

The Chemistry of Plant and Animal Dyes

Margareta Séquin-Frey

Dominican College of San Rafael, San Rafael, CA 94901

Recent years have seen renewed interest in dyes that are derived from natural sources, especially among artists working with textiles but also among laymen who are interested in historical crafts, or who simply enjoy producing different shades of color from plants. This paper provides an historical introduction to the subject, with a chronological account of the development of dye processes. In the second section we discuss the chemistry of the different dye procedures and the chemical structures of important natural dyes, such as the dyes of saffron and of the famous madder root (Fig. 1 and 2). The description will concentrate on those compounds that can be used as dyes on natural fibers such as wool, silk, cotton, and linen (Figs. 3–11).

History of Natural Dyes

Until the middle of the nineteenth century, plants, animals, and minerals were the only sources for coloring agents, be it for dyes or pigments.¹

The first fiber dyes were already used in prehistoric times after the last ice age, around 1000 B.C. They consisted of fugitive stains from berries, blossoms, barks, and roots. They were early examples of so-called *direct dyes* or *substantive dyes*, i.e., dyes that color the natural fiber without special pretreatment of the dye-material or the textile. Accordingly, the dye process itself was simple but resulted in rather limited color fastness, i.e., poor resistance toward color-change after repeated washings or after exposure to light. Thus, examples of prehistoric dyes have been found only in rare situations, where the colors and fibers were preserved by permafrost, by

¹ "Dyes" are generally defined as compounds that undergo chemical interaction with the substrate to be dyed (e.g. with a textile). They are usually dissolved or dispersed in a solvent, and the substrate is treated in this solution. "Pigments" do not form chemical bonds with the substrate; in order to adhere to the surface of a substrate they have to be mixed with an adhesive. "Colorant" is a term used for both dyes and pigments (1).

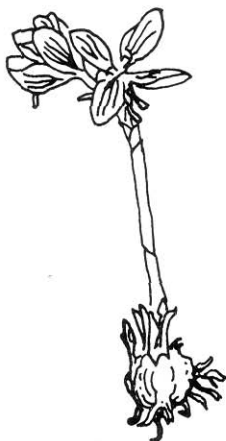


Figure 1. Saffron (*Crocus sativus*), according to a woodcut by Leonhart Fuchs from 1543.

dry desert sand, or under the anaerobic conditions of a swamp.

More sophisticated dyes were developed in later times. Advanced dye procedures were required to produce colors with better fastness.

The blue dye of indigo (Fig. 11), derived from the plant *Indigofera tinctoria*, had been known in India for about 4000 years. Phoenician traders and migrating peoples gradually introduced this dye to the Mediterranean area, from where it spread to Europe. In Northern Europe another blue dye, woad (*Isatis tinctoria*), had been in use since the Bronze Age (2500–800 B.C.). Dyeing with this plant also produces the chemical indigo. However, due to by-products, the resulting blue is not as pure as that from the indigo plant. Around 1500 A.D. indigo was imported for high prices to Northern Europe. In spite of a decree in England that prohibited import of indigo in order to protect local woad growers, indigo completely monopolized the market around 1740.

Indigo is an example of a *vat dye*, and its application to a fiber involved a complicated procedure. The plant had to be fermented, then treated with urine. The fiber was dipped into the still colorless dye bath and then hung out in the sun in order to get a blue, insoluble dye on the fiber. (The chemistry of this process will be explained in the next section.)

Another ancient vat dye was the Tyrian purple (Fig. 11), derived from the Mediterranean shell fish of the genera *Purpura* and *Murex*. The Phoenician towns of Tyre and Sidon were the centers of this dye industry around 800 B.C., and



Figure 2. Madder (*Rubia tinctorum*), according to a woodcut by Leonhart Fuchs from 1543.

Greek dye factories that produced purple existed all along the Mediterranean coast.

