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High-Performance Liquid Chromatographic Analysis of an Ancient Tyrian Purple Dyeing Vat from Israel

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Abstract. The high-performance liquid chromatographic technique is utilized to analyze the dye components of crude "Tyrian Purple" residues obtained from modern *Murex (Trunculariopsis) trunculus* sea snails and from an archaeological source. This is the first time that this technique has been used to analyze these raw pigments. Previously, chromatographic analyses of cloth stains and textile vat dyeings produced from contemporary snails were published. The modern purple pigment analyzed in this study was produced from excised hypobranchial glands of *trunculus* snails, and the archaeological purple residue investigated was found on the interior of a potsherd from Tel Kabri, Israel. The two pigments studied showed nearly identical chromatographic fingerprints: The pigments consisted of the same four indigoid components and with matching compositions. The dyes found were indigotin, monobromoindigotin, dibromoindigotin, and a fourth colorant that may be dibromoindirubin. The following conclusions can be made regarding the archaeological sample: (1) the ancient potsherd bearing the purple pigment was from an ancient dyeing vat; (2) the biological provenance of the archaeological dyestuff was most probably *Murex trunculus* mollusks; and (3) the Mediterranean snails used for the vat were likely collected at or near the Akhziv beach area in Israel. This study indicates that a biological and geographical chromatographic mapping of the dye components of *porphyra* snails can be developed to assist in provenance determinations of archaeological purple pigments.

INTRODUCTION

The chemical identification of any ancient dye must not only be based on an analysis of the relevant chemical properties of the colorant, but, as importantly, must also include the historical record associated with the dye. Of all the natural dyes used in antiquity, the molluskan purple was the most prestigious, and the purple-dye industry was one of the oldest and most complex of biochemical technologies in the ancient world. The "true purple" or "real purple" textile dye was produced from the colorless, whitish, or yellowish hypobranchial glandular secretions or extractions of certain purple-producing sea snails, as discussed by Aristotle (4th century BCE)¹ and Pliny the Elder (1st century CE).² Other authors of the Greek and Roman periods who have described some particulars associated with the purple dyestuff, known as *porphyra* in Greek literature and as *purpura* in Latin, include the Septuagint (3rd century BCE), Josephus (1st century CE), Philo (1st century

CE), Strabo (1st century CE), Plutarch (1st–2nd centuries CE), and Pollux (2nd century CE).

In porphyrology, the terms "purple" and "blue" have more general meanings than their simple color designations would imply. "Purple" is used to describe the general color of the raw pigment and also refers to textiles dyed with this stuff, irrespective of their actual color. The color of the pigment ranges from purple (or "reddish purple") to violet (or "bluish purple"), depending on the relative compositions of the dye components in the product. Dyeing with this dyestuff can produce textile colors ranging from reddish purple, violet, and blue to even turquoise, depending on, in part, whether certain chemical processing of the dyestuff was performed before and/or during the dyeing stage.³ Similarly, the term "blue" indicates a considerable blue content in the dyeing, which can describe violet, blue, light blue, or turquoise dyeings. Along the Mediterranean coasts of modern-day Israel and Lebanon, the three

most common purple-producing mollusks that were used in antiquity were *Murex (Trunculariopsis) trunculus*, *Murex brandaris*, and *Thais (Purpura) haemastoma*.⁴ These porphyra snails can still be found today — the *trunculus* and *haemastoma* in rather shallow waters, and the *brandaris* in deeper waters.⁵ The successful purple-dyer required knowledge concerning the biochemistry of these sea snails. However, to date, the entire process involved with purple-dyeing has not been completely deciphered, although numerous conjectures exist^{6–11} based on, in part, Pliny's account of this craft as performed in the first century Roman empire.

