

I thank Attila Szabo for helpful comments.

Appendix

There are many treatments of the transition from a Langevin equation to the corresponding Fokker-Planck equation. The following one appeals to me as pedagogically simple.

The starting point is the stochastic Liouville equation for $f(C,B;t)$ as in eq 12,

$$\frac{\partial}{\partial t}f = -Lf - \frac{\partial}{\partial B}F(t)f \quad (\text{A1})$$

in which L is an abbreviation for the operator

$$L = \frac{\partial}{\partial C}(-k(B)C) + \frac{\partial}{\partial B}(-\lambda B) \quad (\text{A2})$$

Integration over time leads to the operator equation $f(C,B;t) =$

$$e^{-tL}f(C,B;0) - \int_0^t ds e^{-(t-s)L} \frac{\partial}{\partial B}F(s) f(C,B;s) \quad (\text{A3})$$

By iterating, one can develop a series expansion of f in powers of F . This is substituted in the last term of eq A1,

$$\frac{\partial}{\partial t}f(C,B;t) = -Lf(C,B;t) - \frac{\partial}{\partial B}e^{-tL} F(t) f(C,B;0) + \frac{\partial}{\partial B} \int_0^t ds e^{-(t-s)L} \frac{\partial}{\partial B}F(t) F(s) f(C,B;s) \quad (\text{A4})$$

Now we average over Gaussian white noise. The average $\langle f(C,B;t) \rangle$ is $g(C,B;t)$. Because the initial distribution $f(C,B;0)$ does not contain any effects of noise, the average $\langle F(t) f(C,B;0) \rangle$ is first order in the noise and

vanishes. Then we need only the average $\langle F(t) F(s) f(C,B;s) \rangle$.

Here is where the two properties "Gaussian" and "white" are used. The average of any product of an odd number of Gaussian random variables will vanish. The average of a product of an even number of Gaussian random variables, for example, $\langle F_1 F_2 F_3 F_4 \rangle$, can be found by taking all possible pairings of the variables, for example, $\langle F_1 F_2 \rangle \langle F_3 F_4 \rangle + \langle F_1 F_3 \rangle \langle F_2 F_4 \rangle + \langle F_1 F_4 \rangle \langle F_2 F_3 \rangle$. Next we use the "white noise" property: $\langle F(t_1) F(t_2) \rangle$ is proportional to the δ function $\delta(t_1 - t_2)$,

$$\langle F(t_1) F(t_2) \rangle = 2\lambda\theta \delta(t_1 - t_2) \quad (\text{A5})$$

Consider now the average $\langle F(t) F(s) f(C,B;s) \rangle$. The first noise factor $F(t)$ can be paired with the second, $F(s)$, or it can be paired with noise factors contained in $f(C,B;s)$. But $f(C,B;s)$ can depend on $F(s')$ only for those times s' that are earlier than s . This pairing leads to $\delta(t-s')$ and requires that a time t that is later than s must be equal to a time s' that is earlier than s . Thus there are no contributions from such pairings, and only the first pairing, of $F(t)$ and $F(s)$, will contribute. Then for present purposes we can write $\langle F(t) F(s) f(C,B;s) \rangle = \langle F(t) F(s) \rangle \langle f(C,B;s) \rangle$. This introduces $2\lambda\theta \delta(t-s)$ and removes both the operator $e^{-(t-s)L}$ and the time integral. The time integral from 0 to ∞ picks up half of the δ function and removes the factor 2. The result is the Fokker-Planck equation,

$$\frac{\partial}{\partial t}g = -Lg + \lambda\theta \frac{\partial^2}{\partial B^2}g \quad (\text{A6})$$

which is eq 13.

Royal Purple Dye: The Chemical Reconstruction of the Ancient Mediterranean Industry

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Royal purple, 6,6'-dibromoindigotin (DBI, structure III in Figure 1, X = Br), is the most renowned of ancient dyes.¹ Even before Nero issued a decree in the first century A.D. that gave the emperor the exclusive right

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to wear royal purple garments, the association of this dye with royalty and high ecclesiastics was well established. As one example, biblical texts² incorporating Iron Age traditions prescribed that the tabernacle curtains and the high priest's vestments were to be dyed with royal purple.

The sociopolitical and religious significance of royal purple was closely tied to its economic value. In some periods, it was worth as much as 10-20 times its weight in gold.³ This circumstance can be traced to the fact that the precursors of DBI, which convert to the dye in air and light (see Figure 1), are found in nature only in the hypobranchial secretions of certain marine mollusks (Figure 2).⁴ As many as 10 000 animals are

(1) Brunello, F. *The Art of Dyeing in the History of Mankind*; Neri Pozza Editore: Venice, 1973; pp 13, 57, 79.

(2) See: Exod. 26:1, 31; 28:4-6; 39:1, 28-29. 1 Kings 5:1-12; 7:13-14; 9:10-14, 26-28; 10:11, 22. 2 Chron. 2:7, 14; 3:14. Ezek. 27:7, 16, 24.

(3) Born, W. *Ciba Rev.* 1937, 1, 106-111, 124-128.