Many shades of red could be created with the madder root, from the Mediterranean and Asian plant *Rubia tinctorum* (Fig. 2). Madder contains alizarin (Fig. 10) and is an example of a "mordant dye." This type of dyestuff produces only a weak coloration on untreated fibers. Strong and fast colors can be obtained, if the textile is first immersed in a solution of a so-called "mordant." These are metal salts, like alum, copper, chromium, tin, and iron salts, and tannins (Fig. 7). In ancient times, mordanting was achieved by carrying out the dye process in copper or tin vessels, or by adding iron nails. Most natural dyes belong to the group of mordant dyes. Other examples of red mordant dyes were kermes, the scarlet red dye from the Mediterranean scale insect *Kermes ilicis*, recorded already in 1727 B.C., and lac, from the insect *Coccus lacca*, found in India and southern Asia.

Ancient dyes and dye procedures have been recorded mainly by two historians of the first century A.D. The Roman naturalist Pliny, the Elder, refers in his writings to indigo as well as woad, a common dye used among Gallic tribes. The Greek physician Dioscorides describes the dyes of madder for red, saffron (from the stigmas of *Crocus sativus*) for yellow (Fig. 1 and 8), weld (from *Reseda luteola*) for yellow (Fig. 4), woad for blue, and dyers' bugloss (*Alkanna tinctoria*) for red (Fig. 9). Bark of oaks, walnut hulls, and oakgalls, all rich in tannins (Fig. 7), provided both dye and mordant and produced brown to black colors. Note that many of the systematic names of dye plants contain the word *tinctorius* or *tinctorum* or similar, which is translated to "the dyer's."

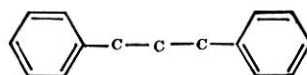
During the middle ages, until about 1250 A.D., the well developed dye procedures were recorded by medieval monks. At this time dye plants and herbs of medicinal usage were often the same. Superstition was also part of the dye process, e.g., certain dye plants were supposed to be most effective when collected at the time of full moon. The preference for particular dyes was highly influenced by the local availability of the corresponding plants.

As the medieval trade unions, the "guilds," grew in power, they took over the tradition of dye processes. Many a dyers' guild carried the saffron crocus in its coat of arms. Dye procedures were developed further and kept as highly guarded secrets. Famous centers of dye production and trade were Venice, Florence, Genoa, Basle, Frankfurt, Nuremberg, Antwerp, and London. In medieval fairs, saffron, madder, indigo, woad, and other dyes, and dye ingredients were traded. A famous historical record, "Plictho de Larti de Tentori," written by the Venetian Giovanni Ventura Rosetti, describes the recipes of the Venetian dyers' guild in great detail. For a comprehensive history of dyes in Europe see (2).

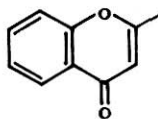
Early pueblo dwellers in the Southwest of the North American continent were experts in fiber arts, including dye processes. After the discovery of the New World, dyes were exported to Europe, among them the deep-yellow fustic, chemically the compound morin (Fig. 4), from *Chlorophora tinctoria*, a large tree of the mulberry family, and logwood (*Haematoxylon campechianum*), containing the dye hema-tein (Fig. 6). The most important exported dye was cochineal or "carmine red" (Fig. 10), prepared from the dried cactus insects of *Coccus cacti*. The first dyers' handbook written in America was "The Dyer's Assistant" by Asa Ellis, published in 1798.

In 1930, the Museum of Northern Arizona and the Bureau of Indian Affairs of the U.S. Department of the Interior, started a program to revive ancient fiberarts among Indian people. Since then Hopi and Navajo Indians have successfully continued and developed the tradition of dyeing with natural products (3), (4).

