Solution of the enigmas of dyeing Tyrian purple and the biblical *tekhelet*

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Introduction

Ancient dyes and dyeing continue to attract attention. This work began with the aim of reconstructing the biblical *tekhelet*. Our starting point was a simple premise: that *tekhelet*, being a blue shade of purple, was obtained from similar molluscs to the famous Tyrian or Royal Purple. The exact technique of dyeing Tyrian Purple had, however, remained a puzzle up to the present day. Willy-nilly we had first to solve this puzzle.

The necessary molluscs, the banded dye-murex, *Phyllonotus (Murex, Trunculariopsis) trunculus*, and the rock-shell or dogwinkle, *Thais (Purpura) haemastoma*, were obtained from the seashore in the vicinity of Haifa, thanks to cooperation with Dr E. Spanier, Head of the Maritime Civilisation Department of Haifa University.

The species that provides *tekhelet*

We suspected the existence of a particular shellfish species which would provide the *tekhelet* colour. Since it would probably be some as yet unrecognised relative of *Ph. trunculus*, we examined each mollusc separately.[1] This tactic led us by serendipity (after hundreds of tests) to the discovery of hermaphrodity in *Ph.trunculus* — a property not mentioned in the literature.

This mollusc is a protantic, sequential hermaphrodite, which means that the male of the species appears periodically and changes its sex after one season. This may explain why the old Hebrew literature mentions that the mollusc appears periodically only. The hypobranchial gland of the *Ph.trunculus* male yields a mixture of dibromoindigotin with a considerable quantity of indigotin, so that the colour obtained is a purplish blue — a colour accepted by many as *tekhelet*. The ratio between these two colorants changes with time, that is, with the sex-transition to female, until only dibromoindigotin remains. Such a limited quantity of only male molluscs (10,000 are needed to provide one gram of the dye) may not have covered the demand for *tekhelet* and other means of producing the colour will be discussed.

The technology of ancient purple dyeing

To prevent any misunderstanding, the molluscs have to be divided into two separate categories, S (substituted) and NS (non-substituted). To the S category belong almost all known purple-yielding molluscs all over the world.[2] In these, the precursor indoxyl has a substituent, usually a sulfur-containing group, at position 2 (fig.1). The only purple-bearing mollusc in the NS category as yet known to us is *Ph.trunculus*. This mollusc has non-sub-

TYPE	SUBSTITUENTS at A	SUBSTITUENTS at B
II	H	H
IV	H	SCH_3
III	Br	H
I	Br	SO_2CH_3
V	Br	SCH_3

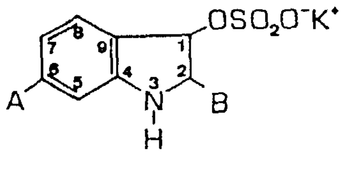

Fig 1: the precursor of dye in S-type molluscs is potassium indoxyl sulfate, with substituents as shown

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stituted indoxyl of type II and/or III at position 2 (fig.2). This division into S and NS categories is crucial in understanding and performing the correct dyeing procedure.

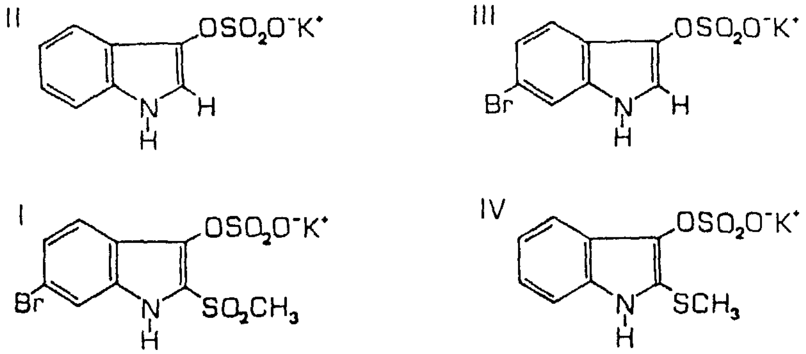

Fig.2: The precursors of dye in Phyllonotus trunculus *are as follows:*
II potassium indoxylsulfate, III 6-bromo-potassium-indoxylsulfate, I 6-bromo 2-methylsulfonyl potassium indoxylsulfate, IV 2-methylthio-potassium indoxyl-sulfate. Presence of I and IV according to Fouquet[3]

