a modern problem

J. T. Baker

The production of Tyrian purple from various species of shellfish was once a considerable industry in the Mediterranean countries. Although the use of the dye has long been abandoned, the process by which it was made and the chemistry by which the colourless precursor in the mollusc is converted into the richly coloured dye are of much interest. The author of this review has both familiarized himself with the history of the dye and investigated its chemistry experimentally.

Tyrian purple, purple of the ancients, and royal purple, are all synonyms for a dye of molluscan origin which has been known since pre-Roman times [1] and has featured significantly in the development and history of civilizations flourishing on the shores of the Mediterranean Sea and in many other parts of the world [2]. (figure 1).

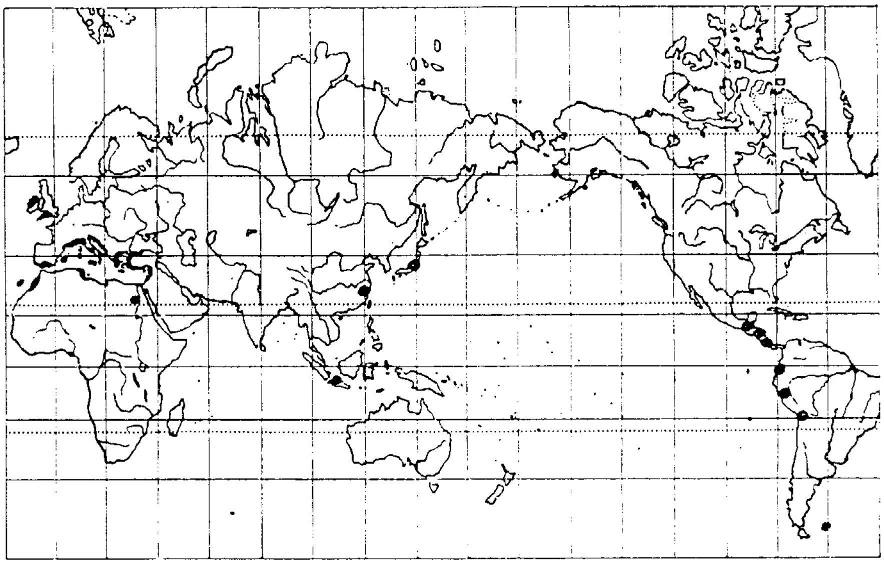
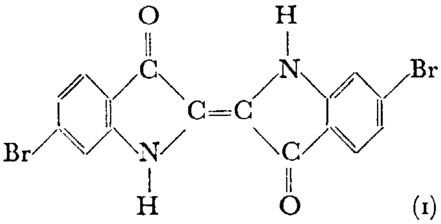


Figure 1 Map of world showing sites of ancient dyeing works (after J. W. Jackson).

Details of methods used for the preparation of purple garments have been lost through confused translations and through the cessation of commercial dyeing operations subsequent to the edict of Gratian, Valentinian, and Theodosius in A.D. 383, by which the making of higher quality purples became a State monopoly. Although the dye itself has now no commercial significance, chemical investigations have proceeded since the seventeenth century in an effort to clarify the sequence of reactions involved in its production.

There is no purple compound as such within the dye-producing hypobranchial glands of the various species of molluscs of the genera *Murex* of the families *Muricidae* and *Thaisidae* which are the principal sources of the dye. The chemical constitution of the dye itself has been accepted as 6,6′-dibromoindigotin, following the careful work of P. Friedländer [3] published between 1906 and 1909.



(1)

Even today, however, the full understanding of the sequence of events by which the colourless precursor is converted to purple dye remains to be elucidated.

In 1685 the physician William Cole [4] noted that exposure to light was necessary to produce the purple substance from an original white fluid which 'will presently appear a pleasant light green colour; and if placed in the sun will change into the following colours: light green, deep green, full sea green, watchet blue, purplish red, very deep purple red'. Subsequently, many investigations [5] were undertaken of the type of light most efficient for effecting these transformations. It was found that not all shellfish of the species studied give gland fluid in which the process leading to purple colours requires light (figures 2 and 3). The processes involved in production of purple from the hypobranchial glands of different species are as open to question as is the true colour of the 'purple' so highly prized in ancient times.

Earlier writings [6, 10] have referred in detail to the problem of defining the colour of Tyrian purple. On historical evidence, the colour had been described by C. E. Pellew [7] as ranging from 'brownish red to bluish grey through violet, purple and even deep indigo blue'. H. de Lacaze-Duthiers has illustrated [8] a series of purple colours produced from different species of molluscs, and stresses the impossibility of agreement on any one colour unambiguously representing the Tyrian purple of ancient times.

