The Chemical Processing of Royal Purple Dye: Ancient Descriptions as Elucidated by Modern Science

R. H. MICHEL AND P. E. MCGOVERN
Museum Applied Science Center for Archaeology (MASCA),
University Museum, University of Pennsylvania, Philadelphia,
Pennsylvania 19104

ABSTRACT Royal Purple, the most famous indigoid dye of antiquity, was derived from hypobranchial gland extracts of various marine gastropod mollusks. The extracts were processed by a lengthy, elaborate procedure, according to the Roman writer of the first century A.D., Pliny the Elder; other, more cursory texts are known from the Classical Greek period up until Byzantine times. In order to obtain fast, intense textile colors, as described in the ancient texts, a soluble precursor or derivative must have been used, which was then converted to the dye within the fiber. Present knowledge of the chemical compounds and reactions involved in indigoid dye processing and in the formation of Royal Purple from hypobranchial gland extracts suggests how this might have been accomplished by controlling the oxidative, photochemical, and/or enzymatic/hydrolytic pathways to the dye. Because of the imprecision and ambiguity of the ancient texts, however, the dyeing process can only be reconstructed by assuming that certain additives entered into specific reactions (e.g., a tin [not lead] reducing system in Pliny’s account). Inferences are even more difficult to draw about the earliest known Royal Purple dye processing, based on the archaeological evidence from a thirteenth century B.C. industrial context at the site of Sarepta in Lebanon.

INTRODUCTION Royal Purple (chemically known as 6,6’-dibromoindigo) and related indigoids of molluscan origin are, as the most famous dyes of antiquity, frequently mentioned in ancient texts. One of the earliest references occurs in a letter (Knudtzon 1907–1914: I.162–163 [Letter no. 22]) which is part of the large corpus of international correspondence found at el-Amarna, the capital city of Akhenaten (1350–1334 B.C., following the lower chronology of Wente and Van Sijen 1976). The letter to Akhenaten’s father, Amenhotep III, from Tushratta of Mitanni, an Indo-European kingdom on the upper Euphrates, mentions a shipment of violet-colored goods (Semitic tekel, probably a mixture of dibromoindigo purple and indigo blue; see Zderman 1981). About the same time, the dye is also referred to in the extensive literary corpus found at Ras Shamra (Thureau-Dangin 1934; Schaeffer 1950), ancient Ugarit, on the Syrian coast, as well as in Linear B texts from Crete (Stiglitz 1986: 183–184). Beyond the fact that Royal Purple, especially in the form of dyed fabrics, was an important commercial item and extensively traded, no information about the actual process of dyeing is provided in these texts.

In the succeeding centuries of the Iron Age, Canaanite city-states (Tyre, Sarepta, Sidon, etc.) on the Levantine coast came to dominate the dyeing industry (Bruin 1970; Pritchard 1978; McGovern and Michel 1984, 1985). Royal Purple was so intimately associated with these peoples that the name by which they called themselves (Canaanites), as well as their later historical appellation (Phoenicians), very likely derived from ancient Semitic and Greek roots for “purple” (Speiser 1936; Landsberger 1967). Perhaps as much as the Semitic alphabet or the seafaring by which the latter was transmitted to the West, purple dyeing was a distinctive element of Phoenician culture, and to promote the industry, dye factories were set up at colonies throughout the Mediterranean (Reese 1979–80). Given the importance attached to Royal Purple, it is somewhat surprising to find that the dye is rarely referred to in the known Phoenician texts, and that the
process of dyeing itself goes totally unmentioned. Indeed, Biblical texts, which incorporate Iron Age traditions, are more informative about the involvement of Phoenician city-states, especially Tyre (Ezekiel 27:7, 16, 24; II Chronicles 27:14), in the industry. The use of Royal Purple in early Israelite religion (e.g., in the tabernacle curtains and the High Priest’s vestments in II Chronicles 26:11; 28:4–6; 31:1, 28–29; etc.; II Chronicles 3:14) shows considerable Phoenician influence, which was especially strong during the time of Solomon, when craftsmen from Phoenicia were employed to construct the Temple in Jerusalem, using imported Lebanese cedar and other materials (I Kings 5:1–12; 7:13–14; 9:10–14, 26–28; 10:11, 22). The apparent textual omission of Royal Purple could reflect the very limited archaeological investigation of Iron Age sites in Lebanon. In addition, industrial processes might have been held in low esteem by writers, or they might have been closely guarded secrets of the initiated; in either case they were not properly in the domain of written documentation. As is evident from the glassmaking texts of the early second millennium BC. (Oppenheim et al. 1970), however, the manufacturing procedures of some ancient crafts could be described in great detail, with a highly specialized vocabulary.

