The Photochemistry of Royal Purple

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Why Study Royal Purple?

Why should the photochemistry of an ancient dye, albeit the most famous and expensive dye that the world has known, be of interest to modern science? To be sure, Royal Purple--6,6'-dibromoindigotin (DBI: Compound III in Figure 1)--was crucial to the economic success of the first millennium B.C. Phoenicians, to whom we are indebted for our alphabet, among other cultural and technological advances. From their homeland in Lebanon, the Phoenicians plied the waters of the Mediterranean, and wherever they went they carried textiles dyed with Purple. Dye factories were established at many Phoenician colonies along the coasts of Tunisia, Malta, Sicily, and Spain. Moreover, Purple played an important role in ancient Semitic religion, which has been passed down to us in biblical tradition (see, e.g., Exodus 26:1, 31; 28:4-6; 39:1, 28-29; II Chronicles 3:14, describing the Israelite High Priest's garments and the Tabernacle curtains). Since mollusks that yield the dye occur throughout the world's oceans, many other ancient peoples, including the ancient Chinese and Peruvians, appear to have independently discovered purple-dyeing and also to have ascribed special religious and economic value to the dye.

Yet, purple-dyeing in the Mediterranean disappeared over 500 years ago, with the fall of Constantinople in A.D. 1453, and had been in decline for 800 years before then, following the Islamic conquest of the seventh century. Even after the synthetic route to DBI was developed in the early twentieth century, this dye was not produced as a commercial product.

Does the Dye Have a Biological Function?

The biological effect or purpose of purple dye formation in the hypobranchial gland of the live mollusk is also poorly understood. Several side-products of indigoid dye formation, specifically choline sulfates and serotonin (a neurotransmitter) and related amines, might enable the animal to ward off predators, or to bore through shells and paralyze (anesthetize) its prey. Since hundreds of mollusks come together to form spawning mounds, in which a yellowish egg mass with a distinct purplish color forms, possibly a dye precursor or the dye itself is a pheromone. On the other hand, secretion of the hypobranchial gland, through the mantle cavity of the animal to the outside, could simply be a detoxification mechanism.

Royal Purple: A Unique Natural Material Undergoing Photodevelopment

Possibly, it is our insufficient scientific understanding of what was clearly a material of great historical significance that should prompt us to look at the photochemistry of DBI more closely. From a human, if not a molluscan, perspective, what is most striking about molluscan Purple is that it yields a highly unusual and intense coloration, especially when exposed to light. The mollusks were and are a common food source, and in opening the shell, one can easily come away with purple hands.

In 1685, the first "modern" investigator of the dye, William Cole, noted that exposure to light led to the development of purple from the hypobranchial glandular secretions of a north Atlantic species, *Nucella (Thais) lapillus*. Ancient dyers must also have observed that textiles dyed with the secretions of certain mollusks developed a deeper color very quickly in light, especially under the intense Mediterranean sun. Surprisingly, only one short reference in the writings of the Roman scholar Pollux mentions the effect of light on the dye, and this reference does not specify the stage of the process at which light is critical. Could it be that lighting conditions were a closely guarded trade secret?