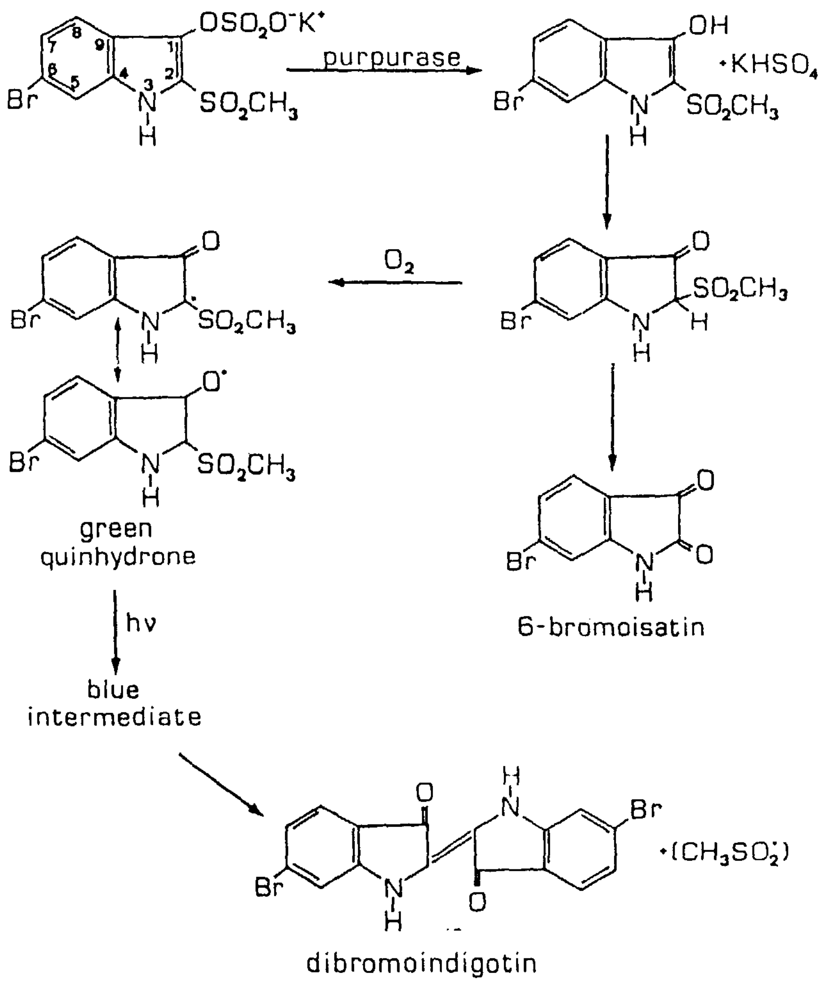

Fig.3: the formation of the dibromoindigotin purple dye from indoxyl precursors substituted at position 2

Dyeing with S-type molluscs, such as *Th.haemastoma*, does not require reduction of the dye (vatting).[4] We found that the blue intermediate product of the enzymatic, oxidative and photochemical reactions (fig.3) exhibits an affinity towards wool; it may be stabilised by acidification of the dye bath, so that the dye is taken up by the wool and then oxidised by air to the typical reddish purple colour of dibromoindigotin (RP according to the Munsell catalogue). The colour obtained by this method is, however, not as brillant as, and often less fast than, that obtained by the vatting method.

In the case of NS, that is, *Ph.trunculus* molluscs, the formation of the dye does not require a photochemical stage (fig.4) and proceeds so quickly that direct dyeing is impossible. The NS type of mollusc requires vatting, as indigo does. However the reduction potential of dibromoindigotin is much higher than that of indigotin. Consequently, the purple dye cannot be reduced by fermentation or by glucose as indigo is. We suspected that the reduction was performed by the ancient dyers by exploiting the sulfur compounds also provided by the molluscs and our experiments were directed that way. The results obtained gave some credence to our theory, but these compounds proved insufficient to secure reduction of the dye or to prevent re-oxidation of the dye precursor by air. After a series of experiments, we worked out conditions for the vatting of dibromoindigotin. The fleshy material from the molluscs was boiled in an alkaline solution, with low-grade wool (keratin), sugar and urea added to help reduction; water was then added to reduce the dye-bath temperature to 50°-60° C; and the material for dyeing then entered.[5]

