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Experiments with the dyes from European purple-producing molluscs

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Introduction

For those of us who don't have easily available molecular analytical methods such as infrared and mass spectrometry, reference materials are still very important. We all know how difficult it can be to find reference samples of some ancient dyes. If they are not available commercially, then practically the only option left is to go out and try to find them in nature.

I had already tried out this approach with kermes in 1986 and it was quite successful.¹ This led me to try the same approach on the other famous ancient dye, the shellfish or 'Tyrian' purple. Therefore, in 1987 my wife and I went to the east coast of Spain, with the double purpose of trying to find (a) kermes in Spain, and (b) the Mediterranean mollusc species which produces the ancient purple. We found both of them, although this paper is only concerned with the shellfish purple. The present paper describes the methods used for obtaining reference samples of the purple dyes from four mollusc species living in the European seas.

Some zoological information

Most mollusc species producing the purple colour belong to the gastropod family Muricidae, as it was originally understood. Later, this family was split up into several families, into subfamilies, genera and subgenera. This nomenclature splitting has resulted in a situation that, for non-specialists, may seem rather confusing. For example, the names *Murex trunculus*, *Hexaplex trunculus* and *Trunculariopsis trunculus* all pertain to one and the same species, the banded dye-murex, nowadays generally called *Phyllonotus trunculus*.²

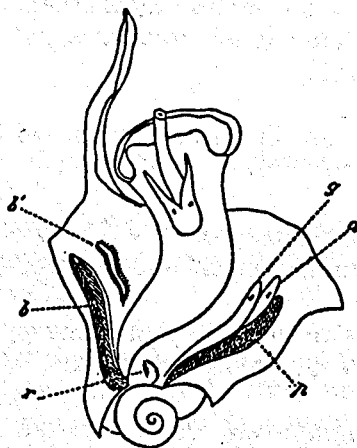


Fig.12: Spiny dye-murex, *Phyllonotus* (*Bolinus*, *Murex*) *brandaris*, with the mantle wall cut open. a: anus; b, b': gills; g: genital opening; p: hypobranchial gland; r: kidney

A very important point is that no animal of the purple-producing species contains any purple pigment as long as it is alive and well. Snails have, near the periphery of the body, a cavity called the mantle cavity, which is in direct contact with the outer world, and in which some organs, for example the gills and the genital opening, are located. In this mantle cavity, most of the marine snails also have a gland, called the hypobranchial gland,

the location of which is indicated in the sketch of a dissected spiny dye-murex, *Phyllonotus (Bolinus, Murex) brandaris* (fig.12). In this hypobranchial gland the species we are concerned with here produce a whiteish viscous secretion.

Chemistry

This secretion, starting from one or more almost colourless precursors, produces purple colorants, under the successive action of (a) an enzyme, (b) oxygen and (c) light.³ The hypobranchial gland contains the precursor or precursors and the enzyme, but the healthy living animal somehow manages to keep them separate, so that no reaction can occur. Depending on the precursors and reactions, two groups of species can be distinguished: the *trunculus*-type where light is not necessary, and the *brandaris*-type needing both light and oxygen.⁴

As far as textile dyeing is concerned, there are two methods for dyeing mollusc purple. The first and most simple is to produce the dye on the fibres, starting from the precursors. But, since the molecular structure of mollusc purple is indigoid, there is also the possibility of starting with the complete purple colorant, reducing it in an alkaline bath, and dyeing it just like indigo. Both methods were applied in this project.

Experimenting

In June 1987 we were on the east coast of Spain, in the fishing harbour of San Carlos de la Rapita, south of Tarragona. In the fishing nets we found dead animals of *Ph. brandaris* and *Ph. trunculus*; both had a purple spot on their shell. This was formed when the dying animal lost control over the content of its hypobranchial gland, so that the enzyme and precursor got mixed and the reactions could start. It was fairly easy to obtain the living molluscs we needed, since *Ph. brandaris* is considered to be a delicacy by the Spanish, and can be purchased in the local fish-market. And the animals of *Ph. trunculus*, also taken in the nets when fishing for *brandaris*, are used by the fishermen as bait for line-fishing. We could purchase what we needed directly from the fishermen.