Purple-dyeing has a royal history. Purple-dyed robes and textiles were the pride of the ancient Assyrian and Babylonian kings.¹² The Biblical book of Esther vividly describes the colorful opulence of royal purple-dyed Persian robes and palaces festooned with purple fabrics. Roman emperors and Caesars who were ceremonially robed with colors obtained from the purple dyestuff also allowed some high government officials and generals to attire themselves with togas or cloaks that were completely dyed with purple.¹³ This Royal Purple or Imperial Purple dyestuff was also the source of the red-purple *Argaman* and bluish *Tekhelet* Biblical textile dyes that were used in the vestments of the High Priest and in some of the textiles used to adorn the Tabernacle.¹⁴ According to the Biblical passages, these dyes were prescribed soon after the Exodus of the Israelites from Egypt, which has been estimated to have occurred about 3,300 years ago.¹⁵ These Biblical dyeings required a "craftsman",¹⁶ which indicates that purple dyeing was already an established scientific art at that time, as has been confirmed through archaeological findings.

Though the Aegean theory of purple-dyeing insists that the Minoans of Crete originated this industry probably before 1750 BCE,¹⁷ the Phoenicians are nevertheless credited with perfecting this craft and making the textile dyeings produced by this exclusive industry prized above all others.¹⁸ The preeminent role that the Phoenician craftsmen enjoyed and the high esteem in which these purple dyers were held can be seen from various Biblical passages. In one of these, it is related that King Solomon, who was preparing to build the Temple in Jerusalem, asked King Hiram (also "Hiram") of Tyre for the following:¹⁹ "Now, send me a craftsman to [supervise] work in gold, silver, copper [bronze?], and iron, and in purple, scarlet, and blue, and who knows how to grave [all manner of] engravings, alongside the craftsmen I have with me in Judah and in Jerusalem, who were provided by David my father." Hence, the name "Tyrian Purple" has also been used to describe that snail dyestuff or dyeings produced from it. The industrial know-how of the Phoenicians is evident

from the various dyeing installations that these peoples left along the Mediterranean coastlines of modern-day Israel and Lebanon.²⁰ The oldest chemically confirmed purple pigments discovered thus far were found on potsherds from a 13th century BCE Phoenician site at Sarepta (Biblical Zarephath and modern-day Sarafand, Lebanon).^{21,22} In Israel, the oldest purple-pigmented shard is from Tel Akko in an area that has been dated to the 13th–12th centuries BCE.²³

In this study, the high-performance liquid chromatographic (HPLC) technique is utilized to analyze the dye components of raw Tyrian Purple residues obtained from modern *Murex trunculus* sea snails and from an archaeological source. This is the first time that the HPLC technique has been used to analyze these crude pigments. The modern pigment was produced by extracting the glandular fluid without any subsequent treatment or application to a textile. Previously, this chromatographic method has been used to analyze stained cloths and vat dyeings produced from modern *Murex* species.^{24,25} In that study, the purple stains were produced by smearing the colorless fluid containing the dye precursors of certain snails onto a cotton cloth and allowing the color to develop under the influence of sunlight and air. The woolen dyeings were produced by immersing the textile into a reduced dye solution (a "vat") obtained by reducing the indigoid dyestuff with sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and caustic soda (NaOH) and, after removal of the textile from the bath, allowing the solubilized dye in the fibers to undergo air oxidation to the final purple color. Analyses of these cloth stains and dyeings may not be representative of the chemical dye composition of the raw pigment itself. Cloth stains caused by the glandular fluid are often unevenly colored, and different results may be obtained depending on which part of the cloth was used for the analysis. The analysis of a vat dyeing may also not reflect the true composition of the crude pigment due to the varying chemical affinities that each indigoid component has for different textile fibers. For example, it has been found that dibrominated indigotin has significantly more affinity to wool than does indigotin,³ both being components of the dyestuff obtained from *Murex trunculus*.^{25–28}

The instrumental identifications of brominated indigoids in archaeological samples have been previously performed by means of the following techniques: visible spectrophotometry on a painted Paracas cotton textile from pre-Columbian Peru,²⁹ on a late Hellenistic / early Roman period Cypriot textile from Salamis (or Enkomi),³⁰ and on a small piece of stained limestone from a 6th century BCE Tel-Dor (Israel) dyeing installation;³¹ infrared (IR) spectrometry on a pigmented potsherd from a 9th–8th century BCE Tel Shiqmona

