Marginalia

Blue as the Sea

Roald Hoffmann

It is hard to imagine a world without color. Color is all around us, in the steady background of the brown shades of the earth, the green of plant life, the blue of sky and sea. It's there in the highlights of birds, butterflies and flowers. No wonder that a reasoning animal would desire the variety of color in its environment, from the pigments of our houses and art works to the clothes we wear. But producing those hues is not so simple. Most vegetable and animal colors are not fast. In a mid-19th-century compendium on practical chemistry that I have, the longest chapter by far is on dyes and dyeing. There's a craft, and art, and industry there.

In Republican Rome the restrictions on the wearing of clothes dyed in purple were extremely rigorous. Only the two censors and triumphant generals could wear togas or cloaks completely dyed in purple; consuls and praetors had to make do with purple-edged clothing. The manufacture of royal or Tyrian purple was highly restricted in the succeeding Empire. In fact, by an edict of the emperors Valentian, Theodosius and Arcadius it was a capital offense to manufacture the royal purple other than in the Imperial Dye-Works. The privilege of wearing the true purple (more below on what's "true" and what isn't) was restricted to the emperor. In A.D. 301 a pound of Tyrian purple-dyed wool cost 50,000 denarii, about a thousand days' wages of a baker.

Meanwhile, the Hebrews wrote a prescription for a blue into the Old Testament. Here is how the Lord spoke to Moses (Numbers 15:38): "Speak unto the children of Israel, and bid them make fringes in the corners of their garments, they and their children's children, and into the fringes they should work in a thread of blue [*tekhelet* in Hebrew]. And it shall be a fringe to you and whenever you see it you shall remember all the commandments of the Lord, and obey them."

Consistent with the specificity of Biblical and Talmudic concepts of holiness, these blue strands must be colored with the particular blue mentioned, *tekhelet*, which is a dye from a snail. Just how important this prescription and its observance were to the Hebrews in their everyday life may be judged from the fact that the very first tractate of the Talmud inquires: "From which moment may one recite the Shema [the prayer of creed] in the morning?" And as the first answer gives: "When one can distinguish between *tekhelet* and white."*(1)*

In Jewish tradition the lore of making *tekhelet* was lost by A.D. 760. Since then the most orthodox prayer shawls have included no colored strands in their tassels, for there is no substitution in the eyes of the Law. The Byzantine imperial purple works, and the art of making Tyrian purple, vanished with the fall of Constantinople in 1453.

Meanwhile the world turned, many times. Blue and purple were or became available from other sources, not the least of which, in the last century, is that piece of human ingenuity called chemistry. And we have also found out what natural Tyrian purple and Biblical blue were.

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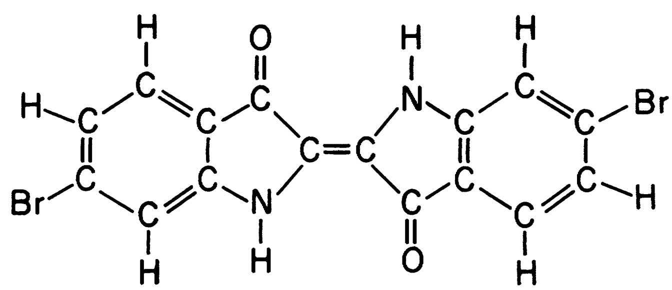
These pigments are of animal origin. They were extracted painstakingly, and therefore expensively, from three species of gastropod snails, *Truncalariopsis trunculus*, *Murex brandaris* and *Thais haemastoma*. In one of the body structures of these beautiful shelled snails, the mantle, there is a hypobranchial gland. This chemical factory has numerous functions, producing a mucoid substance that cements particles as they are expelled by the snail, as well as several neurotoxic chemicals used in predation. And it emits a clear fluid, which is the precursor of the dyes. On exposure to the oxygen of the atmosphere, under the action of enzymes, and, importantly, sunlight, the fluid changes from whitish to pus-like yellow, then green, and finally blue and purple. Aristotle, a careful observer, and Pliny give good descriptions of the snails and the process of dye extraction.

There is an ancient tale concerning the discovery of Tyrian purple, that of Hercules and his dog. The dog's mouth was stained on crushing a sea-snail with its teeth. Or, if not Hercules, then a shepherd or a Tyrian nymph. Given these tales, and Aristotle's account, it is incredible that the biology of the purple trade remained lost for so long. It was rediscovered accidentally in 1856 by Félix Henri de Lacaze-Duthiers, a French zoologist. He noticed a fisherman draw a yellow design on his shirt with a shellfish of the *Thais* species. The fisherman knew the pattern would turn red.

A century later we know much about these pigments. Not about the utility of their precursors to the snail, nor yet about the marvelous chemistry of the series of color changes. But the pigments at the end of the series are indigo (sometimes called indigotin) and a brominated derivative (there is a good bit of bromine in the sea!), 6,6′-dibromoindigo. The structure of the latter is shown below:



The brominated compound is Tyrian purple. *Tekhelet*, the Biblical blue, is probably some mixture of the two compounds. There is substantial variation in the color obtained from the molluscs, depending on the species, the climatic conditions and the method of processing the dye. Remarkably, even the sex of the specimens matters; for the rock murex *T. trunculus* Ehud Spanier and Otto Elsner find that the male secretes a liquid yielding mainly indigo, but the female's secretion differs, leading to the brominated purple dye.

