PURPLE DYESTUFFS OF ANTIQUITY

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ROLE OF 6-BROMOINDIGOTIN IN DEFINING THE NATURE OF BIBLICAL *TEKHELET* BLUE DYE

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Ancient Purple Dyes from Mediterranean Murex Shellfish

Purple dyes were among the most precious treasures of Antiquity.

Throughout the 2,000 years before the Common Era, ancient sources record two types of murex purple as commercial merchandise and as regal tribute:

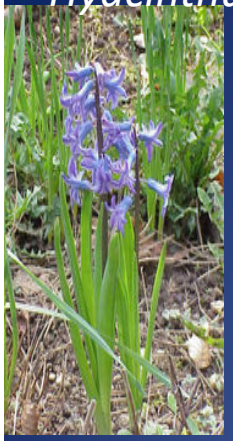
- Tyrian purple – a reddish purple
- Hyacinthine purple – a bluish purple

Tyrian Purple

- Biblical “purple” (Heb. *argaman*)
- Made from **spiny dye-murex** (ABOVE LEFT, *Bolinus brandaris*), often in admixture with dogwinkle (rock-shell, *Stramonita haemastoma*).
- Chemically, it is **6,6’-dibromoindigotin** (DBI), formed from the natural bromoindoxyl precursors.
- All other species of porphyrogenic shellfish also give only DBI,

except for *Hexaplex trunculus*, the banded dye-murex (ABOVE RIGHT)….

