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TYRIAN PURPLE FROM MARINE MURICIDS, ESPECIALLY FROM *PLICOPURPURA PANSA* (GOULD, 1853)

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ABSTRACT A review of the literature discloses that most marine snails of the family Muricidae produce in the hypobranchial gland a viscous secretion containing, besides mucus and biologically active compounds, minute amounts of chromogens. These chromogens develop enzymatically and under the influence of light and oxygen into a purple pigment known as "Tyrian Purple", "Royal Purple" or shellfish purple. In the hypobranchial gland the enzyme purpurase is kept apart from the chromogens, so that no pigments are formed under normal conditions. Different species of muricids produce different pigments, depending on the number and concentration of different chromogens and on the varying light intensity and oxygen availability during pigment formation. The main pigments obtained from the hypobranchial gland from muricids are indigoids. The pigment of *P. pansa* is mainly 6,6′-dibromindigo with smaller amounts of 6-bromoindigo and 6,6′-dibromoindirubin, similar to that of *Murex brandaris*.

KEY WORDS: "Tyrian Purple", gastropoda, muricidae, *Plicopurpura pansa*, hypobranchial gland

INTRODUCTION

A review of the hypobranchial gland of muricids, its secretions, including "Tyrian purple", seemed justified in view of the growing interest in natural dyes and marine products with pharmacological properties.

The majority of purple producing marine snails belong to the family of Muricidae and most, if not all, produce a colorless secretion in the hypobranchial gland, which turns purple on exposure to air and light (Fretter & Graham 1994).

In antiquity, the purple from the muricids *Murex trunculus*, *M. brandaris*, and *Purpura haemastoma* was produced in the eastern Mediterranean countries – now called, Crete, Lebanon, and Israel. Through the Phoenicians the art of purple production was spread from the Mediterranean to West Africa and Ireland (Jackson 1917). Purple dyes were used extensively by Egyptians and subsequently by Greeks and Romans. In view of the enormous quantity of marine snails needed to produce a minute amount of the dye, the scarcity of the animals, and the high costs of production, Tyrian purple was at that time a most expensive luxury article. In addition there was the symbolic importance of purple as a sign of royalty, power and wealth, and the belief that it could possess magic and supernatural powers (Reinhold 1970). At that time it was the only known fast vat dye, other than indigo. With the Arab conquest of Palestine in 638 A.D., and finally with the fall of Constantinople in 1453 A.D. the use of Tyrian purple became, with a few exceptions, extinct in the Old World (Herzog 1919; Born 1936b; Clark et al. 1993). Through archaeological studies it was confirmed that during the Middle Ages on the west coast of France the muricid *Nucella lapillus* was used as a source for purple (Gruet 1993). From the 16th to the 18th century the artisanal use of purple for marking linen was widespread in Ireland, South Wales and Cornwall, as well as in Scotland, France, Norway and other parts of Europe (Cole 1685; Jackson 1917).

In Japan, the muricid *Rapana bezoar* was of importance in ancient dyeing processes (Baker 1974). On the Japanese peninsula Shima, professional seafood collectors stained their diving suits, made of cotton, with the purple from marine snails believing that it contained supernatural powers (Yoshioka 1974).

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The use of muricids for dyeing on the pacific coast of the Americas dates at least from pre-Columbian times. In the same way as the now extinct Mediterranean purple industry the exploitation of the dye of marine snails led also on the pacific coast of the Americas to a product of high economic value.

Today, however, there is not much general interest existing in Tyrian purple derived from marine snails, since similar pigments can be obtained from synthetic substitutes at much less cost (Born 1936c). However, two remarkable exceptions have to be mentioned: (a) the dark violet-blue tekhelet color, which is relevant to Jewish religious rituals derived from the Mediterranean muricids *Murex erinaceus* and *M. trunculus*, and b) on the Pacific coast from Peru to Mexico, the hypobranchial secretion of the muricid *Plicopurpura pansa* (Gould 1853) has been exploited since pre-Columbian times by Indians for dyeing cotton yarn, which until now is subsequently woven into traditional dresses (Martens v. 1874, 1898; Schunck 1980a; Nuttall 1909; Jackson 1917; Born 1936c; Gerhard 1964; Turok et al. 1988; Yoshioka 1974; Thompson 1994; Garay 1996; Sandberg 1997). v. Martens (1898) pointed out that the use of the pigments from *P. pansa* for dyeing in Central America must have had a very long and pre-Columbian tradition and were not brought by the Spanish conquistadors from Europe to the New World. Its presence in archaeological textiles and pictures confirmed his finding.