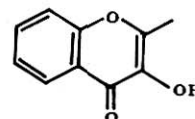
For a comprehensive history of textile dyes see (5). The excellent booklet published by the Brooklyn Botanic Garden (6) describes the history, the botanics, and dye procedures of important plant dyes. For a more popular description of local



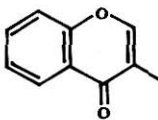
Flavonoid skeleton



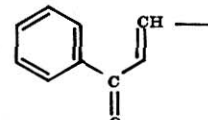
Flavones



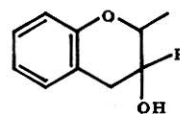
Flavonols



Isoflavones

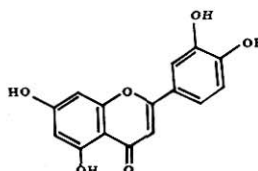


Chalcones

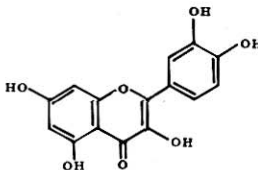


Catechins

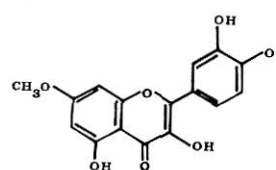
Figure 3. Flavonoids and related compounds provide the largest group of plant dyes, usually yellows. All flavonoids contain the $C_6-C_3-C_6$ unit. Subgroups providing plant dyes are the flavones, the flavonols, the isoflavones, the chalcones, and the catechins. The illustration shows the characteristic C_6-C_3 part of each subgroup.



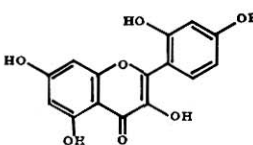
Luteolin



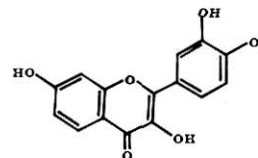
Quercetin



Rhamnetin



Morin



Fisetin

Figure 4. Luteolin, from weld (*Reseda luteola*), an ancient yellow dye, is an example of a flavone. Examples of flavonols are quercetin, widely found in plants, e.g. in onion (*Allium cepa*), oakbark, and in *Ericaceae*; Rhamnetin, from *Rhamnus cathartica*; Morin, the yellow dye from fustic (*Chlorophora tinctoria*); Fisetin, from sumac (*Rhus*).

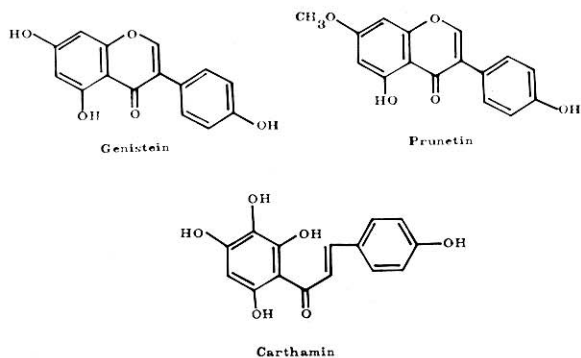


Figure 5. Genistein, from dyer's broom (*Genista tinctoria*) and Prunetin, from the leaves of the tree *Prunus cerasifera*, are examples of isoflavones. Carthamin, or "safflor," the dye from the dyer's thistle (*Carthamus tinctorius*), is a chalcone.

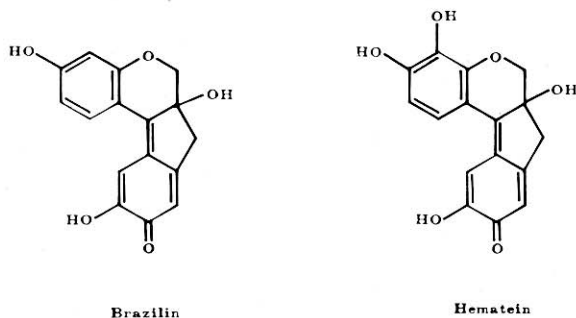


Figure 6. Brazilin, the red dye from brazilwood (*Caesalpinia brasiliensis*), and Hematein, from logwood (*Haematoxylon campechianum*), for blue, browns, and black, are chemically related to the flavonoids.

dye plants and dye processes see Ida Grae's book "Nature's Colors" (7). The article by F. Zaehring lists a large number of natural dyes, their sources, the colors produced, methods of application and several chemical structures (8).