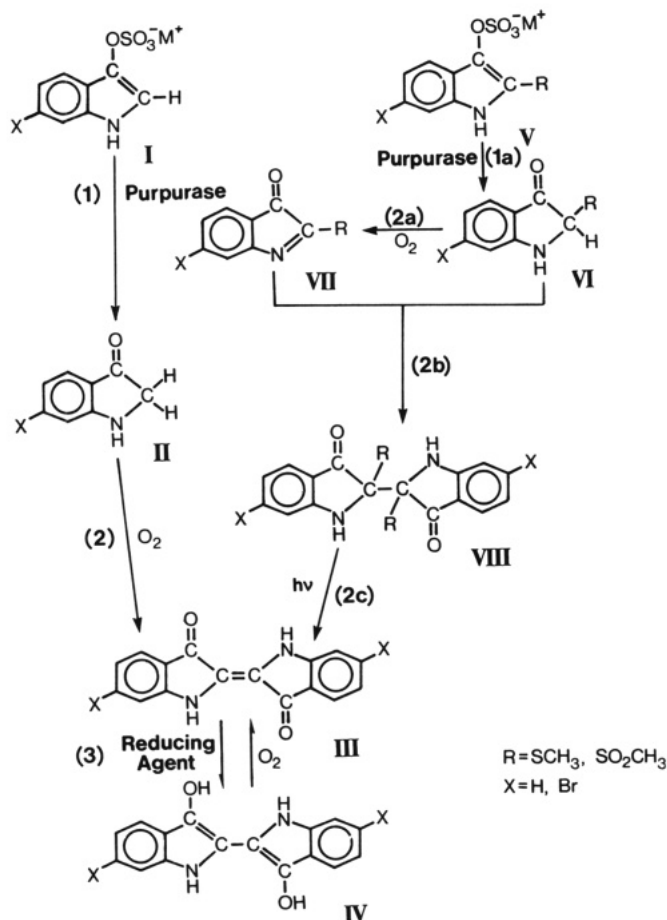


Figure 1. Chemical pathways for the production of indigoid dyes, beginning with the precursors of the molluscan glandular secretions.

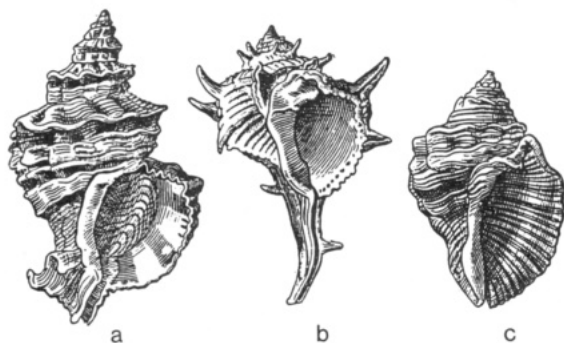


Figure 2. Principal Mediterranean molluscan species, yielding 6,6'-dibromoindigotin (DBI) and related indigoids: (a) *M. trunculus*; (b) *M. brandaris*; and (c) *P. haemastoma*. Reprinted from Besnier, M. *Dictionnaire des antiquités grecques et romaines*; Daremberg, C., Saglio, E., Eds.; Hachette: Paris, 1877-1919; Vol. 4, p 770, Fig. 5887.

needed to produce 1 g of the dye.^{5,6}

The mollusks occur worldwide, including the Mediterranean Sea and the Pacific and Atlantic Oceans, and the chemistry of the dye precursors has been shown to be similar in many respects for the various species.⁴ Since the mollusks were a common food source, the unusual and intense coloration of the secretions and their suitability for dyeing would have been readily

appreciated. Ancient peoples from around the globe, including the Phoenicians, Chinese, and Peruvians,⁷ discovered dyeing processes that employed the molluscan secretions.

Royal purple is especially associated with the Phoenicians in history^{6,8,9} and legend.¹⁰ Their preeminent role in the Mediterranean industry has been substantiated by the chemical identification of DBI on the interiors of "Canaanite" jars, used for storage and shipment of goods, from a 13th century B.C. dyeing factory at Sarepta, a site on the coast of Lebanon.^{11,12} This is the earliest attestation of the dye from anywhere in the world, and significantly, it was found in the homeland of the Phoenicians.

Despite the importance of purple dyeing to the Phoenicians, they rarely mentioned it in their writings, perhaps in order to protect closely guarded secrets,¹³ or perhaps it seems that way because only a small textual corpus has been recovered from excavations. The first lengthy, probably eyewitness, account of the industry occurs over 1000 years after it had begun, in Pliny the Elder's *Historia Naturalis* (Book IX, Sections 60-65, Chapters XXXVI-XLI)¹⁴ of the mid first century A.D. The Roman scholar recounts in marvelous detail how the mollusks were captured by using baited wicker baskets; how the best time to capture the animals was in the spring, after the rising of the Dog Star, Sirius; how the glands were removed and the extracts heated for 10 days in a large vat with added salt and water, with periodical skimming off of refuse materials from the surface and testing of the liquid for its dyeing properties; how a double dipping of the wool was able to produce the "Tyrian color", reputedly the finest and most expensive dye of all; how human urine modified the coloration; and so forth.