The carnivorous muricid *Plicopurpura pansa* (Gould 1853), according to Kool (1993) conspecific with *Purpura pansa* (Gould 1853), inhabits intertidal rocks exposed to the open sea with high impact waves. The range of *P. pansa* extends at the Pacific from the north-west coast of Mexico (Baja California Sur) (Clench 1947; Keen 1971) to northern Peru (Peña 1970; Paredes et al. 1999).

Hypobranchial or Mucous Gland

Since the mid 18th century the hypobranchial gland of muricids has attracted the interest of natural scientists, investigating its functional role, and the astonishing production of Tyrian purple. Fretter and Graham (1994) consider the main function of the hypobranchial gland to be a secretor of mucus for trapping and cementing particulate matter sucked into the mantle cavity with the respiratory water current, prior to its expulsion.

The hypobranchial or mucus gland is an elongated epithelial structure located in the dorsal mantle cavity between the gills and recto-genital organs, immediately below the shell. In the gland three distinct anatomical and functional areas have been described: two lateral regions composed of eight distinct cell types, among them many active secretory cells (mucocytes), ciliated on the ventral surface, and possessing pores through which the mucus and other secretory products are released into the mantle cavity, and a central area where the formation of the "purple" precursors takes place and where secretory products accumulate prior to their release from the snail (Bolognani Fantin & Ottaviani 1981; Roller et al. 1995). The purple precursors (tyrindoxyl sulphate) and the enzyme (aryl sulfatase = purpurase) that induce the transformation of the purple precursors into pigments are only localized in the median zone of the hypobranchial gland (Erspamer 1946) and are kept separate, so that no reaction occurs. Mollusk purple as such does not occur in the live animal, but it is formed during a sequence of chemical reactions from the secretions produced by the animal. When the animal contracts vigorously the cells are massively liberated, burst open by mechanical or osmotic pressure, and their contents dispersed into the mucus (Lacaze-Duthiers 1859). These observations were later refined by the histological work of Bernard (1890), who found a well-developed innervation in the gland, suggesting a role in perception (Verhecken 1989).

The pharmacological action by extracts of the hypobranchial gland was discovered by Dubois (1909), and he described for the first time their toxic and paralyzing action in both warm- and cold-blooded species. The secretion of the hypobranchial gland from a large number of muricids contains, besides mucus, the precursors of the purple dye, proteins (aryl sulfatase, purpurase), and toxins and narcotizing agents, like serotonin (5-hydroxytryptamine), murexine (urocanylcholine,), choline ester and biogenic amines (Erspamer 1952; Erspamer & Benati 1953; Whittaker 1960; Malaszkiewicz 1967; Huang & Mir 1971; Roseghini et al. 1996; Shiomi et al. 1998).

The secretion from the hypobranchial gland of *P. pansa* can be obtained by "milking" without harming the animals. It is a milky-white liquid, which turns on exposure to air and light, at first yellow, then greenish, bluish and finally purple ("Tyrian purple"). During personal field observations (unpublished) we observed that *P. pansa* uses the secretion to immobilize prey (*Nerita* sp., *Littorina* sp.) in the intertidal zone, and does not resort to drilling through the shells of other snails. Additionally interesting to notice is the fact that during the predation no purple color is formed on the prey, despite the presence of oxygen and intense light radiation.

The chromogens containing the hypobrancial secretions seem to be purely incidental, and their functional role, if any, is presently unknown (Clench 1947). The volume of secretion obtainable from *P. pansa* depends not only on the size and sex of the animals, the time interval between the each "milking", but also on the season. Its production and use may be in proportion to the type of food the snails feed on. From small animals of less than 2 cm shell length can be obtained about 0.5 ml of secretion, from 5–6 cm large animals up to 4 ml (Rios-Jara et al. 1994). It has to be kept in mind however, that in this volume only a minute proportion consists in the dye precursors.

Chemistry of Tyrian Purple Formation

Several preliminary studies on the chemical composition of the pigments of *P. pansa* are available. The comparison between the chemical composition of the hypobranchial secretion of other muricids will lead to a better understanding of the metabolic pathways that lead to the final production of Tyrian purple.

