

Formation of Anthocyanins in Plants*

By Prof. R. Robinson, F.R.S.

DISTINCT lines of investigation converge on the problem of the formation of anthocyanins in plants, our information being derived from studies in plant physiology, in genetics and in the organic chemistry of the pigments and related members of the flavan group. Anthocyanins are frequently produced when photosynthetic activity at the site of eventual pigmentation is diminished through seasonal changes or various kinds of injuries to the plant (mechanical, fungus disease, etc.). Under such conditions, carbohydrates and other synthetic products tend to accumulate as the result of interference with the translocation currents. Abundant nutriment favours anthocyanin formation, which can, in many cases, be accelerated by artificial feeding with sugars.

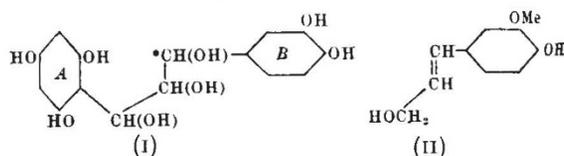
To all generalisations in this field of experiment there are exceptions, but the formation of anthocyanin from simple carbohydrates may be regarded as established. A low temperature, light, and access to oxygen favour the appearance of the colouring matter; plants which form abundant anthocyanin in the dark are equipped with reserves of food-stuffs, an example being the tulip.

Experiments on vines have made it very probable that the anthocyanin forerunners are synthesised in the leaves, but undergo specific modifications in the coloured fruits.

There is no physiological evidence of an essential stage of *reduction*, whereas *oxidation* is definitely indicated as a step in the phytosynthetic mechanism. The state of oxidation of pelargonidin derivatives is that of normal carbohydrates, whereas cyanidin and delphinidin glycosides are more oxidised to the extent of one and two oxygen atoms in the molecules respectively.

Biogenetic schemes for the anthocyanins, flavones, catechins and related substances were advanced by the author in 1921 at the Edinburgh meeting of the British Association, and these require no modification at the present time. The C_{15} system ($C_6-C_3-C_6$) is regarded as built up from hexoses and triose by means of aldol condensations; if neither oxidation nor reduction by external reagents occurs, this requires that one, and only one, of the aromatic nuclei eventually produced will retain the carbohydrate state of oxidation. The other nucleus is auto-

matically reduced giving (I) as the normal (hypothetical) intermediate, in which ring *A* is unreduced and ring *B* reduced (one oxygen atom less than a hexose).



The three central carbon atoms are unprotected, and are found in various natural products in almost every possible state of oxidation. Thus oxidation of the asterisked $\cdot\text{CH}(\text{OH})$ to CO and dehydration gives rise to cyanidin derivatives.

An important corollary of this hypothesis is that the phytosynthetic process is a condensation of $C_6(B)$ with C_3 followed by one of $C_6(B)C_3$ with $C_6(A)$.

Now many C_6-C_3 substances (in which C_6 is benzenoid) are known among natural products, and coniferyl alcohol (II) is cited as a single example because many chemists take the view that lignin is largely constructed from coniferyl units; hence (II) may be a plant product of fundamental significance. The interesting point is that the range of orientation of phenolic groups in all the C_6-C_3 types is the same as that in the *B*-nucleus of the anthocyanins and flavones. Such biogenetic schemes are based on statistical surveys of groups of plant products and can only indicate the broad lines of molecular architecture; more searching analysis is the task of the biochemist.

In the meantime, reinforcements have arrived from a somewhat unexpected quarter, and Lawrence and Scott-Moncrieff in their studies of the garden *Dahlia* have founded what is in effect the new subject of chemical genetics. It is not suggested that genetics and chemistry have never previously been considered together; but this pioneering work shows not only how to apply chemical methods of examination to the routine of genetic work but also, what is much more novel, how to interpret the results so as to throw light on the actual mechanism of synthesis in the plant.

