Anthocyanins and their Sugar Components.

By J. B. Harborne, Hertford, England.

With 5 Figures.

Contents.

I. Introduction ...................................................... 165

II. Isolation .......................................................... 168

III. Properties of Anthocyanins ..................................... 169

   General Remarks .................................................. 169
   Spectral Characteristics ......................................... 170
   Chromatographic Properties ...................................... 175
   Hydrolysis Products ............................................... 176
   Enzymic Degradation ............................................... 177

IV. Identification of Anthocyanins .................................. 178

V. Natural Occurrence .................................................. 179

   Monosides ........................................................... 179
   Biosides ............................................................. 182
   Triosides ............................................................. 183
   Acylated Anthocyanins .............................................. 184
   Anthocyanin-like Compounds ....................................... 185

VI. Distribution of Anthocyanins .................................... 186

   Systematic Relations .............................................. 186
   Tissue Variation ................................................... 188
   Intraspecific Variation ............................................ 188

VII. Anthocyanins and Plant Colour ................................ 189

   Colour and Structure ............................................... 190
   Metal Complexes .................................................... 190
   Copigmentation ..................................................... 191
   Concentration ....................................................... 191

VIII. Biosynthesis of Anthocyanins ................................ 192

IX. Conclusion .......................................................... 194

References ..................................................................... 195

I. Introduction.

Anthocyanins are water soluble pigments which are responsible for most of the pink, red, mauve and blue colours of plants. They are all
based on a single aromatic structure—that of the 3,5,7,3',4'-pentahydroxyflavylium cation, cyanidin (I). The colour of this substance is altered by the addition or removal of a hydroxyl group or by methylation or glycosylation. Such modifications in structure are known to be controlled in the flowers of many higher plants by single gene substitutions. The anthocyanins present in series of colour mutants of garden flowers are thus suitable material for studying the biochemical effects of gene action.

![Chemical diagram](image)

(I.) Cyanidin.

Such studies have in fact provided most of the present knowledge of the biochemical genetics of higher plants (34). Flower and fruit colours are undoubtedly of adaptive value in relation to animal pollen vectors, and the primary function of the anthocyanins is to attract insects and birds to plants. The suggestion of Moewus (68) that anthocyanins play an active part in the sexuality of plants by acting as hormones has not been substantiated by later workers (81).

Besides providing much permanent pigmentation in plants, anthocyanins sometimes appear transiently in young leaves and other organs in response to environmental changes. Production in this instance seems to be directly related to the accumulation of excess carbohydrate in the plant. Since up to 67% of their weight is sugar in bound form, it is not surprising that anthocyanins should play a (minor) rôle in carbohydrate metabolism.

It has long been known that the sap solubility and stability of anthocyanins depend on the presence of the sugar residues attached to them. The aglycones (anthocyanidins) produced on hydrolysis of anthocyanins are both unstable to light and insoluble in water. The classical studies of Willstätter and Everest (100), of Karrer and Widmer (54–56) and of Robinson and his colleagues (59, 79, 80) were at first concerned with establishing the chemical structure of the six anthocyanidins commonly found in garden flowers. The 3-glucosides, 3:5-di-glucosides and 3-biosides of most of these anthocyanidins were then synthesized by Robinson’s team and it was established that these glycosides were widespread in nature. Surveys (24, 59) showed that most of the structural variation in anthocyanins resided not in the nature of the aglycones but in the nature, number, and position of attachment of sugar and other residues. In consequence of the lack of suitable methods

References, pp. 175—199.