Colouring Matters of Plants.

IN view of the fact that many of Nature's most striking colour effects are produced as the result of harmonious groupings of highly coloured plant life, and that it is to the various plant pigments that these fine tints owe their origin, it is not surprising that chemists have striven, from quite early days of the science, to elucidate the chemical structure of these colouring matters, and botanists to discover their relationship to the vital activities of plant life.

During recent years our knowledge concerning plant pigments has been rapidly and greatly enlarged, and observations have been made that are of great significance to chemist and botanist alike, whilst the horticultural possibilities which they seem to indicate should be of interest to even the most casual lover of Nature's beauties.

When referring to plant colouring matters it must be borne in mind that it is necessary to distinguish between the plastid pigments (chlorophyll, carotin, etc.) and the water-soluble sap-pigments. The present article will deal only with the latter group—sap-pigments—but it must not be imagined that this indicates that progress has not been made in the researches upon plastic pigments; indeed, much knowledge concerning them has resulted from the extended and intricate work of Willstätter and others.

The sap-pigments may be divided into two main classes: (i) Derivatives of flavone or of flavonol—sometimes called anthoxanthines—which are pale yellow or colourless when in faintly acid solution, but bright yellow when dissolved in alkalis; and (ii) the anthocyans, which are red when in acid solution, violet to red-violet when neutral, and of varying tints from dull red, or red-brown, to purple and pure blue when in solution in the form of alkali salts. In both groups the individual pigments differ from each other in the amount of oxygen which they contain in the form of phenolic hydroxyl groups and the arrangement of these groups in the molecule.

We owe most of our knowledge of the distribution in Nature of the yellow sap-pigments—which usually occur in plant life in chemical combination with various sugars—to the work of A. G. Perkin, whilst the actual synthetic production of a number of these colouring matters by Kostanecki has confirmed our ideas concerning their chemical structure. How widely these pigments are distributed in Nature will be gathered from the fact that members of this group have been isolated from the following sources: Heather wallflower, clover flowers, cotton flowers, delphinium flowers, onion skins, violas, poplar buds, parsley, etc. Although yellow sap-pigments derived from flavone have been isolated from a large number of plants and flowers, it is quite certain that pigments of this group are present in a very much larger number of plants than those from which they have up to the present been isolated.

When we turn to consider the pigments of the anthocyan class—the purples, reds, and blues of plant life—the fact of their extremely wide distribution is obvious to everyone. Their presence in petals or leaves is noticeable even where only a small fraction of 1 per cent. of the pigment exists in the flower. That this is so will be fully realised when the fact is considered that the blue cornflower contains only about 0·75 per cent. of its dry weight of the blue pigment cyanin. In contrast with this is the case which has come to light in recent investigations, where as much as 25 per cent. of the flower's dry weight of a yellow sap-pigment was present in a yellow viola, yet this large quantity was completely masked by a mere fraction of 1 per cent. of a plastid carotin colour that was present in the same flower.

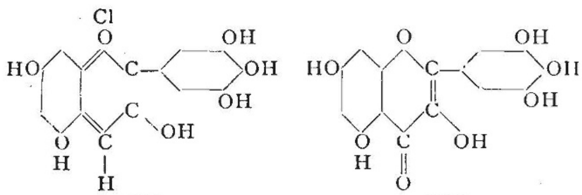
The great beauty of the anthocyan pigments has given rise to very numerous attempts to obtain an accurate knowledge of their chemical structure and also of their function in plant life. The name "anthocyan" dates back to 1835, and appears to have been introduced by Marquart. Despite the very numerous attempts that were made to isolate these pigments in a pure condition, it was not until 1903 that an anthocyan pigment (the colour of the pelargonium) was obtained in a crystalline condition by Griffiths. In 1913 Willstätter and Everest described their investigation of the pigment of the blue cornflower—which they called cyanin—and laid the foundation of the fuller investigation of the anthocyan pigments that has been developed since that date. It is to Willstätter, to his collaborators, and to Everest that we owe most of our knowledge of these pigments. The identity of a considerable number of the anthocyans has now been established, and pigments of this group have been prepared synthetically. Among others, the colouring matters of the cornflower, rose, pelargonium, viola, peony, hollyhock, cherry, and grape have been obtained in a pure condition and investigated. In almost every case these pigments occur in Nature chemically combined with sugars.

As the result of these chemical investigations the relationship that exists between the yellow sap-pigments derived from flavone and the anthocyan colouring matters has been made clear. This relationship has been the subject of much study by botanists, particularly by Keeble, Armstrong and Jones, and Wheldale, and it is interesting to note that, whilst botanical work appeared to point to the anthocyan colours being oxidation products of the yellow sap-pigments of the flavone series, chemical investigations have proved that the relationship is the reverse of this—the anthocyans are reduction products of the yellow sap-pigments.