Only short, often cryptic, references are found in other Greek and Roman writings. Plutarch¹⁵ notes in his biography of Alexander that the well-preserved textiles recovered by the conqueror at the Persian court of Susa had been dyed 190 years earlier at Hermione in Greece, by using either honey or oil. The alchemical texts written in Egypt in the third century A.D., in particular Papyri Leidensis¹⁶ and Graecus Holmiensis,¹⁷ with probable roots in much earlier tradition,¹⁸ also mention specific materials and procedures that entered into the processing of purple dyes. But since a goal of

(7) Jackson, J. W. *Mem. Manchester Phil. Soc.* 1915-1916, 60(Part II), 19-29.

(8) Reese, D. S. *Libyan Stud.* 1979-1980, 11, 79-93.

(9) Jensen, L. B. *J. Near Eastern Stud.* 1963, 22, 104-118.

(10) Pollux, J. *Onomasticon*; Bekker, I., Ed.; F. Nicolai: Berlin, 1846; Book 1, pp 45-49.

(11) Pritchard, J. B. *Recovering Sarepta, A Phoenician City*; Princeton University: Princeton, 1978.

(12) McGovern, P. E.; Michel, R. H. *Anal. Chem.* 1985, 57, 1514A-1522A. McGovern, P. E.; Michel, R. H. *MASCA J.* 1984, 3, 67-70.

(13) The relative openness of some ancient crafts is well illustrated by the second millennium B.C. glass industry. See: Oppenheim, A. L.; Brill, R. H.; Barag, D.; von Saldern, A. *Glass and Glassmaking in Ancient Mesopotamia*; Corning Museum of Glass: Corning, NY, 1970.

(14) Pliny the Elder. *Pliny's Natural History*; Bostock, J., Riley, H. T., Trans.; H. G. Bohn: London, 1855.

(15) Plutarch. *Lives of the Noble Greeks*; Fuller, E., Ed.; N. Doubleday: New York, 1959; pp 240-314. See: Blümner, H. *Technologie und Terminologie der Gewerbe und Künste bei Griechen und Römern*; Teubner: Leipzig, 1942; note 15.

(16) Berthelot, M. P. E. *Collection des anciens alchimistes grecs*; G. Steinheil: Paris, 1887.

(17) Lagercrantz, O. *Recepte für Silber, Steine, und Purpur*; Almquist and Wiksells: Uppsala, 1913.

(18) Reinking, K. *Milliand Textilber.* 1925, 6, 349-351.

(4) Baker, J. T. *Endeavor* 1974, 33, 11-17.

(5) Friedländer, P. *Ber. Dtsch. Chem. Ges.* 1909, 42, 766.

(6) Bruin, F. *Sociétés et Campagnes de Commerce en Orient dans l'Océan Indien*; Mollat, M., Ed.; S. E. V. P. E. N.: Paris, 1970; pp 73-90.

the dyeings was to produce less expensive substitutes for royal purple, these papyri likely describe plant- or insect-derived dyes rather than molluscan royal purple. Talmudic descriptions of the same period and later refer to marine animal dyes, probably including royal purple, that were processed by heating the "blood" of the animal (presumably, the hypobranchial glandular secretions) and tested for authenticity in a mixture of urine, alumina, and fenugreek, or in fermented barley-flour dough.¹⁹

On the basis of available scientific, historical, and textual knowledge, scholars have attempted to reconstruct the ancient Mediterranean industry from Pliny's account and the other ancient references, with varying degrees of success. To assess current interpretations and direct future research, this Account reviews the field from the perspective of modern chemistry.

The Chemistry of Royal Purple

As early as 1685, it had been noted by Cole²⁰ that a colorless fluid in the hypobranchial glands of marine mollusks, found off the coast of Britain, was converted to a red color on exposure to light. Subsequent research²¹ substantiated the photochemical nature of the process. During the 19th century, as one of the earliest chapters in the emerging field of archaeological chemistry, an attempt was made to identify the chemical structure of the dye.²² Finally, in 1909, Friedländer determined that DBI was the dye obtained from one of the Mediterranean molluscan species, *Murex brandaris*. Later research of Friedländer²³ and others^{24,25} showed that this compound was also a major component of the dyes from other Mediterranean species (*Murex trunculus* and *Purpura haemastoma*), as well as molluscan species occurring in other parts of the world (e.g., *Purpura patula* and *Nucella (Purpura) lapillus* from the Gulf of Mexico and the Atlantic Ocean, respectively).

The isolation and structures of the individual precursors were first effectively investigated by Bouchilloux and Roche²⁴ and later more completely elucidated by Baker and Sutherland²⁶ and Fouquet and Bielg.²⁵ The precursors were found to be sulfate esters of indoxyl, 6-bromoindoxyl, and derivatives of these substituted in the 2-position with methylthio or methylsulfonyl groups (see compounds I and V in Figure 1). Hydrolysis of these sulfate esters by the enzyme purpurase (step 1 in Figure 1) was studied by Dubois and Erspamer.²⁷ Baker and Sutherland²⁶ also showed that the oxidatively formed greenish compound from 2-substituted indoxyls converted to dye by a photochemical process

(19) Herzog, I. *The Royal Purple and the Biblical Blue: Argaman and Tekhelet*; Spanier, E., Ed.; Keter: Jerusalem, 1987; pp 17-131. Herzog, I. *Proc. Rep. Belfast Nat. Hist. Philos. Soc.* 1919-1920, No. 2, 21-33.