(Israel) dye vat;³² mass spectrometry on 3rd–4th centuries CE Egyptian Coptic textiles and on Peruvian textiles;²⁸ HPLC on a textile from 3rd century CE Egypt, a 1st century BCE Black Sea coast textile, and a textile from a Cologne museum collection;²⁵ and a combination of proton-induced X-ray emission (PIXE) spectroscopy, electron spectroscopic chemical analysis (ESCA), and diffuse reflectance Fourier-transform IR (FTIR) spectroscopy on the 13th century BCE potsherd from Sarepta (Lebanon) mentioned above.^{21,22} However, spectrometric techniques generally provide an “overlap of information” that can mask the minor components present in a mixture of substances. This is particularly problematic when isomeric mixtures are involved. A chromatographic method, such as HPLC, on the other hand, can produce an efficient “separation of information”. This method has been successfully applied to the separation and identification of various indigoidal components from modern dyestuffs²⁶ and it has been expanded to include dyestuffs from other chemical classes.³³ This HPLC method was used in the current study.

ARCHAEOLOGICAL SAMPLE ANALYZED

The archaeological purple pigment analyzed was on the interior of a basin shard (no. 3438/3) from Tel Kabri (Israel).³⁴ This site is about 5 km inland from the modern coastal city of Nahariya and about 6 km southeast of Akhziv Beach, which itself is about 5 km from the Lebanese border. This potsherd was found in a casemate room (Area E, Locus 890) with other clay vessels. Another purple-pigmented potsherd (no. 3425/100) was found in a nearby but nonadjoining room (Locus 1309). Both fragments are dated to the 7th century BCE — the Iron Age. The top of each curved fragment was finished and smooth. In addition, black soot stains were present on the exterior of each fragment. As of the 1994 season, no other shards bearing purple pigmentation were found at Tel Kabri.

The purple-pigmented potsherds were found at a site that was part of a Phoenician settlement estimated to have been founded at about 1,000 BCE which existed until it was destroyed by the Babylonian army at the beginning of the 6th century BCE.³⁵ Tel Kabri has been identified with the Biblical settlement of Rehob in the territory that was to be the inheritance of the Tribe of Asher (Joshua 19: 30) who was unable to secure it from the Canaanite, i.e., Phoenician, inhabitants who controlled the area (Judges 1: 31–32).³⁵

EXPERIMENTAL

The modern purple residue analyzed in this study was produced from excised *Murex (Trunculariopsis)*

trunculus hypobranchial glands obtained in the following way. About a hundred *trunculus* snails were collected in May of 1992 in water about 1–2 m deep at Akhziv Beach, Israel. These live snails were left in sea water for about 4 h and transported to Jerusalem. At the end of the day and continuing into the night, the snail shells were strategically broken and the hypobranchial glands removed under the open Jerusalem sky. The purple color developed naturally from the originally colorless fluid. The pigment was then separated from the fleshy parts of the gland by repeated rinsings of the mixture with tap water and pouring the mixture through a coarse strainer until no more purple was visible in the wash water. The latter procedure lasted about a week. The coarse purple dispersion was then centrifuged and, after decanting the supernatant liquid, the remaining sediment was freeze-dried.

The following treatments were performed on a small sample that was removed from the ancient clay fragment and on the modern pigment: The purple colorant was extracted with about 200 μ l of near-boiling *N,N*-dimethylformamide (DMF) solvent for 1 min. (The resulting blue color of each solution indicated the presence of a brominated and/or an unbrominated indigoid dye.) This mixture was then clarified through a 0.45- μ m nylon syringe filter and analyzed via the reverse-phase HPLC technique described below.

