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Revival of Biblical *Tekhelet* Dyeing with Banded Dye-Murex (*Ph. trunculus*): Chemical Anomalies

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Abstract

Biblical t*ekhelet* was a violet-blue dyed wool of mysterious origin. The precious dye disappeared in the seventh century. During the19th century it was identified as the hyacinth purple of antiquity, made from the hypobranchial gland of the banded dye-murex (*Ph. trunculus*). Chemically, the dye has been shown to be a mixture of indigotin and 6,6`-dibromo-indigotin, originating respectively in the male and female snails. *Tekhelet* dyeing has been revived in modern Israel for renewing the Jewish religious observance of tying *tekhelet* tassels to the corners of four-cornered garments. Experimental anomalies plague the manufacturing process: the crude dyestuff is usually coloured purple that turns blue on heating. Possible causes of these phenomena are discussed. It is proposed that the formation of 6-bromo-indigotin may rationalise these anomalies as well as the historic controversy between Bizio and Lacaze-Duthiers 150 years ago regarding the nature of antique hyacinth purple.

1. Historical Introduction to Identifying Biblical *Tekhelet*

A trio of dyeings (ancient Hebrew *tekhelet, argaman* and *tola'at-shani)* are listed thirty times in the Bible for use in constructing sacred textiles for the Tabernacle[1]. *Tola'at-shani* is kermes, a crimson dye obtained from scale insects resident on oaks in southern Europe. *Argaman* is Tyrian purple, made from the hypobranchial glands of two species of littoral sea snails, usually the spiny dye-murex (*B. brandaris*) and sometimes together with the rock-shell (*Th. haemastoma*): the chemical composition being 6,6`-dibromo-indigotin (DBI). These creatures and their dyeings are illustrated in the colour-plate on the cover of this journal.

Biblical *tekhelet* was a violet-blue dyed wool of mysterious origin. Besides these ceremonial uses in the Tabernacle, *Numbers 15* adds an obligation for every individual Israelite to tie a *tekhelet* tassel on each of the four corners of his garment. The last *tekhelet* dyehouses were closed down in the 7th century[2]. Since then the technology has been lost, the dye's source forgotten and even its colour is unknown.

Ancient sources lead to identification of the source of *tekhelet*. Jewish Oral Law *(tosephta*) necessitates that ritual *tekhelet* be dyed only with a sea snail[3], and the Talmud reports that the shellfish appears every seventy years[4]. Contemporaneous Greek translations of the Hebrew Bible all consistently render *tekhelet* as "hyacinth"[5], which then was one of the two primary products of dyeing with sea snails[6], namely hyacinth-purple (a bluish purple, now designated violet) and Tyrian purple (a reddish purple, now designated purple).

Archaeological remains of purple-dyeing have been identified at scores of sites on the Mediterranean coast, including vats carved in rock, deposits of DBI and countless broken shells of spiny or banded dye-murex or rock-shell[7]. Banded dye-murex is the species *Ph. trunculus*. At the Phoenician port of Sidon, two enormous mounds were found – one of banded dye-murex and the other a mixture of spiny dye-murex and rock-shell. This striking separation was understood[8] to indicate separate utilisation in dyeing, one to produce hyacinth-purple and the other Tyrian purple.

In 1832, Bartolommeo Bizio, professor of pharmacy at the University of Venice, discovered the tinctorial assignments of these murexes[9]. He collected the shellfish species from the sea and prepared their dyestuffs. In Bizio's hands, spiny dye-murex gave a homogeneous purple – "Tyrian purple", while banded dye-murex gave a violet – "hyacinth purple", that he separated analytically to a mixture of indigo blue (indigotin) and purple.

Twenty-six years later, the French zoologist Henri Lacaze-Duthiers[10] began examining dyeings from shellfish. He insisted that reddish purple alone was the basic colour obtained from all species, including the banded dye-murex. This anomalous observation led him to a furious and unresolved controversy with Bizio, who had found a unique bluish shade with the banded shells. Alexander Dedekind[11], keeper of the Imperial Egyptian Museum in Vienna, sided with Bizio on this issue, maintaining that *tekhelet* be identified specifically as the violet product from the banded dye-murex.

In 1909, Paul Friedlander[12] proved that the molecular structure of Tyrian purple from spiny dye-murex was DBI. He found[13] the same compound in the banded murex-dye, but failed to identify conclusively the blue ingredient present.

The renowned archaeological chemist Rod. Pfister[14] examined the murex dyes in 1937. He found the same results as Bizio regarding the unique blue shading of the banded murex dye to a violet colour due to the presence of indigotin, as did Bouchilloux and Roche[15] in 1954 in their chromatographic study. Thus it was proven that hyacinth *tekhelet,* as made with banded dye-murex, is a mixture of two dyestuffs, namely DBI and indigotin.

So far, five archaeological textile specimens have been identified that are dyed with a *tekhelet* mixture of DBI and indigotin: from 7th-century Ein Boqeq (Dead Sea), 4th-century Palmyra, 3rd-century Britain and two from 1st century BCE Enkomi (Cyprus). [16]

In 1971 Fouquet and Bielig[17] published a definitive investigation of the biochemistry of the murex dyestuffs. They proved that formation of an indigo-blue ingredient is no artefact due to inadvertent debromination of DBI during processing, but rather a result of the unique composition of natural precursors, indoxyl and bromo-indoxyl, that are present in the banded dye-murex. Thus, two molecules of indoxyl combine to form the dimer molecule indigotin, while two molecules of bromo-indoxyl combine to form DBI.

