

chromogens are doubtless colorless but must not on this account be confused with the leucoanthocyanins.

Finally we remark that attention was pointedly drawn to the importance of colloid association of anthocyanins in the Presidential Address to Section B of the British Association (Leicester, 1933).⁶ We showed *inter alia* that cyanin is blue in the acid cornflower cell-sap because it is adsorbed on colloidal particles which stabilize the anions at a pH of 4.9.

Co-pigmentation is, however, a different phenomenon and is observable in dilute, strongly acid solutions. In the heterogeneous systems of a flower petal the two factors probably merge and in addition surface phenomena become important in relation to flower color. In this connection it is interesting to note that all the colors of hydrangeas (blue, violet, red) can be exactly reproduced by pouring acid solutions of synthetic delphinidin 3-monoglucoside⁷ (now recognized as the hydrangea anthocyanin) on filter paper. The best results are obtained with optimum concentrations of organic acids and in the presence of tannin. Dilute (red) solutions give blue on the paper, more concentrated solutions, red, and the hydrangea violet is intermediate. Blue margins are noted in all cases unless the acid concentration is too high. Hence we reject the view that the blue color is due to ferric salts, physical conditions being obviously paramount. The function of iron salts, etc., added to the soil is probably to initiate physiological disturbances whereby the anthocyanin concentration is diminished. Further relevant facts are reported in the following note.

(6) Cf. Report of the British Association for the Advancement of Science, 1933, and *Nature*, **132**, 625 (1933).

(7) Reynolds and Robinson, *J. Chem. Soc.*, 1039 (1934).

DYSON PERRINS LABORATORY
OXFORD UNIVERSITY
OXFORD, ENGLAND

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Notes on Variable Colors of Flower Petals

BY GERTRUDE M. ROBINSON

These notes refer to variations not due to change in the basic anthocyanins.

It has already been noted that a factor for flower color is the concentration of the anthocyanin and the ratio of this to the concentration of co-pigments of the tannin and flavonol classes. A good example is the ordinary lilac in which the co-pigment remains substantially constant. The

pale mauve colored flowers contain much less anthocyanin than the red flowers.¹ In the latter case the co-pigment is unable to modify the color of all the anthocyanin present. A second factor is colloid association, probably with polysaccharides (see the preceding note) and in this case too the development of much anthocyanin may produce a new shade. A third factor is virtual change of pH due to surface phenomena (diffusion of mobile ions), and fourth and fifth may be dyeing of the fibers and crystallization of the pigment, respectively. Modifications due to traces of elements such as iron are also possible but have not yet been recognized with certainty in any one case. A common phenomenon is that of a red bud which becomes mauve, purple, violet or blue when the flower opens or a little later; changes due to fading and loss of vigor are not under consideration. This sequence has only been observed in flowers characterized by *relatively high pH* (about 6.0). The following are representative observations and some notes on exceptional cases are appended. pH was determined after trituration of the material (3 g.) with distilled water (14 cc.).

Ageratum.—Young red buds (pH 6.0) develop into violet flowers (pH 5.8). The anthocyanin is an acylated cyanidin diglucoside. The concentration of anthocyanin is higher in the buds than in the flowers but the ratio of flavone to anthocyanin is higher in the flowers than in the buds.

Anchusa (Dropmore var.).—Red buds (pH 6.35) become blue flowers (pH 6.2). The flavone remains constant but the ratio of anthocyanin in buds to flowers is 34.4:22.5. In this case colloid association in the flowers, as in the cornflower, is indicated.

Centaurea.—The concentration of anthocyanin in purple flowers of the annual cornflower is higher than in the blue flowers.

Cheiranthus mutabilis.—The color changes are due to the gradual formation of anthocyanin superposed on the yellow ground of the petals; subsequently the anthocyanin is destroyed. This anthocyanin is an acylated glucoside of an acylated cyanidin. The reddish bracts contain unacylated cyanidin diglucoside.

Delphinium (vars. Dr. B. Crane, Lorenzo di Medici, Blue Bird).—Blue petals or parts of petals (pH about 5.6) contain less anthocyanin and relatively less flavone than violet petals (pH about 5.7) of the same plant. Here again colloid association is indicated.

Hydrangea.—Red and blue flowers contain the same anthocyanin, namely, delphinidin 3-monoglucoside. There is a little more flavone in the red than in the blue flowers. The ratio of anthocyanin concentrations, red to blue, is usually from 6:1 to 7:1 and using a specially deep-colored blue variety it was still 4:1. The pH of hydrangeas is

(1) Robinson and Robinson, *Nature*, **130**, 21 (1932).

variable, the red flowers being slightly more acid than the blue; varieties which do not blue have unusually low pH . If the petals of a blue variety are allowed to develop in a weak light more anthocyanin is produced and a red color partly masks the blue.

Ipomea Learii.—Young red buds (pH 6.4) become blue flowers (pH 6.2–6.3) and the pigment concentration diminishes slightly. This process does not occur in cut flowers kept in hard tap water, but always when distilled water is used. Here again the change of color is associated with a flower of unusually high pH . The range in the majority of flower petals is from 4.0 to 5.0.