A Varian Vista 5500 LC instrument was used for the chromatographic measurements, with a Merck 150 \times 4 mm Lichrosorb 15537 RP-18 standard column (7 μ m), a 10- μ l sample loop, and a 1.0-ml/min flow rate. Data processing was on a PC using LabCalc software (Galactic Industries). The linear gradient elution scheme used consisted of a constant 10% of phosphoric acid (5% w/v) and the following methanol / water ratios: 30 / 60 (0–1 min); 30 \rightarrow 60 / 60 \rightarrow 30 (1–3 min); 60 \rightarrow 90 / 30 \rightarrow 0 (3–15 min); 90 / 0 (\geq 15 min). The detector wavelength used was 600 nm. These chromatographic and spectrometric detection conditions have also been described elsewhere.³³

RESULTS AND DISCUSSION

This section presents the qualitative and quantitative results obtained from the HPLC analyses on the purple pigments and a discussion regarding the clay fragment.

Indigoidal Content

The results of the HPLC analyses are recorded as chromatograms and are shown in Fig. 1. A chromatogram depicts the absorption of light of the washing solvent with or without different solutes, as it elutes out of the separation column. The time spent by each solute in the column, the retention time (R_t), under the chro-

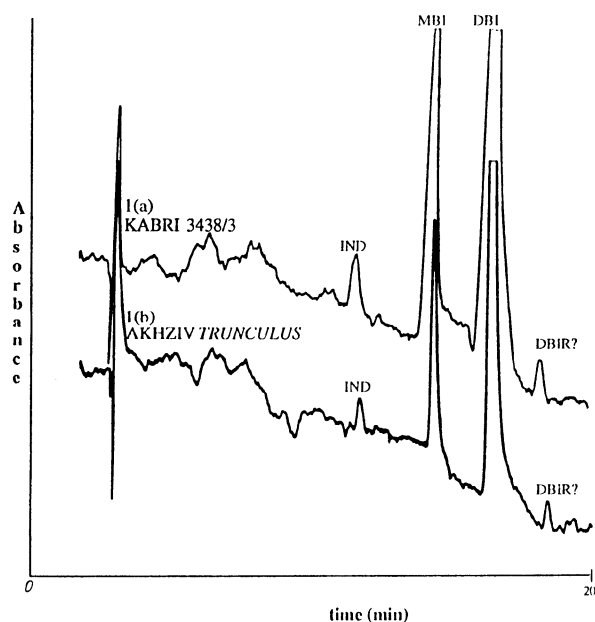


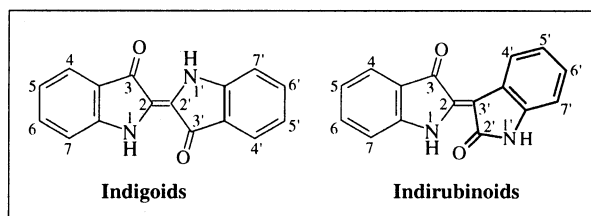
Fig. 1. HPLC chromatograms of DMF extracts of purple pigments detected at 600 nm: (a) ancient Tel Kabri potsherd sample; (b) modern sample from *Murex trunculus* snails from Akhziv.

matographic conditions and elution program used in this study, is characteristic for each indigoidal substance. Figure 1 shows the chromatograms of DMF extracts of (a) the archaeological pigment and (b) the modern purple pigment.

Figure 1 clearly shows that an extremely close match exists between the modern and the archaeological purple pigments. Each pigment actually consists of four indigoidal dye components. After calibrating this HPLC separation method with reference dyes,³³ three indigoids can be definitely identified: blue indigotin (IND), monobromoindigotin (MBI), and reddish-purple dibromoindigotin (DBI). (The color of MBI is probably similar to that of DBI as inferred from a comparison of the hue angle differences obtained from the "L, a, b" color coordinates³⁶ derived from the reflectance curves of woollens dyed with the purple pigment.³) The structures of these indigoids are given in Fig. 2. The fourth dye found is a reddish color and is chromatographically and spectrally consistent with the expected properties of 6,6'-dibromoindirubin (DBIR), which is an isomer of DBI.³³ As previously described,³³ this new dye's λ_{\max} is at about 550 nm, which is indicative of an indirubinoid (indigoids absorb in the 600 nm region), and its relative R_f as compared with dibrominated indigotin is nearly identical to the relative R_f of indirubin as compared with indigotin. This component is also similar to dye X found in purple-produced stains and dyeings from *brandaris*