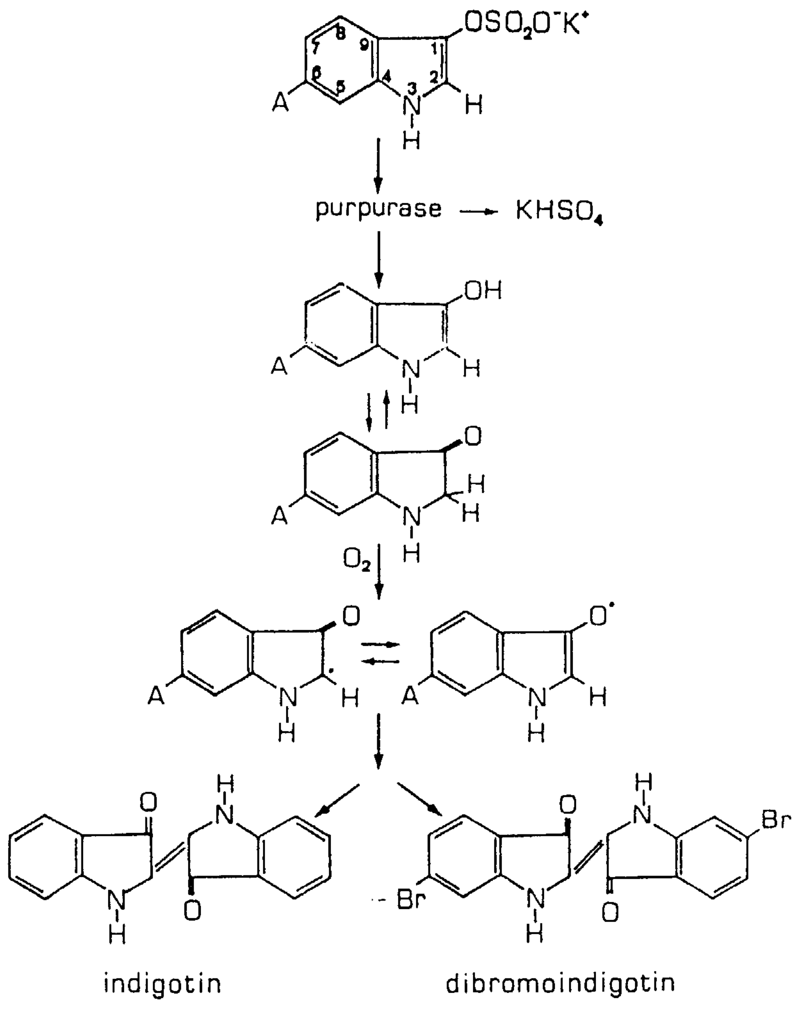

Fig.4: dye formation from indoxyl precursors unsubstituted at position 2. A = H or Br

probably used the keratin of wool as the reducing agent. The same experiments explain why archaeologists often find kilns for the production of calcium oxide at the ancient dyeing places.[6] It is true that mollusc shells provide a good raw material for such lime-kilns but much more important was the necessity of producing on site the alkali needed for the reduction vat. The two products of these kilns, the potash of burned wood and the calcium oxide from the shells, provided this alkali.

The elaborated system using keratin and alkali works excellently for *Ph.trunculus*, since no photochemical reaction is needed. However, if molluscs of the S category are added, complications occur and this was certainly the reason why the *Th.haemastoma* mollusc was used relatively little, despite the fact that it is easier to catch and is also bigger. Pliny has already claimed inferiority for this mollusc. The chemistry was too complicated for the ancient dyers to manage: the photochemical step required by molluscs of type S, which is very difficult to carry out in the presence of *Ph.trunculus* due to its shielding effect, was a particular problem.

Technology of *tekhelet* dyeing

We suspected that the ancient dyers also knew how to debrominate purple dyes for the production of *tekhelet*.[7] This step would have been easy to perform once the method of operating the reduction vat was known. Any watchful dyer working with vats of halogenated dyes exposed to light will sooner or later discover a change of colour in the vat and then in the resulting dyed yarn. Depending upon the amount of illumination, and therefore the amount of debromination, the colour obtained will vary from Munsell's reddish purple (RP), through purple (P), bluish purple (BP) and violet (V), up to blue (B).

Spectrum of colours obtained using purple molluscs

Since Pliny's writings, literature has described the various beautiful colours produced by the ancient Tyrian Purple dyers. Almost all authors accepted the explanation that the various colours were obtained chiefly by mixing various species of the molluscs. In fact, dibromoindigotin gives reddish-purple (Munsell's RP) and the bi-products that can be formed from the precursors are also reddish. The only mollusc giving blue shades is the masculine *Ph.trunculus*, because it also yields indigotin. It is impossible to obtain from mixtures of species a more bluish colour than that from the masculine *Ph.trunculus*.

As already described a range of hues is available by the gradual conversion of the purple dye into indigotin by debromination. For example, the following transformations were obtained: Munsell 2.5 RP 6/4 reddish purple was transformed into 7.5 B 5/6 blue; or 10 P 4/6 purple into 7.5 PB 6/6 purplish blue (estimated visually). This shows that the whole gamut of colours from Munsell's RP up to B could be easily produced. Consequently, it is relatively easy to obtain *tekhelet* of desired hue, or, if preferred, a pure sky-blue. Pure blue is, however, of little interest (except maybe for Jewish religious ritual) — since the indigo dye is much cheaper than the shellfish — but the various violets are certainly very attractive. Large quantities of dye can also be built up on wool, giving an even black colour.

