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A BRANCHED TRISACCHARIDE IN THE BETACYANINS OF *BOUGAINVILLEA GLABRA*

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Key Word Index—*Bougainvillea glabra*; Nyctaginaceae; betacyanins; 2^G-glucosylrutinose.

It was reported [1] that the total betacyanin fraction isolated from bracts of *Bougainvillea glabra* var. *sanderiana* gave on alkaline hydrolysis, besides hydroxycinnamic acids and two sophorosides, a diastereoisomeric mixture of two 6-triglycosides (DP1 and DP2) of betanidin and isobetanidin. In the present study the sugar moiety of these pigments has been investigated in more details and found to be the branched trisaccharide 2^Gglucosylrutinose.

Earlier work [1] proved that DP1 is a betanidin derivative and DP2 the corresponding isobetanidin derivative and that the hydroxyl group at position 5 of the aglycones is free. Controlled acid hydrolysis of the DP1–DP2 mixture (10% HOAc for 3·5 hr under reflux) gave rhamnose, glucose, rutinose sophorose, and a sugar (S_5) which was isolated by preparative PC. This sugar gave, on complete acid hydrolysis, glucose and rhamnose; mild acid hydrolysis gave sophorose and rutinose. These results are in agreement with S_5 being a trisaccharide. Methylation of S_5 with MeI/AgO in $HCONMe_2$ followed by acid hydrolysis gave 2,3,4-tri-*O*-methyl-L-rhamnose, 2,3,4,6-tetra-*O*-methyl-D-glucose and 3,4-di-*O*-methyl-D-glucose identified by TLC and PC [2]. Hence S_5 is the branched trisaccharide 2^Gglucosylrutinose. Since controlled hydrolysis (1N HCL; 10 min at 80°) of the DP1–DP2 mixture gave, in addition to the products of total hydrolysis, small amounts of gonphrenins I and II (6-*O*-β-D-glucopyranosides of betanidin and isobetanidin), the trisaccharide-aglycone linkage is β. All observations are completely consistent with DP1 being betanidin 6-(2^Gglucosylrutinoside) and DP2 being isobetanidin 6-(2^Gglycosylrutinoside).

Branched trisaccharides are relatively rare in Nature and such sugars have not previously been found in association with betacyanin pigments. As previously reported [1], the bracts of *Bougainvillea glabra* contain, besides the 6-triglycosides, two 6-sophorosides; but the 6-rutinosides, which might be expected to occur, have not been found. These results suggest, but do not prove, that in the biosynthesis of the 6-triglycosides, the 6-sophorosides are intermediates and that the final step in synthesis is transfer of rhamnose.

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BETANIN 3'-SULPHATE FROM *RIVINIA HUMILIS*

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Key Word Index—*Rivinia humilis*; Phytolaccaceae; betacyanins; betamin 3'-sulphate.

The first betacyanin sulphate, prebetanin, was reported from *Beta vulgaris* L. var. *rubra* [1]. In a previous paper on the distribution of betacyanins in the Centrospermae [2], it was reported