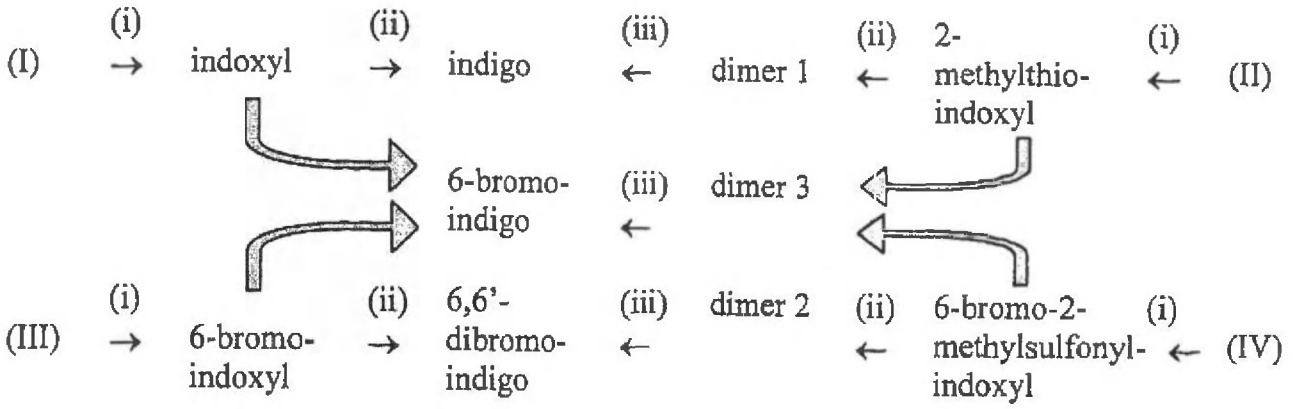
Since the re-discovery by Cole (1685) of "Tyrian Purple" from *Nucella (Purpura) lapillus* a number of researchers have worked on the determination of the chemical composition of the secretion of the hypobranchial gland. Most remarkable, considering the limited knowledge of organic chemistry at the beginning of the 19th century, is the analytical work by Bartolomeo Bizio about the origin and properties of Tyrian purple from the Mediterranean muricids *Murex trunculus* and *M. brandaris* (Ghiretti 1994). When collecting the glandular secretion of the snails he made the important observations, first, that as soon as the colorless fluid is exposed to light and air it becomes immediately yellow and greenish, and soon afterwards it turns into deep emerald green, blue, deep blue and finally reaches the purple color. Next, that during the production of the purple dye, a highly odorous compound is released. In comparing the color differences between the purple from *Murex trunculus* and *M. brandaris* he discovered that they are species specific. Bizio also determined that Tyrian purple is a substance with chemical properties similar to indigo. Schunck (1879) isolated and crystallized the pigment from the "ink" of *Nucella (Purpura) lapillus*, and determined the chemical properties. He called the pigment punicin. To obtain 7 mg of punicin he extracted the hypobranchial gland of 400 animals, after which he reports "my patience was exhausted". Friedländer (1909) isolated 1.4 g of the pure pigment from 12,000 hypobranchial glands from *Murex brandaris*, and showed that it was 6,6′-dibromoindigo.

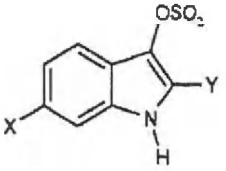
Recently, using advanced analytical methods, Fouquet (1970), Baker and Duke (1973), Michel et al. (1992) and Koren (1994, 1995) among others, have confirmed that the major pigment from all studied muricids is 6,6′-dibromoindigo.

Different species of muricids produce different color qualities of the dye, depending mainly on the number and concentration of the different chromogens. Fouquet (1970) found four different chromogens in the hypobranchial gland of *M. trunculus*: I) indoxyl sulfate, II) 2-methylthio-indoxyl sulfate, III) 6-bromoindoxyl sulfate, and IV) 6-bromo-2-methylsulfonyl-indoxyl sulfate, and he described the chemical pathway leading to Tyrian purple: The first step in the purple production is hydrolysis of the sulfate group with purpurase (aryl sulfatase). Indoxyl sulfate (I) and 6-bromoindoxyl sulfate (III) are then oxidized by oxygen to give indigo and 6,6′-dibromoindigo, respectively. With 2-methylthio-indoxyl sulfate (II) and 6-bromo-2-methylsulfonyl-indoxyl sulfate (IV) oxidation is followed by dimerisation and the dimer is photolysed in light to give indigo and 6,6′-dibromoindigo respectively together with methanethiol or dimethyl disulfide. These reactions as described by Foquet (1970) are shown in Figure 1.

