

Developments in the Chemistry of the Anthocyanins

It is a remarkable fact that almost the whole range of anthocyanin pigments of flowers, fruits, and blossoms is derived from the three fundamental anthocyanidins, namely, pelargonidin, cyanidin, and delphinidin, by various substitutions in the hydroxyl group. A very extensive survey of the colouring matters of this class conducted during the last two seasons has only served to emphasise the prevalence of the three known types.

Nevertheless, the existence of exceptions has already been recognised by Willstätter, who found that the bluest anthocyanins occurring in the beet, in *Celosia cristata*, and in *Atriplex hortensis* are nitrogenous pigments. At the other end of the scale, the most yellow anthocyanin was noted in *Papaver alpinum*, and a similar substance which colours the yellow Iceland poppy is in progress of investigation in this Laboratory by Miss R. Scott-Moncrieff. Quite a different anthocyanin has now been found to occur in the orange-red flowers of *Gesnera fulgens* (or *G. cardinalis*). This anthocyanin we propose to term *gesnerin*, and it is a 5-saccharide (unidentified sugar residue) of 4' : 5 : 7-trihydroxyflavylium chloride. On hydrolysis it yields the anthocyanidin chloride which was readily identified as apigeninidin chloride,¹ the synthesis of which was effected in 1925 because it was thought probable that a derivative of the substance would occur in Nature. The major anthocyanidins are related to naturally occurring flavonols and it was thought probable that similar substances derived from the flavones in a similar way might be encountered; this expectation has now been realised in the case of the anthocyanidin related to the flavone apigenin. A further search among the Gesneriaceae and other families of the Personales will be made, since it seems very probable that the anthocyanin derived from luteolinidin will also be encountered.

The suggestion first made in these columns, that some of the more important anthocyanins are 3 : 5-diglucosides, has been amply confirmed by synthesis.

Dr. A. R. Todd in collaboration with one of us has already succeeded in synthesising hirsutin, malvin, and cyanin chlorides, and synthetic indications have been obtained in regard to peonin and pelargonin chlorides; all these pigments bear two glucose residues separately attached to oxygen atoms in positions 3 and 5 of the anthocyanidin molecule. An independent confirmation of the correctness of these views is obtained from the work of Prof. Karrer and his colleagues, who have been able to show that the process of oxidation of many anthocyanins by hydrogen peroxide, followed by hydrolysis, results in the detachment of only one hexose unit, obviously that attached to position 3 (private communication). The hypothesis that anthocyanins of the mecocyanin type are 3-biosides has also been confirmed by synthesis of representatives of all the possibilities (for example, cyanidin 3 : 7-diglucoside, 3-cellobioside, and 5 : 7-diglucoside), and by an examination and comparison of their properties.

We were naturally much interested in the letter of Mr. W. J. C. Lawrence² on the subject of the co-pigments which modify the colour of dahlias, pelargoniums, etc., as we have long been of the opinion that the chief co-pigments are the tannins and anthoxanthins, including the flavone and flavonol glucosides. Until, however, these substances have been isolated and identified, speculation as to their nature seems premature. Nevertheless, experiments with pure anthocyanins and pure flavonol derivatives have proved very suggestive, and, for example, the appearance and properties of a co-pigmented violanin solution from purple violas can be simulated by means of a synthetic anthocyanin in association with quercitrin.

We have found the phenomenon of co-pigmentation

almost universal in flower colours, almost all of which are bluer than they should be at the pH obtaining in the cell sap. The degree of the effect is, however, very varied in different flowers, and, as we have already suggested, a genetic factor for flower colour is frequently connected with the development (or, it may be, the suppression) of a co-pigment.³

In addition, we pointed out that the co-pigment might remain as a constant factor in certain cases, and that a change of colour tone might result from an increase in the concentration of the anthocyanin. Thus in the ordinary lilac there is a co-pigment, found also in the white flowers, which with a low concentration of anthocyanin produces the familiar pale mauve colour; the deeper red shades are the result of an increased proportion of colouring matter, and the deep bluer red varieties contain both pigment and co-pigment in greater concentration. An alternative to the latter part of this statement is obviously that a new and more efficient co-pigment has been developed.

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¹ Pratt and Robinson, *J.C.S.*, 127, 128.

² NATURE, 129, 834, June 4, 1932.

³ *Biochem. J.*, 25, 1687; 1931.

Mass-Spectra of Helium and Oxygen

In the course of my analyses of leads of different origins I have had opportunity of making some interesting observations on these two elements. While preparing a new discharge tube by preliminary running, a mixture of helium and oxygen was used and a search was made for the line due to He⁺⁺. The occurrence of doubly charged helium atoms in the discharge was inferred during the early work of Sir J. J. Thomson¹ and has recently been very beautifully demonstrated by Conrad,² but the evidence in each of these cases was indirect, namely, the prolongation of the normal helium parabola. All attempts so far made to photograph the line of He⁺⁺ as a satellite of the line H₂ by means of the mass-spectrograph have been unsuccessful.

These failures I have ascribed to my use in the past of cooled charcoal (incapable of absorbing helium) for the high vacuum parts of the apparatus. This explanation appears to be correct, for by reducing the pressure in the slit system and the camera to a much lower value by a diffusion pump and lowering the intensity of the H₂ line by continuous washing with oxygen and helium, the doubly charged line of the latter has now been found. It is indeed still much too faint compared with H₂ for accurate measurement, but there is now reasonable hope that with a setting of the discharge tube more favourable to atomic lines and more careful washing it will be possible to reduce the pair to approximately equal intensity. The distance between these lines will then afford a really direct and trustworthy measure of the ratio of the masses of the helium and hydrogen nuclei, a figure of fundamental importance in nuclear physics.

During these experiments it was noted that the helium-oxygen mixture gave much stronger oxygen lines than did pure oxygen, and since the oxygen molecular line was so bright that it could be seen on the willemite screen, conditions were very favourable for the detection of the two faint isotopes of oxygen. The atomic lines 17 and 18 are unsuitable for this, owing to the presence of OH and OH₂, but the molecular lines 33 and 34 due to O¹⁶O¹⁷ and O¹⁶O¹⁸ respectively may be expected to be fairly free from