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ROYAL PURPLE AND THE PRE-PHoenician DYE INDUSTRY OF LEBANON

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Introduction

Purple dyestuffs have probably been produced by chemical processing of the secretions of the hypobranchial glands of Mediterranean gastropod mollusks (Murex trunculus, Murex trunculus, and Purpura haemastoma) since the mid-second millennium B.C. (Fig. 1). Shell heaps on Crete and elsewhere in the Mediterranean (Reese 1979-80) and along the Levantine coast (e.g., at Ras Shamra, Sidon, and Tyre) have provided the primary archaeological evidence for the industry, which is also attested to in Akkadian and Ugaritic texts from the Late Bronze Age (e.g., Thureau-Dangin 1934; Schaeffer 1950). While the middens may be prima facie evidence for the industry, particularly if they are of one species, they could possibly represent a food source. The archaeological identification of an industrial complex and/or the chemical confirmation of the ancient dye would provide much less ambiguous evidence for the origins and development of the industry.

Fig. 1: a, M. trunculus b, M. brandaris c, P. haemastoma
(Altes Museum 1877-1919)
of a spouted vat (Plate 2) with a purple sediment on its interior came from a square (II-B-6) 10 m north in a stratigraphically related context. In Area II-B-9, approximately 10 m to the southeast, three more such vats of a similar or larger type from the transitional Late Bronze—Early Iron Age (Stratum V), were recovered. Associated with the latter was a large pile of crushed *M. trunculus* in Area II-C-9.

The vat from II-B-6 is similar in shape to pot bellows from metallurgical installations (Daeye 1979), but may well have had industrial purposes. Some sort of pre-processing of the mollusc material would obviously be required to separate the dye-producing gland extracts from extraneous animal matter, perhaps according to methods described in much later writings (e.g., Pliny the Elder). The spouted vat would be an ideal vessel to drain aqueous extracts, while removing solid residues which floated on the surface.

The chemical composition of the dyes from the three Mediterranean mollusc species has been previously investigated (Fouquet and Bietig 1971, Baker 1974, Zitterman 1981). *M. brandaris* and *P. haemastoma* yield mainly 6,6'-dihydroindigo (X = Br in Structure 1 below), while *M. trunculus* gives the substituted indigo (X = H) in addition to the dibromo compound. The proportions of the two dyes from *M. trunculus* can vary widely, depending upon how the mollusc extracts are processed. For example, prolonged exposure to air (oxidation) will leave primarily precursors for the dibromo compound in solution, whereas the major indigo (X = Br) is converted to the dye, which is insoluble and would probably be removed with the mollusc residues. Exposure of the remaining content of the solution to sunlight would then yield the dibromo compound, since about half of its precursor requires ultraviolet light to go to the insoluble dye. Consequently, the color of the dye derived from the *M. trunculus* can range between reddish purple (6,6'-dihydroindigo) and bluish violet (indigo).

**Structure 1**

![Chemical structure of 6,6'-dihydroindigo and indigo.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding energy (eV)</th>
<th>Structural environment of the element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unknown purple</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>353</td>
<td>532</td>
</tr>
<tr>
<td>N</td>
<td>401</td>
<td>400</td>
</tr>
<tr>
<td>C</td>
<td>289</td>
<td>289</td>
</tr>
<tr>
<td>Ca</td>
<td>103</td>
<td>104</td>
</tr>
<tr>
<td>Si</td>
<td>103</td>
<td>104</td>
</tr>
<tr>
<td>Al</td>
<td>74.2</td>
<td>74.2</td>
</tr>
<tr>
<td>Br</td>
<td>70.2</td>
<td>70.0</td>
</tr>
</tbody>
</table>

**Spectroscopic investigations**

All the Sarepta sherd were extremely small and had very thin accumulations of the purple material on their interior surface. A sherd from Area II-A-4, which measured about 5 cm square and whose purple coloration was slightly more intense than other examples, was chosen for the initial analysis. Because of the small sample, non-destructive spectroscopic techniques were first employed.

Proton-induced x-ray emission spectroscopy (PIXE) confirmed the presence of unusually high levels of bromine in the purple layer (0.32%) versus 0.002% for the exterior surface lacking the color). Elements with atomic weights less than sodium, however, could not be detected by this method.

The specific chemical environment of the bromine was determined by electron spectroscopic chemical analysis (ESCA). As a reference for the unknown ancient specimen, a sample of synthetic 6,6'-dihydroindigo, which had been deposited from a sodium hydroxide solution onto an uncoated Sarepta storage jar sherd from the same locus, was also tested. As can be seen from Table 1, the ancient purple is virtually identical to the 6,6'-dihydroindigo. Specifically, the compound is composed to a large extent of nitrogen, of carbonyl and hydroxyl groups, and of organic bromine. Other elements (Ca, Si, and Al) are lower than in the modern material. Elements with atomic weights less than sodium, however, could not be detected by this method.