At the time of Fouquet's studies the possibility of cross-coupling of the indoxyls which accounts for the large percentage of 6-bromoindigo in the pigment of *M. trunculus*was was unknown.

The composition of the chromogens of other muricids is less complicated. *Thais clavigera*, *T. bronnii*, *Dicathais orbita*, *M. brandaris* and *N. lapillus* contain 6-bromo-2-methylthio-indoxyl sulfate (IV); *M. erinaceus* contains a single different chromogen and *Purpura haemastoma* and *Rapana bezoar* contain two other different chromogens, but the chemical structures are not known (Baker 1974; Hiyoshi & Fujise 1992). The reaction pathways of





X=H, Y=H, (I) indoxyl sulfate
X=H, Y=SCH_3, (II) 2-methylthio-indoxyl sulfate
X=Br, Y=H, (III) 6-bromoindoxyl sulfate
X=Br, Y=SO_2CH_3, (IV) 6-bromo-2-methylsulfonyl-indoxyl sulfate

Figure 1. The chromogens from *Murex trunculus* and their reactions to give indigoid pigments (Fouquet, 1970).

6-bromo-2-methylthio-indoxyl sulfate (tyrindoxyl) to give indigoid pigments are shown in Figure 2.

The composition of the different chromogens is not only dependent on the species of muricids, but also environmental, and physiological condition of the animals. The light intensity and oxygen availability also play a role during pigment formation. According to historical reports the best seasons to exploit the purple snails in the Mediterranean are autumn and winter. During summer the animals are hidden and in spring they lay eggs, at which time the hypobranchial secretion presumably is losing its coloring power and is not suited for color production (Born 1936; Cardon & du Chatenet 1990). Fouquet (1970) cites Schaefer (1941 "Neuere Ansichten über den antiken Purpur" Chemiker Zeitung, 273) and O. von Fürth (1903 "Vergleichende chemische Physiologie der niederen Tiere". Verlag G. Fischer, Jena, page 377) who stated that there are seasonal changes in the chromogens of snails from the "trunculus" and "brandaris" types, due to age, gender, and food.

Chemistry of Tyrian Purple from P. pansa

For more than a hundred years the chemical composition of "Tyrian Purple" from *P. pansa* has attracted the interest of chemists. Edward Schunck (1880a) obtained a sample of cotton yarn dyed on the west coast of Nicaragua with the extract of *Purpura patula* (now *P. pansa*). From 24 g of dyed material he obtained 99 mg of pure crystalline pigment with all the properties of punicin, which he had earlier obtained from *Purpura capillus (Nucella lapillus)* (Schunck 1879). Thirty years later it was shown by Friedländer (1909), that Schunck's punicin was 6,6′-dibromindigo. In 1922 Friedländer obtained from Mexico a sample of yarn dyed with the excretion of *P. aperta* (the zoological description has to be *P. pansa*, since *P. aperta* does not occur on the Pacific coast of the Americas). The analysis of the dye showed no differences in solubility, color, and absorption spectrum between the dye from *M. brandaris*, which he had analyzed before and for this reason he concluded with some certainty the dye of *P. pansa* consists mainly of 6,6′-dibromoindigo (Friedländer 1922).

Saltzman (1992) showed that the reflectance spectrum of cloth dyed with the "ink" of *P. pansa* had a maximum absorption at 520 nm. Very similar results obtained Withnall et al. (1993) and Clark et al. (1993) for synthetic 6,6′-dibromoindigo. Mass spectrometry was used by McGovern et al. (1991) to confirm that the major colorant of the cotton sample from Saltzman, was 6,6′-dibromoindigo with traces of 6-bromoindigo. It was found that direct introduction of the cotton sample into the mass spectrometer led in addition to the detection of large amounts of 6-bromoindigo also to some indigo. This artifact arose from interaction of the cotton fiber and 6,6′-dibromoindigo at the high injection temperatures, leading to debromination and the formation of indigo. The problem can be avoided by extraction of the dye from the fiber with hot quinoline, or with dimethyl sulfoxide (McGovern et al. 1991). Using this extraction methodology, it was observed that apart from the major 6,6′-dibromoindigo component there were also smaller amounts of monobromoindigo and indigo which have been previously obscured by other low molecular weight materials.