Hyacinthus orientalis, natural form



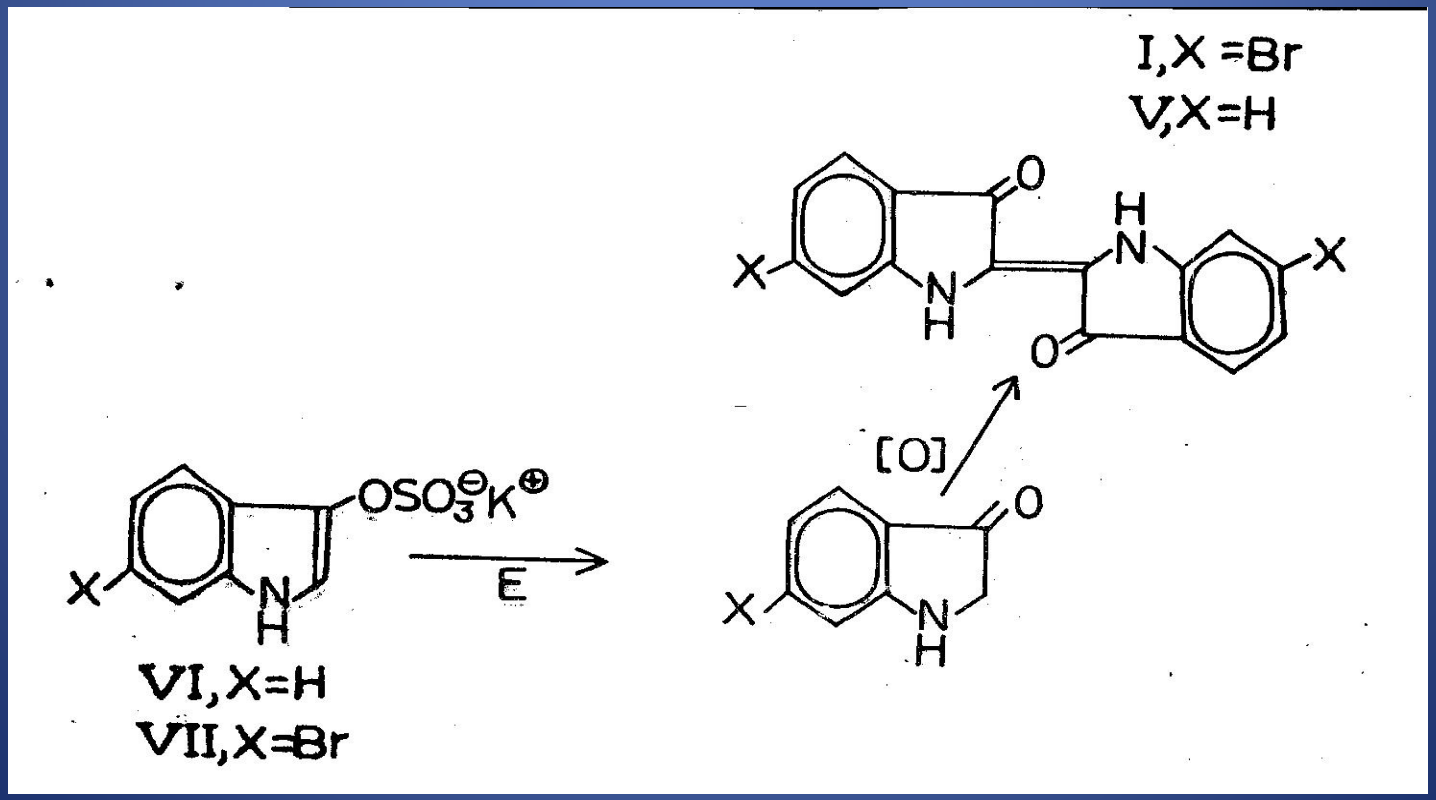
Hyacinthine Purple

Man and Mollusc Site and Paul Monfils

- It is a violet blue - a shade called 'Royal Purple' (*Wikipedia*), the colour of the hyacinth flower (ABOVE ,LEFT).
- More precious than Tyrian purple; the bluish purples were extolled by Pliny the Elder.
- Made from *H. trunculus* (*ABOVE, FAR RIGHT*), collected on rocky sea-beds off Mediterranean shores: archaeological finds show that this was the most widely used species for purple in antiquity.
- Accordingly, may we suggest that the classical term 'Imperial Purple' may refer to hyacinthine purple rather than to Tyrian purple?
- In contrast to Tyrian purple, exposure to sunlight is not required for hyacinthine dye formation, because most of its natural indoxyl precursors lack a molecular *C-2* substituent that would require photolysis.

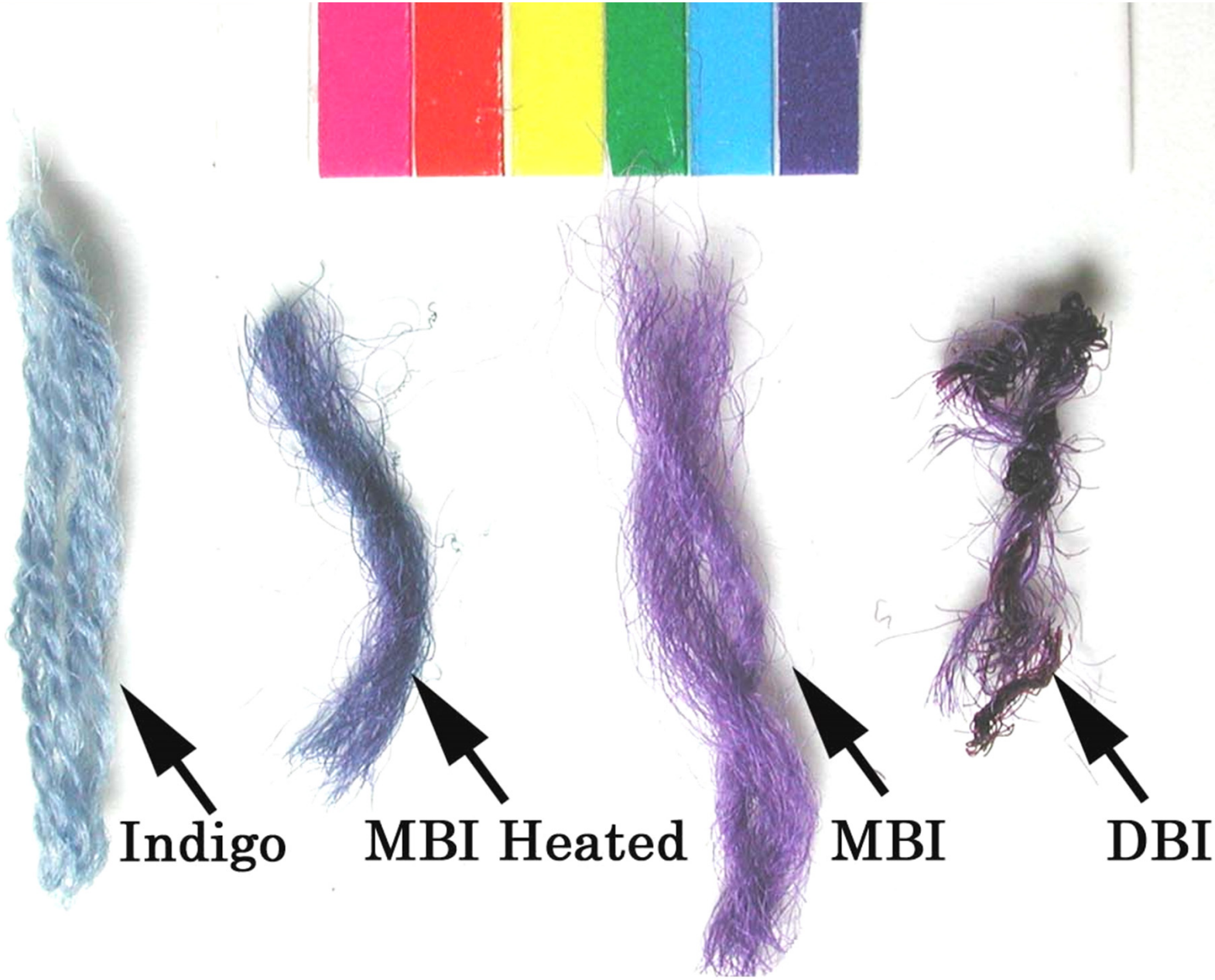
Non-photochemical formation of purple indigoids from *H. trunculus* indoxyl precursors