Modern ideas that the colour of Tyrian purple was violet over a deep-red background may well have arisen from such old descriptions as *purpura hyacinthea* (a violet shade like that of the hyacinth blossom) and those due to E. Ploss [9] who called it 'bluish-red merging into violet'. The elder Pliny [10] considered Tyrian purple best when 'it is the colour of clotted blood, dark by reflected and brilliant by transmitted light'.

Our own work on the different species of purple-producing molluscs of the Mediterranean confirms that a wide range of colours is in fact possible, depending on the choice of shellfish and on the method of preparation.

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The origin of the name Tyrian purple

Abbreviated reference to the historical and mythological derivation of 'Tyrian' may be found in several articles [11], but only Ploss [12] has reproduced the translation from the fourth-century Greek romance 'Leucippe and Clitophon' by Achilles Tatius to give the historical derivation, and from the *Onomasticon* of Julius Pollux—a ten-volume Greek dictionary of the second century—to give the derivation from Greek mythology. Regardless of which origin is correct, the name is now commonly associated with the city of Tyre, and it is significant that Virgil called the same colour *sarranus*, from Sarre, the former name of Tyre.

J. W. Jackson [13], however, does not believe that Tyre was the site of the original purple-dyeing works. He believes that Leuke, a small island to the south-east of Crete was producing purple before 1600 B.C., and quotes the findings of the Currelly and Bosanquet expedition to Leuke in 1903, when shells of *Murex trunculus* were found in association with pre-Phoenician artifacts [14].

The origin of the word 'purple' is even more obscure. It is possible that the Latin *purpura* is derived from the Greek *perphýra*, which can be related to *phýro* (to wet, or mix) and *phorphýro* (to be combined). Thus the word could have been originally a professional term of the earliest Greek dyers [12]. Possibly, the true origin is a term, now lost, used to describe the species giving the dye. It has been claimed that the *purpura* was not only a species of purple-producing shellfish, but also the purple itself, both as an industrial product and as a colour.

Methods of dyeing used by the Ancients

In this review, discussion is confined to the Mediterranean dyeing industry, for which several authors have given widely differing accounts of the methods used [5, 15].

The source of the dye, at least, is not in doubt. It is described as a small whitish 'vein' situated transversely under, but in immediate contact with, the shell. The best results were obtained working with live animals. The glands of the larger shell-fish were separated from the rest of the animal, but smaller varieties were crushed whole, shell and all. There is evidence that where the gland was removed intact, special instruments were used. Neither Pliny the Elder [10] nor Pliny the Younger [16] described a method for the removal of the gland but they did report that only the gland was used for the dyeing process.

The confusion existing as to the method of dyeing used by the ancients may well stem from the elder Pliny's writings, in which he described three distinct methods; in subsequent accounts these have often been confused. It is therefore worth considering Pliny's original writings, as translated by K. C. Bailey [17]. Cap. XXXVIII, sect. 62, states:

133. 'The vein already mentioned is then extracted and about a sextarius [approx. 7 lb] of salt added to every hundred pounds of material. It should be soaked for three days, for the fresher 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.

134. Meanwhile the flesh which necessarily adheres to the veins is skimmed off and a test is made about the tenth day by steeping a well-washed fleece in the liquefied 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 tinge of black. The wool drinks in the dye for five hours and after carding is dipped again and again until all the colour is absorbed'.

Pliny then speaks of the need to use both the 'non-fast' *Buccine* dye and the fast *Pelagian* dye to obtain the best results. The amounts required are surprisingly large: '200 lb of *Buccine* extract and 110 lb of *Pelagian* are used for every 50 lb of wool'. It is clear that operations were conducted on a considerable scale.

The Tyrian method is also described: 'the Tyrian colour is obtained by first steeping the wool in a raw and unheated vat of *Pelagian* extract, and then transferring it to one of *Buccine*'.

138. 'Conchyliated garments are prepared by a similar method to the first, but no buccine extract is used and the dye is diluted simultaneously with water and human urine. Only half the usual amount of dye is used'. This method gave a paler shade, which was fashionable in Pliny's time.

The ancients introduced several modifications to produce different colour tones. Many of the dyes developed by the ancients were the result of steeping the fibres in vats derived from glands of different species of shell fish; in some cases, kermes, (derived from an insect parasite of the kermes oak) was used as well. The Ancients applied the dye to fibres and never to a piece of material, ensuring a maximum intensity and uniformity of colour. Pliny indicates that urine was used only in the preparation of 'conchyliated' purple, but it is probable that it was used more extensively.