Chemistry

In this section we shall provide the chemical background of the different dye processes. Subsequently, the chemical structures of some natural dyes will be discussed and compared with the main categories of natural products chemistry.

Many dyes in plants are glycosides: The dye molecule is linked to a natural sugar, e.g. to glucose (see carminic acid in Fig. 10), which increases the water solubility in the aqueous plant system. During the dye process, the glycosidic bond is broken, and new bonds are formed between the fiber and the dye, thus producing a water insoluble, washable coloration.

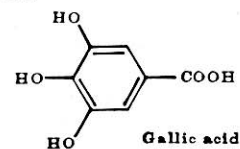
Direct dyes or *substantive dyes* are compounds that form a direct chemical bond with the fiber. The cellulose molecules of plant fibers are linked to these dyes by means of hydrogen bonds. Animal fibers, like wool and silk, contain acidic and basic positions in their protein molecules. Thus, dyes with basic or acidic groups (so-called *cationic* and *anionic* dyes, a subgroup of direct dyes) undergo salt-formation with the acidic and basic positions, respectively, in the textile. Examples of direct dyes are carthamin (Fig. 5) and bixin (Fig. 8). Both are also applied as mordant dyes. A natural basic dye is berberine (Fig. 11).

In the *mordanting* process, fibers are treated with a metal salt solution (aluminum, chromium, copper, iron, and tin salts) before the actual dye process. The metal ions form strong complexes between the fiber and the later applied dye. Different metal salts produce different color shades with the same dye. Most natural dyes can be applied as mordant dyes.

Vat dyes have to be reduced first to a water-soluble form.

Hydrolyzable tannins

Derivatives of



Catechin tannins (condensed tannins)

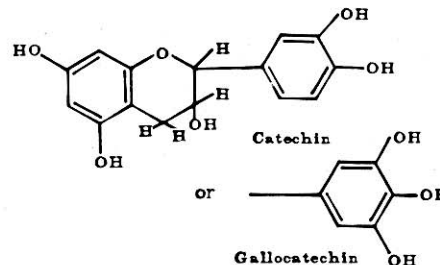


Figure 7. Tannins comprise a complex group of chemical compounds. Hydrolyzable tannins are derivatives of gallic acid. Catechin tannins or condensed tannins are derived from the flavonoid catechins. Examples are Catechin, from the Asian tree *Acacia catechu*, a brown dye, and Gallocatechin.

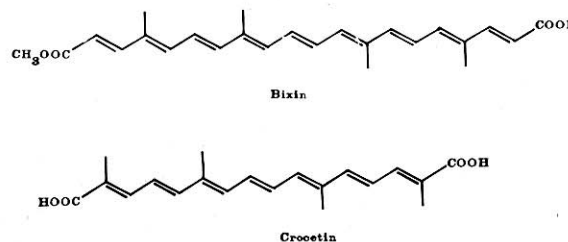
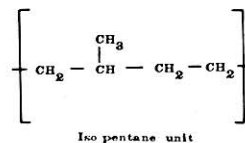


Figure 8. Terpenes or isoprenoids are biochemically synthesized from isopentane-units. Examples of terpenoid dyes are Bixin, the red dye from the fruit of the tropical tree *Bixa orellana*, and Crocetin, the ancient yellow dye saffron from *Crocus sativus*.

The textile is then treated in the aqueous solution. Oxidation of the dye on the fiber creates the desired water-insoluble colorant. In the case of indigo, the treatment with urine transfers the glucoside indican into the water-soluble indoxyl (Fig. 11). The action of sunlight on the fiber causes oxidation of indoxyl to the insoluble dye.

Chemists divide compounds found in nature into categories of substances that have a common biochemical background. Examples are the categories of carbohydrates, terpenoids and steroids, amino acids, and proteins. For a detailed treatise see (9). Natural dyes are included in the categories of flavonoids, tannins, terpenoids, naphthoquinones, anthraquinones, and alkaloids.