The analytical technique of choice for the characterization of mixtures of indigoid dyes is the application of the High Performance Liquid Chromatography (HPLC), pioneered by Wouters and Verhecken (1991). This technique allows the characterization of pigments by retention time and absorption spectrum. Koren (1994) applied this technique to a sample of Dr. Saltzman's material containing the Mexican purple from Oaxaca. He could only detect 6,6′-dibromoindigo. A recent chemical study of the pigments of *P. pansa* confirmed the finding that the main component of the dye is 6,6′-dibromoindigo (90%); with 9% monobromoin-

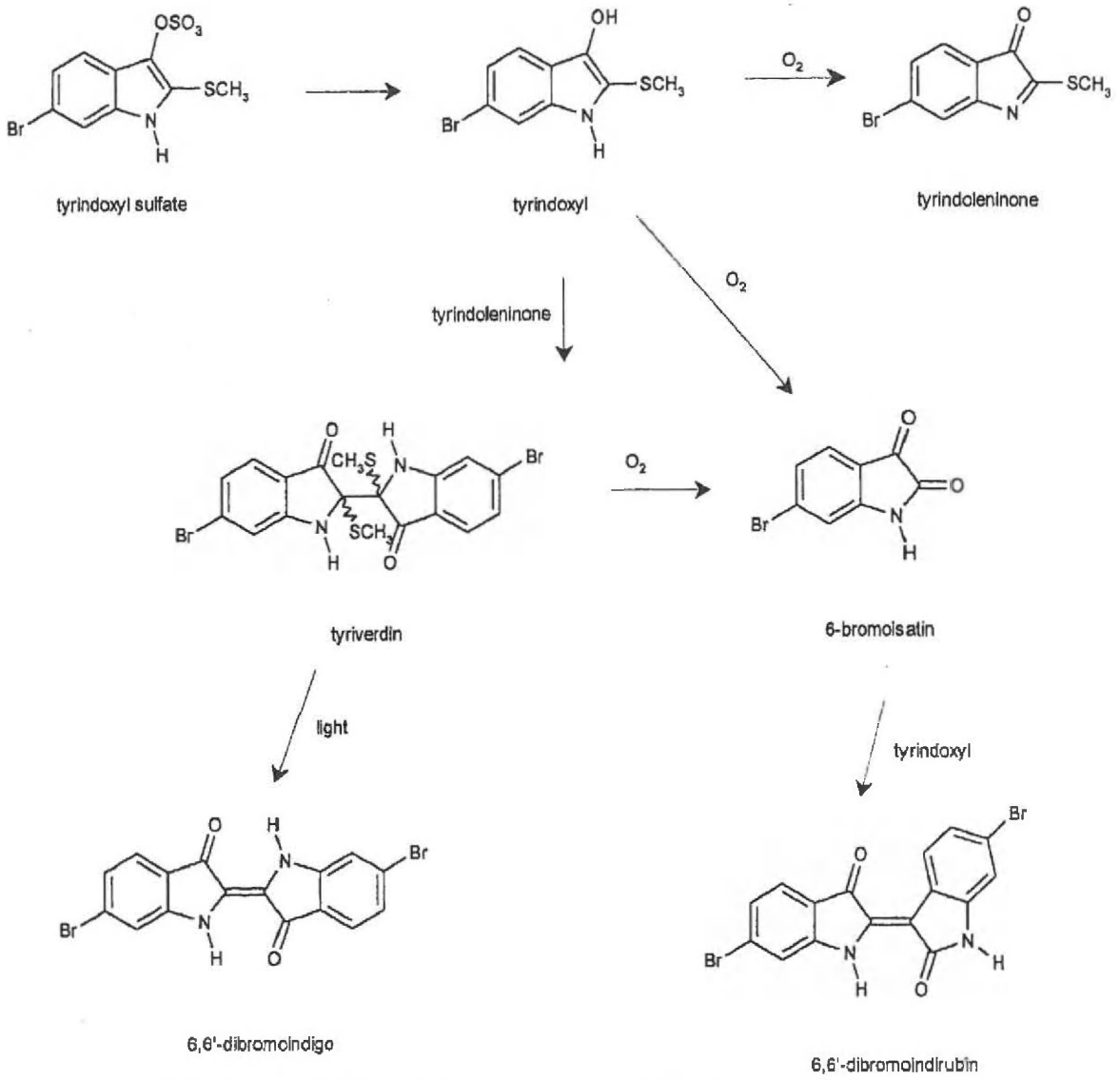


Figure 2. The production of indigoids from tyrindoxyl sulfate in "brandaris-type" mollusks.