Three additional possibilities for regulation of the hue may also be demonstrated. All three are based on more sophisticated dyeing techniques and depend on the difference in properties of both colorants, dibromoindigotin and indigotin: in vat dyeing, whether using masculine *Ph. trunculus* or not, indigotin always appears by accidental debromination.

The first method, which we call the 'differential dyeing method', exploits the different affinities of the two colorants. Under the correct conditions the dibromindigotin is taken up and the indigotin remains and accumulates in the bath. In this way, after a series of first purple dyeings (giving reddish shades), a more or less blue colour can be finally dyed by changing the dyeing conditions so that they are suitable for the take-up of the indigotin.

The second, so-called 'exclusion dyeing process' exploits the various solubilities of the sodium salts of the two dyes. It was noticed that at a pH of less than 9.8 the leuco-form of the indigotin salt precipitated and could be separated from the soluble leuco-form of dibromoindigotin.

In the third method the indigotin was first eliminated by reducing it, using for example glucose, and then separating it by decanting it from the insoluble unreduced dibromoindigotin. It is of course questionable whether the ancient dyers were able to manage these more sophisticated methods.

The biblical *tekhelet*

As to the question whether the biblical *tekhelet* was produced according to our methods, our answer inclines to be yes. In support we may quote a line from the book Midrash, truma ev 211, a sentence which concerns *tekhelet* and is written as follows, in transcription and verbatim translation: '*Vetekhelet* [and tekhelet] *ve argaman* [and purple]. *Tekhelet shezovin oto* [tekhelet that is dyed] *b-dam* [with blood] *zacher/zachar* [memory/masculine] *l-ot* [for or in memory] *she-kvar* [that already] *hitkinu* [mounted] *avot* [fathers].... Since usual Hebrew writing does not include vowels (punktation), the word was read as '*zacher*', i.e. 'memory'. This, however, makes the sentence illogical since immediately after this word appears *l-ot*, which also means 'for memory'. However, up to our finding and interpretation, to read it as '*zachar*' was considered an even bigger nonsense. We can now suggest the following free translation: 'Tekhelet and purple: tekhelet is dyed with blood of males, from memory as our fathers have done.'

Another supporting chapter has been found in the Talmudic writings: according to Talmudic literature, during the Roman occupation Jews living in Israel supplied *tekhelet* to Jews in Babylon. A report has been found of a conversation between Abayi, who probably came from Babylon, and Rabbi Samuel ben Judah:[8] 'Abayi said to Rabbi Samuel, "that *tekhelet* — how do ye dye it?" He said to him "We take hillazon blood and drugs, put them into a kettle, boil the mixture, and then take out something of the liquid in an egg-shell, and test the sample with a bit of wool. We throw away that egg-shell and burn the trial sample of wool."'

Werner Keller called his book *Und die Bible hat doch recht* and this conversation may be regarded as depicting the truth: the problem is — explanation. The following is our interpretation of this discussion. The drugs include the alkali and some keratinous material. Heating of the mixture causes reduction of the dye to its leuco-form. The Tyrian Purple dyeing was carried out in the open, since it produces very strong odours (sulfur compounds). So, in a sunny Mediterranean climate debromination proceeds rather quickly. However, the degree of debromination cannot be fixed visually, since in reduced state both the purple and the indigotin have a similar colour. To control the process, the dyers from time to time performed a dyeing test in an egg-shell (because if not good it must be destroyed). When the proper colour (*tekhelet*) had been achieved, they started the dyeing proper.

Is this the biblical *tekhelet*? This is our way of producing the *tekhelet* colour, but whether it was biblical *tekhelet* we leave to those who have the authority and better understanding of religious affairs.

Acknowledgements

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Notes

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3. Fouquet, H., 1970, *Bau und Reaktionen Natürlicher Chromogen Indigoider Farbstoffe bei Purpurschnecken* (Dissertation, University of Saarlandes)

4. Elsner, O., and Spanier, E., 1985b, 'The dyeing with *Purpura haemastoma*', *International Symposium on Fiber Science and Technology*, September 1985, Hakone, Japan

5. Elsner, O., 1990, 'Pliny's description of the Tyrian purple and the biblical Tekhelet in view of our recent research results' *International Workshop on the History of Chemical Technology*, Jerusalem

Incidentally, reduction and dyeing by this method were also performed with sulfur and vat dyes with good results.

6. Reese, D.S., 1979/80, 'Industrial exploitation of murex shells, purple dyes and lime production at Sidi Khrebish-Bengazi (Berenice)' *The Society for Libyan Studies, 11th Annual Report*

7. Elsner and Spanier 1985a (see note 1, above)

8. The Babylonian Talmud, *Menachot* 42b;
Spanier, E., 1987, in J.Herzog (ed), *The royal purple and the biblical blue* (the study of Chief Rabbi Jsaac Herzog with recent scientific contributions, Jerusalem

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