(20) Cole, W. *Philos. Trans. R. Soc. London* 1685, 15, 1278-1286.

(21) de Lacaze-Duthiers, H. *Ann. Sci. Nat., Zool. Biol. Anim.* 1859, 4th Series 12, 5-84.

(22) Negri, A.; de Negri, G. *Gazz. Chim. Ital.* 1875, 5, 437-438. Schunck, E. *Chem. Soc. Trans.* 1879, 35, 589-595; *Chem. Soc. Trans.* 1880, 37, 613-617.

(23) Friedländer, P. *Ber. Dtsch. Chem. Ges.* 1909, 42, 765-770; *Monatsh. Chem.* 1909, 30, 247-253; *Angew. Chem.* 1909, 22, 2321-2324; *Ber. Dtsch. Chem. Ges.* 1922, 55, 1655-1658.

(24) Bouchilloux, S.; Roche, J. *Bull. Inst. Océanogr. Monaco* 1955, No. 1054, 1-23.

(25) Fouquet, H.; Bielg, H.-J. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 816-817.

(26) Baker, J. T.; Sutherland, M. D. *Tetrahedron Lett.* 1968, 43-46.

(27) Dubois, R. *Arch. Zool. Exp. Gen.* 1909, 5th Series, 2, 471-590. Erspamer, V. *Pubbl. Stn. Zool. Napoli* 1947, 20, 91-102.

(step 2c in Figure 1), evolving long-observed, odoriferous sulfur compounds. The structure of this intermediate was identified by Christophersen and co-workers²⁸ as a 2,2'-bissubstituted 2,2'-diindoxyl (compound VIII in Figure 1), the dibromo derivative being referred to as tyriverdin. Indoxyls not substituted in the 2-position were shown to form indigoids directly by oxidative coupling in air. Whereas *M. trunculus* secretions contained both indoxyls and 6-bromoindoxyls, substituted and unsubstituted in the 2-position, secretions from *M. brandaris* and *P. haemastoma* contained primarily 2-substituted 6-bromoindoxyl. Consequently, *M. trunculus* yields both indigotin and DBI, while *P. haemastoma* and *M. brandaris* produce almost exclusively DBI.

As indigo vat dyeing is practiced today, the indigoid is reduced to the almost colorless, soluble leuco base (step 3, going from compound III to IV, in Figure 1), in which form it is absorbed by the textile to be dyed. Reoxidation by exposure to air yields the colored dye, which is wash-fast and resistant to rubbing. This procedure is to be contrasted with direct application of the molluscan secretions to a textile with subsequent color development in the sun, the preferred method of the pre-Columbian inhabitants of Peru, dating back to 500 B.C.,²⁹ and very recently, of Indians in Mexico.³⁰

Any process that does not use the molluscan secretions directly must in some manner avoid the formation of the insoluble dye until the textile fiber has been impregnated. This might be accomplished in a number of ways:

1. The substituted or unsubstituted dye, once formed, could be converted to the leuco base by chemical or fermentative reduction (step 3 in Figure 1). Even with excess reducing agent present, however, care would be needed to minimize exposure of the reduced solution to air.

2. For those molluscan secretions containing primarily 2-substituted indoxyls or for those that were obtained by separating the unsubstituted indoxyls after oxidative coupling (step 2 in Figure 1), the avoidance of light would prevent the conversion of diindoxyls to indigoid dye (step 2c, going from compound VIII to III, in Figure 1).

3. The formation of the diindoxyls from indoxyls (starting with step 2a in Figure 1) might be blocked by antioxidants, i.e., stabilizers to oxidation of the intermediates (compound VI).

4. The hydrolysis of the sulfate ester precursors might be blocked by the deactivation of the enzyme purpurase (step 1 in Figure 1).

Although the ancient dyer lacked an understanding of the chemistry of royal purple, the time-consuming, elaborate procedures detailed by Pliny and in other sources go far beyond the simple application of the molluscan secretions and probably have a basis in pragmatic observations on how best to produce an uncontaminated, fast, attractive textile dye. The task of the interpreter is to determine whether any of the above

(28) Christophersen, C.; Watjen, F.; Burchardt, O.; Anthoni, U. *Tetrahedron* 1978, 34, 2779-2781.

(29) Saltzman, M. *Textile Conservation Symposium in Honor of Pat Reeves*; McLean, C. C., Connell, P., Eds.; The Conservation Center, Los Angeles County Museum of Art: Los Angeles, 1986; pp 27-39.

(30) Nuttal, Z. *Putnam Anniversary Volume*; G. E. Strechert: New York, 1909; pp 368-384. Gerhard, P. *New York Shell Club Notes* 1977, No. 229, 4-5.

chemical methods aids in the understanding of a given ancient text.