digo, and 1% dibromoindirubin (Withnall et al., unpublished). Results obtained by different authors (Wouters 1992; Cooksey et al. 1992; Koren 1995, Withnall et al. unpublished) using HPLC to determine the chemical composition of the indigoid constituents of the purple dye from various muricids are shown in Table 1.

Since the values in Table 1 were obtained using a variety of HPLC protocols, close comparison is not justified, but some trends can be noted: *P. pansa* belongs to the *M. brandaris* group containing no indigo in the pigment, some 6,6′-dibromoindirubin, and showing a higher proportion of 6-bromoindigo than the average.

TABLE 1.

The composition (in %, obtained through HPLC analysis) of the indigoid constituents of the purple dye from various muricids.

	Indigo	Indirubin	6-Mono Bromo Indigo	6,6′-Dibromo Indigo	6,6′-Dibromo Indirubin	Reference
Murex brandaris	0	0	3	83	14	Wouters (1992)
Thais haemastoma	0	0	3	91	6	Wouters (1992)
Nucella lapillus	0	0	3	88	9	Cooksey et al., (1992)
Nucella lapillus	8	0	1	77	14	Withnall et al., (unpublished)
P. pansa	0	0	9	90	1	Withnall et al., (unpublished)
P. pansa	0	0	16	77	7	Wouters (pers. com).
Murex trunculus	55	7	35	3	0	Wouters (1992)
Murex trunculus	3	0	15	63	2	Koren (1995)

Textile Dyeing with "Tyrian Purple"

In using the "ink" for dyeing materials two significant differences have to be mentioned between the Mediterranean muricids and *P. pansa*: (a) the Mediterranean snails have to be killed to obtain the chromogens, whereas *P. pansa* can be "milked" to obtain the dye without harming the animals; and (b) the "milk" from the *P. pansa* can be applied directly on textiles where the final pigments are formed in the presence of light and oxygen.

In textile dyeing, there are two methods for dyeing with mollusk purple. The most simple is to have the chromogens react in the presence of light and air to obtain directly the final pigment on the fiber, as is the case with *P. pansa*. Since the molecular structure of mollusk purple is indigoid, there exists also the possibility of starting the dyeing process with the final oxidized purple colorant by reducing it in an aqueous alkaline bath, and applying the highly water soluble, and almost colorless leuco-form as a vat dye, just like indigo. Exposure to air oxidizes the leuco-form back to the indigoid pigment (Verhecken 1993; Clark et al. 1993; Schweppe 1998). In sunlight, the brominated leuco-indigoids can be photodebrominated, leading to 6-bromoindigo or indigo after aerial oxidation and changing the purple color to blue. This chemistry of reduction and photodebromination of 6,6'-dibromoindigo, was first described by Driessen (1944), as shown in Figure 3.

DISCUSSION

Different species of muricids produce different color qualities of the ink (Born 1936a), depending on the number and concentration of different chromogens. According to Verhecken (1993) depending on the precursors and chemical reactions for the formation of the pigments, two groups of dyes from marine muricids can be distinguished: the "trunculus type" where light is not necessary, and the "brandaris type" requiring both light and oxygen. Since for the formation of the dye of *P. pansa* light and oxygen is necessary, the dye of *P. pansa* according to this definition belongs to the "brandaris type". Another fact supports this characterization: the pigments of the "brandaris type" contain mainly 6,6'-dibromoindigo. The pigments of *P. pansa* contain 90% 6,6'-dibromindigo, confirming that the snails are forming part of the "brandaris type". This is in contrast to the purple pigment derived from *M. trunculus*, which is exceptional in containing non-