and *haemastoma* species reported in ref 25. The first three indigoids found are consistent with other analyses performed on extracts from stains produced on a cotton cloth and woolen dyeings obtained from Mediterranean *trunculus* species from Spain^{24,25} and from filter paper stains of the same species from France.^{27,28} However, some indirubin was found in the dyeing but not in the staining from the Spanish snail, whereas no indirubin was found in the Israeli species investigated in this study. Hence, it can be concluded that the presence of the indirubin in the dyed wool reported in ref 25 is probably a result of the dyeing process ("vatting") and is not associated with the natural biochemistry of the glandular extract. Detection of a fourth colorant in the Israeli *trunculus* extract was a surprising result of this study. This is the first time that this dye has been found in this species. Previously, only the Spanish *brandaris* and *haemastoma* snails showed this type of colorant.

A quantitative comparison of the relative uncorrected compositions (r.u.c.'s) of the dye components in each pigment extract as determined by this study is depicted in Fig. 3. The unmodified compositions indicated are the ratios of the integrated peak areas from Fig. 1 and are uncorrected for the molar absorptivity ϵ of each dye at that wavelength. These values *can* be used to compare the relative compositions of the *same* dye obtained from different sources (but not for comparisons of the compositions of different dyes). Thus, each set of r.u.c.'s obtained from a particular source can be used as



Chemical class Dye (abbreviated symbol)	C.I. Constitution Number ¹	Substituents R ₆ R _{6'}	
Indigoids			
Indigotin (IND)	75 780	H	H
6-Monobromoindigotin (MBI)		Br	H
6,6'-Dibromoindigotin (DBI)	75 800	Br	Br
Indirubinooids			
Indirubin (INR)	75 790	H	H
6-Monobromoindirubin (MBIR)		Br	H
6'-Monobromoindirubin (MBIR')		H	Br
6,6'-Dibromoindirubin (DBIR)		Br	Br

¹Dye classification number according to *The Colour Index*, 3rd ed.; Society of Dyers and Colourists: London, 1971; Vol. 4; p. 4639; Vol. 8; p. 8133.

Fig. 2. The chemical structures of indigoids and indirubinooids.

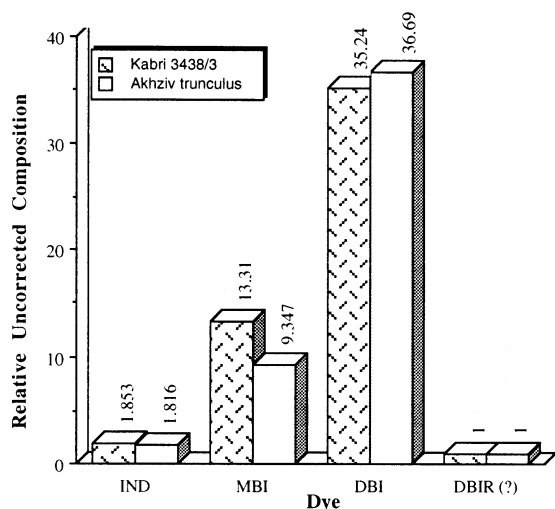


Fig. 3. Relative uncorrected compositions of the indigoidal dyes in extracts of the purple pigments from ancient Tel Kabri and modern Akhziv snails (obtained from Fig. 1).

a *quantitative fingerprint*, where each relative number is characteristic for a specific dye component. It can be seen from Fig. 3 that a very close match exists between the r.u.c.'s of the four colorants from the archaeological pigment and those from the modern pigment. Assuming that the absorptivities of the indigoids (at 600 nm) are not too different, then that figure clearly indicates the preponderance of DBI in the purple pigment, followed by MBI and then IND. This trend in the Israeli *trunculus* snail from Akhziv is different from that found in the Spanish and French snails. In those European snails the IND content is comparable to the DBI content. However, geographical differences associated with the *trunculus* species have also been found within Israel. Preliminary investigations have shown that *trunculus* snails from Dor beach, which is about 50 km south of Akhziv, while producing the same four colorants as that from Akhziv, yield significantly more indigotin and less DBI than that of the Akhziv snail.³⁷ These quantitative observations provide further strong evidence that the purple pigment present on the archaeological sample from Tel Kabri was probably produced with the Akhziv *trunculus* species. The proximity of the tel to Akhziv also corroborates this chemically based conjecture.

