NCW 2001: Celebrating Chemistry and Art

Indigo and Tyrian Purple—In Nature and in the Lab

by Paul F. Schatz

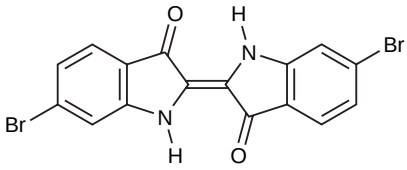
Both indigo and Tyrian purple were used as dyes in antiquity. Indigo was available from plants, and both dyes were obtained from snails found in the Mediterranean Sea. Some of the interesting history of these two dyes was described recently in a report on a talk by Roald Hoffmann at an ACS national meeting (*1*). Tyrian purple (**1**) is the 6,6′-dibromo derivative of indigo (**2**). However Tyrian purple cannot be prepared from indigo by simple bromination. Substitution will occur at every open position of the aromatic ring except the 6 and 6′ positions. The positions of the bromine atoms in Tyrian purple have a dramatic influence on its color. Tyrian purple is the only brominated derivative of indigo that has a reddish cast. If bromines are placed at any position of the aromatic ring other than the 6 and 6′ positions, the dye is blue. Color experts opine that these bromo derivatives have a greener shade of blue than indigo. As can be seen in the photos on this and the facing page, the color of 5,5′-dibromoindigo (**3**) is very similar to that of indigo (**2**).

Friedländer determined the structure of Tyrian purple by synthesizing 6,6′-dibromoindigo, demonstrating its identity to the dye extracted from snails (*2*). From 12,000 snails he was able to isolate 1.4 g of dye.

Because it could only be made from snails, Tyrian purple was scarce and expensive. Robes made of cloth dyed with it were signs of wealth and nobility in antiquity. On the other hand, indigo, derived from plants, was one of the earliest and most common dyes. Rather than being a sign of wealth, indigo proved to be a source of wealth. First, for the British, who in the nineteenth century dominated the indigo dyestuff market as a result of huge indigo plantations in India. And then for the Germans, who took over control of the indigo market at the turn of the century with synthetic indigo. The structure determination and synthesis of indigo were triumphs of the burgeoning German chemical industry of that time. Adolf von Baeyer was awarded the Nobel Prize of 1905 in recognition of his contributions to chemical synthesis, citing his synthesis of indigo specifically.

Background material on both of these dyes can be found in the *Journal of Chemical Education* (*3–9*). The information about Tyrian purple is mostly historical, while the information about indigo also includes its synthesis (*10*) and methods of dyeing with it (*11*, *12*). A multi-step synthesis of Tyrian purple suitable for the advanced undergraduate organic chemistry laboratory has been published in *Education in Chemistry* (*13*) and used by the author.

Tyrian purple



1

Each dye discussed in this article is shown above with its chemical structure. From left: Tyrian purple, indigo, and 5,5′-dibromoindigo. The compounds were prepared by students in the advanced undergraduate organic laboratories at the University of Wisconsin–Madison under the author's guidance.

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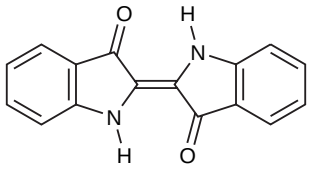
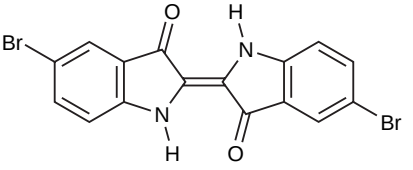
indigo



2

5,5′-dibromoindigo



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Photos by J. J. Jacobsen and R. J. Wildman