DIOSCIN AND GRACILLIN FROM TAMUS COMMUNIS

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In our investigation of the chemical composition of Dioscoreaceae (1-3), we report here the isolation of two known spirostane triglycosides, dioscin and gracillin (4), from the rhizomes of *Tamus communis* L. While gracillin was never isolated from *T. communis*, dioscin was isolated, previously only by enzymatic hydrolysis of a more complex saponin (5), and identified by paper chromatography. In studies currently in progress (6), we have not found more complex saponins with diosgenin as the aglycone.

EXPERIMENTAL

PLANT MATERIALS.—The rhizomes of *T. communis* were collected at Agerola (Naples) in September. Voucher specimens of the plants are deposited in the Herbarium at Naples University, Faculty of Pharmacy.

EXTRACTION AND ISOLATION.—Lyophilized rhizomes of T. communis (750 g) were extracted in a Soxhlet apparatus with light petroleum (bp 40-70°), CHCl₃, CHCl₃-MeOH (9:1), and then with MeOH.

The residue from the CHCl₃-MeOH extract (14 g) was chromatographed on a Si-gel column (CHCl₃ and CHCl₃-MeOH in varying proportions) and rechromatographed on a Sephadex LH-20 column (MeOH) to give 90 mg of a mixture of dioscin and gracillin. The mixture of two triglycosides was separated by preparative hplc (μ -bondapack C-18 column, 30 cm×7.8 mm id, H₂O-MeOH 25:75) to afford 24.5 mg of dioscin and 10 mg of gracillin.

STRUCTURAL ELUCIDATION.—Dioscin and gracillin were identified as diosgenin-*bis*- α -L-rhamnopyranosyl-(1 \mapsto 2 and 1 \mapsto 4)- β -D-glucopyranoside and as diosgenin- α -L-rhamnopyranosyl-(1 \mapsto 2)- β -Dglucopyranosyl-(1 \mapsto 3)- β -D-glucopyranoside, respectively, by spectral (¹H and ¹³C nmr, fabms) and chemical data (methanolysis and glc analysis of the persilylated methyl glycosides of the sugars).

The exact position of the linkages of terminal sugar units in gracillin was clarified by partial acid hydrolysis followed by permethylation and methanolysis of the resulting glycosides. The permethylated derivatives were gas-chromatographed in comparison with authentic standards.

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Received 15 October 1984

THE FLAVONOIDS OF STEVIA MICROCHAETA, STEVIA MONARDIFOLIA, AND STEVIA ORIGANOIDES

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In our continuing chemical studies of *Stevia* species (Compositae, Eupatorieae) (1,2), we report the isolable flavonoids from three North and Central American species namely, *Stevia microchaeta* Sch. Bip., *Stevia monardifolia* H.B.K., and *Stevia origanoides* H.B.K. All the flavonoids recorded have been isolated

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