The Vat and the Dyeing Process

The morphology of the two pigmented clay fragments, the locations of the pigments on the interior of the two fragments, the soot stains on the outside of the shards, and the chemical analysis of the purple pigment indicate that, undoubtedly, the excavated potsherds were originally parts of the mouth of the same dyeing vat or the mouths of different vats. The presence of black soot stains on the exterior of each fragment is

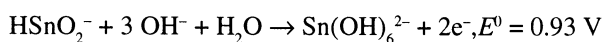
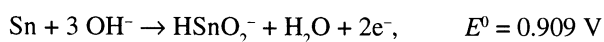
typical of a dye vat; soot stains were also found on the pigmented potsherds from Tel Shiqmona.³⁸ Charcoal was also found in an area near the Shiqmona purple-pigmented shards. These stains indicate that the vessel was directly heated using a wood fire and/or with hot charcoal. Heating the dye bath while the woolen fleece is in the solution will speed the dyeing process by increasing the diffusion of the dye molecules to the fibers and into them. Heating of the vat may have also been performed while processing the dye prior to the actual dyeing stage itself.

The purple woolens produced from these vats and archaeological findings in Israel reveal the commercial aims of these Phoenician dyeings. No woolen dyeings that have been unambiguously shown to contain authentic purple have been discovered thus far in Israel, whereas industrial-sized purple dyeing installations have been found at or near the Israeli coast. This indicates that these expensive dyeings were mostly intended for export and not for the local market.

The formation of a purple residue on the interior walls of the dyeing vat is consistent with the chemistry of indigoid dyeing. In order to perform any dyeing, which results in relatively strong physico-chemical bonds between the dye molecules within the textile fibers and the fibers, the dye must first be in a soluble form in order to penetrate into the fibers. The indigoidal dyestuff may have been introduced into the vat prior to the dyeing in one of two ways:^{8,10} (1) initially, as a purple pigment, or (2) in the soluble precursor form (prior to the final color development). Each of these two possible methods, which are discussed below, can yield an oxidized pigment that will adhere to the inside vat walls.

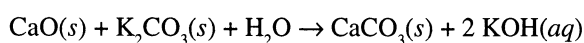
Dyeing with the final pigment. The purple indigoidal residue naturally formed from the extracted glandular fluid could have been added to an alkaline vat and reduced by means of a natural reducing agent to a soluble form, the so-called *leuco* ("white") reduced form (see Fig. 4), which produces a yellow-green solution — a "whiter" color than the original pigment. (This reduction is necessary because indigotin and its brominated derivatives are not otherwise soluble in aqueous media in their oxidized form.) The natural reducing agent that might have been used, if purple dyeing proceeded according to this method, has still not been unambiguously identified. Fermentation vats which are effective for the reduction of indigotin from indigotin-producing plants³⁹ have not been successful for the reduction of DBI⁹ because the magnitude of DBI's reduction potential is higher than that of indigotin.^{7,11} If a metal served as a reducing agent, then the most likely candidate was tin in the presence of an

alkaline solution,^{6,9,11} which reacts according to:⁴⁰



Tin was a metal already mentioned in the Bible (Numbers 31: 22).

Natural basic solutions could have been obtained by means of (1) stale urine (a source of ammonia); (2) aqueous solutions of one or more of the following materials: potash (K_2CO_3) from wood ashes; soda ash (Na_2CO_3) from plant ashes; lime (CaO) — produced by heating limestone (CaCO_3) — which, when hydrated, produces lime water, $\text{Ca}(\text{OH})_2$; (3) a combination of lime + wood and/or plant ashes, which in water yields the strong base KOH and/or NaOH according to, for example:



Dyeing of wool would have been performed by adjusting the pH to below 10 so as not to decompose the proteinic textile. Once the wool has been removed from the dye vat, the reduced leuco indigo in the wool will become oxidized and form the pigment within and on the textile fibers (see Fig. 4). Washing the dried dyeing will remove the pigment that has adsorbed onto the surface of the fibers, and the final fast, stable, dyeing will be ready for spinning into threads which will be woven to the final garment.

