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SHORT COMMUNICATION

PINOCEMBRIN 7-β-NEOHESPERIDOSIDE, A FLAVANONE GLYCOSIDE FROM *SPARATTOSPERMA VERNICOSUM*

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Abstract—A glycoside isolated from the fruit of *Sparattosperma vernicosum* was shown to be pinocembrin 7-β-neohesperidoside (I). The natural occurrence of this bitter compound has not previously been reported.

INTRODUCTION

WE ARE examining the chemical constituents of various members of the Brazilian Bignoniaceae. *Sparattosperma vernicosum* is reputed to receive some use in the treatment of skin diseases. This paper reports the isolation and identification of a major constituent of the fruit of this plant.

RESULTS AND DISCUSSION

An ethanolic extract of the fruits of *Sparattosperma vernicosum* was partially decolorized with activated charcoal and subsequently purified by chromatography on silica gel. A colourless crystalline compound, $C_{27}H_{32}O_{13}$ m.p. 277–280°, with the u.v. spectrum of a flavanone, was obtained. Acid hydrolysis yielded equimolar amounts of pinocembrin, L-rhamnose and D-glucose. Examination of the NMR spectrum of the hexatrimethylsilyl derivative confirmed that the compound had structure I. The flavanone B-ring protons appear at τ 2·62 (5H, singlet) and those attached to C-8 and C-6 at 3·77 (2H, doublet of doublets, $J=2{\cdot}2$ c/s). A phenolic hydroxyl proton at τ 1·88 is characteristic[1] in its chemical shift and sharpness of a C-5 hydroxyl proton which is hydrogen bonded to the C-4 carbonyl. This is supported by the u.v. data.[2, 3]

The compound is thus a 7-rhamnosyl-glucoside of pinocembrin and the configuration of the disaccharide and stereochemistry of its attachment are also established by the NMR spectrum. Naturally occurring rhamnosyl-glucosides are reported to have an α-L-rhamnose moiety in which the rhamnose C-1 proton has an equatorial–equatorial coupling, giving rise to a doublet with $J=2$ c/s. Furthermore, the spectra of trimethylsilylated rutinosides and neohesperidosides (6- and 2-*O*-α-L-rhamnopyranosyl-D-glucopyranose respectively) are characteristically different in the positions of the signals of the rhamnose C-1 proton.[1] In

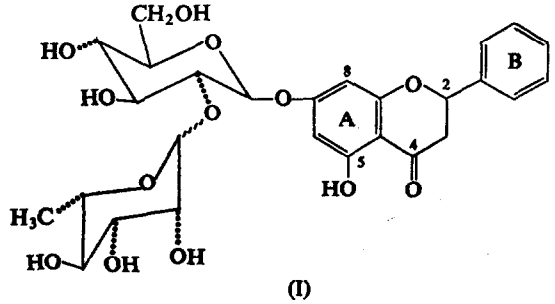
[1] T. J. MABRY, J. KAGAN and H. ROSLER, *Nuclear Magnetic Resonance of Flavonoids*, University of Texas Publication 6418 (1964).

[2] H. L. HERGERT and O. GOLDSCHMID, *J. Org. Chem.* 23, 700 (1958).

[3] *The Chemistry of Flavonoid Compounds* (edited by T. A. GEISSMAN), pp. 151–153, MacMillan, New York (1962).

the former it appears at τ 5·65–5·75 and in the latter at about τ 5·15. In our case, the compound shows a doublet (J=2 c/s) at τ 5·05, indicative of a neohesperidose most probably with equatorial–equatorial coupling at the C-1 position of rhamnose. This latter assignment must be made with some caution since the alternative, equatorial–axial coupling is also expected to be small. The rhamnose methyl signal (3H, doublet, J=7 c/s) at τ 8·76 confirms the neohesperidose moiety, since this signal commonly appears as a doublet at τ 8·8 in neohesperidosides and as a broad singlet at τ 9·05–9·2 in rutinosides. The glucose C-1 proton at τ 4·96 is a doublet with J=6·3 c/s, indicative of an axial–axial coupling, so that glucose must form a β-linkage to C-7.

The above evidence establishes the isolated compound as pinocembrin-7-β-neohesperidoside (I). To the best of our knowledge this substance has not been previously reported.



(I)

EXPERIMENTAL

Isolation of Pinocembrin 7-β-Neohesperidoside

Dried whole fruits of *Sparattosperma vernicosum* were crushed and extracted with hot ethanol. A portion (20 g) of the crude gum obtained was refluxed with Norite (0·5 g) in methanol (100 ml) for 30 min and the solution filtered and evaporated. The residue was chromatographed on silica gel (Woelm, 1 kg) by gradient elution using $CHCl_3$–MeOH (5–30%) mixtures. Fractions were examined by TLC and those containing the desired compound combined to yield a yellow gum (5·2 g) which was further purified by preparative TLC (silica gel, 0·5 mm, developed twice in $CHCl_3$–MeOH, 3:1) to yield a colourless solid, m.p. 277–280° (ethanol), λ_{max}^{EtOH} 286 nm (log ϵ 4·24), 330 (log ϵ 3·51), $[\alpha]_D$ − 110° (*ca.* 0·41, pyridine). Found: C, 57·14; H, 5·37. $C_{27}H_{32}O_{13}$ required: C, 57·45; H, 5·67%.

Hydrolysis of Pinocembrin 7-β-Neohesperidoside

Pinocembrin 7-β-neohesperidoside (3 g) was refluxed with H_2SO_4 (100 ml) for 6 hr. The solution was filtered and the residue and filtrate extracted with ether and EtOAc. The combined extracts yielded pinocembrin (1·21 g), m.p. 193–194° (ethanol), which sublimed giving colourless plates, m.p. 194–195°. Found: C, 70·22; H, 4·70. $C_{15}H_{12}O_4$ required: C, 70·30; H, 4·72%. No depression in m.p. resulted on admixture of authentic pinocembrin, and the u.v. and i.r. spectra of the isolated and authentic materials were superimposable.

The filtrate from hydrolysis was then neutralized with $BaCO_3$, filtered and passed successively through columns of Amberlite IR 120 and Duolite A4 ion-exchange resins. The resulting aqueous solution was evaporated to yield a mixture of sugars (1·70 g). A portion (0·72 g) was separated by TLC (silica gel, Me_2CO–EtOAc, 2:1, developed twice) giving D-glucose (251 mg) which crystallized from water as the monohydrate, $C_{16}H_{12}O_6 . H_2O$, m.p. 81–33°, $[\alpha]_D$ + 49° (*c.* 1·0, water, final value) and L-rhamnose (240 mg) which crystallized from water as the monohydrate $C_{16}H_{12}O_5 . H_2O$, m.p. 79–83°, sublimes 105° (2 mm Hg), $[\alpha]_D$ + 7° (*c.* 1·4, water, final value). In each case these sugars were identical in R_f and showed no depression in m.p. on admixture with the corresponding authentic material.

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