Chemical and Fermentative Reduction Systems

The ancient extraction process for royal purple as described by Pliny has often been understood as a vat process.³¹ Actual experiments³² according to the recipes and procedures outlined by Pliny, however, are only able to produce a true vat dye under certain circumstances that may or may not conform to the intended meaning of the text. For example, the word *plumbum*, which the heating vessel is said to be made of, can be translated as "tin"³³ or "lead",³⁴ depending upon whether one supplies the adjective *album* ("white") or *nigrum* ("black"), which is lacking in Pliny's text. The choice of adjective is critical in deciding whether a reducing system is being described by Pliny. Lead and a moderately alkaline solution (pH 10–12), with decreased air supply, at ca. 90 °C will not reduce indigoids, but tin under similar experimental conditions is effective.³² Although Pliny does not mention any specific steps taken to restrict the air supply (e.g., covering the vessel, minimal stirring), he implies that fairly large amounts of extracts were processed in a single vessel, and as such, less air would have reached indigoids lower in the vessel (i.e., with a lower surface-to-volume ratio). Under these conditions, prolonged heating of the molluscan extracts in an alkaline solution in a tin or tin-coated vessel could have reduced the indigoid to the leuco base. Different colors could have been achieved by dipping the textile in the leuco base solutions from different molluscan species or by varying the extraction time. Pliny, however, does not explicitly state that an alkali was used, and the alkalinity of the additives (e.g., urine and salt) he does mention are not sufficient for reduction to occur. Possibly, this was an oversight in his text, since strong alkalis (potash, soda, and lime) were available to the Romans.

Natural reducing agents³⁵ present in the molluscan secretions might have contributed to an alkaline vat dyeing. Methyl mercaptan, a byproduct of tyriverdin photolysis (see Figure 1, step 2c), is hypothesized to be the reducing agent. Experiments with a more easily handled, higher boiling synthetic mercaptan, 1-dodecanethiol, have demonstrated that DBI is reduced by a mercaptan in strong alkali at about 80 °C.³² We have also observed recently that the glandular secretions of *M. brandaris* were effective in decolorizing indigoids from *M. trunculus* secretions at room temperature, in the absence of any added alkali. This suggests the presence of a reducing agent in *M. brandaris* secretions, but the active ingredient and its mode of action have yet to be determined.

Since only a finite amount of mercaptan from the 2-substituted indoxyls is available for reduction and in

order to preserve the soluble, reduced form of the dye, the leuco base (compound IV in Figure 1), Elsner and Spanier added a reducing sugar (glucose from grape juice) to their mixture.³⁵ The addition of glucose is relevant to the note by Plutarch mentioning the use of honey (a mixture of glucose and fructose) in royal purple dyeing.¹⁵ The reducing capability of honey is known for indigotin;³⁶ recently, the first evidence was obtained that this is also true for DBI.³²

The possibility of tin, natural mercaptans, and honey serving as reducing agents to form vat dyes of DBI does not exclude their use in other stages of the process. The antioxidant properties of honey, for example, may provide a means of preserving the molluscan secretions in a soluble, precursor form for a period of time.³⁷

An iron filing/fermented urine mixture at 90 °C has been shown to be effective in reducing indigotin, but not DBI.³² The purple dye processed with iron and urine, described in Papyrus Leidensis, must then not have been a molluscan purple. Furthermore, iron and urine form iron salts and might have served as mordants for red dyes from madder or kermes.

Reinking¹⁸ translated the Greek words in Papyrus Leidensis for the iron additive (*σκαπίας σιδήρου*) as *Eisenhammerschlag* (German), "smithing scale", which is a mixture of ferrous and ferric oxides. Lagercrantz³⁸ rendered the phrase as *Eisenfeilstaub*, "iron filings", whereas Berthelot³⁹ read *scories de fer* (French), "iron slag". Steigerwald's recent study⁴⁰ supports Reinking's translation. Reduction of DBI with various forms of iron showed that DBI was not reduced in fermented urine with a pH of about 8.5.³² Steigerwald has argued that a much higher pH was required, but the highest pH recorded for fermented urine is 9.5.⁴¹

Honey and other organics might also have entered into a fermentative reduction process. A very clear description of a fermentation vat in the processing of woad plant, a source of indigo, is found in Papyrus Graecus Holmiensis.¹⁷ Starting with either woad or *Indigofera*, another common plant source, indoxyl is liberated, indigo formed by oxidative coupling, and the latter then reduced by a fermentative, enzymatic process to the soluble leuco base. Fermentation systems for synthetic indigo were operated into the early part of this century and generally utilized madder and bran, as well as a small amount of woad.⁴² The bran nourished the bacteria, which presumably derived from the woad.⁴³ Madder (*Rubia tinctoria*) is a plant source for reddish mordant dyes of the alizarin (anthraquinone derivative) family, but probably functions here as a redox intermediate facilitating the reduction of indigotin.⁴⁴

Mollusk dyers might well have been acquainted with the fermentation process using indigo plants and used

(31) Heinisch, K. F. *Fibres* 1957, 18, 203–206. Forbes, R. J. *Studies in Ancient Technology*; E. J. Brill: Leiden, 1964; Vol. 4, pp 98–142. Bruin, F. *Sociétés et Campagnes de Commerce en Orient dans l'Océan Indien*; Mollat, M., Ed.; S.E.V.P.E.N.: Paris, 1970; p 83. Reese, D. S. *Libyan Stud.* 1979–1980, 11, 79–93. Contrast: Baker, J. T. *Endeavor* 1974, 33, 11–17.