If these interpretations are correct, the true Tyrian method did not involve a vat dye: that is, one soluble only in its reduced, colourless, form. There is, however, evidence of a vat-dyeing scheme of the following kind. The glands were excised, placed in a lead vessel, and covered with about 7 per cent of their weight of salt; the mixture was ground together, and allowed to stand for three days. The yellow-brown suspension was then diluted with water and urine and heated gently for about ten days. Meat particles, fat, etc., rose to the surface as a foam which was removed periodically. After ten days, the volume had reduced to about one-tenth of the original; urine and honey were added to produce a satisfactory viscosity, and heating was continued. The liquor was tested by steeping a well-washed, degreased fibre in it, and then exposing it to bright sunlight. If the colour shade was not satisfactory, other liquors were added.

Elsewhere in the ancient world it would appear [13] that methods of dyeing were less well developed, and involved a greater use of direct gland secretion than did methods in major dyeing works on the Mediterranean.

Our own work with Mediterranean species would suggest that a far more detailed consideration of dyeing methods may be desirable because of the widely differing glandular constituents of Mediterranean species, which may have been of importance in ancient times.

Molluscs used by the Ancients

Pliny's descriptions of the shells used by the Ancients...

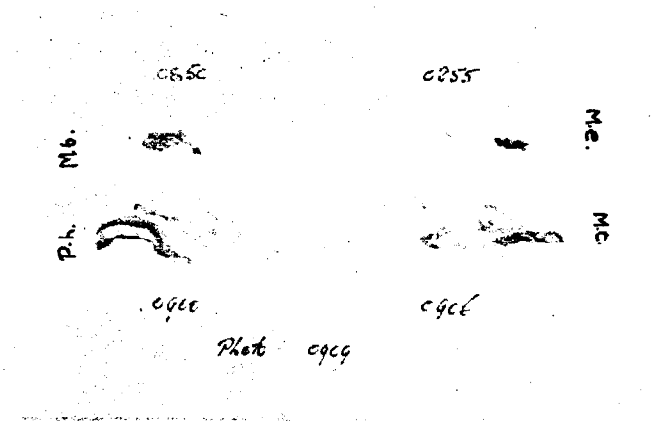


Figure 2 Glands from *Murex brandaris (M.b.), M. erinaceus (M.e.), Purpura haemastoma (P.h.),* and *M. trunculus (M.t.)* showing times of dissection.

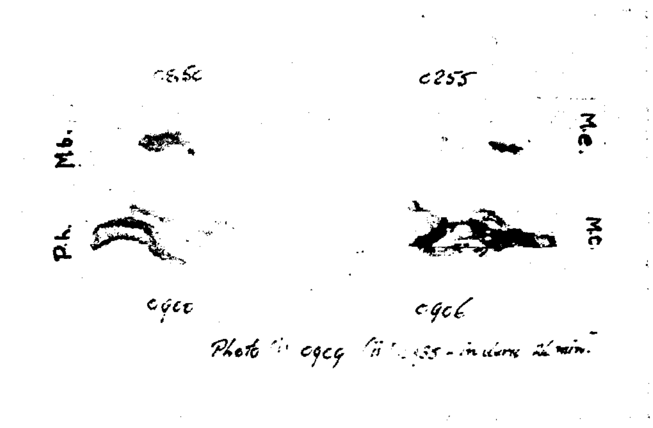


Figure 3 Glands, as in figure 2, left in dark 29 minutes after gland from *M. trunculus* dissected. Note production of purple by *M. trunculus.*

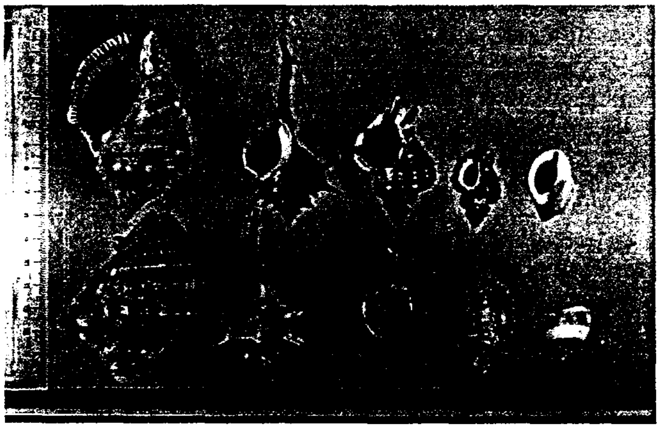


Figure 4 Molluscs reported to be important in ancient times. From largest to smallest, *P. haemastoma, M. brandaris, M. trunculus, M. erinaceus, P. lapillus.*

Figure 5 The Japanese mollusc *Rapana bezoar* related to the *Purpura.*

not make clear which molluscs were actually used, and different authors attach importance to different species. It must be accepted, of course, that the current distributions of the various species are not necessarily the same as those in former times.