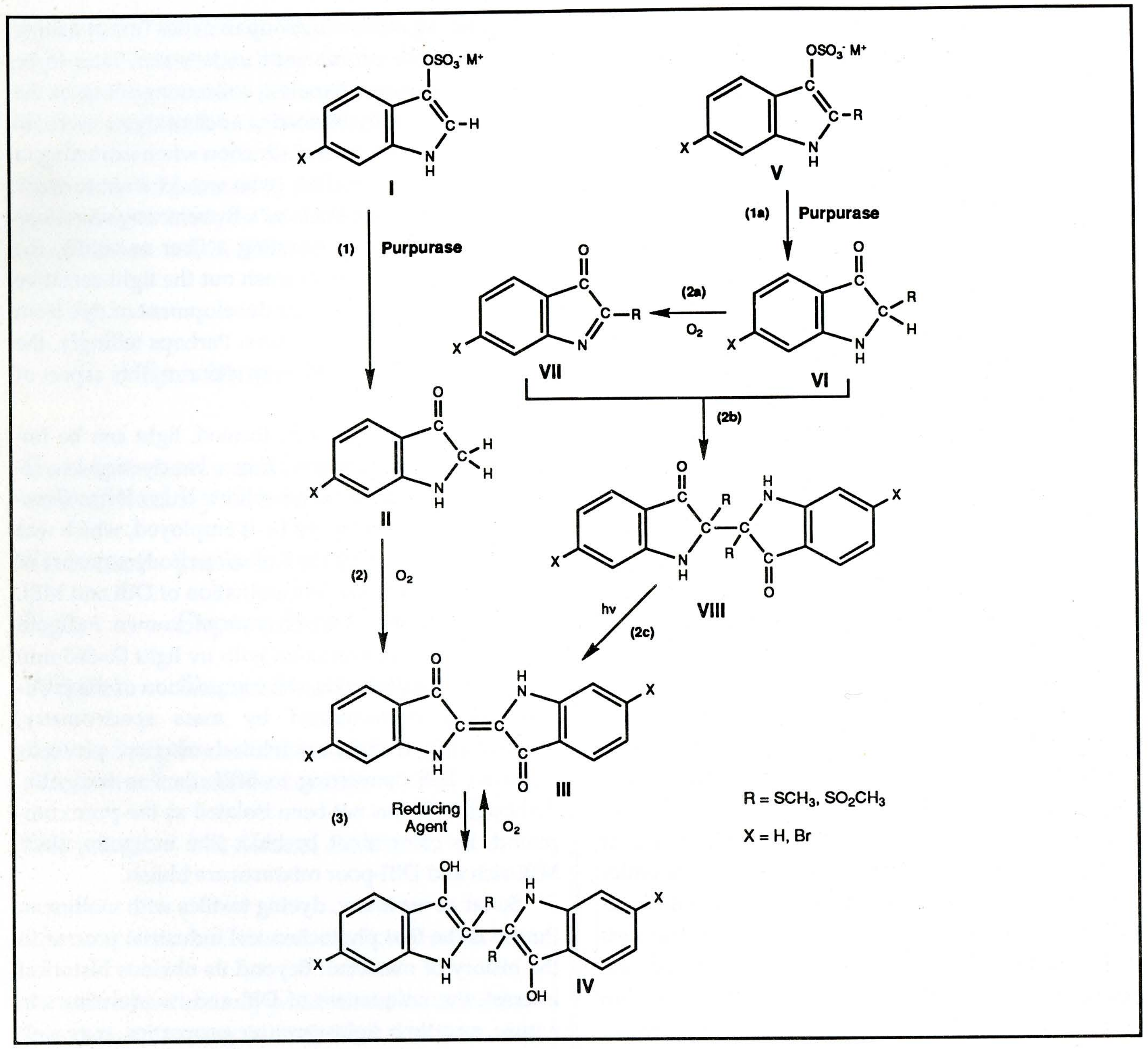

Figure 1. Chemical pathways for the production of indigoid dyes from hypobranchial glandular secretions of Muricidae.

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To understand how light enters into the conversion of the molluscan glandular precursors to indigoid dye, several preliminary comments about the reaction pathways in Figure 1 are in order. Firstly, the reaction pathway on the left (Steps 1 and 2), starting from indoxyl sulfate esters which are **not** substituted in the 2-position, does **not** require light to form the dye, but only air. Of the Mediterranean species, only *Murex trunculus* produces such precursors, and, since bromine is often not present in the 6-position, the glandular sections of this animal usually result in a mixture of indigotin, 6-monobromoindigotin (MBI), and DBI.