(32) For details of the experiments described in this and the following sections, see: Michel, R. H.; McGovern, P. E. *Archeomaterials* 1987, 1, 135–143; 1987, 2, 93; 1990, 4, 97–104.

(33) Reference 14, Vol. 2, p 446, n 93.

(34) Bailey, K. C. *The Elder Pliny's Chapters on Chemical Subjects*; E. Arnold: London, 1929.

(35) Elsner, O.; Spanier, E. *Proc. 7th Int. Wool Tex. Res. Conf. Tokyo* 1985, 5, 123, 125–126.

(36) Davidson, A., A.; Hailwood, J.; Henesey, F.; Shepherdson, A. U.S. Patent 1,861,382; Imperial Chemical Industry, 1932.

(37) Bizio, A. C. R. *Hebd. Séances Acad. Sci.* 1842, 15, 1007–1009.

(38) Reference 17, p 113.

(39) Reference 16, p 43.

(40) Steigerwald, G. *Traditio* 1986, 42, 38–39.

(41) Doumet, J. A. *Study on Ancient Purple*; Imprimerie Catholique: Beirut, 1980; p 39.

(42) Knecht, E.; Rawson, C.; Lowenthal, R. *A Manual of Dyeing*; C. Griffin: London, 1910; p 321.

(43) Wendelstadt, H.; Binz, A. *Ber. Dtsch. Chem. Ges.* 1906, 39, 1630.

(44) Friedländer, P. *Fortschr. Teerfarbenfabr. Verw. Gebiete* 1911, 10, 424–425 (German patent 240,266, Farbwerke vormals Meister Lucius & Bruning in Höchst am Main).

it in the processing of royal purple.⁹ Certainly in extraction of the molluscan secretions, the animal residues could also have fermented, especially if large amounts of the materials were involved and the processing took place over several days. Following an old commercial process for synthetic indigo⁴³ that controlled the supply of oxygen, experiments³² demonstrated that fermentation vats with indigotin work very well, whereas those with DBI do not. There is still the possibility that a different bacterium, perhaps not found on the woad plants of these experiments, would be able to reduce DBI, and further experimentation is needed. Moreover, if the molluscan extracts were boiled, as described by Pliny, then fermentation would be halted and the solution sterilized; if temperatures were kept well below 100 °C during the remainder of the process ("an even and moderate heat by placing the vessels [with the extract] in a flue communicating with a distant furnace"), then fermentation might have been reinitiated.

Some modern investigators^{45,9} conjecture that the marine lichen orseille acted as a reducing agent or a stabilizer for intermediates. This has never been tested chemically, and the various ancient references^{46,17} rather suggest that orseille, a reddish purple dye itself (a phenolic phenoxazine derivative used to make litmus), was a source of ground color for the royal purple.

Photochemical Control

By processing the molluscan extracts in the dark or at least in subdued lighting (with lower levels of ultraviolet radiation), it might have been possible to block the photolysis of the diindoxyl (step 2c in Figure 1). This procedure would have been only partially successful in preventing dye precipitation in species (viz., *M. trunculus*) producing both 2-substituted and unsubstituted indoxyls, but more so in species (*M. brandaris* and *P. haemastoma*) that primarily secrete 2-substituted indoxyls. Although ancient dyers must have observed that textiles dyed with certain molluscan extracts developed a deeper color more quickly in sunlight than in the dark, surprisingly only one ancient text makes reference¹⁰ to the effect of light on the dye, but it does not specify the stage of the process in which light is critical.

Indoxyl Stabilization

Besides preserving the dye in the leuco form (compound IV), reducing agents might also have been used to block the oxidative pathways from the indoxyls to the indigoid (step 2, going from compound II to III, in Figure 1) or to the indolinone (step 2a, going from compound VI to VII). The work of Doumet⁴¹ indicates that the precipitation of the dye can be avoided during room-temperature extraction of the glandular materials if mild alkaline, aqueous media in vessels of lead alloyed with tin, antimony, or arsenic are utilized. During extract concentration at higher temperatures (40–50 °C) and for longer periods, conditions similar to those described in Pliny's account, formation of the dye could not be prevented unless pure tin was used. On the other hand, starting with the dye, it could not be dissolved

under either set of conditions. The implication of Doumet's experiments is that precursor oxidative pathways could be blocked under the appropriate conditions.

Deactivation of Purpurase

It has been shown that the enzyme purpurase, which occurs naturally in the molluscan secretions and is essential for the hydrolysis of the precursors (step 1 in Figure 1), can be deactivated by placing the freshly excised hypobranchial glands in 75 °C water. An effective dyeing process might then have been to impregnate the textile with the deactivated precursor solution and somehow to add back purpurase to reinitiate the dyeing process. This suggestion, however, is not supported by the ancient textual evidence, the most complete account by Pliny indicating that the mollusks were in fact soaked in a cold brine before extraction.