Classical Greek sources also give little more than brief notations about Royal Purple. Aristotle (Historia Animalium, book V, chapters 12, 45–49), and that the dye was derived from a specific organ of various marine gastropod mollusks, which had to be removed with extreme care from beneath the shell. The Greek legend about the discovery of the dye, which was repeated in various versions in later texts (see especially that of Julius Pollux of the second century A.D. (Onomasticon I, 45–49), was that a dog belonging to Herakles, the god of Tyre, bit into a large sea-snail, staining its mouth red, whereupon Herakles promptly dyed a garment with the dye so reddened. Subsequent accounts report that the fact that a red mollusk extract could be used to dye a textile by direct application, this story sheds no light on the processing of Royal Purple.

It is only in the time of the early Roman Empire, as much as 1500 years after the industry began, that the process is first described in some detail. The longest account is found in the Historia Naturalis of Pliny the Elder (book X, sections 60–65, chapters XIX–XXI), as translated in the edition of Bulley (1929), written in the mid-first century A.D.:

Two kinds of shell-fish furnish the purple and the cochylis dyes—the colours used for both are the same, only that they are mixed in different proportions. . . .

Purples are caught with a sort of small wicker basket cast into the deep, and containing a bait of small bivalves which snap their shells together, as mussels are known to do. These bivalves, though half-dead, revive on returning to the sea and open gape greedily. The purples seek them out and attack them with protruding tongue, and the mussel shuts up as soon they feel the sting, and hold their assailing fast. Thus suspended, the purples are taken up, caught by their own greed.

The best time to catch them is after the rising of the dog-star or before spring arrives, for, when they have produced the knob-like excrescence, the juice is too thin. Yet this fact, although of the utmost importance, is not recognized in the dye-factories. The vein already mentioned is then extracted and a sextarius [cn. 7 lb.] of salt added to each hundred pounds of material. It should be soaked for three days, for the freer the extract, the more powerful the dye, then boiled in a leaden vessel. Next, five hundred pounds of dye-stuff, diluted with an amphora [about 8 gallons] of water, are subject to an even and moderate heat by placing the vessels in a flue communicating with a distant furnace.

Meanwhile the flesh which necessarily adheres to the veins is skimmed off and a test is made about the tenth day by steeping a wall-washed flax in the liquid contents of one of the vessels. The liquid is then heated till the colour answers to expectations. A frankly red colour is inferior to one with a deep black. The wool drinks in the dye for five hours and after carding is dipped again and again until all the colour is absorbed. . . .

The Tyrian colour is obtained by first steeping the wool in a raw and unheated vat of pelagion extract, and then transferring to one of buccinum . . . .

Conchylated garments are prepared by a similar method to the first, but no buccinum extract is used and the dye is diluted simultaneously with water and human urine. Only half the usual amount of dye is used . . . .

Considering the wealth of detail in Pliny's account, greatly exceeding that of any other contemporary document, he must have either observed the industrial process firsthand or received information about it from a knowledgeable source. In brief, he describes the capture of certain mollusk species and the removal of a colorless organ from each specimen. These organs were then subjected to a sequence of operations with salt and water in vessels of lead (as translated, but see below). The mixture was then heated over a ten-day period, refuse organic materials were skimmed off the surface, and the liquid was tested for its dyeing properties. The use of varying amounts of extract from different mollusk species, as well as the dilution of the mixture with water and urine, suggests that the coloration could be changed by modifying the process.

Relatively little additional information about the Royal Purple dyeing process can be obtained from other Roman writings. In Plutarch's biography of Alexander, the fastness of the dye is attested by Alexander's recovery of 5000 talents of very well preserved purple textiles from the Persian court at Susa, which are said to have originated 190 years earlier, in Greece. A possibly significant note by Plutarch is that this cloth was dyed by using honey in some instances and oil in others (see also the commentary in Blümner 1942). The alchemical texts written in Egypt in the third century A.D., in particular Pappuriy Leidenas and Graecus Holmien- siss (editions of Berthelot 1887 and Lager- crantz 1913, respectively), with probable roots in much earlier tradition (Reinck 1925; Forbes 1964), mention specific materials and procedures that entered into the processing of purple dyes. But since the goal of these experiments was evidently to manufacture an economical substitute for Royal Purple, it is unclear whether the precursors of mollusk-, plant-, or insect-derived dyes are being described in a given passage. Talmudic descriptions of the same period or later refer to marine animal dyes, probably including Royal Purple, that were processed by heating the "blood" of the animal (most likely, the hypobranchial secretions) and tested in a mixture of urine, alumina, and fenugreek, or in comminuted barley flour dough (Hersch 1919–20).