Working on the snails turned out to be a smelly (methylmercaptan is formed by the reactions) and rather disgusting business, since in the act one has to kill the animals, to which I object ethically, and their shells must be broken, to which I object on aesthetic grounds. With a small hammer, a hole is made in the shell at about a quarter of a whorl from the aperture, so that the mantle wall becomes visible. Cutting open the mantle wall with a small pair of scissors shows the white-to-yellowish hypobranchial gland. With a small hard brush the contents of this gland was brushed on to a white silk or cotton cloth. Then starts the chain of reactions, changing the almost colourless gland material gradually into the purple, passing through yellow, red and greenish shades. However, the reaction occurs only when precursor and enzyme are brought together by diffusion in the viscous mucus of the hypobranchial gland, and this does not happen at the same moment everywhere in the sample. Consequently, most of the time several colours can be seen together, but near the end of the sequence only the purple remains. The difference between the reddish purple of *Ph. brandaris* and the blueish purple of *Ph. trunculus* is very clear.

The third Mediterranean species, *Thais (Purpura) haemastoma*, cannot be obtained from fishermen, since it lives on rocks and cannot be taken with a net. These shells were taken by skin-diving, at a depth of about three metres; in one locality near San Carlos there were plenty of them and I could easily collect enough specimens for my purposes. The same working method was applied; and here the changes in colour were photographed as a series over time. A selection of these photographs has been published elsewhere in colour.⁵ It was thus shown that the transformation from the colourless to the purple compound in the bright noon sunlight in Spain had already started after one minute, and was complete after nine minutes.

So much for the first method of dyeing mollusc purple: preparing the dye on the fibre, beginning with the precursor(s). The second method, which consists of first preparing the dyestuff and then reducing it in an alkaline bath, is somewhat more complicated. The working procedure was partly inspired by Pliny's description of the ancient method of purple dyeing, but also partly based on experiences from the first method.

The hypobranchial glands of about twenty animals per species were dissected and collected in seawater to which 7% (w/v) sodium chloride (NaCl) was added. This mixture was macerated for two weeks at ambient temperature. A rather dark liquid was obtained which, however, was free of the strong stench of decomposing mollusc tissue. When exposing this liquid to sunlight, the purple pigment is formed, and can be collected on a filter.

The material thus obtained may possibly correspond to the purple dyestuff that, according to some authors, was traded over long distances⁶ (although it is probable that most of the material traded was purple-dyed wool). There is a vast debate on the question of exactly how the ancients reduced their mollusc purple. I chose the easiest solution and used alkaline sodium dithionite, with strong direct light excluded in order to avoid the well-known debromination of the reduced species. Dyeing wool in this bath, followed by air oxidation, yielded purple samples from the three species. *Ph. trunculus*, however, stands out by the blueish shade of its dye, as compared with the two other species.

The samples of dyed textiles prepared by both methods have been analysed by HPLC.⁷ One of the main results was the discovery in the dye from *Ph. trunculus* of monobromindigotin, a compound we had expected but which had never before been demonstrated in untreated mollusc purple.

Apart from the Mediterranean species, there is also the species *Nucella lapillus*, also referred to as *Thais lapillus* or *Purpura lapillus*. This shellfish is called dog-whelk or dog-winkle in English; it lives on rocky shores of the western coasts of France, especially in Brittany (Bretagne), and on the British coasts. The purple from this species had already been described by William Cole in 1685⁸ and more recently Su Grierson has described her tests with shellfish of this species collected on the west coast of Scotland.⁹ In 1990 we worked on this species in Brittany, giving it the same treatment as before. Despite its size, this small species produces a relatively large amount of dye, which has the reddish-purple hue of the *Ph. brandaris* purple.

As an example of a non-European and non-Murex species, there is the case of *Oliva bulbosa*, collected in Dubai by Bill Charter, a commander of the British Navy. He was walking with his wife along the seashore and found some nice little shells. His wife held them in her hand while walking back. Once home, they found that two remarkable things had happened: she had a purple spot on the palm of her hand, and this spot was numb, as if it had been anaesthetised. He published this experience in a malacological journal,¹⁰ and so I got in contact with him. He prepared the dye on a textile according to my indications and thus I obtained the purple from this tropical *Oliva bulbosa*: it is also a reddish purple, but it has not yet been analysed.

Although this example is clearly out of the scope set by the title of this paper, I couldn't resist including it. It shows that mollusc-purple dyed ancient textiles from the Persian Gulf area need not necessarily be dyed with purple from *Ph. brandaris* or other Mediterranean species. In fact, a number of mollusc species from Japan, Australia and Central America are known to yield a purple dye,¹¹ and most probably several more have the same property but have not yet been mentioned in this context.

Notes

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