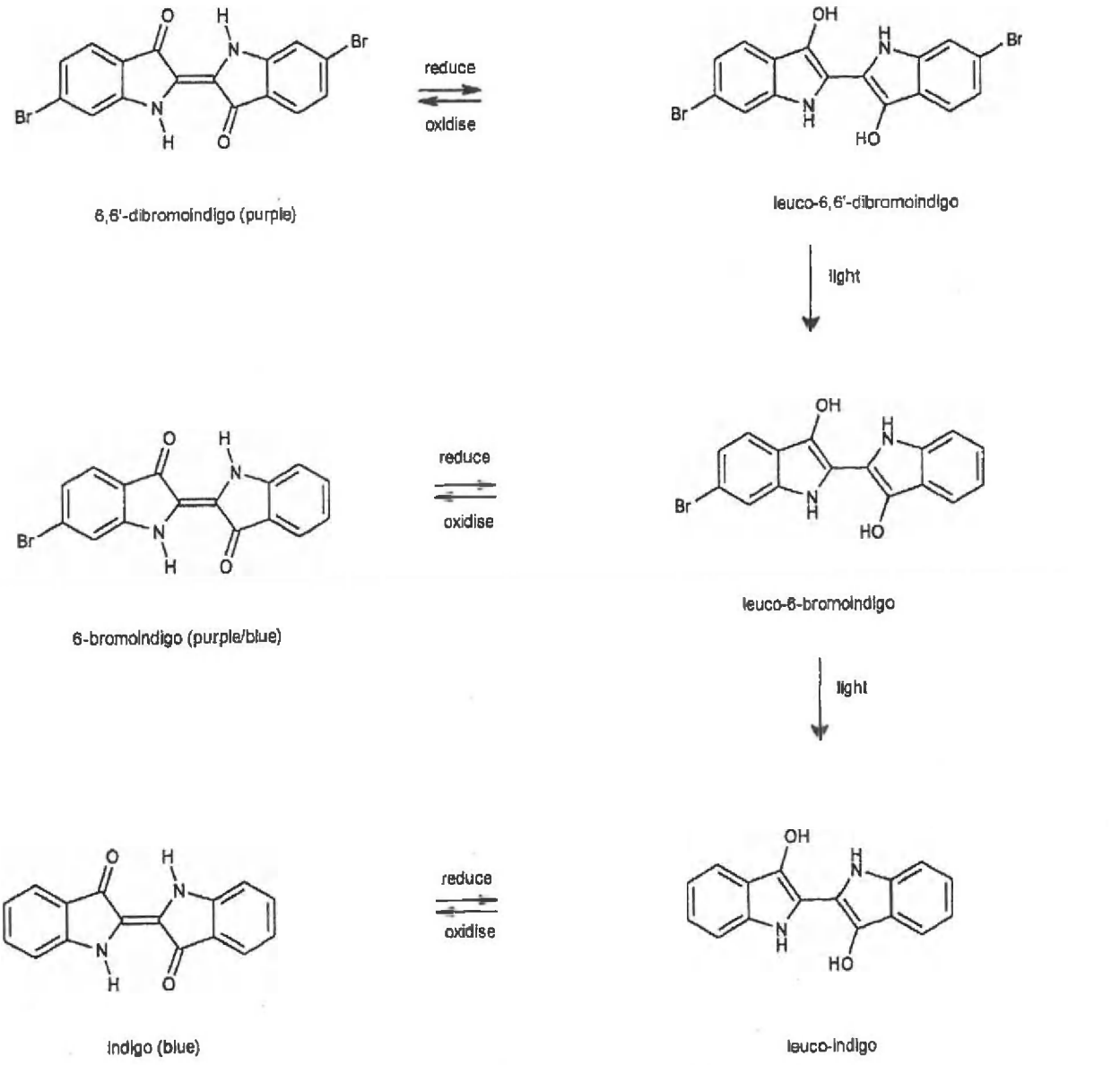


Figure 3. The reduction and photodebromination of 6,6'-dibromoindigo.

brominated precursors, leading to widely varying mixtures of indigoid pigments, including indigo and indirubin (Malaszkiewicz 1967).