1 = DBI. V = indigotin. VI = indoxyl 3-sulphate. VII = 6-bromoindoxyl 6-sulphate.
E = aryl sulphatase. [O] = aerobic oxidation.
6-bromoindigotin = 1 ,with 6-Br and 6'-H.



WHO IDENTIFIED THE SOURCE OF HYACINTHINE PURPLE?

- **In 1832, the Venetian Professor of Pharmacy and Chemistry B. Bizio was the first to identify the source of hyacinthine purple as the Mediterranean shellfish *H. trunculus*.**
- **Although contested by his contemporary Lacaze-Duthiers, his finding was confirmed by later researchers [Pfister 1937; Bouchilloux & Roche 1954; Fouquet & Bielig 1971; Elsner 1992].**
- **The dye from *H. trunculus* is characterized by a high content of 6-bromoindigotin (MBI), admixed with variable proportions of indigotin and DBI.**
- On gentle heating, MBI spontaneously undergoes a discontinuous thermochromic transition from violet to blue [Ziderman 2001].
- These variations account for the range of shades obtained from *H. trunculus* – purplish, violet or bluish.
- **Contrary to past belief, the authentic dyeing-process is now recognized to have required a bacterial fermentation vat [Edmonds 2000; Boesken-Kanold 2005].**


Indigo
MBI Heated
MBI
DBI

Shells of Banded Dye-Murex (*H. trunculus*)
Source of Hyacinthine Purple (*Tekhelet*)

Dyed on Wool

What is Ritual *Tekhelet*?

- The Bible [*Num*. 15:37; *Deut*. 22:12] commands to tie a *tekhelet* cord to tassels on the corners of garments.
- This Jewish practice was discontinued in the 7th century, because its source was lost.
- With the rediscovery of the molluscan source and the dyeing process, there is a unique opportunity to revive this religious practice and the industry of hyacinthine purple manufacture.

THE *TEKHELET* PROJECT

- The goal will be to be able to set up full-scale installations to breeding the snails and to produce the dye; for purposes of painting and of its use as a natural textile dye, particularly to dye the ritual *tekhelet* cords .
- The mollusk must be conserved, as it is threatened by extinction in Nature, due to pollution of the Mediterranean Sea.
- The sea cannot be fished for *H. trunculus* in Israel, because it is a protected species.
- A regular and reliable supply of hundreds of thousands of snails will be required each year
- So the central initiative of the *Tekhelet* Project is an R&D program to investigate how to rear and farm banded dye-murex in artificial pools using mariculture.

OPERCULA FOR INCENSE

Muricidae were used not only for making purple.

- Near Kas, by the southern shores of our host-country Turkey, a 14th century BCE-shipwreck was excavated, and found to contain a shipment of opercula of *H. trunculus*.

- After being the subject of conjecture as to the usage of this freight, opercula are recognized as the onycha constituent of incense [Ziderman 1988].

Accordingly, the same shellfish would have provided the raw material for two lucrative industries, purple-dyeing and incense- fabrication.

Operculum in shell orifice

RELATED SUBJECTS FOR RESEARCH

The project may also deal with related subjects, such as:

1. **Developing a laboratory assay for the content of dyestuff precursors in the shellfish**
2. **Chemical synthesis of 6-bromoindoxyl and 6-bromoindigotin**
3. **Clarification of the mechanism of the thermochromic transition of 6-bromoindigotin**
4. **Explaining variations in the color as obtained from individual snails**
5. **Defining optimal conditions for the formation of the dye**
6. **Utilising a fermentation vat for dyeing**
7. **The biology of the fermentation process**
8. **Alternative mariculture and biological methodologies for making the dye**