NATURAL DYES

by Clair G. Wood

Thou shalt make the tabernacle with ten curtains of twisted linen, and blue and purple and scarlet....

—Exodus 26:1

The human race has always been fascinated with color. As early as 180,000 B.C., the Neanderthal tribes prepared their dead for burial by coating them with red ochre (iron [III] oxide). Their successors, the Cro-Magnon peoples, made elaborate cave paintings using yellow and red iron oxides, black manganese dioxide, and white clays. For tens of thousands of years, humans obtained their coloring agents exclusively from rocks and salts, and earth tones predominated—until weaving was invented.

Pigments had been made by combining colored minerals with a *vehicle,* such as oil or mud, that would adhere to a surface. When the pastelike pigments were applied to fabric, the cloth became stiff, and the coloring material soon washed or fell out. Pigments wouldn't work—cloth could only be colored by dyes, organic molecules that bond directly to the textile.

Animal dyes

One of the earliest and most important of the animal dyes came from several species of snails found along the shores of the Mediterranean. *Tyrian purple* (Figure 1) was discovered by the Phoenicians about 1500 B.C. and became, for the next 3000 years, the most important dye of the civilizations that rose and fell in the area. The mollusks were avidly gathered as dye factories sprung up along the Mediterranean and west African coasts, and Phoenician traders carried the dye to Spain, France, and Italy. According to Pliny the Elder (ca. 50 A.D.), the dye was extracted by crushing the shellfish and boiling them in salt water for ten days. Cloth was dipped in this solution, then exposed to sunlight. The yellow color changed to greenish-blue, then to purple. The Roman emperors prized the dye and decreed that only members of the royal family could wear clothing colored by it, hence the expression "born to the purple." Among those who wore Tyrian purple were Alexander the Great, Julius Caesar, and Cleopatra.

Other animal dyes were obtained


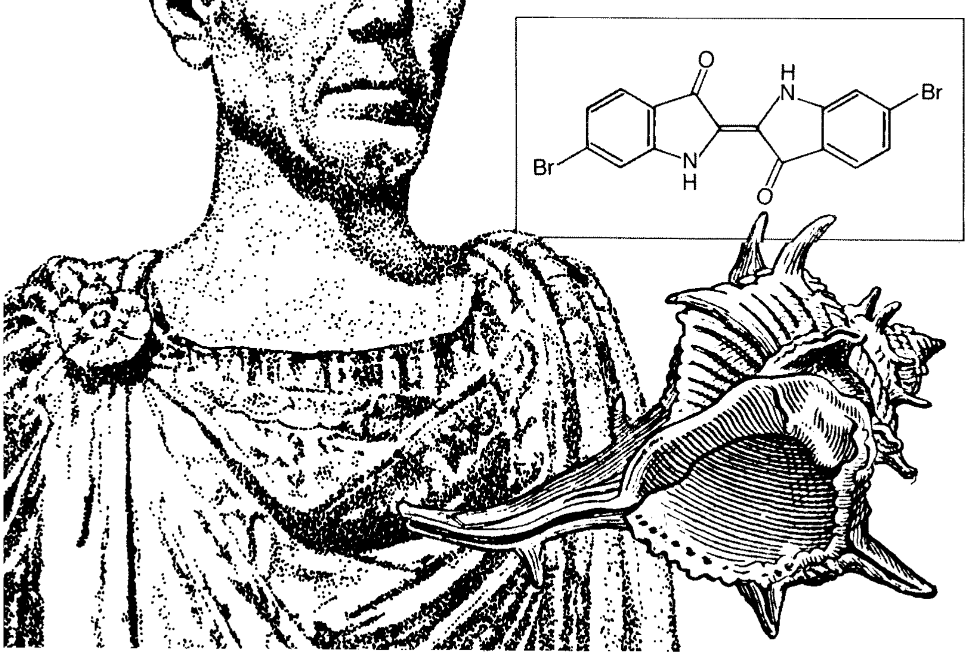

Figure 1. **Tyrian purple, which is known chemically as 6,6′-dibromoindigo, is an ancient dye that was extracted from a Mediterranean mollusk. The Roman Empire decreed that only members of the royal family (such as Julius Caesar, above) could wear robes dyed with Tyrian purple.**