Flavonoids constitute the largest group of plant dyes (Fig. 3-6). They are usually yellow to orange-yellow in color and contain all a C₆-C₃-C₆-unit. Flavonoids are divided into subgroups, dependent upon their different states of oxidation (i.e., oxygen content). Plant dyes are included in the groups of flavones, flavonols, isoflavones, chalcones, and catechins (Fig. 3).

The structures of brazilin, the red dye from brazilwood (*Caesalpinia brasiliensis*), and hematein, the blue to dark-

brown dye from logwood (*Haematoxylon campechianum*) also contain a C₆-C₃ unit and are related to the flavonoids.

Catechins often form so-called *condensed tannins*, as opposed to the *hydrolyzable tannins*, which are esters of a sugar, usually glucose, with one or more trihydroxybenzene carboxylic acids (Fig. 7). The chemistry of tannins is complex and non-uniform (10). Tannins are often used in combination with other dyes, as a pretreatment to the fiber, and produce mostly brown to black colors.

Flavonoid dyes are usually mordant dyes, except for the catechins, which also can be used as direct dyes.

Terpenoids or *isoprenoids* (Fig. 8), form an important category of natural products. The *isopentane*, *isoprene*, or C₅ unit is the biochemical building stone for these compounds. Crocetin, from saffron, equally important as a food ingredient, is an example of a terpenoid compound. At this point, note the large number of conjugated double-bonds, a characteristic

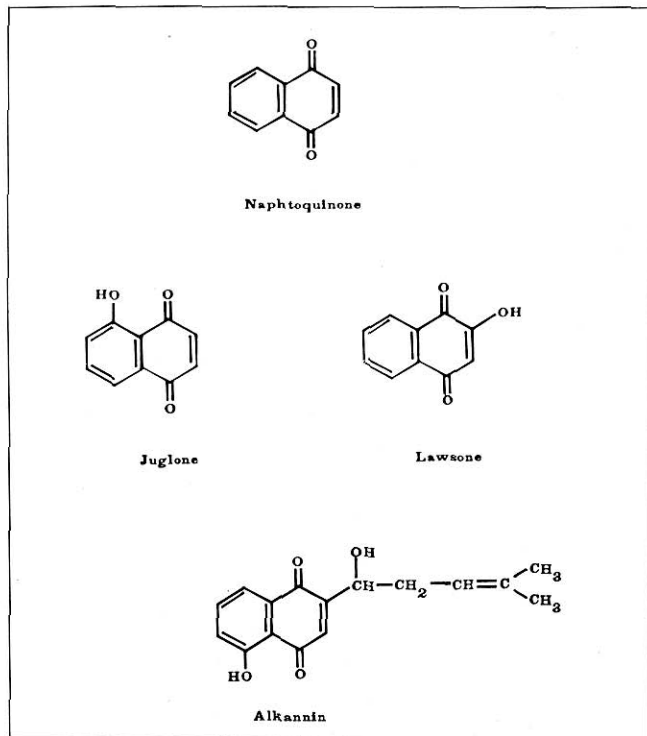


Figure 9. The basic structure of naphthoquinone is found in the following natural dyes: Juglone, for green to brown dyes, from walnut trees (*Juglandaceae*), Lawsons, the red dye from henna (*Lawsonia inermis*), and Alkannin, from the old-time dye plant alkanet (*Alkanna* or *Anchusa tinctoria*), also for reds.