Schaeffer lists the most important *Purpura* species as:

Type	Source
P. haemastoma	Atlantic Ocean (African Coast)
P. lapillus	Atlantic Ocean
P. madreporarum	Atlantic Ocean
P. patula	Gulf of Mexico
P. persica	Gulf of Mexico
P. aperta	Gulf of Mexico

Although it has been reported that *Purpura haemastoma* does not occur in the Mediterranean, Jackson [13] believes that it is widely distributed in this area—in Provence, Corsica, Sardinia, and Sicily. Certainly it is now readily available off Southern Italy.

The most important *Murex* species are:

Type	Source
M. brandaris	Mediterranean
M. trunculus	Mediterranean
M. erinaceus	Coast of Normandy
M. cornutus	Atlantic Ocean (African Coast)

Species most often referred to as of major importance in ancient dyeing works are *M. brandaris*, *M. trunculus*, *M. erinaceus*, *P. haemastoma*, and *P. lapillus*. These are illustrated in figure 4; the first four were collected in the Bay of Naples and the last named in Cornwall, England. In Japan, *Rapana bezoar*, closely allied to *Purpura*, was of importance in their ancient dyeing processes (figure 5).

On the basis of shell mounds found near sites of ancient Mediterranean dyeing works, *M. brandaris* and *M. trunculus* were the principal molluscs used, some use being made also of *M. erinaceus*, *P. haemastoma*, and *P. lapillus*. *Murex brandaris* lives on sandy or muddy bottoms and in considerable depth of water (10 to 150 metres) whereas all other species listed are found in relatively shallow water (0 to 15 metres). Pliny described the method of catching *Murex* in wicker baskets and Möhres in 1963 reported [15] that *M. brandaris* was still caught in mussel-baited baskets for the Venice markets. Near Venice and Naples today, vast quantities of *M. brandaris* are collected by trawlers with dredges, but the market is for human consumption and not for dyeing.

Our recent investigations in Naples reveal that *M. brandaris* yields considerably less dyestuff precursor per gland than does *M. trunculus* or *P. haemastoma*. Further, because *M. trunculus* and *P. haemastoma*, as shallow-water dwellers, are more accessible than *M. brandaris*, one wonders if the Ancients may not have first worked with *M. trunculus* and *P. haemastoma* to produce purple dyes

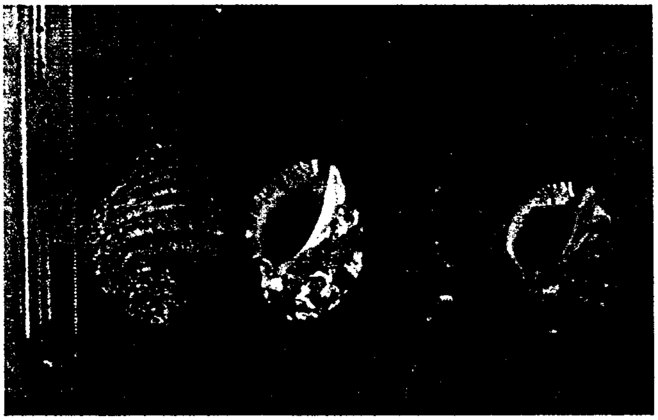


Figure 6 Two of the Australian species studied, *Dicathais orbita* (larger), *Mancinella bufo* (smaller).

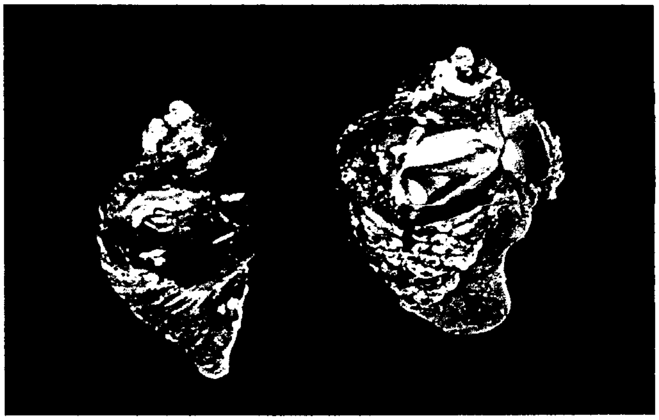


Figure 7 *D. orbita*, illustrating that in the live animal dissection exposes a light-coloured under-side of gland. In the dead animal (left) the gland is already yellow.

and sought the deeper water *M. brandaris* only when supplies of the other species became less abundant. The rock-dwelling *P. haemastoma* and *M. erinaceus* would have been particularly accessible. Unless the smaller *M. erinaceus* was once available in certain localities in vast numbers, it is unlikely that this species was economically significant.

