doi:10.2533/chimia.2019.760 Chimia 73 (2019) 760–762

Chemical Education

A CHIMIA Column

Topics for Teaching: Chemistry in Nature

The Colour Violet: Chemistry or Physics?

Catherine E. Housecroft*

**Correspondence*: Prof. C. E. Housecroft, Department of Chemistry, University of Basel, BPR 1096, Mattenstrasse 24a, CH-4058 Basel, E-mail: catherine.housecroft@unibas.ch

Abstract: Violet iridescence in purple emperor butterflies arises from structural order in the wing-scales in contrast to the chemical pigments responsible for some violet colours in Nature.

Keywords: Chemical education · Iridescence · Structural order · Violet pigments

The natural world is full of colour, but its origins are not always simple. In this article, we look at the colour violet, using examples from butterflies and flowers. Before continuing, we review the part of the electromagnetic spectrum that covers ultraviolet (UV) and visible light. The visible region is from 380 to 750 nm (Fig. 1). The UV region lies beyond the shortest wavelength (highest energy) of the visible spectrum (Fig. 1). If visible light of a given wavelength, λ, is *reflected*, we see the colour corresponding to this wavelength. If visible light of a given wavelength is *absorbed*, we see the complementary colour, *i.e.* white light minus the absorbed radiation. The difference between reflected and absorbed light is critical to the discussion that follows.

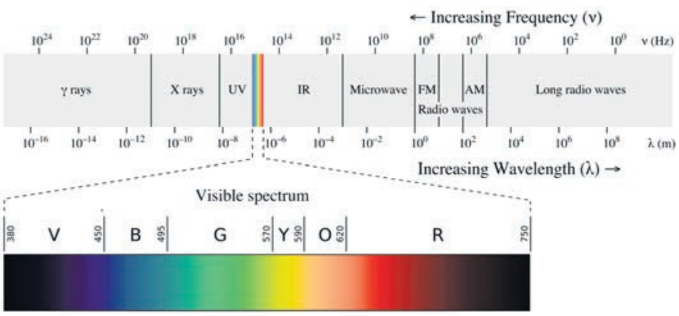


Fig. 1. The electromagnetic spectrum highlighting the visible region from 380 to 750 nm. Credit: Philip Ronan, Gringer [CC BY-SA 3.0 (*https://creativecommons.org/licenses/by-sa/3.0*)].

Butterflies and moths belong to the order *Lepidoptera*. Many moths are night-flying and we often fail to appreciate the beauty of their colours. Day-flying butterflies stun us with their beautiful displays of colours, some of which are *iridescent*.[1] An iridescent material is one that appears to change colour with the angle from which it is viewed. The appearance of butterfly wings arises from several features: (i) pigments that absorb light, (ii) scattering of light, (iii) *luminescence* (the emission of light from a material after it has been *excited* by absorbing light) and (iv) iridescence.[2] The colour of light absorbed by a pigment depends on its chemical structure and pigments are widespread in the plant kingdom (see later). Scattering of light, luminescence and iridescence arise from nanoscale structures made of *chitin* on the wings of butterflies. Fig. 2 shows scanning electron microscopy (SEM) images of the wing-scales of different butterflies at various magnifications. Scales cover both the upper and lower sides of the wings and overlap one another as shown in the SEM image in Fig. 2a. The detailed structure of the scales is visible at higher magnifications (Figs. 2b–d). Although the detailed construction is highly variable across the several thousand species of *Lepidoptera* that live in Europe, a general description can be given in terms of parallel ridges (seen in Fig. 2c) connected by cross ribs.