Conclusions

One can, by clearly distinguishing between the various chemical compounds and reactions involved in indigoid dye processing, assess the information provided in ancient texts, especially that of Pliny the Elder, in terms of the dyeing procedures carried out in antiquity. Very often, the mention of a material (e.g., honey, tin or lead, orseille), even in the context of an industrial process, is not sufficient to establish the exact purpose of that material, whether as a chemical or fermentative reducing agent in a vat process, an additive to block oxidative pathways to the indigoid, or a color additive, and so forth. The available ancient texts dealing with royal purple are probably too equivocal or imprecise in their vocabularies and descriptions ever to provide precise correlations with modern chemical knowledge. Nevertheless, other texts may eventually be found that will aid in better understanding the ancient processing of royal purple. For example, a statement about the approximate temperature at which the concentration of the extracts was carried out would help in deciding whether a specific reducing system could have been operative. The role of darkness and sunlight in the ancient process is also not clearly specified in ancient texts, and yet this is crucial to understanding whether some of the dye precursors could be kept in solution.

If problems persist in relating the descriptions of Pliny and other Greek and Roman writers to the known chemistry of DBI, then extrapolating the Roman process back into Phoenician times is even more fraught with difficulties. We¹² have previously discussed the implications of the 13th century B.C. dyeing factory for royal purple at Sarepta, Lebanon. Since the dyeing facility was in the midst of a large group of kilns in which pottery was fired to a temperature at least above 500 °C, possibly the fresh secretion mixture was exposed to temperatures near 100 °C, which would have deactivated the enzyme purpurase or aided reductive reactions under appropriate conditions. The apparent contradiction between the presence of exclusively DBI on the interiors of the jars and the finding of only *M. trunculus* shells, whose secretions contain a mixture of brominated and unbrominated precursors, led to another hypothesis. If the *M. trunculus* secretion solution were kept in the dark, the indoxyls not substituted in the 2-position, which form about 90% of the indigotin blue, could have been prematurely converted to the dye

(45) Heinisch, K. F. *Fibres* 1957, 18, 203–206.

(46) Theophrastus of Eresos. *De Historia Plantarum*; Sprengel, K., Trans.; J. F. Hammerich: Altona; Book IV, Chapter 6, Paragraph 5. Reference 14, Book XXVI, Section 103, Chapter LXVI.

and then separated from the solution containing mostly the dibromo compound.⁴⁷

More exact information on the effect of reducing systems, natural antioxidants, heat, and various additives (e.g., salts, acids, and bases) on the stability of the indoxyl precursors is needed in testing such hypotheses. The reactivity of indigotin, which has recently been compared to that of DBI in our laboratory,^{48,32} must be better characterized. Analyses of secretions from different molluscan species and sexes at various seasons of the year are crucial in determining the relative amounts of precursors, enzymes, and other substances that could affect the reaction. Even as the basis of speculation is improved by continued chemical experimentation, however, our understanding of the ancient processing of royal purple will always be inherently limited by the available textual evidence.

Note on the Analytical Identification of DBI and Related Indigoids

A variety of physical and chemical techniques have been employed in the identification of indigoid dyes, specifically DBI. These include mass spectrometry (see below), ultraviolet (UV),^{49,50} visible,^{29,51} and infrared^{52,12} spectroscopy, electron spectroscopic chemical analysis,¹² electron spin resonance,⁵³ thin-layer chromatography,^{54,4} and qualitative chemical tests.⁵⁵ Each technique requires relatively small samples, which is particularly important in the analysis of valuable archaeological materials. Each technique can at times positively identify an unknown compound as an indigoid dye, depending upon whether or not it is part of a mixture and according to the specific experimental procedures employed. When several techniques are used to analyze the same sample, complementary information can often be obtained that will confirm the presence or absence of specific indigoids.⁵⁶

We have found that high-resolution mass spectrometry provides an expeditious and precise technique for positively identifying indigoid dyes of molluscan origin.^{57,48} Individual indigoids in a mixture are clearly distinguished, and indigoid dyes on textile fibers can

(47) This possibility is suggested by Pliny: Pliny the Elder. *Historia Naturalis*; Rackham, H., Ed.; Harvard University: Cambridge, 1961; Book XXXV, Section 27, Vol. 9, p 295. See: McGovern, P. E.; Michel, R. H.; Saltzman, M. *Bull. Am. Sch. Orient. Res.* 1988, 269, 81-84, 88-90. Contrast: Ziderman, I. I. *Bull. Am. Sch. Orient. Res.* 1987, 265, 25-33; 1988, 269, 84-87.

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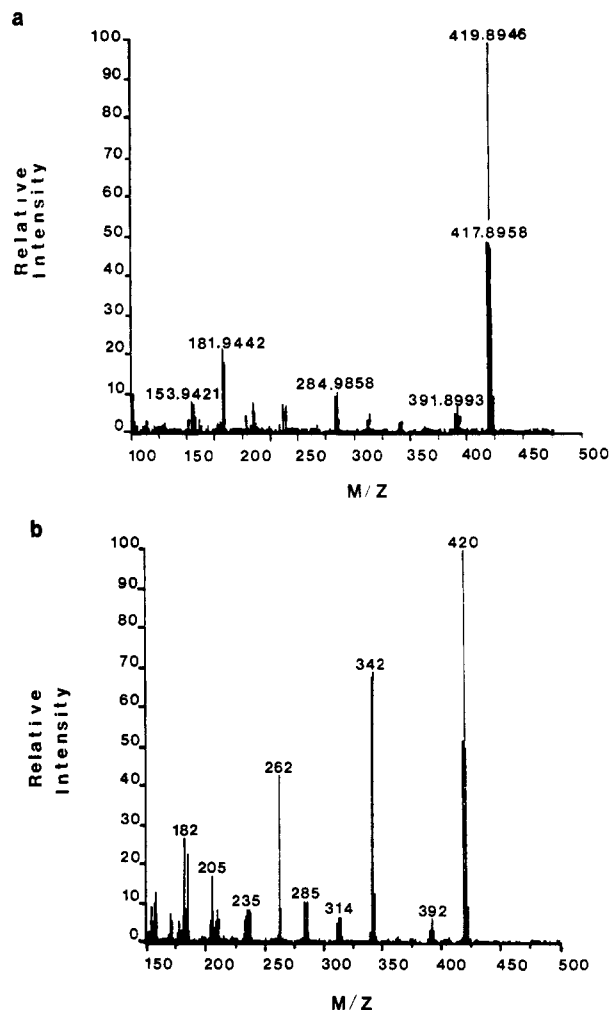