The facts cited here come from a remarkable book, *The Royal Purple and the Biblical Blue (2)*. Its centerpiece is an unpublished 1913 D.Litt. thesis from London University. The author of that work was Rabbi Isaac Halevy Herzog, a broadly educated scholar who in his time was Chief Rabbi of Ireland and Israel. Herzog's thesis, entitled "Hebrew Porphyrology," is accompanied by six diverse papers. The book is ably edited by Ehud Spanier, a marine biologist at the Centre for Maritime Studies at the University of Haifa, who also is the co-author of several of the accompanying studies. These range over topics as diverse and relevant as the textiles and dyes of antiquity, the modern biology of muricid snails and the consequences to religious observance of reviving the *tekhelet*-making industry.

Oh, if all theses were like Herzog's! Adroitly weaving his way through the classical descriptions of the dye-producing snails, in full command of the sometimes contradictory Talmudic references, aware of the complex zoology of the snails, he achieves nothing less than a synthesis. Sometimes the flood of information makes for heavy going, as in the elaborate excavation from circumstantial evidence of the actual color that the Biblical blue conveyed. But common sense and strong opinions save the text. And the poetic content of the material presses through, whether it is in the variant attribution by the great Franco-Jewish commentator Rashi of the color of *tekhelet* as green, as leeks. Or the quotation (in eight recensions!) of a saying by Rabbi Meir, "Why has *tekhelet* been singled out from all other colors? Because *tekhelet* is like unto the sea and the sea is like unto the sky and the sky is like unto the sapphire, and the sapphire is like unto the Throne of Glory...."

All along, there has been another, much more economical, source of the same dye. It is the genus *Indigofera* of herbs of the pea family, widely dispersed in warm climates. This plant was an important product of the India trade, for it is readily cultivated there. Again the naturally occurring primary chemical is not indigo but a derivative that is easily converted to the dye after extraction. Byzantine edicts and Talmudic authorities describe tests to distinguish purple dyes extracted from snails from those of plant origin. These tests don't work, because the chemical is the same. And what is a pea plant doing making a molecule identical to that synthesized by a snail? That problem remains to be solved, but surely it has to do with the common biochemical pathways shared by living organisms, and the wondrous games evolution plays *(3)*.

Still another chemical curiosity in this tale of the Blue and the Purple: In 1887 a remarkable person, Rabbi Gershon Chanoch Leiner of Radzin, claimed that he had rediscovered the Biblical *tekhelet*. Leiner was unusual among Hassidic rabbis in that he knew several European languages and was familiar with mechanics and medicine. Herzog makes the astute observation that in another place, another time, Leiner might have been a great scientist. He obtained his pigment in Italy from *Sepia officinalis*, a cuttlefish, subjecting the ink to a reasonably well-described chemical treatment.

A 1913 analysis (commissioned by Herzog) of the Radzin sect's pigment showed it to contain not the ink of the cuttlefish, but the oldest synthetic pigment known, Prussian blue, $Fe_4[Fe(CN)_6]_3$ *(4)*. Did the rabbi cheat, or was he deceived by his suppliers of cuttlefish, who might have spiked the ink with a little Prussian blue? No, according to a suggestion by Israel I. Ziderman *(2)*: The Radzin rabbi's chemical works *made* the Prussian blue in its processing of the ink. The Hassidic chemists fused the organic material with iron filings and potash. This process would generate potassium cyanide (KCN) as well as the ferrous and ferric ions Fe^{2+} and Fe^{3+}, the necessary components of Prussian blue. The same cyanide of iron was first made in 1704 from bullock's blood in a similar way. Any source of carbon and nitrogen—almost any organic material—would do. It's all in the chemistry *(5)*.

References

1. Berakhot 9a. I am indebted to Shira Leibowitz for this reference.
2. E. Spanier, ed., 1987, *The Royal Purple and the Biblical Blue. Argaman and Tekhelet. The Study of Chief Rabbi Dr. Isaac Herzog on the Dye Industries in Ancient Israel and Recent Scientific Contributions*, Jerusalem: Keter Publishing House. For a modern account of the ancient royal purple industry see P. E. McGovern and R. H. Michel, 1990, *Accounts of Chemical Research*, 23:152.
3. For accounts of species of very different phyla making the same complex molecules see nepetalactone, the active principle of catnip, from the mint and from a walking stick: R. M. Smith, J. J. Brophy, G. W. K. Cavill and N. W. Davies, 1979, *Journal of Chemical Ecology*, 5:727; T. Eisner, 1964, *Science*, 146:1318; the cardiotonic bufadienolides, from the venom of toads and from fireflies: T. Eisner, D. F. Wiemer, L. W. Haynes and J. Meinwald, 1978, *Proceedings of the National Academy of Sciences of the U.S.A.*, 75:905; K. Nakanishi, T. Goto, S. Itô, S. Natori and S. Nozoe, eds., 1974, *Natural Products Chemistry*, Vol. 1, Tokyo: Kodansha, pp. 469–475.
4. The story of Prussian blue is fascinating in itself. Gmelin's "Handbuch der Anorganischen Chemie" (Eisen B., 1932, pp. 670–723) had more than 50 pages on this subject in 1932! The formula cited is the correct one of the so-called "insoluble" Prussian blue (see H. J. Buser, D. Schwarzenbach, W. Petter and A. Ludi, 1977, *Inorganic Chemistry*, 16:2705). The "soluble" Prussian blue is $KFeFe(CN)_6$. Essential is the "mixed valence" ferrous and ferric iron; the potassium content of dye preparations can be quite variable.
5. The material in this essay was published in a slightly different form as a review of Reference 2, appearing in *Liber*, 1989, No. 2 (December 1989), different pagination in English, French, Italian, German and Spanish editions.