Very interesting in connection with the function of these sap-pigments in plant life is the fact that, whilst chemical investigations have made it clear that the anthocyan pigments are reduction products of the yellow sap-pigments, botanical work strongly points to the conclusion that these very anthocyan pigments occur in plant life in positions that are the seat of oxidising influences.

It has been noticed by many who have investigated the anthocyan pigments that there is always at least a trace of yellow sap-pigment present alongside the red, purple, or blue of the anthocyan. From this has arisen the belief that the anthocyans are produced in Nature *via* the yellow sap-pigments, and recent work has shown that there is very considerable ground for thinking that this belief may prove to be correct.

To even the most uninitiated, the chemical formulæ representing a typical anthocyan [*e.g.* delphinidin (I.)] and the corresponding yellow sap-pigment [myricetin (II.)] make it obvious that a relationship exists between them—



(I.) (II.)

Naturally, to the horticulturist the interrelationship of the various sap-pigments to one another is of great interest; also the effect of these colours upon the tints produced by the plastid pigments that occur with them in plants and flowers. The proof, by chemical investigation, that the blue cornflower owes its colour to the same pigment as the red rose is of the greatest interest, for does it not raise hopes of success in the endeavour to produce a pure blue rose? In the rose the colour is red because the sap is acid, whereas the cell-sap in the cornflower is in such a condition that the pigment can take up enough alkali to form its blue alkali salt. Can the latter condition be reproduced in the rose?

It is often erroneously stated that the yellow sap-pigments are responsible for the yellow tints in flowers and berries, but in reality the bright yellows are almost exclusively due to plastid colours related to carotin, whilst the orange and brown tints are produced by combinations of these colours with those produced by pigments of the anthocyan group. In some few instances, however, it is probable that sap-pigments give rise to fairly strong yellows, but, in general, members of this class of compound produce pale yellow tints such as the colour of the primrose, or are present in an almost colourless condition in the acid cell-sap of white- or cream-coloured flowers. It is exceedingly difficult, even for one who has studied the pigments minutely, to be certain by mere observation which of the anthocyan pigments is present in any flower that may be examined. Chemical work has shown that plants of the same botanical group may produce different pigments, and, indeed, that more than one anthocyan, or yellow sap-pigment, may be present in the same flower.

Very naturally the clothing of Nature in such beautiful tints, as the result of the presence of these colours, led to the desire on the part of man to use them for the colouring of garments and other textile materials. Many of the members of the yellow sap-pigments are capable of industrial use as mordant dyes, and were largely so used before the synthetic colours became available. Some of them—*e.g.* fustic—are still employed in considerable quantities even in European countries. In the East quite a number remain in use. Concerning the dyeing properties of the anthocyan pigments, much doubt seems to have existed, but it appears certain that in 1850-60 the colour of the hollyhock was largely used in Bavaria for dyeing purposes. Quite recently these colours have been more fully investigated in respect of their dyeing properties, and it has been found not only that they dye wool, but also that they are capable of giving very fine shades when used on cotton with a tanning mordant. Although they have considerable tinctorial power, and the dyeings produced by them are fast to light, they do not stand washing sufficiently to make it possible for them to hold their own against synthetic colours.

Apart from the two main groups of sap-pigments, with which the above remarks have been concerned, there are quite a considerable number of coloured compounds that exist in plants in some soluble form—usually as glucosides. It should be noted that, whilst flavone or flavonol derivatives are very widely distributed, and the anthocyan pigments almost equally so, the remaining colours are much more restricted in their distribution. What *rôle* the flavones, either alone or accompanied by anthocyans, play in plant life, other than that of decoration, has not yet been discovered. Wide distribution is no indication of commercial importance as regards plant colouring matters, and some colours that are by no means widely distributed are of considerable importance. Furthermore, the question of plant colouring matters does not end with the consideration of those colours that exist ready-formed in the plant. Indigo, the most important of all plant colouring matters, exists in plant life as a soluble, colourless glucoside called indican, which produces indigo only when it loses the sugar with which it is chemically combined, and is oxidised by contact with air or other oxidising medium. The archil or cudbear group constitutes another class of colours that were formerly of commercial importance, and are produced from soluble colourless products present in various lichens. In conclusion, the important dye alizarine should not be omitted; this product was formerly obtained exclusively from plant sources—chiefly madder-root, in which it occurs partly as the glucoside ruberythric acid—whereas almost all the alizarine that is now used is prepared synthetically from the coal-tar product anthracene. It would appear that the time is not far distant when all plant pigments that are used for technical purposes will be displaced by synthetic products, but the recent shortage of synthetic dyes has certainly somewhat prolonged the commercial life of the various natural colouring matters.