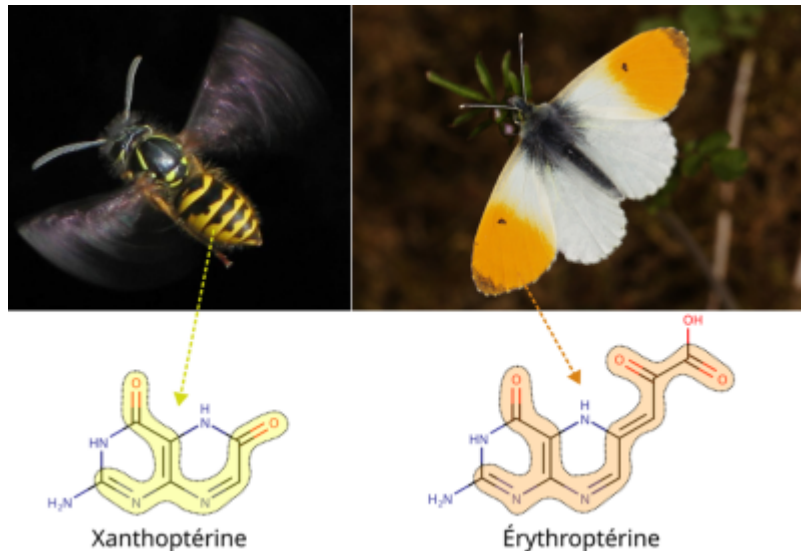


Figure 3. The differences between two pigments in the same family illustrate the impact of chemical structure on colour. Xanthopterin and erythropterin have the same basic chemical structure (common to all pterins, some of which are not pigments), but it's thanks to an extension of the conjugated bonds (represented by coloured solid areas) that erythropterin has electrons excitable at lower energies and therefore absorbs at higher wavelengths, giving its colour orange-red rather than yellow. [Sources: Wikimedia wasp ©/soebe, licence CC BY-SA 3.0 ; Aurore © Wikimedia/Kjetil Fjellheim, licence CC BY 2.0]

We can go a step further by pointing out that we've limited ourselves here to a wavelength range between 400 and 700 nm, simply because our human eyes are insensitive to wavelengths below and above that (as you'll have gathered by now, pigments are at work in our retinas, and these are only specific to a small range of wavelengths, due to the properties of their electrons; full circle!) However, there's no reason why the rest of life should be limited to these wavelengths. For example, bees and birds are often capable of perceiving the near ultraviolet (UV; between 350 and 400 nm), while some snakes are able to see in the near infrared (IR; between 700 and 1,000 nm).

So there's no clear dividing line between what's visible and what's invisible, only a gradient of absorption in the light spectrum according to the characteristics of the organic molecules (in this respect, pigments are nothing really special compared to all other organic molecules, apart from delighting our eyes).

In fact, when we look at the wavelengths actually absorbed by a pigment (using the UV/visible/IR spectroscopy technique that produces absorption spectra; Figure 4), we see that pigments don't absorb at a single wavelength, but often at several points in the spectrum and over continuous ranges, forming more or less broad peaks around a mean value (Figure 4). This is because pigment electrons are influenced by the complexity of their environment (solvent, matrix, protein, etc.), enabling them to absorb a whole range of wavelengths relatively close to one another.

Ultimately, the energy levels of a pigment's electrons dictate its total absorption spectrum in the UV-Visible-IR, which, together with other colouring mechanisms not discussed here, is what gives an organism its visible colour (Figure 4).