Dyeing with the precursors. The other possibility of purple-dyeing was by temporarily halting the natural biochemical development of the precursors within the gland to the final pigment. This would have been accomplished soon after the original localized break of the snail's shell and extraction of the glandular fluid. The purple pigment, which consists of dibromoindigotin as the major dye component, is actually an artifact of the snail because the purple dyestuff is not contained in the

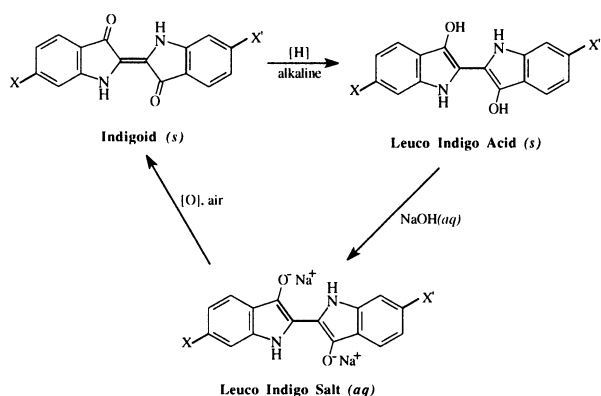


Fig. 4. Reduction of an indigoid to a soluble leuco salt and reverse air oxidation back to the original insoluble pigment.

animal. Rather, it is the precursors, which are unbrominated and brominated derivatives of potassium indoxyl sulfate (see Fig. 5) that are contained within the hypo-branchial gland of the animal.⁴¹ Following the break in the shell, the exposed gland could then have been punctured in situ or punctured after its excision from the animal. As a result of the rupture in the gland, the enzyme purpurase, an aryl sulfatase, comes in contact with the indoxyl sulfates and hydrolyzes each to the enol form,⁴² which then probably undergoes tautomerization to the keto structure. If these indoxyls are left to themselves at this point and exposed to air and light, they will eventually undergo photochemical oxidation to the final purple pigment. This is first brought about by oxidative coupling of the indoxyls or indolinones (or further oxidized species) to the greenish tyriverdins,^{43,44} which develop into the final brominated and unbrominated indigotins.⁴³ The full mechanism of this process, especially the kinetic roles of oxygen and light at various stages of the reaction, has still not been totally determined. If the indoxyls, however, can be stabilized and not allowed to undergo oxidation, then a solution containing these precursors can be used for dyeing.⁸ The stabilization would be favored if the quantity of oxygen could be minimized. This can be accomplished by using antioxidants, such as reducing sugars, for example, honey (fructose + glucose) and/or grape sugar (glucose),⁷ or by fermentation.

The process that will lead to the final pigment could have also been temporarily or permanently arrested by either inhibiting or completely denaturing the enzyme. This stoppage could have been accomplished by means of a relatively high temperature⁷ and/or manipulation of the pH of the solution. The wool could then be dyed by immersion in the precursor solution and upon removal of the fleece, the soluble indoxyls that have penetrated the fibers could then be allowed to undergo photochemical oxidation in the air.

The pigment formed at the top of the vat. Whichever dyeing method was employed, the formation of a purple scum on top of the solution would be nearly unavoidable. This "skin" would be produced whether the dye solution consists of the reduced form of the indigoids or of the unoxidized precursors, because when air comes in contact with either of these reduced forms, it will oxidize them to the final pigment. Thus, the surface oxidation of the dye solution will form a darkly colored layer on top of the solution. (This is a common occurrence when dyeing with an indigoid.) This pigmentation, which cannot be used in the dyeing process, will adhere to the parts of the dyeing vat with which it comes in contact. Hence, after thousands of years, the residual pigment on the interior of the potsherd from the dyeing