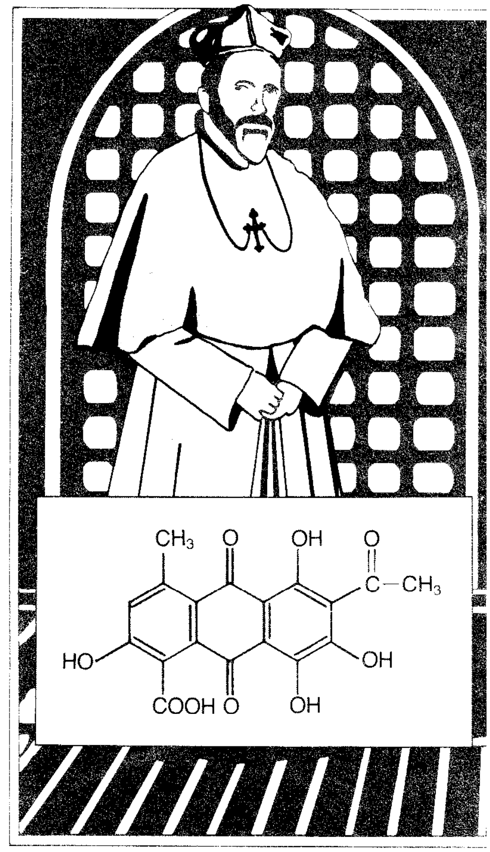

Figure 2. **Kermesic acid, derived from the kermes insect, so impressed Pope**

Other animal dyes were obtained from insects. Kermes was a scarlet dye obtained from Coccus ilicis, a tree scale that lived on oak. Moses mentioned its use in Egypt, and other writers referred to it as captured booty in 1400 B.C. Kermes varied in color from bluish-red to brilliant scarlet depending on the mordant used (more about mordants below).

A dye very similar to kermes was discovered by Mexican dyers around 1000 B.C. Cochineal is derived from another scale insect, Dactylopius coccus, that lived on cactus. The insects were collected by hand, about 200 pounds per acre of cactus, and dried in the sun. The dried insects resembled rust-colored grain seeds and gave scarlet dye when soaked in water. The Spaniards learned of cochineal in 1518 A.D. and brought it to Europe, where it rapidly replaced kermes. The scarlet obtained with a tin mordant is particularly beautiful and was used until 1954 to dye the uniforms of the British Brigade of Guards uniforms.

