Phytochemistry, 1967, Vol. 6, pp. 1583 to 1584. Pergamon Press Ltd. Printed in England

SHORT COMMUNICATION

PHENOLIC COMPOUNDS OF *SMILAX GLYCYPHYLLA*

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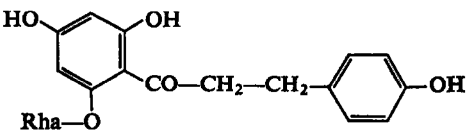
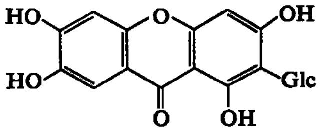
(*Received* 10 *May* 1967)

Abstract—The presence of a phloretin rhamnoside in some samples of *Smilax glycyphylla* leaf has been confirmed, and its detailed structure elucidated. Other samples of the same species are devoid of glycyphyllin but contain the xanthone mangiferin.

IN 1886 Rennie isolated glycyphyllin from the leaf of the Australian plant *Smilax glycyphylla*, and showed it to be a rhamnoside of phloretin.[1] At that time, only two other dihydrochalcone glycosides were known: phloridzin(phloretin 2′-glucoside) isolated by de Koninck[2] from root bark of the apple tree, and asebotin (4′-*O*-methyl ether of phloridzin) obtained by Eykman[3] from the leaf of *Pieris japonica*. Following the isolation of two more dihydrochalcone glycosides from the leaf of certain *Malus* species,[4] the other recorded occurrences of dihydrochalcones were checked; most were confirmed but a few found to be erroneous.[5] Samples of *S. glycyphylla* leaf gave different results according to the geographical location of the source; material from New South Wales contained glycyphyllin (I), but samples from Queensland were devoid of it, containing instead other phenolic compounds of which the major one proved to be the xanthone mangiferin[5] (II).



(I) Glycyphyllin



(II) Mangiferin

Rennie's identification of glycyphyllin as a phloretin rhamnoside has been confirmed and its detailed structure shown to be phloretin 2′-α-L-rhamnoside. Quantitative acid hydrolysis showed one molecule of phloretin to be combined with one molecule of rhamnose, while alkali breakdown of glycyphyllin gave phloretic acid and phloroglucinol rhamnoside. Comparison of the u.v. spectrum in neutral and in alkaline solution shows that it is not a 4′-glycoside; the λ_{max} shifts by 40 nm thus resembling phloretin 2′-glucoside (phloridzin) with an alkali shift of 44 nm rather than phloretin 4′-glucoside with a shift of 9 nm. Since naturally occurring

[1] E. H. RENNIE, *J. Chem. Soc.* 857 (1886).
[2] L. DE KONINCK, *Ann. Chem.* **15**, 258 (1835).
[3] J. F. EYKMAN, *Rec. Trav. Chim.* **2**, 99 (1883).
[4] A. H. WILLIAMS, *J. Chem. Soc.* 4133 (1961).
[5] A. H. WILLIAMS, *Nature* **202**, 824 (1964).

L-sugars always seem to exist in the α-configuration in higher plants, glycyphyllin would be expected to be an α-L-rhamnoside and this structure is supported by comparison of its molecular rotation, $[M]_D^{19}$ −137°, with those of α-methyl-L-rhamnoside, $[M]_D^{20}$ −112°, and β-methyl-L-rhamnoside $[M]_D^{20}$ +169°.

Mangiferin was identified by comparing its melting point, chromatographic properties and u.v. spectrum with those of authentic material.

EXPERIMENTAL

Glycyphyllin. Dried leaf (900 g) of *Smilax glycyphylla* from New South Wales was extracted three times for 24 hr at room temperature with ethanol–water (4:1), the bulked filtrate evaporated under reduced pressure and the aqueous concentrate extracted with petrol ether and then twice with *n*-butanol. The butanol extract was evaporated under reduced pressure to give a brown solid. This was crystallized several times from 40% methanol–water to give a pale yellow solid (6 g) which after drying in vacuum at 100 melted over the range 115–120°, $[\alpha]_D^{19}$ −33° (2 per cent in ethanol).

Hydrolysis with 0·5 N HCl for 2 hr at 100° gave phloretin 64·9 per cent and rhamnose 33 per cent (Phloretin rhamnoside $C_{21}H_{24}O_9$ requires phloretin 65·2 per cent, rhamnose 39·0 per cent. Phloretin was identified by its mp., 262° underpressed by authentic material m.p. 264 ; and by reaction with acetic anhydride and sodium acetate[6] to give 5,7-diacetoxy-3-(4′-acetoxybenzyl)2-methylchromone, m.p. and mixed m.p. 173 . Rhamnose was identified by paper chromatography in three solvents and by its rotation, $[\alpha]_D^{16}$ +8 (5 per cent in water). From the products of alkaline decomposition of glycyphyllin (15% w/v barium hydroxide, 6 hr at 100) phloretic acid and a rhamnoside of phloroglucinol were identified by paper chromatography in three solvents. In recording the u.v. spectra, the λ_{max} of the principal bands in 95% ethanol are given, followed by the bathochromic shift in M/500 ethanolic sodium ethoxide: glycyphyllin 287, 327, shift 40 nm; phloretin 2′-glucoside 287, 331, shift 44 nm; phloretin 4′-glucoside 283, 292, shift 9 nm. Acetylation of glycyphyllin with acetic anhydride and pyridine at room temperature (2 hr) gave the *hexa-acetate* (80% yield) m.p. 136° (from ethanol). (Found: C, 58·6; H, 5·5. $C_{33}H_{36}O_{15}$ required: C, 58·9; H, 5·4%.)

Mangiferin. Dried leaf of *S. glycyphylla* from Queensland was extracted as for glycyphyllin. Paper chromatography showed the presence of several phenolic compounds, but no glycyphyllin. About 50 mg of the major compound, which showed the distinctive u.v. fluorescence of mangiferin, was isolated by chromatography on thick paper; m.p. 266–268 , literature value 268–270°.[7] The u.v. spectrum was very distinctive showing peaks at 242, 258, 315, 365 nm. The shifts obtained by addition of the recognized reagents (acetate, acetate-borate, ethoxide, aluminium) agreed closely with those published.[8]

Acknowledgements—Thanks are due to Dr. W. Bottomley and Mr. W. E. Hillis for their help in obtaining samples of *Smilax* from known localities in Australia.

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[6] F. E. KING and A. ROBERTSON, *J. Chem. Soc.* 1704 (1931).

[7] E. C. BATE-SMITH and J. B. HARBORNE, *Nature* **198**, 1307 (1963).

[8] J. B. HARBORNE, *Methods in Polyphenol Chemistry*, p. 29. Pergamon Press, Oxford (1964).