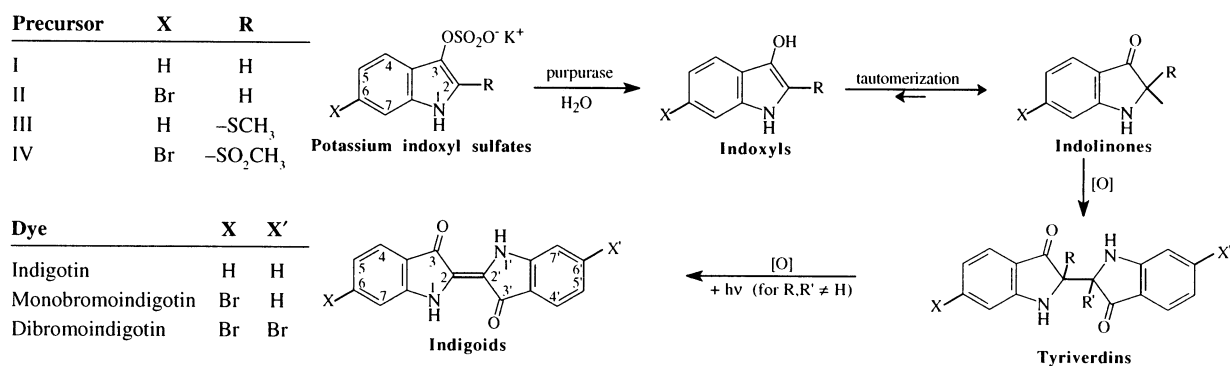


Fig. 5. General scheme involved in the biochemical formation of indigoids in the Tyrian Purple dyestuff from the precursors of the *Murex trunculus* species.

vat is still visible. This phenomenon, though unwanted by the dyer, is quite fortunate for modern-day analysts as these residues are the evidence that scientists need to identify a clay fragment as being part of a dyeing vat.

The presence of the archaeological purple pigments on clay fragments that were parts of the mouth of a vessel indicates that these colorants were formed close to the very top of the dyeing vat. As this pigmentation mark indicates the highest liquid level in the vessel, the inference is that the dye solution was filled nearly to the top. This finding implies that the liquid was not boiled, for that would have undoubtedly caused the expensive dye solution to bubble over. One possible reason why the dyer may have wanted to almost fill the vat to the top may have been a desire to minimize the premature oxidation of the reduced dyestuff or of the unoxidized precursors. This could have been accomplished by sealing the vat with a wooden lid or cloth cover so as to reduce the air space above the solution.

CONCLUSIONS

This study has shown that a chromatographic fingerprint may be obtained for an archaeological purple pigment that would assist in the determination of both its biological and geographic provenance. A full analysis that should be conducted in the future will need to consider the various factors that could have a qualitative and quantitative effect on the indigoidal compositions. These factors include ageing effects on the archaeological pigment or textile dyeing, such as temperature, humidity, illumination, and washing.²⁵ Additional factors relate to the environment in which the snail is growing and include the physical and chemical properties of the sea water, such as salinity, temperature, mineral and organic compositions, and pH. Seasonal factors, age, sub-species, and sex of the collected snail are also important, as are the lighting and processing conditions

associated with the extraction of the glandular secretions and the dyeing process itself. Finally, the analytical method used to investigate the dyestuff may itself also affect the dye contents.

Pliny the Elder has described the practice of Tyrian Purple dyeing in the Roman period in detail, though several key pieces of information are still missing. The only passage in the Talmud (Menahot 42b), dated to the early 4th century CE, that describes the dyeing of *Tekhelet*, the bluish form of purple, seems to indicate a different process:⁴⁵ “*Abbaye said to Rabbi Samuel son of Rabbi Judah: ‘That Tekhelet, how do you dye it?’ He said to him: ‘We bring sea-snail blood and compounds, and put them into a vat (and we boil the mixture). We then take out a little [of the liquid] into an egg-shell and test [the liquid] with a fleece of wool. We then throw away that egg-shell and burn the [trial sample of dyed] wool.’*” This cryptic Talmudic passage is the focus of future scientific research that will hopefully decipher this purple puzzle.

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