Malcomia maritima.—The buds and young flowers are red and change to dullish violet. The pH in both cases is about 6.4. The anthocyanin concentrations, red to violet, are about in the ratio 3:2. Flavone is present in approximately the same concentration in both cases. It is very interesting that the variety "Crimson King," which does not blue, has pH 5.17. All varieties of the virginian stock are colored by cyanidin diglucoside.

Meconopsis Baileyi.—The purple flowers contain more anthocyanin than the blue.

Rosa.—The "Veilchen" rambler rose has red buds (pH 6.3) changing to dullish violet flowers (pH 6.3). The anthocyanin ratio, red to violet, is 29.6:22.9. In a dry season the flowers become violet almost as soon as they open but in a wet season the change occurs just before fading. In the latter case the anthocyanin concentration is higher than in the former.

The rose, Madame Ed. Herriot, has salmon-pink young flowers changing to bluish-pink. The pH in both cases is 5.9. The anthocyanin ratio of young to older flower petals is 44:26. Flavones are present but show little change.

The rambler "Excelsior," like "Veilchen," is colored by cyanin but the pH is 5.6 and the color change does not occur.

Chlorogenic Acid.—The method of Gorter² has been employed and it appears that this plant constituent may have some significance in relation to flower color. Blue hydrangea flowers do not contain any chlorogenic acid but the red flowers have a substantial amount.

Blue flowers of *Ipomea Laurii* are free from the acid but fading, accompanied by reddening, causes the development of this substance. Red buds and purple flowers of *Centaurea* contain chlorogenic acid but there is none in blue cornflowers.

Arnebia cornuta.—This plant, known as Mahomet's Fingers, produces yellow flowers and shortly after opening (incipiently also in the bud) dark purplish-brown areas appear on each petal; the colored spots later disappear. The anthocyanin is malvidin diglucoside. The colored areas are opposite the anthers and in the bud follow their shape. If tissue paper is interposed at an early stage between anther and petal, the spot does not develop. Also, if the petal is tied away the same result is achieved in a large majority of cases. The petals on which this operation is performed grow, but do not reach full normal size. It would appear that the anther contains a stimulant (? volatile) to anthocyanin formation although this view is necessarily tentative because the normal physiology of the plant may have been modified by the mechanical operation.

(2) Gorter, *Rec. trav. chim.*, **31**, 281 (1912).

In one case the anthers were successfully excised and a good flower developed. It was always pure yellow.

DYSON FERRINS LABORATORY
OXFORD UNIVERSITY
OXFORD, ENGLAND

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The Identity of Pyrethrosin with Chrysanthin and Non-identity with Geigerin

BY MILTON S. SCHECHTER AND H. L. HALLER

A crystalline compound isolated from pyrethrum flowers (*Chrysanthemum cinerariaefolium*) has been described recently by Rose and Haller.¹ The compound was named "chrysanthin" because its physical properties appeared to be identical with those of a compound obtained by Chou and Chu² from benzene extracts of pyrethrum flowers, and named by them "chrysanthine."³ The compound described by Rose and Haller melted at 201° when crystallized from ethyl acetate and at 177–178° when crystallized from ethanol. Its optical rotation in chloroform was $[\alpha]^{20}_D -30.5^\circ$. Analyses and molecular weight determinations showed it to have the molecular formula $C_{17}H_{22}O_5$.

Chou and Chu stated that the compound isolated by them had a melting point of 200° and a rotation of $[\alpha]^{20}_D -30^\circ$ in chloroform. The empirical formula, $C_{10}H_{13}O_3$, assigned by them was based on combustion analyses only, no molecular weight determinations having been made.

Thoms⁴ in 1891, during a study on the insecticidal principle of pyrethrum flowers, isolated an insecticidally inert product which he termed "pyrethrosin," and which he regarded as being identical with one obtained by Marino-Zuco⁵ in a similar study. Thoms found that pyrethrosin had a melting point of 189° and suggested the provisional formula $C_{34}H_{44}O_{10}$ on the basis of four combustions but no molecular weight determination. This formula is exactly twice that proposed for chrysanthin by Rose and Haller.

In the course of a chemical study of *Geigeria aspera*, a plant that causes "vermeersickte" or vomiting disease of sheep, Rimington and Roets⁶ isolated a bitter principle which they called

(1) Rose and Haller, *J. Org. Chem.*, **2**, 484 (1937).

(2) Chou and Chu, *Chinese J. Physiol.*, **8**, 187 (1934).

(3) The final e was dropped by Rose and Haller in accordance with present standards of nomenclature.

(4) Thoms, *Ber. deut. pharm. Ges.*, **1**, 241 (1891).

(5) Marino-Zuco, *Atti accad. Lincei*, 1 Sem., 571 (1890); abstr. in *Ber.*, **24**, 201 (1891).

(6) Rimington and Roets, *Onderstepoort J. Vet. Sci. Animal Ind.*, **7**, 485 (1936).