Vegetable dyes

Vegetables dyes can be found in almost any plant. Historically, three of the most important were madder, woad, and indigo. Madder (Rubia tinctorum), a bright red dye, comes from a plant of the same name also known as “dyer’s root.” Though its origin is lost in antiquity, it was used to dye the wrappings on Egyptian mummies. It is said that Alexander the Great used madder to help him defeat the Persians in 350 B.C. He had many of his soldiers dye their cloaks with splotches of red and stagger onto the battlefield. As the jubilant Persians fell on the “badly wounded” enemy, they were soundly defeated. Madder appeared in Europe in the seventh century and was the dominant red dye for more than 1000 years. It provided the red for the famous British redcoats during the American Revolution. The chemical responsible for the color is alizarin. The natural dye quickly lost favor in the late nineteenth century as it was replaced by the cheaper synthetic version of the same compound. When Julius Caesar arrived in Britain in 55 B.C., he described the fierce warriors he found there: “All Britons stain themselves with woad which grows wild and produces a blue color which gives them a terrible appearance in battle.” Nor was it only the warriors who painted themselves blue, for Pliny the Elder writes, “There is a plant like plantain, the juice of which the wives and daughters of Britain paint themselves and go naked resembling Moors and Ethiopians.” Woad, a dye from the European plant Isatis tinctoria, has been found on some of the most ancient textile fragments ever unearthed. It was used to dye the robes of the high priests of Jerusalem in Biblical times, but it was in Europe that it was extensively cultivated. The dye was obtained by first air-drying the woad plants and grinding them to a powder. The powder was then moistened, placed in a warm, dark place, and stirred frequently. Several weeks of fermentation produced a black paste, from which a blue dye was extracted. The European woad plant had indigo as its main chemical constituent. Woad was the principal European dye for centuries, and dyers became quite skilled at mixing it with other dyes to obtain new colors. Saxon green was the result of dyeing a fabric with woad, then overdyeing it with weld, a yellow dye from another plant. When woad was overdyed with madder, a purple shade resulted. Indigo, from the plant Indigofera tinctoria, is much richer in the indigo molecule. This dye worked its way from India to Egypt, the Holy Lands, and eventually Europe, where it arrived around 1200 A.D. Its introduction was bitterly opposed by woad growers. Many laws were passed against use of the “devil’s dye,” and it was widely believed to harm both the cloth and its wearer. So successful was the anti-indigo lobby that the dye did not become established in Europe for more than 500 years. Then King George II chose indigo for the British naval uniform, giving the world “navy blue” forever after. Indigo was one of the few natural dyes of commercial importance to America. In 1744 Eliza Pickney grew indigo from seeds her British army officer father brought from the East Indies to the colonies. Later, the enterprising young woman persuaded plantation owners around Charleston, S.C., to grow indigo and set up the Winyah Indigo Society. This cooperative shipped great quantities of the dye to England, until introduction of synthetic indigo destroyed the market for the natural product. Today indigo has been largely replaced by other blue dyes, though it is still used in cosmetics (D & C Blue #6), as a laboratory indicator solution (indigo blue), and as the dye of choice for coloring blue jeans.

Synthetic dyes

The synthetic dye industry began with a serendipitous discovery. In 1856, William Perkin, an 18-year-old student at the Royal College of Chemistry in London, was trying to synthesize quinine, a drug used to treat malaria, by reacting aniline sulfate with potassium dichromate. He obtained a black paste which, when extracted with alcohol, gave a violet residue that dissolved in water to give a brilliant purple color. Perkin observed that the dye had a strong affinity for silk. He quickly realized the commercial possibilities and left college to go into business for himself. The dye, mauve, rapidly proved to be a commercial success; Queen Victoria preferred mauve-colored silk for her gowns. Perkin’s discovery was even more fortuitous than it first appeared. If his aniline had not been contaminated with toluidine, an essential step in the synthesis of mauve could not have taken place.

Perkin’s discovery opened the floodgates for similar research throughout Europe. By 1870, cloth could be purchased in many more colors than was ever possible with natural dyes. Initially the British were the leaders in factory-produced dyes, but the Germans soon dominated the field, obtaining 950 patents between 1880 and

1900. The effect of this deluge of man-made dyes on the natural dye market was devastating. No better example can be found than the story of indigo. In 1893, India had 76 indigo factories and 250,000 acres of the plant under cultivation. In 1883, Adolph von Baeyer
(who started his chemistry career at age 13) synthesized the indigo molecule. His method was not economical, but it paved the way for chemists at the German BASF Corporation to find an alternate route, and synthetic indigo was marketed in 1900. The market for natural indigo collapsed almost overnight. Today more than 6000 synthetic dyes are available, and most are cheaper and more effective than the dyes found in nature. However, for craftsmen and amateur scientists, natural dyes still have one major advantage—they are as close as the garden.

VOCABULARY

Indigo

Because indigo is not soluble in water, it is applied by a multistep process known as vat dyeing. The indigo is first chemically reduced to a form that is colorless but soluble (B).
Traditionally, this reduction was done by fermentation or treatment with urine, but today it is done by application of sodium hydrosulfite. The cloth is soaked in this pale yellow solution, then “skyed” by
hanging it in the air. Oxygen in the air oxidizes the indigo back to the brilliant blue form (C), which is insoluble and difficult to dislodge from the fibers.