The complex data cannot be conveniently summarised, but the main conclusions are fully justified by the experiments. The anthocyanins and flavones are regarded as produced divergently from two plant substances. One of these is present in limited amount, and is a component for all the

* Substance of a lecture at the University of Liverpool under auspices of the Chemical Society on Dec. 10, and of a paper to the Glasgow University Alchemists Club on Dec. 11, 1935.

pigments. The second component is produced in amount and variety dependent on the factorial influences and interactions. This interpretation is in good agreement with the views expressed above. The limited, common intermediate would be $C_6(A)$ at some stage in its history; $C_6(B)C_3$ corresponds to the variable component in the hypothesis of Lawrence and Scott-Moncrieff.

Little can be advanced in favour of most of the special theories that have been proposed to account for anthocyanin formation in plants. There is, for example, a curiously persistent idea that anthocyanins result in Nature from the reduction of flavonols. But the physiological evidence shows that oxidation rather than reduction is requisite, and the fact of occurrence of analogous flavones and anthocyanins together in a plant has no unique applicability to the flavonol-reduction theory. We must anticipate it also on the basis of the parallel formation-mechanisms mentioned above. Thus the $C_6-C_3 \rightarrow C_6$ hypothesis of partly independent routes to anthoxanthin and anthocyanin implies the probability of similar orientations of phenolic groups in the aromatic nuclei of the xanthic and cyanic pigments. Accordingly we might expect to find, as we do, pelargonin with apigenin; the flavonol-reduction theory, however, requires the anthoxanthin to be a derivative of kaempferol in this case.

Actually, the constitutions of congeneric cyanins and flavones do not often correspond closely, and the flavones (flavonols) cover a wider structural range than the anthocyanins. It is especially to be noted that correspondence of *unusual* structures in the two groups is not observed; the joint appear-

ance of cyanidin and quercetin derivatives is not surprising because these are the most widely distributed representatives of their types.

Hypotheses depending on oxidation of known flavan types such as the catechins (state of oxidation of tetrahydro-anthocyanins) are in better accord with the facts, although there is little positive evidence in favour of them. Tetramethylcatechin affords bromotetramethylcyanidin bromide on treatment with bromine in dioxan containing peroxide, but the conditions for the oxidation of catechin itself to cyanidin have not been ascertained. More significant perhaps is the recognition of the wide distribution of leuco-anthocyanidins (probably possessing the state of oxidation of dihydro-anthocyanins) which are found in almost all kinds of plant material. Inevitably the transformation of these substances into colouring matters of flavylum type must occur in Nature occasionally, but it does not follow that this route represents the standard mechanism. Two dihydroanthocyanidins, namely, cyanomaclurin and peltogynol, have been isolated and characterised; these are stabilised by the possession of a glucose-like oxide ring, and the related anthocyanidins are not found in the form of naturally occurring anthocyanins. The true leuco-anthocyanidins usually afford cyanidin on hydrolysis and autoxidation.

It is too early to attribute a predominant role to the leuco-anthocyanidins, but it is already safe to assume that their modification represents an auxiliary pigmentation process. It is possibly operative in autumnal reddening and in the coloration following injuries or decortication of leaves.

The Fulmar Petrel

By Seton Gordon

THE spread southwards of the fulmar along the coasts of the British Isles during recent years is remarkable. The earliest known British colony of fulmar petrels was on St. Kilda. This, indeed, was the only known colony in the British Isles until the year 1878, when a dozen fulmars founded a colony on Foula, in Shetland. In the following year the colony had increased to 20 pairs (*Zoologist*, 1879, p. 380). From that time until the present day the fulmar has spread, and is still spreading, down the coasts of Britain, and is establishing new colonies yearly along the rock-bound coasts of Scotland, England and Ireland.

Whence has come this great stock of birds? It is generally supposed that they are descendants of the St. Kilda colony, which has overflowed east and south. Harvie-Brown's notes in his "Vertebrate Fauna of the North West Highlands and Skye", published in 1904, are therefore interesting. At that time the fulmar was only beginning to extend its range, but even then Harvie-Brown was inclined to question the generally accepted belief that St. Kilda was the birthplace of these new colonists.

He writes:

"While there may be reasonable and probably just cause for supposing that SOME AT LEAST