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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.

Acknowledgement— I thank Professor M. Piattelli (Catania, Italy) for his interest in this work.

REFERENCES

1. Piattelli, M. and Imperato, F. (1970) *Phytochemistry* **9**, 2557.
2. Minale, L., Piattelli, M., De Stefano, S. and Nicolaus R. A. (1966) *Phytochemistry* **5**, 1037.

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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

that the red fruits of *Rivinia humilis* L. contain, besides betanin and isobetanin, a red–violet pigment (rivinianin). In the present study the rivinianin has been shown to be betanin 3′-sulphate.

Rivinianin was isolated from aqueous extracts of fruits by preparative electrophoresis. Since the pigment (λ_{max} 253 541 nm; mobility relative to betanin 1·78 at pH 2·4 and 1·34 at pH 4·5) gave on complete acid hydrolysis a mixture of betanidin and isobetanidin, it is a betanidin derivative; the hydrolysate also contained glucose identified by PC (six solvents) and sulphate identified via $BaCl_2$. Alkaline hydrolysis of rivinianin in the absence of oxygen gave, besides sulfuric acid, a mixture of betanin and isobetanin identified by paper electophoresis, analytical column chromatography on polyamide and treatment with β-glucosidase which gave glucose and a mixture of betanidin and isobetanidin [3,4]. Since diazomethane methylation of rivinianin followed by alkali fusion gave 5-hydroxy-6-methoxyindole-2-carboxylic acid, it was inferred that the hydroxyl group at position 6 of the aglycone is free. In order to ascertain the position of the SO_3^- group in the glucose residue, rivinianin was treated with MeI in $HCONMe_2$ in the presence of AgO. The permethylated product on acid hydrolysis gave 2,4,6-tri-*O*-methyl-D-glucose; from this it follows that only one SO_3^- group is present in the molecule and this is linked to the hydroxyl group at position 3′ of the glucose residue.

Acknowledgement—The author thanks Prof. M. Piattelli for his interest and criticism.

REFERENCES

1. Wyler, H., Rosler, H., Mercier, M. and Dreiding, A. S. (1967) *Helv. Chim. Acta* **50**, 545.
2. Piattelli, M., and Minale, L. (1964) *Phytochemistry* **5**, 547.
3. Minale, L., Piattelli, M., De Stefano, S. and Nicolaus, R. A. (1966) *Phytochemistry* **5**, 1037.
4. Minale, L., Piattelli, M. and De Stefano, S. (1967) *Phytochemistry* **6**, 703.

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ADINA ALKALOIDS: ISOLATION AND STRUCTURE OF ANHYDROADIRUBINE

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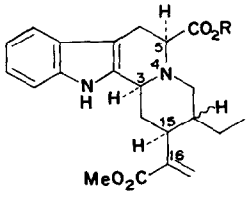
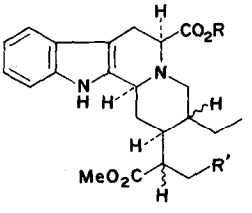
Key Word Index—*Adina rubescens*; Rubiaceae; carboxyindole alkaloid; anhydroadirubine.

The Malaysian tree *Adina rubescens* has yielded several indole alkaloids with novel structural features. In particular, a unique group containing a carboxyl function constituted the first representatives of a hitherto unknown series with standard monoterpenoid C_{10} units but derived directly from tryptophan rather than the ubiquitous tryptamine [1–3]. We now report the discovery of a second tetracyclic carboxy *Corynanthe* alkaloid —anhydroadirubine, for which structure **1a** is suggested.



(1a) R = H
(1b) R = Me



	R	R′
(2a)	H	OH
(2b)	Me	OH
(2c)	Me	OAc
(2d)	Me	H

Chromatography of a methanolic extract of the heartwood from *A. rubescens* on ion exchange resins, followed by gel permeation afforded an amino-acid concentrate. After methylation and preparative TLC a small amount of an amorphous alkaloid $C_{23}H_{28}O_4N_2$ $[\alpha]_D^{25}$ −28° was obtained. Its UV spectrum indicated an indolic chromophore, confirmed by NMR signals for four aromatic protons in the τ 2·5–3·1 region and an indolic NH at τ 2·18, with a corresponding IR band at 3480 cm^{-1}. Two IR carbonyl absorptions at 1745 and 1720 cm^{-1} and a pair of methoxyl singlets in the NMR spectrum at τ 6·20 and 6·23 suggested two methyl esters, one of which was