The other two historically important Mediterranean species, *Murex brandaris* and *Purpura haemastoma*, primarily produce sulfate esters of 6-bromoindoxyl which are substituted in the 2-position with a methylthio or methylsulfonyl group. These precursors form the greenish 2,2'-bissubstituted-6,6'-

dibromo-2,2'-diindoxyl (tyrindoxyl: Compound VIII in Figure 1), which then photochemically forms DBI (Steps 2a-c in Figure 1).

The photolysis of tyrindoxyl to indigoids has been shown to have a high quantum efficiency, suggesting a chain reaction.The formation of tyrindoxyl itself is also undoubtedly photochemically initiated. Filter paper impregnated with molluscan glandular secretions has been stored by us for up to a year and remained unaltered in appearance until exposed to light. The greenish tyrindoxyl then forms in about one minute; conversion to DBI requires another four minutes. It is not known whether light initiates the oxidation of the 2-substituted indoxyl to an indoleinone (Step 2a in Figure 1), or takes part in the subsequent addition reaction of these two compounds (Step 2b). Based on the well-known photo-oxidation of indoxyl to isatin, the first possibility is the more likely.

Photochemical Control in the Ancient Dyeing Industry?

Ancient dyers might have exploited the light sensitivity of the indole derivatives involved in molluscan dye formation in several ways. The formation and photolysis of tyrindoxyl could have been blocked or slowed by extracting the secretions in subdued light or darkness. When impregnating a textile or fibers under these conditions, species which produce mainly 2-substituted indoxyl sulfate esters, such as *M. brandaris* and *Purpura haemastoma*, will not form dye until exposed to light. The dye formed within the fiber from molecules of the absorbed precursors is fast to washing and rubbing.

By following a similar procedure and distinguishing male and female secretions, species producing greater amounts of the 2-unsubstituted indoxyl sulfate esters, such as *M. trunculus*, can also be made to yield a range of colorations from blue to purple, dependent on the relative amounts of unsubstituted 6-bromoindoxyl and indoxyl. Recently, we have observed that the final colorations of Mediterranean *M. trunculus* glandular samples collected and stored in the dark are probably differentiated by sex. Secretions from pseudohermaphroditic females* (i.e., females with non-functional male sexual organs) are predominantly blue, whereas the secretions of true males are mainly purple. Since the animals congregate by sex during mating season (a group of males first attaching itself to a rocky prominence underwater, later to be joined by a group of females), collections of one or the other sex can easily be made. Ancient dyers were no doubt aware of the color distinction when extracting in subdued light or the dark (who would want to work all day long under a hot sun?). By selecting secretions from one sex for impregnating a fiber or textile, the dyer then needed only to wash out the light-sensitive precursors following the air development of dye from the 2-unsubstituted precursors. Perhaps tellingly, the ancient writers are completely silent on this aspect of the dyeing industry.

Once the dye has been formed, light can be important in yet another way. If true vat-dyeing--i.e., reducing the dye to its water-soluble leuco form (Compound IV, Step 3 in Figure 1)--is employed, which was quite likely at least by the Roman period, exposure of the vat to light causes debromination of DBI and MBI. Our experiments in which vats of known indigoid composition were irradiated with uv light (λ=365 nm) for specific time periods, the composition of the products being characterized by mass spectrometry, showed that the debromination reaction proceeds stepwise, DBI converting to MBI, then to indigotin. Although MBI has not been isolated as the pure compound, its color must be blue, like indigotin, since MBI-rich and DBI-poor mixtures are bluish.

So far as we know, dyeing textiles with molluscan Purple is the first photochemical industrial process in the history of mankind. Beyond its obvious historical interest, the uniqueness of DBI and its precursors in nature, and their light-sensitive properties, may well point to more far-reaching significances.

*True females were rare in the area (Banyuls-sur-Mer, on the French Mediterranean coast close to the Spanish border) where we collected mollusks. Pseduohermaphroditism or protandry is believed to result from high tin pollution in the marine water.

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