My late colleague, Professor Otto Elsner, later discovered[18] that banded dye-murex males furnish indigotin, while the females furnish purple DBI. Therefore the natural precursors are segregated in nature: the male's hypobranchial gland contains the indoxyl precursor, while the female contains the bromo-indoxyl precursor.

2. <u>Revival of *Tekhelet* Dyeing with Banded Dye-Murex</u>

The first effort to revive *tekhelet* was due to Rabbi G.H. Leiner[19] of Radzin, Poland. In 1887, he re-established the religious practice of *tekhelet* tassels among his followers, who have continued the observance until the present day. However, the process he utilised is unacceptable historically since the sepia he used is not obtained from a sea snail used in dyeing in antiquity but from cuttlefish!

In 1913 Chief Rabbi Isaac Herzog submitted to London University his D. Litt. thesis on the subject of *tekhelet.* In it he published[20] the chemical analyses of "*tekhelet*" from Radzin, that had been performed for him by Friedlander, by Green and at the Gobelins factory. They found that it had nothing to do with an animal source but was in fact merely dyed with Prussian blue, a modern synthetic pigment that consists of iron cyanide: the sepia ingredient had been destroyed[21] during the chemical process. Herzog concluded that the scientific evidence, as expounded by Bizio and Dedekind, proved the *tekhelet* source to be banded dye-murex. However, he considered that this species should be disqualified since it lacked - he claimed – two features required by Talmudic law: a coloured shell and an infrequent emergence. Herzog suggested that Janthina species might be a more suitable choice, but it was later found[22] to be unacceptable.

A critical reappraisal[23] of the various views has lead to the conclusion that banded dye-murex is indeed the historical source of *tekhelet*. In its natural habitat, the shell is encrusted with a richly coloured biological fouling. Furthermore, it was concluded[24] that the snail's rare emergence from the sea refers to its inaccessibility on the seabed from where it necessitates a special fishing technique. Herzog`s two Talmudic objections are thus answered.

Certain religious circles in Judaism have therefore accepted this identification, and attempted to recreate the dyeing process. However, the dyestuff so prepared is usually coloured purple, like the Tyrian purple from spiny dye-murex! In fact, the required violet blue of hyacinth *tekhelet* **was** obtained from banded dye-murex on rare occasions and also when prepared according to the procedure described by Fouquet. This anomalous difference mirrors the controversy described above between the views of Lacaze-Duthiers and Bizio 150 years ago! In order to obtain a blue product, the dyers now routinely prepare a hydrosulphite vat from the crude purple dye in a transparent glass vessel, that is then exposed to sunlight in order to facilitate photochemical debromination to a blue colour. Such a process was not available in antiquity due to the absence of a strong reducing agent like hydrosulphite and of glass reaction vessels.

A second anomaly found is that the purple dyeing with crude banded dye-murex turns blue when the wool is heated (in order to stabilise dimensions).

3. Discussion

The colour change to blue on heating purple dyed wool would appear to be due to loss of bromine to form indigotin. A possible explanation would be debromination of DBI after chemical reduction by residual hydrosulphite in the wool or by sulfhydryl groups of the wool protein: this is however unlikely in the absence of sunlight that is required for photochemical debromination of a reduced DBI.

As regards to the anomalous purple usually obtained from banded dye-murex, it is hereby suggested that this crude product contains a significant amount of 6-bromo-indigotin (MBI), a purple substance, which has indeed been, identified[25] in banded murex dyes. To form the violet *tekhelet* mixture of indigotin and DBI, the respective precursors indoxyl and bromo-indoxyl must remain separate during their dimerisation, as they were in the hypobranchial glands of the male and female snails. Otherwise, premature admixture of the two precursors may form MBI, which is coloured purple and being asymmetrical is presumably less stable than DBI and more readily loses its bromine thermally to form indigo blue.

The hypothesis that enough MBI may be formed from banded dye-murex to give a purple product provides a rationale for the historic disputation between Bizio and Lacaze-Duthiers (see above) regarding the colour of the dye from banded dye-murex. Lacaze-Duthiers evidently obtained product rich in MBI that he found indistinguishable visually from Tyrian purple. Bizio not only obtained a product poor in MBI, but was able to utilise his training in chemistry so as to analyse the chemical constitution, thereby paving the way for the later researches mentioned above that have conclusively established the unique status of banded dye-murex as the source of *tekhelet*.

Further research is required to find a reliable process that will give the mixture of indigotin and DBI required for dye authentic *tekhelet* to a violet hyacinth colour.

Addendum (30/9/2001)

The experiment proving the hypothesis proposed in the Discussion has now been successfully performed. The following results were presented on 11th September 2001 before the International Conference on Colours in Antiquity, held at the Department of Classics, University of Edinburgh.

In his article in this volume, Chris Cooksey has reported the chemical synthesis of MBI. He kindly provided me with wool samples that he had dyed with MBI. On gentle heating in water, the violet-coloured wool dyed with MBI readily changed colour to blue, just as had been hypothesised.

It may therefore be concluded that, when the hypobranchial gland contents of male and female banded dye-murices are mixed before all precursors present have formed DBI and indigo-blue, MBI may be formed. Now, if enough MBI is thus produced, the dyeing will not be violet but purple. Furthermore, the bromine substituent is labile and the colour readily changes to indigo-blue.

Such an indigo-blue dyeing with banded dye-murex should not be considered the best shade for *tekhelet*. An exactly identical result was readily available in antiquity by use of the relatively inexpensive and convenient agricultural product woad, without requiring any murex at all!

Renewed chemical research is required to define experimental conditions that will prevent formation of MBI during *tekhelet* manufacture. Thereby a more authentic violet hue would be achieved.

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