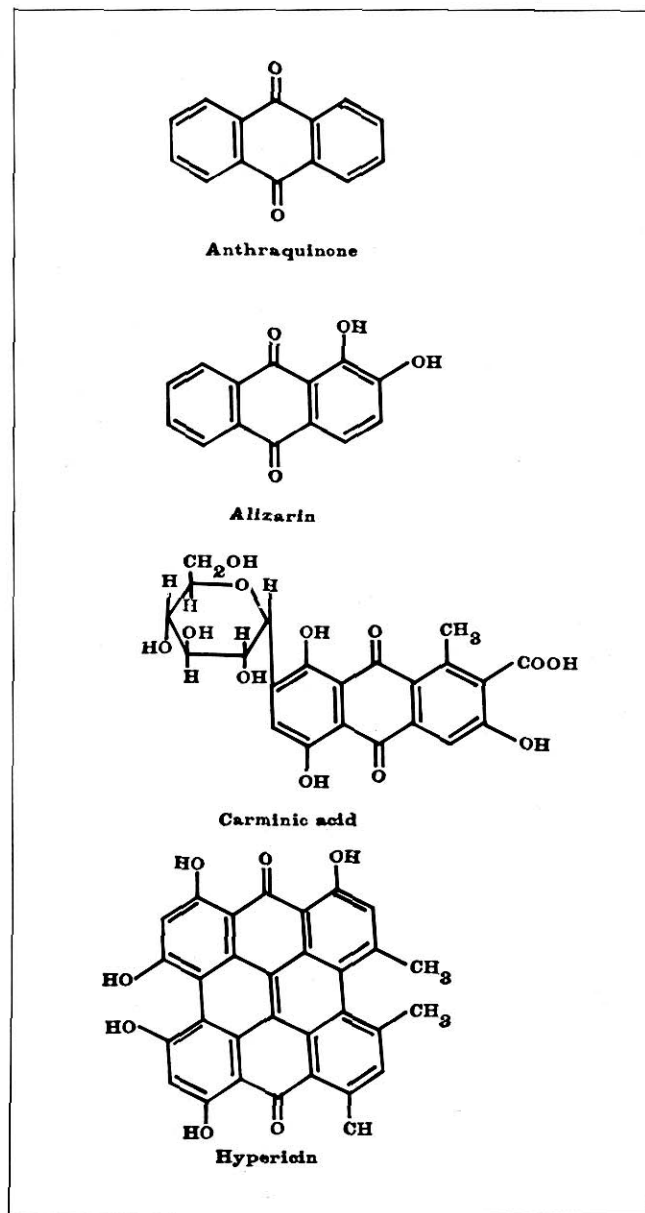


Figure 10. The basic structure of anthraquinone is found in: Alizarin, the red dye from madder (*Rubia tinctorum*), in Carminic acid, "cochineal," a glucoside from the cactus insect *Coccus cacti*, and in Hypericin, the yellow dye from St. John's wort (*Hypericum perforatum*).