Popularity and use of Tyrian purple from ancient times

The Bible frequently refers to the colours blue, purple, and scarlet, the latter usually being the colour obtained from kermes. Purple is often referred to in connection with Tyre and appears to mean the colour developed from the 'purple shellfish'. The Old Testament gives examples of the variety of uses of purple in connection with important buildings, people, and events. Exodus refers to the purple curtains of the Tabernacle and to the purple in Aaron's garment. Purple is connected with Tyre in Chronicles II. Ezekiel refers to purple of Syria and of Tyre and Judges mentions purple worn by royalty. Purple was also used to honour people; in Esther, King Ahasuerus honoured Mordecai the Jew by giving him 'a garment of fine linen and purple'.

Purple dyes were used by Egyptians at an early date. A papyrus dating from the time of Rameses II (1400–1300 B.C.) mentions the purple-dyeing trade. Subsequently both the Greeks and Romans used the purple colour extensively and the famous Greek infantry—the Hoplites—wore purple tunics both to impress the enemy because of their splendour, and to conceal blood from their wounds. At sea, the Admiral's vessel was distinguished by purple sails.

In Rome, the *Equites* (or Knights) wore a narrow band of purple on their togas, whereas the senators were distinguished by a single broad band of purple down the front of the tunic. The Imperator (or Commander-in-Chief) wore a purple cloak which, hoisted on a spear, was a rallying point in times of danger. A victorious general on return to Rome would receive a purple cloak with gold embroidery.

Sixty years before the reign of the Emperor Augustus (63 B.C.–A.D. 14) the violet-purple was fashionable (cost 100 denarii a pound); then came Tarentine red, and finally the Tyrian *dibapha* (twice dipped) which cost more than 1000 denarii a pound. Purple dyes from various sources were used in almost every house at this time, and Lentulus Spinther in 62 B.C. used the *dibapha* for the *praetexta* (an outer garment worn by the children

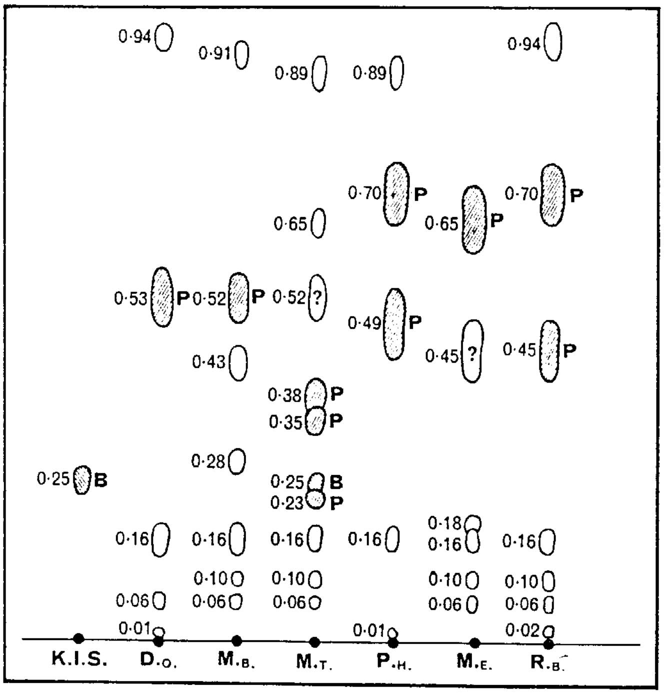
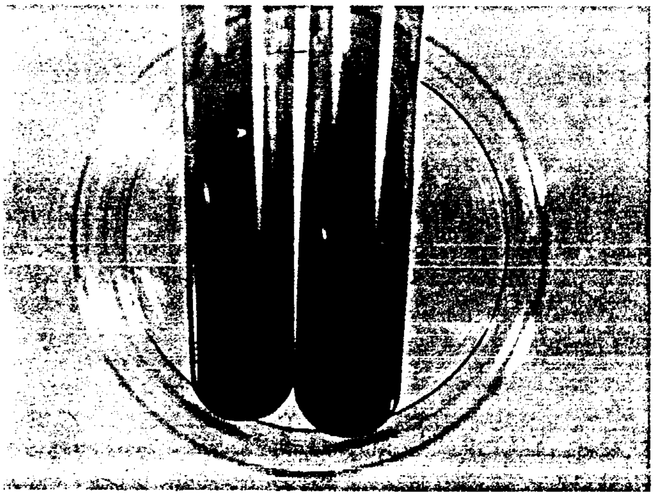
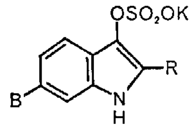


Figure 8 Paper chromatogram of ethanol extracts of glands





R = SCH_3	B = Br	*Dicathais orbita*	
R = H	B = H	*Murex trunculus*	Fouquet and Bielig Nov. 1971
R = SCH_3	B = H	" "	
R = H	B = Br	" "	
R = SO_2CH_3	B = Br	" "	
R = SO_2CH_3	B = H	Not yet confirmed	

Figure 10 Precursors found in different species of molluscs.

of nobility)—only to incur the disapproval of the court for using so common a dye.