Following the Islamic conquest of the Middle East in the early seventh century AD., Royal Purple production was curtailed. Even Mediterranean dye works, unaffected by the invasions, ceased to operate, because of the increased availabil- ity of less expensive substitutes. Conse- quently, medieval references are primarily dependent on earlier writings. Production ceased altogether after the fall of Constantinople in A.D. 1453. In 1464, Pope Paul II issued an edict instructing cardinals to substi- tute cochineal scarlet for Royal Purple in dyeing their vestments (see Jensen 1963 and Born 1937).

In this brief historical overview of the written references to the processing of Royal Purple, Pliny's account stands out as the most lengthy and authoritative. Mod- ern writers on the subject, like their ancient counterparts, consequently turned to it in attempting to reconstruct or describe the dyeing process. Since Pliny did not claim to give a complete account of the process, however, writers have felt justified in supplying additional details in light of the scientific, historical, and linguistic data available to them. In the ongoing process of understanding Pliny's account, it is to be expected that sometimes the text was elaborated upon or that unwar- ranted inferences were drawn from it. In order that inquiry not be prejudiced by past interpretations, and to direct future research in the most fruitful directions, it is necessary to reappraise the evidence and its direct relevance to the ancient text from time to time. The remaining part of this article is such an interpretative effort from a perspective of modern science, first outlining the chemistry of Royal Purple, as currently known, and then suggesting ways in which specific chemical compounds and reactions might be related to Pliny's account and other more cursory or ambigu- ous ancient texts.
THE CHEMISTRY OF ROYAL PURPLE

As early as 1685, it was noted by Cole 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 research (Lacaze-Duthiers 1859) substantiated the photochemical nature of the process. During the nineteenth century, as one of the earliest chapters in the emerging fields of chemical and biological chemistry, an attempt was made to identify the chemical structure of the dye (Negri 1875; Schunck 1879). Finally, in 1899, Friedländer determined that 6,6'-dibromoindigo was not the dye obtained from one of the Mediterranean mollusk species—Murex brandaris. That this compound was also a major component of the dyes from other Mediterranean species (Murex trunculus and Purpura haemastoma), as well as from mollusk species occurring in other parts of the world (e.g., Purpura aperta and Nucella lapillus from the Gulf of Mexico and the Atlantic Ocean, respectively), was supported by later research of Friedländer (1922) and others (Bouchilloux and Roche 1955; Fouquet and Bielig 1971).

The isolation and structures of the individual precursors were first effectively investigated by Bouchilloux and Roche (1955), and later more completely elucidated by Baker and Sutherland (1969) and Fouquet and Bielig (1971). The precursors were found to be sulfates esters of indoxyl, 6,6'-dibromoindoxyl, and derivatives of these substituted in the 2 position with both in Fig. 1), in the procaryol groups (see compounds I and V in Fig. 1). Hydrolysis of these sulfate esters by the enzyme purpurase (step 1 in Fig. 1) was studied by Dubois (1969) and Esramer (1947). Baker and Sutherland (1968) also showed that the oxidatively formed greenish compound from 2-substituted indoxyl converted to dye by a photochemical mechanism (step 2c in Fig. 1), in the procaryol groups long-observed, odiferous sulfate compounds. The structure of this intermediate (compound VIII in Fig. 1) was identified by Christophersen and co-workers (1976) as a 2,2'-bisindoxyl 2,2'-dihydrindoxyl, the dibromo derivative being referred to as tyri-nerindoxyl. Indoxyls not substituted in the 2 position are formed by oxidative coupling in air. Whereas Murex trunculus secretions contained both indoxyl and 6,6'-dibromoindoxyl, substituted and unsubstituted in the 2 position, extracts from Murex brandaris and Purpura haemastoma contained only 2-substituted 6,6'-dibromoindoxyl. Consequently, Murex trunculus yields both indoxyl and 6,6'-dibromoindoxyl, while Purpura haemastoma and Murex brandaris produce exclusively 6,6'-dibromoindoxyl.

As indigo vat dying is practiced today, the indigotin is reduced to the almost colorless, soluble leuco base (step 3, going from compound III to IV in Fig. 1), in which form it is absorbed by the textile to be dyed. Reoxidation by exposure to air yields the colored dye, which is so well bonded to the textile that it is wash-fast and resistant to rubbing. This procedure is to be contrasted with direct application of the mol- lusks extract to a textile with subsequent color development in the sun, such as was observed in the British Isles in the seventeenth century by Cole (1685), or in Mexico as still practiced by the Indians (Nuttall 1909; Gerhard 1977).

