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Bathochromic Effect of Heat on 6-Bromoindigotin:

Key to Understanding Purple Dyeing with Banded Dye-Murex

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Abstract

The purple dye from banded dye-murex is typically tinted blue, and is therefore identified as the hyacinthine purple of antiquity, biblical *tekhelet*. Chemical reactions between indoxyl and bromoindoxyl precursors, which are largely segregated respectively between males and females of the species, compete to form a mixture of 6,6`-dibromoindigotin, 6-bromoindigotin [MBI] and indigotin.

In the hands of some workers, a reddish purple has been obtained from banded dye-murex that readily changes colour to blue on heating, a phenomenon attributed to a hypothetical tinctorial lability of MBI.

Wool dyed violet with synthetic MBI indeed turns blue on mild heating. Visible adsorption spectroscopy shows a bathochromic shift after heating. Gas MS, SIM and X-ray fluorescence spectroscopy reveal no change in chemical composition, showing that no indigotin is formed by debromination of MBI. Pure MBI also undergoes an irreversible change in colour from violet to blue at 60°C.

The bathochromic effect of heat on MBI is the key to understanding the nature of hyacinthine purple and to rationalising conflicting findings regarding the colour of the dye from banded dye-murex.

Introduction

Banded dye-murex [*Phyllonotus trunculus*] was the major source for dyeing purple in the ancient Mediterranean world.[1] Purple from this shellfish is found typically to have a blue tint, giving it a violet colour. It is therefore identified as "hyacinthine purple" of antiquity, biblical *tekhelet*.[2]

The other shellfish-dye of antiquity "Tyrian purple" [biblical *argaman*] was made from two species, spiny dye-murex [*Bolinus brandaris*] and dogwinkle [*Thais haemastoma*, oyster drill].[3] Chemically, it is 6,6`-dibromoindigotin [DBI], which is formed as an artefact by chemical reactions when natural

bromoindoxyl precursors present in the hypobranchial glands of these species is exposed to light and oxygen.

Characteristic features of these two murex purples of antiquity are listed for comparison in the Table.

Hyacinthine purple is a mixture of DBI with indigotin and 6-bromoindigotin [MBI], the latter two accounting for its blue tint. Chemical coupling reactions between indoxyl and bromoindoxyl precursors, which are largely segregated respectively between the male and female snails, compete to form the three dyestuffs, as illustrated in Fig. 1. The dye obtained contains the three dyestuffs in varying proportions, depending on the reaction conditions prevailing, such as temperature, pH, illumination, ionic strength and relative concentrations of precursors.

The dye composition also depends, of course, on the ratio of males to females in the shellfish catch used. But this factor is further complicated by protandric sequential hermaphroditism, the males undergoing sex reversal to functioning females.[4] Since its penis is retained, such a female may be erroneously scored as male, even though it now contains predominantly bromoindoxyls.

Furthermore, the ratio of the amounts of dyestuffs actually dyed on to the textile, and the resulting colour, will be determined by additional factors, such as their affinity for the fibre substrate under the reaction conditions used, and, in vat dyeing, by their redox potentials and the illumination. Accordingly, the dye composition obtained on the textile will become enriched in one of the three ingredients, making it more homogeneous than that it is in the initial dye-bath.

Bathochromic effect of heat on MBI

An additional complication affecting the colour obtained from banded dye-murex, that has recently been discovered, is a colour-change on heating MBI.

In the hands of Lacaze-Duthiers, a reddish purple was sometimes obtained from banded dye-murex, which was visually the same colour as Tyrian purple.[5] This observation was erroneously understood to mean that it was the same dyestuff as obtained from spiny dye-murex, namely DBI.

It has recently been discovered that wool dyed purple with the banded murex has the peculiar property of readily turning blue on heating.[6] Ziderman ascribed the change to a hypothetical tinctorial lability of MBI, which was presumed to be the effective dyestuff in the dyeing. The lability was seemingly due to debromination of MBI to indigotin.

Previously detected only chromatographically without being isolated, synthetic MBI later become available for chemical research.[7] In a test of his proposition, Ziderman discovered that, on being

heated, MBI dyeings on wool also change colour from violet to blue, just as is required to prove the validity of his hypothesis.[8]

Accordingly, reddish purple dyeings obtained with banded dye-murex can be essentially MBI, and not DBI, which, on the other hand, would always be the dyestuff in purples from spiny murex and oyster drill. This conclusion provides cogent substantiation of the uniqueness of the banded murex species as the source of hyacinthine purple dye but not of Tyrian purple. It therefore corroborates Bizio's view, in his disputation on this issue with Lacaze-Duthiers.[9]

In order to prove whether the blue product of heating MBI is merely another physical form of MBI or that it is indeed indigotin, instrumental techniques were employed, including visible adsorption spectroscopy, gas MS and X-ray fluorescence spectroscopy.

Experimental part

MBI and the wool dyed with MBI were made and kindly supplied by Chris Cooksey. For the heating treatment, the dyed wool was placed in an oven at about 100 °C for a few minutes until it changed colour from violet to blue.

Visible spectra were obtained with a Hitachi UV-Visible Spectrophotometer U-3500, with the integral-sphere attachment for the visible reflectance absorption. The reflectance spectrum was automatically transformed into an absorption spectrum by the Kubelka-Munk equation.

X-ray fluorescence spectra were measured with a Horiba XGT2000W X-ray analytical microscope, at 50 kV, 1.0m A, 300 sec, and diameter 100 microns.