But the price of purple dyes continued to increase and imitations were more widely used (see later). By A.D. 300 the prices had risen steeply, as illustrated by a famous Edict of Diocletian (A.D. 284–305) in which he made possibly the first attempt to introduce price control. Mommsen [18] records the prices per constant unit weight as follows:

Doubly-dyed purple silk	150 000 denarii
Doubly-dyed purple wool	50 000 denarii
Red-dyed purple wool	32 000 denarii
Violet-dyed purple wool	10 000 denarii
Imitation purple wool	400 denarii

The doubly-dyed purple garments became used more and more by royalty and less and less by others. Pure purple dyes became protected by laws enacted under the Roman emperors and any person outside the court who wore a garment dyed with pure purple could be convicted of treason and put to death. This purple was called *purpura hyacinthea* and was reserved to the Gods and the Roman Emperors. In the legal code of Theodosius the Great (A.D. 379–395) it appears as '*murex sacer adorandus*' [12] (the sacred purple fish which is to be worshipped). The Byzantine emperors used the purple dye in an ink which was reserved for their use.

When the Eastern Roman Empire succumbed to the Turks, the purple-dyeing factories of Tyre—more than 1000 years old—were destroyed. Tyre was almost completely demolished by the Saracens in 1291 when they recaptured it from the Crusaders. Purple dyes were produced in a few isolated centres until, with the fall of Constantinople in 1453, dyeing with purple from shellfish, in the Mediterranean, ceased entirely.

During the era of purple dyeing on the Mediterranean, many centres grew rich through its production—from the original Tyre (now Sur) and Sidon (now Saida) in Asia Minor, the industry spread to Carthage, to the islands of the Greek Archipelago, to Tarentum in Southern Italy, to Marseilles, and as far west as Cadiz on the Atlantic Coast.

Several modifications were implemented to reduce the cost of purple dyes. One of these was to dye the material first with kermes and then with a vat from the purple shellfish. The term 'hysginus' or 'hysgic purple' was associated with this colour; garments dyed in this manner were about one-tenth the price of the genuine article.

Two manuscripts from 300 B.C., found in an Egyptian tomb—the *Papyrus Graecus Holmiensis* and the *Leyden Papyrus*—give directions for preparing imitation dyes. The recipes indicate that kermes, madder, and indigo (woad) were used as substitutes for purple at that time.

Modern interest in purple dyes from shellfish appears to have arisen from William Cole's report [4], in 1685, of a minor dyeing industry in Ireland, and his subsequent work on *Purpura lapillus*. Since that time only isolated usages of the purple dye have been reported, and the main interest has been in understanding the nature of the purple dye, and the mechanism of its production from the natural colourless precursor.

Recognition of the relationship between indigotin and Tyrian purple

Until the early 1900s, the possibility that Tyrian purple was a derivative of indigotin was not recognized. Some of the reported methods of dyeing for Tyrian purple did not obviously relate to those for indigo, originally obtained from indoxyl glucoside (indican) which occurs in many plants of the genus *Indigofera*. (The term indigo is used for the mixture of dyes obtained from indican and the term indigotin for the pure chemical species).

Baeyer's laboratory synthesis of indigotin in 1883 eventually led to a commercially successful synthesis by *Badische Anilin- und Sodafabrik* (BASF) in 1897 and the