Any process which does not use the mol- lusk secretions directly must in some manner avoid the formation of the insoluble dye until the textile fibers have been impregnated. This might be accomplished in a number of ways:

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

For those mollusk extracts containing only 2-substituted indoxyls or for those that were obtained by separating the unsubstituted indoxyls after oxidative coupling (step 2 in Fig. 1), the avoidance of light would prevent the conversion of dindoxyl to indigotin dye (step 2c, going from compound VIII to III in Fig. 1).

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

4. The hydrolysis of the sulfates ester precursors might be blocked by the deacti- vation of the enzyme purpurase (steps 1 and 2 in Fig. 1).

Although the ancient dyer lacked an understanding of the chemistry of Royal Purple, the time-consuming, elaborate procedures detailed in Pliny and other sources go far beyond the simple application of the mollusk extract 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 chemical methods aids in the understanding of an ancient text.

THE ANCIENT PROCESSING OF ROYAL PURPLE

Chemical and Fermentative Reduction Systems

The ancient extraction process for Royal Purple as described by Pliny has often been understood as a vat process (e.g., Heinisch 1957; Forbes 1964: 99–100; Brunn 1970; and Reese 1979–80; contrast Baker 1974). Actual experiments 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 can be translated as "tin" (Pliny 29–79 CE) or "lead" (Bailey 1929), depending upon whether one supplies the adjective album ("white") or nigrum ("black"); neither appears in Pliny's text. The choice of adjective is critical in deciding whether Pliny is describing a reducing system. Lead and an alkaline solution will not reduce indigo dyes, but, according to experiments carried out in the MASCA laboratories, reduction to the leuco base occurs slowly with metallic tin in a potash solution at ca. 90°C. Accordingly, the prolonged heating of the mollusk extracts in an alkaline solution in a tin or tin-coated vessel could have reduced the indigotin to the leuco base. Different colors could have been achieved by dipping the textile in the leuco base solutions from different mollusk species for varying periods of time. Pliny, however, does not explicitly state that an alkali was used, and the alkalinity of the additives he does mention (e.g., urine and salt) would pot have been 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 (Forbes 1965: 181–183, 243).

An iron filing/fermented urine mixture at 90°C has been shown to be effective in our laboratory studies in reducing indigo, but not 6,6'-dibromoindigotin. The purple dye processed with iron and urine, described in Papyrus Leidensis, must then not have been a mollusk purple. Furthermore, iron and urine form iron salts, and might have served as mordants for red dyes from madder or kermes.

It has been recently proposed by Ebers
and Spanier (1985) that the 2-methylthio-
and 2-methyl sulfonyl-substituted indoxyl
dye precursors from the hypobranchial
gland of the various mollusk species are the
source of reducing agents for indigo dyes,
thus setting up a natural vat system. In the
experiments of Elsner and Spanier, since
only a finite amount of the 2-substituted
indoxyls is available for reduction, reoxida-
tion by the air prevented by a surface
layer of oil or the addition of a reducing
sugar (glucose from grape juice). As noted
above, evidence exists in ancient texts for
the use of such materials in the processing of
Royal Purple. For example, honey,
mentioned by Plutarch, is a mixture of glucose
and fructose, and has been shown to be
an effective reducing agent for indigotin (al-
though thus far undemonstrated for dibro-
moindigotin).

Honey and other organics might also
have entered into a fermentative reduction
process (cf. Jensen 1965). A very generic
description of a fermentation vat in the
processing of the woody plant, a source of
indigo, is found in Papyrus Graecus Holm-
iensi. Presumably, mollusk dyes would
have been known about the same process. In
the mollusk extraction, the animal residues
could also have fermented, especially if
large amounts of the materials were
involved in the process. In the
mollusk extraction, the solution sterilized
by boiling the vessels [with the extract
solution] in a flue communicating
with the vat (see below), then fermentation
might have been reintroduced.