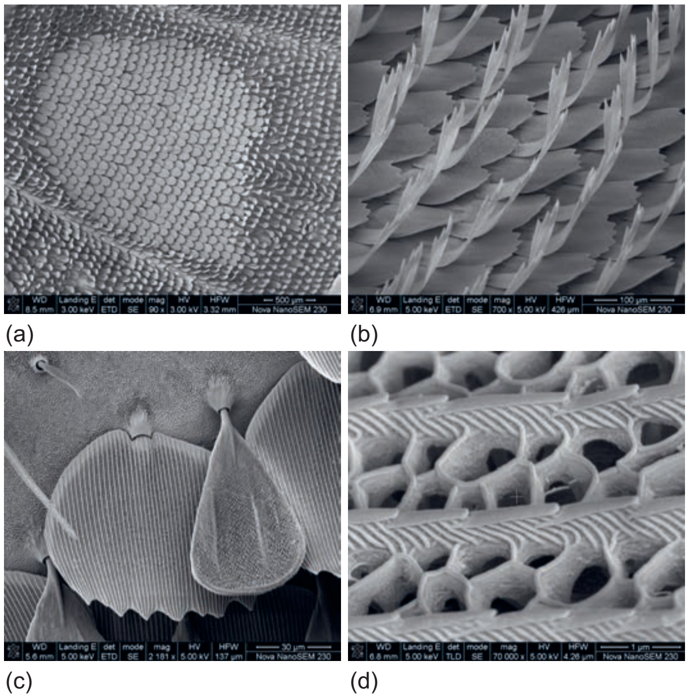


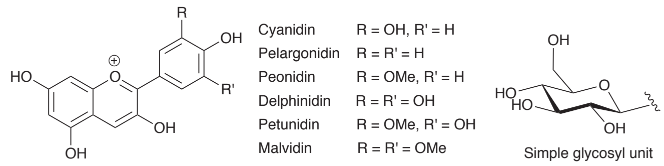
Fig. 2. Scanning electron microscopy (SEM) images of the wing-scales of butterflies: scale bar (bottom right of each image) (a) 500 µm, (b) 100 µm, (c) 30 µm and (d) 1 µm. The images are from different butterflies. (Courtesy of the Nano Imaging Lab, SNI, University of Basel.)

The violet iridescence of male purple emperor butterflies (Fig. 3) is particularly striking. The brown colour (Fig. 3) arises from *melanin* pigments while the violet hue is a *structural colour*. Structural colour arises from the interaction between the wave-like properties of incident light and the intricate structural order present on the butterfly wing-scales. For interference to occur, the periodicity of the structural features must be of the same order of magnitude as the wavelength of the incident light.[3] Scanning electron microscopy (SEM) imaging of the wings of purple emperor butterflies reveals two types of wing-scales: cover and ground scales. As the names imply, the cover scales lie on top of the ground scales, and the micrometric structure of the cover scales is more complex than that of the ground scales.

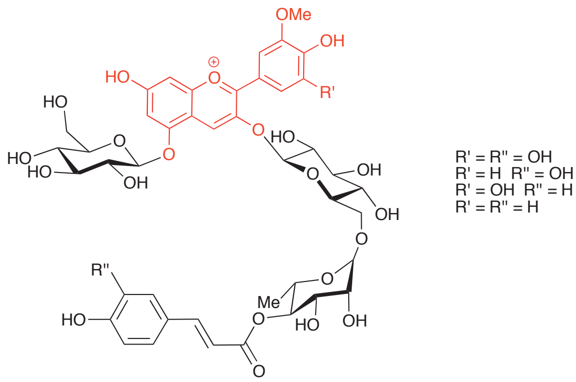
The parallel ridges (analogous to those in Fig. 2c) form a surface diffraction grating with an 820 nm period. Upon each ridge lies a series of lamella which form a Bragg diffraction grating with a periodicity of *ca*. 75 nm. The complex architecture is described in detail in ref. [2] and results in a maximum *reflectivity* at the interface of the UV and visible parts of the spectrum at 380 ± 27 nm, corresponding to violet light (Fig. 1). The relative orientations of the lamellae with respect to the wing scale, and the relative orientation of each scale with respect to the membrane of the wing lead to the violet iridescence being visible only within an angular viewing range of 18°, and so the observation of the violet iridescence in Fig. 3 is highly angle-dependent. Viewed from some angles, the wings appear brown. The large variety of optical nanostructures in *Lepidoptera* has the potential for application as templates for nanophotonic materials.[4]

Fig. 3. A male purple emperor (*Apatura iris*) butterfly. ©Edwin C. Constable 2018.

Fig. 4. Flowerhead of *Allium hollandicum* 'Purple Sensation'. ©Edwin C. Constable 2019.



Scheme 1. Structures of the common natural anthocyanidins. Replacing different numbers of OH groups by glycosyl units produces anthocyanins.



Scheme 2. Structures of the anthocyanins found in certain purple potatoes. Core structures of the anthocyanidins peonidin and petunidin are given in red.