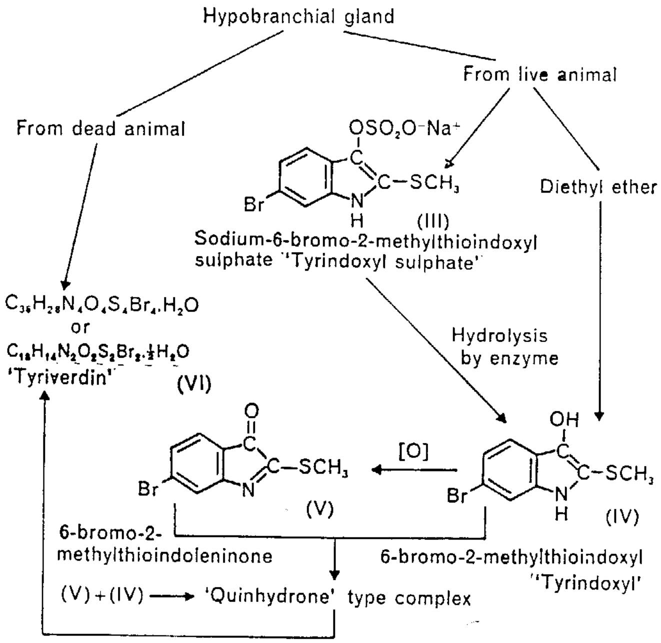


Figure 11 Production of tyriverdin from glands of *D. orbita.*

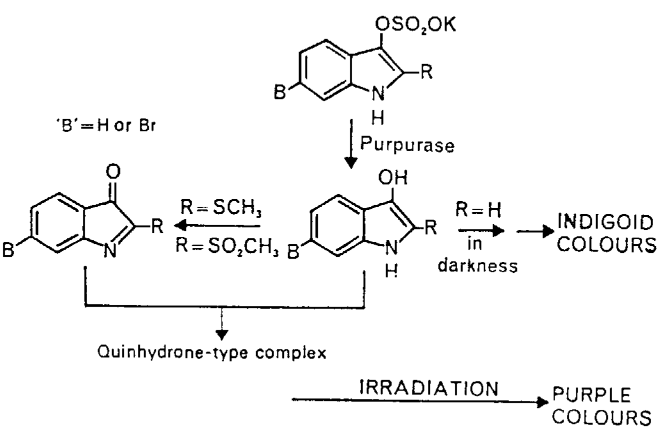


Figure 12 Summary form of pathways to purple from different precursors.

Figure 13 Microphotograph of tyriverdin before irradiation.

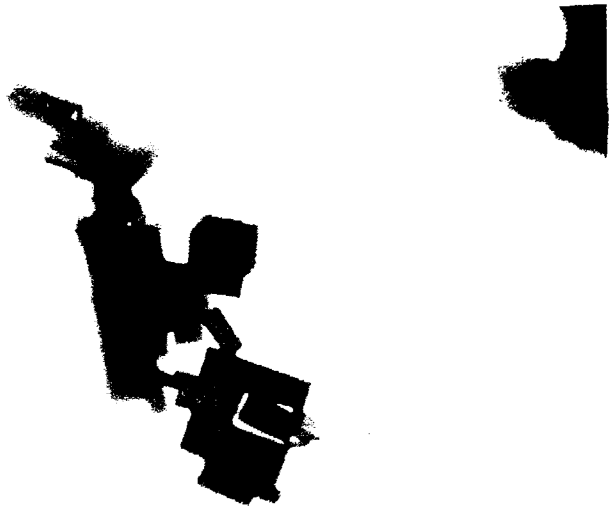


Figure 14 The same as in figure 13, after irradiation.

application of indigo to a variety of fibres is now most often achieved by means of the leuco dye produced by alkaline hydrosulphite reduction of indigotin. A stable disulphuric ester salt of leuco indigotin (Indigosol O) has been available since 1921 [19].

Several halogenated derivatives of indigotin have been prepared commercially and the cheaper chloro derivatives have gained favour over the natural Tyrian purple, which, depending as it does on the molluscs used, must have varied widely in colour standard.

Chemistry of the production of purple dyes from gastropod molluscs

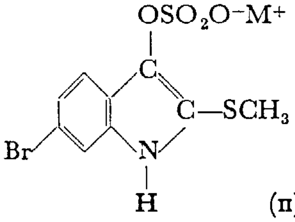
After Cole had awakened interest in the complex colour transformations to purple, a host of workers from Réaumur onwards have contributed to a progressive understanding of the processes involved in production and in the identification of the principal components of Tyrian purple and intermediate compounds. However, the work extends over a number of species and what is found to be true of one species may not necessarily be valid for another.

Our own initial work [20, 21] involved a study of the production of Tyrian purple from an Australian mollusc *Dicathais orbita* Gmelin, not previously investigated by European workers. This mollusc (figure 6) has a clearly defined hypobranchial gland (figure 7) which on extraction, yields only one absolute precursor to 6,6′-dibromoindigotin (I).

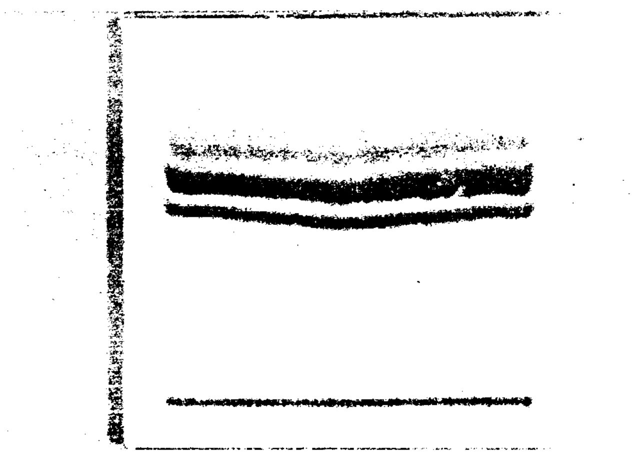
Subsequent investigations on species of historical importance, from the Mediterranean, England, Japan, and Costa Rica reveal not only that *D. orbita* is in no way typical of other species, but also that wide differences exist between species already investigated. H. Fouquet and H.-J. Bielig [22] have also reported briefly of their findings on differences in the Mediterranean species.