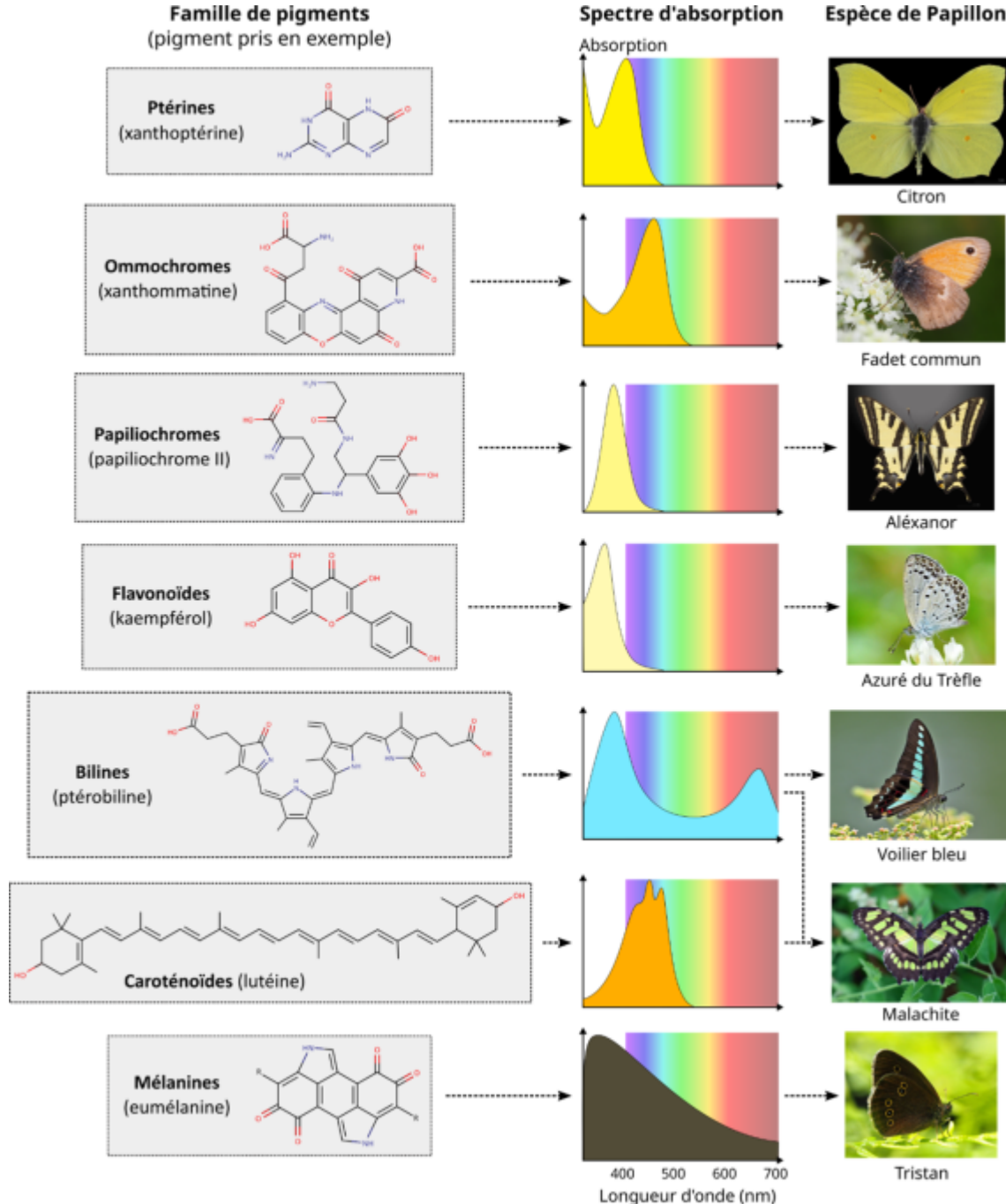


Figure 4. Diversity of pigment families and colour diversity in butterflies. The absorption spectrum of pigments is one of the determinants of colour in butterflies. Due to the diversity of pigment structures, their electrons absorb in a wide range of wavelengths, which partly explains the intra- and interspecific colour diversity of butterflies. It should be noted that the same butterfly generally possesses several families of pigments, that some colours are due to the superposition of several pigments (for example, the green colour of Malachite comes from the joint absorption of a blue bilin and an orange carotenoid, allowing only green wavelengths to pass through) and that other colours are not derived from pigments (for example, the iridescent metallic reflections of Azure butterflies). [Sources: Citron © Wikimedia/Didier Descouens, licence CC BY-SA 4.0; iNaturalist/Florent Figon common © fadet, licence CC BY 4.0 ; Aléxonor © Wikimedia/Didier Descouens, licence CC BY-SA 4.0; Clover © Azure Flickr/Florent Figon, licence CC BY-SA 2.0; Blue © sailboat Flickr/Florent Figon, licence CC BY-SA 2.0 ; Wikimedia/Anne Toll in © Malachi, licence CC BY 2.0 ; Tristan © Flickr/Florent Figon, licence CC BY-SA 2.0]

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- Figon, F. & Lorin, T. (2019) La coloration des Animaux : éléments de physique et de chimie. *Planet-Vie*. <https://planet-vie.ens.fr/thematiques/cellules-et-molecules/biophysique/la-coloration-des-animaux-elements-de-physique-et-de> (in French)
- Valeur, B. & Bardez., E. (2015) *La lumière et la vie, une subtile alchimie*. Paris : Belin. (In French)

Notes and references

Vignette : *Danaus plexippus* [Muséum de Toulouse, Licence CC BY-SA 4.0, via Wikimedia Commons]

[\[1\]](#) From a biochemical point of view, pigments can come directly from food (e.g., green bilines derived from plant chlorophyll, plant flavonoids kept intact; see [Leaf colours](#)) or from the body's own metabolism (e.g., melanins, pterins and ommochromes/papiliochromes are produced from amino acids or nucleic bases, respectively tyrosine, guanine and tryptophan).

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