Chromophores

Why do certain compounds make good dyes? In part because they contain chromophores. Chromophores (Greek: chroma = color; phores = bearer) are groups of atoms within organic molecules that selectively absorb visible light. When light of certain colors strikes the chromophores, electrons are energized and the light is absorbed. Light of other colors is reflected to the observer. Below are a few of the chemical groups that can serve as chromophores:

azo
carbonyl
ethylene
polyenes
nitro
quinoid

To make a good dye, it is not enough for a compound to be colorful. It must also be soluble in water so that its solution can penetrate the fabric. Once in the fibers, it must become insoluble, or attach tightly to the fibers, so it does not wash out. These requirements led natural dyers to use mordants and vat dyeing. Other techniques are used in modern commercial dyeing.

Mordants

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A mordant is a coupling agent. Usually a metal ion, it attaches to both the dye and the fiber and forms a link between them. A mordant can fix a dye that would otherwise come off in the wash. Most mordants are salts of chromium, aluminum, copper, ammonium, iron, and tin. In addition to binding the dye to the cloth, some mordants change its color as well. Alizarin, the crimson color of the British “redcoat,” turns rose color when mordanted with aluminum, purplered with calcium, and violet with magnesium. In this diagram, a chromium ion forms coordinate covalent bonds with electron pairs on the dye and protein molecules. Some effective mordants include potassium aluminum sulfate,
$KAl(SO_4)_2$ (sometimes called alum); potassium dichromate, $K_2Cr_2O_7$ (chrome mordant); iron (II) sulfate, $FeSO_4$ (iron mordant); copper (II) sulfate, $CuSO_4$ (copper mordant); and tin (II) chloride, $SnCl_2$ (tin mordant).

Name________________

"Natural Dyes" – Reading Questions

1. Dyes have been used for a long time. The Neanderthal coated their dead with red ochre which was really____________(rust). Cave paintings used _________and_________ iron _________, black_________and white ________. Humans got their coloring agents from______and________until weaving was invented.

2. One of the most important **animal dyes** came from the __________which formed a __________ color. The dye was extracted by ____________the shellfish and boiling them in _________water for _______days. Cloth was dipped, placed in the sun, and the color changed from ___________ to _______ - ______then to __________. In the beginning only the ________could wear it. Later dyes were formed from_________and it was a _________color. Cochineal was an________and used until 1954 to dye___________________________.

3. **Vegetable dyes** can be made from plants. The three most important were ___________, ____________, and ____________. Madder is a_______color and the chemical it contains is ____________. Woad is a _______color and contains_________as its chemical.

4. Saxon green was a mixture of __________and __________. Indigo is much richer in the __________molecule. The anti-indigo lobby kept the plant out for ________years. Finally it was chosen for the British naval uniform and it gave the world_________forever after. Today indigo has been largely replaced by other blues EXCEPT it is till used for dyeing __________.

5. A college student named _________made the first **synthetic dye** named _________as it was a purplish color. In the beginning the ________ were the leaders in the dye industry, but soon the _______________took over. Today more than _____________synthetic dyes are available.

6. **<u>Indigo</u>** is not soluble in water so is applied by ______________________. Indigo used to be treated by __________but today they use____________. The cloth is soaked, then____________by hanging it in the air. Oxygen _____________ the indigo back to the __________form which is _________ and difficult to wash out.

7. **<u>Chromophores</u>**: When the light of certain colors strikes the chromophores, __________are energized and the light is___________. A good dye must also be__________ so the solution can penetrate the fabric. Once in the fibers it must become ___________or attach itself to the fibers, so it does not wash out. The dyes that we will use for tie dye are fiber reactive. This means that the dye molecules react with the cellulose (cotton) molecules in the shirt.

8. A **<u>mordant</u>** is a ________________. It is usually a _________ion that attaches to both the ________and the __________and forms a________ between them. Most mordants are salts of _________________________- __________________. Some mordants change the __________. Alizarin (red) turns_____________when reacted with __________, or _________with calcium, and ___________ with ___________.