Not all Nature's violet hues arise from the effects of structural order. Violet, red and blue pigments in flowers, fruit and vegetables are often *anthocyanins*, while red, orange and yellow colours frequently arise from *carotenoid* pigments; yellow *flavone* pigments are also important. Since we are focusing on the colour violet, it is the anthocyanin pigments that are of interest and allium flowers provide good examples of such pigmentation. The genus *Allium* includes many species of onions and garlics as well as cultivated flowers such as *Allium hollandicum* 'Purple Sensation' (Fig. 4). The word anthocyanin derives from the Greek ανθος (flower) and κυανος (blue). Anthocyanins are *glycosides* of *anthocyanidins*. Scheme 1 shows the structures of the six common naturally occurring anthocyanidins.[5] Their names derive from genera of plants (*e.g. Pelagonium*, *Delphinium*, *Paeonia*) all of which have bright violet, blue or red flowers. Starting from these six anthocyanidins and replacing different numbers of OH groups by a wide variety of glycosyl units (monosaccharides, or linear or branched oligosaccharides) leads to several thousand water-soluble anthocyanin pigments.[6] These may contain OH groups in the glycosyl units (as shown in Scheme 1, right) or OAcyl groups. Mixtures of anthocyanins are common[7] and, for example, acylated glycosides of petunidin and peonidin (Scheme 2) have been isolated from certain cultivars of purple potatoes.[8]

The violet, blue or red colours of anthocyanins arise because they absorb light in the region 480–550 nm with high molar absorption (or molar extinction) coefficients in the range of 25,000–50,000 $dm^3\ mol^{-1}\ cm^{-1}$ – the higher the molar extinction coefficients, the more intense the colour.[9] Absorption in the 480–550 nm range (see Fig. 1) removes green light from incident white light, leaving violet, blue, or red light being transmitted for the eye to observe depending on the exact wavelengths of light absorbed; the absorption spectra of anthocyanins are pH dependent.

This article highlights how Nature uses reflected light to produce beautiful violet iridescence in butterfly wings, or uses pigments which absorb selected wavelengths of light to produce violet-coloured flowers.

Acknowledgements

I am extremely grateful to Susanne Erpel and Dr Markus Dürrenberger in the Nano Imaging Lab, SNI, University of Basel, for providing the SEM images in Fig. 2.

Received: July 22, 2019

[1] S. Berthier, 'Iridescences: The Physical Colors of Insects', Springer, New York, **2007**.
[2] D. Pantelić, S. Ćurčić, S. Savić-Šević, A. Korać, A. Kovačević, B. Ćurčić, B. Bokic, *Optics Expr.* **2011**, *19*, 5817.
[3] P. Vukusic, *Current Biol.* **2006**, *16*, R621.
[4] Z. Jakšić, D. Pantelić, M. Sarajlić, S. Savić-Šević, J. Matović, B. Jelenković, D. Vasiljević-Radović, S. Ćurčić, S. Vuković, V. Pavlović, J. Buha, V. Lačković, M. Labudović-Borović, B. Ćurčić, *Optical Mater.* **2013**, *35*, 1869.
[5] V. O. Silva, A. A. Freitas, A. L. Maçanita, F. H. Quina, *J. Phys. Org. Chem.* **2016**, *29*, 594.
[6] C. Martin, Y. Zhang, L. Tomlinson, K. Kallam, J. Luo, J. D. G. Jones, A. Granell, D. Orzaez, E. Butelli in 'Recent Advances in Polyphenol Research', Eds. V. Cheynier, P. Sarni-Manchado, S. Quideau, Wiley-Blackwell, Chichester, **2012**, vol. 3, Ch. 5.
[7] C. A. Williams, R. J. Grayer, *Nat. Prod. Rep.* **2004**, *21*, 539; N. C. Veitch, R. J. Grayer, *Nat. Prod. Rep.* **2008**, *25*, 555.
[8] T. Fossen, D. O. Øvstedal, R. Slimestad, Ø. M. Anderson, *Food Chem.* **2003**, *81*, 433.
[9] For an introduction to absorption spectra, absorption maxima and molar extinction coefficients, see: C. E. Housecroft, E. C. Constable, 'Chemistry', 4th Edn, Prentice Hall, Harlow, **2010**, Ch. 11 and 13.

This column is one of a series designed to attract teachers to topics that link chemistry to Nature and stimulate students by seeing real-life applications of the subject.