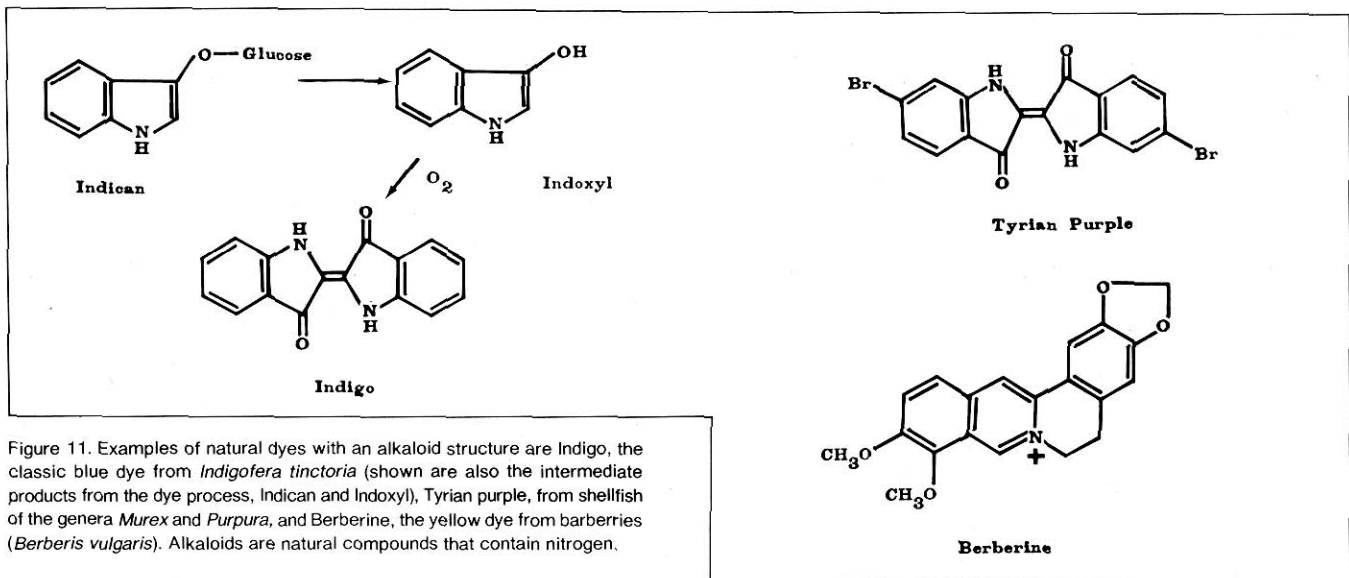


Figure 11. Examples of natural dyes with an alkaloid structure are Indigo, the classic blue dye from *Indigofera tinctoria* (shown are also the intermediate products from the dye process, Indican and Indoxyl), Tyrian purple, from shellfish of the genera *Murex* and *Purpura*, and Berberine, the yellow dye from barberries (*Berberis vulgaris*). Alkaloids are natural compounds that contain nitrogen.

that leads to absorption of light in the visible range, thus making us see a color (11).

Naphthoquinones and *Anthraquinones* (Fig. 9 and 10) are aromatic compounds that comprise a number of strong, red, mordant dyes. It is interesting to compare the chemically close structures of alizarin and carminic acid or cochineal, one derived from a plant, the other derived from an animal source.

Alkaloids are defined as natural products, usually from higher plants, that contain nitrogen. In this chemical group we find the dyes of indigo and Tyrian purple.

Conclusion

In 1856, W. H. Perkin discovered the first synthetic dye, mauvein. Within a few years, natural dyes were replaced completely by synthetic products. The new dyes offered any imaginable shade of color, in great brilliance if so desired, and with exact reproducibility. Lightfastness and washability were excellent, and all types of fibers could be colored. Most natural dyes lack the above qualities. Brilliant colors are rarely obtained, and their fastness varies. Most are applicable on wool or silk, but few dye cotton, polyester, or rayon well. It is practically impossible to obtain repeatedly the same color nuance.

In spite of these drawbacks, natural dyes have experienced a great revival in recent years. Renewed interest in history and traditions on one hand, and increasing appreciation for nature in general have contributed to this trend. The softness of the natural colors attracts many artists. And last, but not least, the pleasure in experimenting with often inconspicuous plants that provide attractive dyes has added to this rediscovery of plant and animal dyes.

Literature Cited

- (1) Orna, M. V., J. CHEM. EDUC., 57, 268 (1980).
- (2) Ploss, E. E., "Ein Buch von alten Farben," Impuls Verlag Heinz Moos, Heidelberg and Berlin, 1962.
- (3) Colton, M.-R. F., "Hopi Dyes," Northland Press, Flagstaff, Arizona, 1965.
- (4) Young, S., "Navajo Native Dyes," U.S. Dept. of the Interior, 1940.
- (5) Robinson, Stuart, "A History of Dyed Textiles," Studio Vista Ltd., London, 1969.
- (6) Editorial Committee of Brooklyn Botanical Gardens, "Dye Plants and Dyeing—a Handbook," Brooklyn Botanic Garden, Brooklyn, N.Y. 11225, 1964.
- (7) Grae, Ida, "Nature's Colors, Dyes from Plants," Macmillan Publishers, London, 1974.
- (8) Zaehring, F., "Mit Achtsamkeit zurueck zur Faerberpflanze," Sandoz Bulletin #53, SANDOZ Inc.
- (9) Robinson, Trevor, "The Constituents of Higher Plants," Burgess Publishing Co., 1975.
- (10) "The Merck Index," Ninth Edition, p. 1172, 1976.
- (11) Orna, M. V., J. CHEM. EDUC., 57, 264 (1980).