The presence of 6,6'-dihydroindigo in the purple deposit was more definitively confirmed by diffuse reflectance Fourier transform infrared (FT-IR) spectroscopy. The spectrum of the ancient purple is compared with synthetic dibromoindigo and indigo (Fig. 2). The N-H absorption band at 3275 cm⁻¹ is a characteristic of dibromoindigo (N-H at 3275 cm⁻¹ from 6,6'-dihydroindigo (N-H at 3375 cm⁻¹)).

![Infrared spectra of unknown purple and synthetic dyes.](image)

The reactions are characteristic of the vat dye family of which the two indigoids discussed here were the only members in antiquity. Halogenated indigo, such as 6,6'-dihydroindigo, also dehalogenate to indigo when their leuco-base solutions are exposed to ultraviolet radiation (sunlight, fluorescent light, etc.).

A sherd about 6 mm across was placed on filter paper on a hot plate and observed under low power magnification. It was heated to 60-80°C, when alcaline hydroxide solution at about the same temperature was dropped onto the surface at a rate that produced some overflow. When a change in the color intensity was observed, the filter paper was examined and found to have a small purple spot. As the filter paper remained...
exposed to daylight and fluorescent light on the laboratory bench, the spot spread slightly and turned blue. The leuco-base of 6,6'-dibromoindigotin, which had not oxidized back to the dye, clearly had undergone photodebromination, followed by oxidation to the blue indigotin.

Conclusions
The combined evidence from the spectroscopic and chemical investigations leaves no doubt that the major component of the purple deposit on the Late Bronze Sarepta sherd is 6,6'-dibromoindigotin. This is the earliest chemical confirmation of the ancient dye. Its archaeological context points to local production of the dye rather than importation. The requisite mollusc species are represented in the loci with the purple-colored sherds, and a suitable industrial vessel, a spouted vat, came from an associated context.

What then was the mollusc source of the Royal Purple at Sarepta? M. brandaris yields a purple dye (6,6'-dibromoindigotin) exclusively. M. trunculus, when processed under reducing conditions as prescribed in modern and Graeco-Roman (Heinisch 1957) literature, will give about a fifty-fifty mixture of the unbranminated (blue) and brominated compounds. If M. trunculus had been used at Sarepta, one might therefore have expected to find blue or violet accretions on pottery. In fact, only purple-colored sherds were recovered.

Wider archaeological exposure would possibly resolve this problem by uncovering accumulations of M. brandaris shells in other contexts. However, it may simply be that the extracts from M. trunculus were exposed to air and oxidized. Then most of the precursors for indigotin would react to form insoluble dye, which might be entirely removed along with other solid residues. A large portion of the brominated precursors would remain in solution until converted to 6,6'-dibromoindigotin on exposure to sunlight. The end result would be a purple-dye derived from M. trunculus. This points to an earlier experimental stage of dye processing, when the importance of a reducing environment and, by implication, of the vat method, was not well understood.

Acknowledgments
The generous contribution of services by E.I. DuPont de Nemours & Co. and its various spectroscopy laboratories in Wilmington, DE, is gratefully acknowledged. Very useful discussions regarding appropriate analytical techniques were held with S.C. Croft and E.G. Brame. R.C. Wendt and D.B. Chase are especially to be thanked for arranging to obtain the ESCA and IR data, and for helping to interpret the spectra. B.B. Baker and C.E. Day also offered valuable advice on interpreting the infrared spectra. The proton-induced x-ray emission spectroscopy (PIXE) was carried out in collaboration with C.P. Swann of the Bartol Research Foundation at the University of Delaware, Newark. Synthetic 6,6'-dibromoindigotin was kindly provided by S.M. Edelstein and D.H. Abrams of Dexter Chemical Corp. A stimulating meeting with I.R. Ziderman clarified a number of points.

The study was first prompted by discussions with I. Khalifeh and J.B. Pritchard. The latter provided the ancient sherd and some of the natural dyestuff which had been extracted and processed from the three Mediterranean species by J.E. Doumet (nd). W.P. Anderson supplied additional samples, as well as detailed stratigraphic information from his dissertation (in press) and that of I. Khalifeh (in press).

Postscript
A purple accumulation has also been noted on the interior of a pithos from Tell Keisan, dated to the eleventh century B.C. (Puch 1980). Infrared analyses of purple-colored sherds from Shiqmona of 9th or early 8th century B.C. date by S.M. Edelstein have identified the purple as 6,6'-dibromoindigotin (personal communications from S.M. Edelstein and N. Karmon). Both sites are located south of Tyre along the Mediterranean coast in Israel, and were occupied by the Phoenicians in the Iron Age.

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