Figure 8 illustrates a comparative paper chromatograph of ethanol extracts of glands from live animals, resolved on Whatman 3 mm paper, using butanol : acetic acid : water (78:5:17) as solvent [23]. Potassium indoxyl sulphate has been used as standard. Spots which are marked with parallel lines yield 'purple' compounds. By *M. trunculus*, but *P. haemastoma* and the Japanese *Rapana bezoar* definitely contain two purple precursors. There is some uncertainty as to the complexity of glands from *M. erinaceus*, where only a very limited supply of samples was available for testing. Figure 9 shows the two 'purple' suspensions obtained from the different fractions of *P. haemastoma*.

Fouquet and Bielig [22] have reported on four constituents of the gland from *M. trunculus*, and when these are compared with the reported [19] precursor to 6,6′-dibromoindigotin in *D. orbita*, there is one obvious precursor which one may expect, though this has not yet been identified (figure 10). Whereas Fouquet and Bielig claim that tyrindoxyl sulphate (II) does not occur in the Mediterranean species, our own unpublished work offers strong evidence that the compound is present in the extracts of *P. haemastoma*.

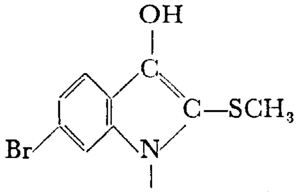


(II)



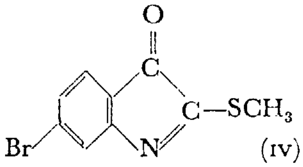
Ethanol extraction of gland material allows isolation of the precursors without further degradation by the purpurase in the glands. On the other hand, ether extraction of gland material produces different compounds, these apparently being modified within the aqueous phase by enzyme hydrolysis, then further modified or extracted into the water-immiscible ether layer.

The first product of hydrolysis would be the corresponding tyrindoxyl (III) in *D. orbita*



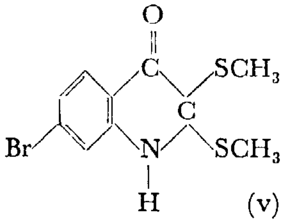
(III)

which could then be dehydrogenated to the corresponding indoleninone (IV).



(IV)

From fresh ether extracts of hypobranchial glands of *D. orbita*, the compound IV has been isolated and characterized. A methanethiol adduct (V) has also been isolated in small amount.



(V)

When the ether solution is allowed to stand in the dark, or when autolysed glands are extracted with methanol/chloroform, *D. orbita* yields a pale-green photosensitive compound, tyriverdin, which in sunlight produces 6,6′-dibromoindigotin, 6-bromoisatin, and dimethyl disulphide. The amount of 6-bromoisatin increases relative to that of 6,6′-dibromoindigotin when oxygen is bubbled through the solution during irradiation, and decreases when the solution is deprived of oxygen.

Tyriverdin is believed to be a quinhydrone type complex of III and IV, and support for this type of structure comes from elemental analysis, proton magnetic resonance, and mass spectrometry.

Figure 11 illustrates the processes envisaged in the production of tyriverdin, from *D. orbita* glands, and figure 12 summarizes the method of production of purple from known precursors. Figure 13 shows crystals of tyriverdin before irradiation by the microscope light source and figure 14 the same crystals after irradiation.

Whereas ether solutions of gland extracts from *D. orbita*, *P. haemastoma*, *M. brandaris*, and *M. erinaceus* give relatively simple mixtures of compounds that are readily accounted for, the ether extract of *M. trunculus* glands from live animals gives a highly coloured solution which when subjected to thin-layer chromatography on silica gel using benzene: acetonitrile (2:1) showed three distinct purple bands and one major blue band on a plate showing eight bands in all (figure 15). All compounds have not yet been identified.

The major end-product of 6,6′-dibromoindigotin is well established. 6-Bromoisatin would be expected to be present in photochemically produced dyes, and some dull colouration could be due to this latter compound. 6,6′-Dibromoindigotin has been characterized in ancient objects, mainly by spectroscopic methods. In infrared analysis we have found that the infrared spectrum will vary significantly, depending on the method of preparation of the pure 6,6′-dibromoindigotin.

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