Gas MS was performed using a Shimadzu QP-5000 gas chromatograph/mass spectrometer. The sample was injected directly without the chromatograph, with electron impact at 70 eV, and ion source temperature at 300 °C.[10] Dyestuff extraction for Gas MS was performed with N,N'-dimethylformamide (DMF).

Results and discussion

The colour deepening exhibited by MBI on being heated is depicted in Fig. 2. In Fig. 3, the absorption spectrum of wool dyed with MBI is shown to change after the thermal colour-shift to blue. The absorption maximum shifts bathochromically from about 510 nm to about 640 nm, from the range for DBI to that for indigotin.

X-ray fluorescence [Fig. 4] reveals the presence of bromine in the dyed wool after dyeing. However, it may be inorganic bromide that has been eliminated from the MBI on heating and not bromine in unchanged MBI.

Gas mass spectrometry was used to prove that the bromine present is in MBI and that indigotin is not formed. In Fig. 5, the extracts of dyed wool before and after the colour-change are compared, both having peaks for MBI at 340 and 342 m/z. This finding was corroborated by single ion monitoring [SIM], which is highly sensitive [Fig. 6]; blue MBI has the same peak as violet MBI, and no indigotin is present.

It was found that, on heating to 60°C, pure synthetic MBI undergoes the same irreversible change in colour to blue, as does the dyed wool. Accordingly, the colour-alteration in dyed wool is not dependent on some interaction between wool and MBI, but is an inherent solid-state property of the dyestuff.

Conclusions

The bathochromic effect of heat on MBI is the key to a renewed understanding of the nature of hyacinthine purple and of conflicting findings that have been reported during the last two centuries regarding the colour of the dye made from banded dye-murex.

Characterisation of the mechanism of the thermal colour-change exhibited by MBI may prove to be an intriguing undertaking. It should be possible to detect and quantify the thermal transformation by differential thermal analysis techniques. A solid–state change in molecular organisation would presumably be the cause of the shift in spectral absorption. The colour-shift may be due to a crystalline transition that could be ascertained by hot-stage polarised microscopy, X-ray powder refraction and crystallography. Alternatively, high power microscopy may detect a change in particle size.

Notes and references

1. Ziderman, I. I. (2002) 'The biblical dye *tekhelet* and its use in Jewish textiles', *Dyes in History and Archaeology* 21, Avignon, France.

2. Bizio, B. (1832) *La porpora (degli antichi) rivocata entro i confini del rosso*, Venezia, Dissertazione critica, Tipografia di Commercio, 53 pp.

Fouquet, H. and Bielig, H.-J. (1971) 'Biological precursors and genesis of Tyrian purple', *Angewandte Chemie International Edition* 10, pp. 816-17.

Ziderman, I. I. (1981) 'Blue thread of the *tzitzit*: was the ancient dye a Prussian blue or Tyrian purple?' *Journal of the Society of Dyers and Colourists* 97, pp. 362-4.

Ziderman, I. I. (1987) 'First identification of authentic *tekhelet*', *Bulletin of the American Schools of Oriental Research* 265, pp. 25-33.

3. Ziderman, I. I. (1986) 'Purple dyes made from shellfish in antiquity', *Review of Progress in Coloration and Related Topics* 16, pp. 46-52.

Ziderman, I. I. (1990) 'Seashells and ancient purple dyeing', *Biblical Archaeologist* 52, pp. 98-101.

4. Ziderman, I. I. (1992) 'Molluscal source of biblical "blue" dyestuff', *Proceedings of the 9th International Malacology Congress*, University of Edinburgh, U.K., 1986, pp. 407-14.

5. Lacaze-Duthiers, H. de (1859) 'Mémoire sur la pourpre', *Annales des Sciences Naturelles: Zoologie* 4, 12, pp. 5-84.

6. Ziderman, I. I. (2001) 'Revival of biblical *tekhelet* dyeing with banded dye-murex (*Phyllonotus trunculus*): chemical anomalies', *Dyes in History and Archaeology* 16/17, pp. xvii and 87-90.

7. Cooksey, C. (2001) 'The synthesis and properties of 6-bromoindigo: indigo blue or Tyrian purple? The effect of physical state on the colours of indigo and bromoindigos', *Dyes in History and Archaeology* 16/17, pp. 97-104.

8. Ziderman, I. I. (2004) 'Purple dyeing in the Mediterranean world: characterisation of biblical *tekhelet*' (presented at International Conference on Colours in Antiquity, University of Edinburgh, U.K., on 11th September 2001) in L. Cleland, K. Stears and G. Davies (eds.), *Colour in Antiquity (British Archaeological Reports)*, Oxford, pp. 38-43, in press.

9. Bizio, B. (1860) 'Réclamation', *Cosmos* 16, p. 624.

Lacaze-Duthiers, H. de (1860) 'Response', *Cosmos* 17, pp. 34-35.

Bizio, B. (1861) 'Notizie concernenti alcune controversie circa la porpora degli antiqui', *Atti del' I. R. Istituto Veneto* 3, 6, pp. 795-802.

10. Sasaki, Y. (2002) 'Dye analyses of braids used for Japanese armours dating from the 14th to 17th century', *Dyes in History and Archaeology* 21, Avignon, France.

11. Born, W. (1937) *Purple*, Ciba Review 4, pp. 112-113.