Figure 3. Mass spectrum of (a) synthetic 6,6'-dibromoindigotin (DBI), recovered from quinoline solution. For comparison, a spectrum (b) of synthetic DBI, which was irradiated as the leuco base with ultraviolet light, has an indigotin peak at m/z 262 and monobromoindigotin peaks at m/z 340 and 342.

be analyzed after recovery from solvent extracts (e.g., with quinoline).⁴⁸ Reductive extraction, on the other hand, has the disadvantage that it is often difficult to prevent debromination of the leuco base by photolysis. A spectrum (Figure 3a) of synthetic DBI, recovered from quinoline solution, has a triplet ion cluster centered at an m/z (mass/charge) of 420 (viz., 418, 420, and 422), representing the three isotope combinations of the DBI. There is no evidence of debromination to monobromoindigotin (m/z 340 and 342) or of indigotin (m/z 262). Exposure of the leuco base of synthetic DBI to UV irradiation (Figure 3b) results in debromination to the lower molecular weight indigoids.⁵⁸

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(58) Reference 55. van Alphen, J. *Recl. Trav. Chim. Pays-Bas* 1944, 63, 95-96.

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Living Ring-Opening Metathesis Polymerization Catalyzed by Well-Characterized Transition-Metal Alkylidene Complexes

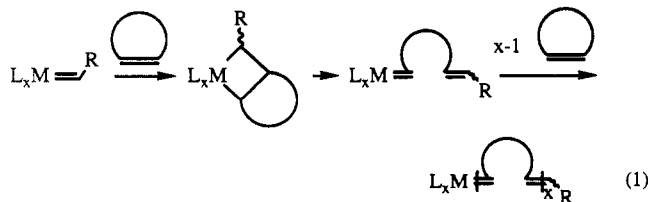
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Organic polymers that have the narrowest possible distribution of molecular weights (a polydispersity approaching 1.00) can be prepared if the rate of initiation is approximately equal to or greater than the rate of propagation, each monomer unit adds irreversibly, and the rates of chain termination and chain transfer are slow on the time scale of the polymerization reaction itself.¹ Such "living" catalyst systems also allow one to add a second monomer after the first is consumed (or a third, etc.) to yield polymers that contain "blocks" of homopolymers connected to one another.² Although narrow molecular weight distributions and the ability to prepare block copolymers are not goals of all polymerization processes, only with such well-defined materials can one be as certain as possible about the polymer's molecular structure and size and, therefore, have the best opportunity to control bulk properties by variations at a molecular level. Surprisingly, living polymerization by transition-metal catalysts were virtually unknown until a few years ago when norbornene was polymerized in a living manner by ring-opening metathesis using a titanium catalyst.³

Ring-opening metathesis polymerization (ROMP) is the process shown in eq 1 (L_x denotes a generalized ligand coordination sphere). If the cyclic olefin is highly strained (e.g., norbornene), then the reaction is essentially irreversible. Ring-opening metathesis polymer-



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ization has been well-studied in systems that employ an empirically derived (here called "classical") Mo, W, or Re catalyst.⁴ However, because of the high activity of most classical catalysts for the metathesis of ordinary olefins, the metal-carbon double bond at the end of the polymer chain reacts with carbon-carbon double bonds in the chain itself, either intramolecularly to give cyclic oligomers or intermolecularly to give linear oligomers. It is also generally true in classical systems that alkylidene complexes are generated in low yield and decompose over the course of a typical polymerization reaction.⁴ All of these factors contribute to the formation of relatively broad molecular weight distributions if highly active metathesis catalysts are employed, and there is no possibility of preparing well-defined block copolymers.

The synthesis of relatively stable, well-defined alkylidene complexes for the metathesis of olefins has been perfected over the last decade.^{5,6} I will focus on one type of catalyst here that contains molybdenum or tungsten, since the reactivity of such species toward olefins can be "tuned" accurately to the point where they become almost perfect ring-opening metathesis catalysts for highly strained monomers.

Catalyst Synthesis and Reactions Involving Ordinary Olefins

Although it has been known for several years that the metal should be in the highest possible oxidation state,⁶ only relatively recently has it become possible to synthesize well-defined four-coordinate alkylidene complexes containing bulky ligands.⁷ For molybdenum and

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