The biosynthesis of the chromogens in the hypobranchial gland of muricids originates from tryptophan, an essential amino acid for animals, which is enzymatically split into indole and pyruvate. After a sequence of chemical reactions different intermediates are formed from indole, which lead finally to the colorless precursor of indigoid pigments tyrindoxyl sulfate, and subsequently through an enzymatic reaction with aryl sulfatase to give the yellowish intermediate tyrindoxyl (Fouquet 1970). In the presence of oxygen the red tyrindoleninone is formed, which reacts together with tyrindoxyl to give the greenish tyriverdin. In the presence of light tyriverdin is photolysed to give dimethyl disulfide and the purple, insoluble pigment 6,6′-dibromoindigo (Verhecken 1989). Additionally, from photolysis of tyrindoxyl or tyriverdin in the presence of oxygen, 6-bromoisatin can be formed which reacts with tyrindoxyl to 6,6′-dibromoindirubin (Withnall et al., unpublished). Oxygen and the light intensity during the chemical reactions of the intermediate substances determine the final composition of the pigments. The higher content of 6-bromoindigo than average in the pigments of *P. pansa* may result from the development of the dye under conditions of high light intensity. Under these conditions, any leuco-6,6′-dibromoindigo would be photodebrominated to give leuco-6-bromindigo, which on aerial oxidation would give 6-bromindigo. Under high intensity light conditions, the photoelimination of dimethyl disulfide from tyriverdin to yield 6,6′-dibromindigo will proceed rapidly, leading to a low concentration of tyriverdin. Consequently, oxidative cleavage of tyriverdin, a bimolecular reaction, to give 6-bromoisatin is a minor reaction pathway, leading to a low concentration of 6,6′-dibromoindirubin in the purple pigments of *P. pansa* (Withnall et al., unpublished).

The importance of the chromogens in the metabolism of the purple snails is unclear. The presence of the enzyme aryl sulfatase, which presumably occurs in all muricids (Erspamer 1946), supports the hypothesis that the chromogens could serve as a storage for the highly unstable indoxyls, which are formed enzymatically by the aryl sulfatase from sulfate esters (Fouquet 1970). Additional attention needs the question about the biological function of the indoxyls and their substituted bromo and methylthio analogs. It could be possible that these bromo and thio substituted indoxyls, like the iodine derivatives of tyrosine could act as hormones in the metabolism of the snails. Since the chromogens, besides mucus and bioactive substances, have their origin in a specialized area of the hypobranchial gland, it is feasible that the gland could have additionally inner secretory activities (Fouquet 1970).

We observed during field work that *P. pansa*, above sea level uses the secretion to immobilize their prey, without the formation of purple pigments (unpublished personal observations). This supports the finding that under normal circumstances the enzyme purpurase is kept apart from the chromogens, and therefore no pigments are formed, despite the presence of oxygen and light (Verhecken 1989). Additionally, in preliminary, yet unpublished personal studies, we could show, that the secretion from *P. pansa* is toxic to nauplii of Artemia, and has gram negative and gram positive antibacterial properties.

From snails of less than 2 cm shell length can be obtained about 0.5 ml of secretion and from large animals 5-6 cm up to 4 ml (Rios Jara et al. 1994). About one liter of secretion is required to dye about 200 g of cotton (Acevedo Garcia et al. 1993; Michel Morfin 2000). Since the average size of *P. pansa* is about 3 cm and a collection of more than 1 ml secretion per animal seems difficult, the enormous number of at least 1,000 snails has to be "milked" to obtain 1 liter of secretion to dye only 200 g of material. Since too frequent "milking" does harm to the animals it was the right decision of the Mexican government to permit only Indian communities the traditional exploitation of *P. pansa* for its pigments and to declare it a protected species.

In contrast with the Mediterranean region, where the use of purple from marine snails has long been forgotten and the craft of dyeing today cannot exactly be reconstructed, in remote Pacific regions of Mexico (in the States of Oaxaca and Michoacan) and with the Indian community of the Borucas in Costa Rica (Turok 1999) its use is continuing now and represents the survival of a knowledge of considerable antiquity. However, as Thompson (1994) observed that this old tradition will be lost in the future. As Thompson (1994) notes "In the early 20th century in Mexico shellfish purple was in much more widespread use than it is now. The beliefs, languages, and crafts of the Mexican Indians are fast disappearing. The progressive 'westernization' of rural Mexico has led people in many villages to abandon their traditional textiles and customs, in favor of factory-made cloth and western-style clothes which are readily available everywhere. Cultural and social decay is continuing to the point that the demand for traditional textiles has almost vanished. Weavers in a few villages formerly noted for their excellent textiles have turned to making more 'commercial' articles, for sale to people, such as tourists, outside their culture—a classic manifestation of the 'airport art' phenomenon."

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