Some modern investigators (Heinis-
ch 1957; Jensen 1965) conjecture that the
marine lichen orselline acted as a reducing
agent or a stabilizer for intermediates (see
below). This has never been tested chemi-

cally, and the various ancient references
(Theophrastus of Eresos, De Historia
Plantarum, book IV, chapter 6, paragraph
5; Pliny the Elder, Historia Naturalis,
book XXVI, section 103, chapter LXVI;
Papyrus Graecus Holmienisi, in Lager-

Deactivation of Purpurase
Elsner and Spanier (1985) have shown
that the enzyme purpurase, which occurs
naturally in the extract and is essential for
the hydrolysis of the precursors (steps 1
and 2a in Fig. 1), can be deactivated by
placing the freshly excised hypobranchial
glands in 75°C water. An effective dyeing
process might then have been to impreg-
nate the textile with the deactivated pre-
cursor solution, and to add back purpurase
to reinitiate the dyeing process. This sug-
gestion, however, is not supported by the
ancient textual evidence, the most com-
plete account by Pliny indicating that the
mollusk was in fact soaked in a cold brine
before extraction.

CONCLUSIONS

By clearly distinguishing between the
various chemical compounds and reactions
involved in indigo dye processing, the
information provided in ancient texts,
especially that of Pliny the Elder, can be
assessed in terms of the dyeing procedures
carried out in antiquity. Very often, the
mention of a material such as honey, tin or
lead, oseille), even in the context of an
industrial process, is not sufficient to
establish the exact purpose of that materi-
al, whether as a chemical or fermentative
reducing agent in a vat process, an additive
to block oxidative pathways to the indi-
gold, a color additive, and so forth. The
available ancient texts dealing with Royal
Purple are probably too equivocal or
imprecise in their vocabularies and de-
scriptions ever to provide the sort of exacti-
tude that can be meaningfully interrelated
with results from modern scientific investi-
gation. This is not to say that other texts
might not eventually be found that will
help in understanding better some of the
stages in 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 spe-
cific reducing system could have been oper-
ating. The role of darkness and sunlight
in the ancient process is also not clearly spe-
cified in ancient texts, yet this is crucial to
understanding whether some of the dye
precursors could be kept in solution.

If problems exist in relating the descrip-
tions of Pliny and other Roman and Greek
writers to the known chemistry of Royal
Purple, then extrapolating the Roman pro-
cess back into Phoenician and earlier times
is even more difficult. The most that can be
done is to hypothesize what processes
might have been employed on the basis of
the archaeological data. We (1984, 1985)
have previously discussed what is thus far
the only documented instance of a dyeing
facility for Royal Purple at Sanape in the
Phoenician homeland of Lebanon, dating
to the thirteenth century B.C. (Pritchard
1980). A spouted vat with 6.6-dibromoin-
digotin on its interior was interpreted as a
processing container by which liquids
could be drained off and solid organic resi-
dues scooped from the surface. Since the
dyeing facility was in the midst of a large
clearing of pottery kilns (Kalifeh in present
which pottery was fired to a temperature
at least above 500°C, possibly the fresh
extract mixture was exposed to tempera-
tures near 100°C, which would have deacti-
ated the enzyme (oseille), tin or lead) or in
reductive reactions under appropriate condi-
tions. The apparent contradiction be-
tween the presence of only the dibromo
compound on the interiors of the pottery
vessels and the fact that only broken shells of
Murex trunculus, whose secretions contain
a mixture of brominated and unbromi-
nated precursors, were found in the vicinity
of the dyeing installation led to another
hypothesis. If the Murex trunculus extract
solution were kept in darkness, the indox-
yl not substituted in the 2-position, which
formation about 90% of the indigotin, could
have been prematurely converted to the
dye and then separated from the solu-
tion containing mostly the dibromo
compound. None of the chemical reconstruc-
tions can be proven, yet they do provide a
framework in which to carry out additional
chemical and archaeological investigation
that may eventually shed further light on
the pre-Roman industry.

Much more still remains to be learned
about the chemistry of the mollusk indi-
gold dyes. The reactivity of indigotin has
been extensively studied in the laboratory, but that of dibromodigotin, which can be expected to have significantly different reaction rates, is only partly known. 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 precursor is also needed. Analyses of extracts from different species and sexes at various seasons of the year would be of value in determining the relative amounts of precursors, enzymes, and other substances that could affect the reaction. Still, even as the basis of speculation is improved by continued chemical experimentation, our understanding of the ancient processing of Royal Purple will always have an inherent limitation in the available textual evidence.

Acknowledgments

The authors wish to thank James B. Fitchard and Lloyd W. Dailey of the University Museum for their very helpful advice on historical and philological matters relating to ancient Purple production.

REFERENCES

Aristotle


Bailey, R. C.

1929 The Elder Pliny's Chapters on Chemical Subjects, E. Arnold, London.

Baker, J. T.


Baker, J. T. and M. D. Sutherland


Berthelot, M. P.


Blumener, H.


Born, W.


Bouchloules, S. and J. Roche


Brün, F.


Caley, E. R.