STUDIES ON NIGERIAN MEDICINAL PLANTS: COMPONENTS OF THE STEMS OF *MYRIANTHUS ARBOREUS*

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Myrianthus arboreus P. Beauv (Urticaceae) is a medicinal plant widespread in tropical West Africa (1). The stems were shown to possess hypoglycemic properties (2), while the leaves possessed antitussive properties (3). However, the components responsible for these activities have not been isolated. Triterpene acids were isolated from the rootwood of this plant (4, 5).

This work deals with the isolation and identification of β-sitosterol, sitosterol 3-*O*-β-D-glucopyranoside, ursolic acid, tormentic acid, euscaphic acid, myrianthic acid, and 2α, 3α, 19α, 23-tetrahydroxyurs-12-en-28-oic acid, for the first time, from the stem of *M. arboreus*. The triterpene acids were isolated as their methyl esters. This is also the first report of the occurrence in the family Urticaceae of 2α, 3α, 19α, 23-tetrahydroxyurs-12-en-28-oic acid (6). Myrianthic acid was also previously found in *Rhododendron japonicum* (7).

EXPERIMENTAL

PLANT MATERIAL.—The stems of *M. arboreus* were collected from Elele-Alimini near Port Harcourt, Nigeria, in March 1984. Voucher specimens are deposited in the Herbarium of the Faculty of Science, University of Port Harcourt, Nigeria.

EXTRACTION AND IDENTIFICATION.—The air-dried, crushed stems (1.4 kg) were successively extracted by soaking in hexane, $CHCl_3$, and EtOH. The solvent was removed in vacuo (40°) to afford crude extracts from hexane (4 g), $CHCl_3$ (6.5 g), and EtOH (10 g). The hexane extract (3 g) was chromatographed on a silica gel column to afford β-sitosterol (50 mg), mp 133-134°. The spectral data were identical to those reported [^{1}H (8) and ^{13}C nmr (9)]. The $CHCl_3$ extract (4 g) was dissolved in aqueous MeOH. The filtrate was acidified with dilute HCl, and the precipitated solid was extracted with 11% *n*-BuOH in $CHCl_3$. Removal of solvent in vacuo gave a solid (3.3 g) which was methylated with ethereal CH_2N_2 and then chromatographed on a column of silica gel to get methyl ursolate (identified by comparison with an authentic sample), methyl tormentate (4) and methyl euscaphate (4). The triterpene acids were identified by their mp, ir, ^{1}H nmr, and tlc.

Further chromatography of a part of the eluate on silica gel gave sitosterol 3-*O*-β-D-glucopyranoside [35 mg, identified by hydrolytic data, ^{1}H and ^{13}C nmr (10)], methyl myrianthate (5,7), and methyl 2α, 3α, 19α, 23-tetrahydroxyurs-12-en-28-oate identified from its ir, ^{1}H and ^{13}C nmr, and ms data (6). The ^{13}C nmr ($CDCl_3$ at 30°) had signals at δ 178.59 (s, C-28), 138.48 (s, C-13), 129.02 (d, C-12), 78.76 (d, C-3), 73.33 (s, C-19), 71.44 (t, C-23), 66.72 (d, C-2), 53.48 (d, C-18), 51.70 (q, OMe), 48.10 (s, C-17), 47.16 (d, C-9), 42.36 (d, C-5), 41.67 (t, C-1), 41.52 (d, C-20), 41.36 (s, C-14), 41.36 (s, C-4), 40.26 (s, C-8), 38.13 (s, C-10), 37.60 (t, C-22), 32.47 (t, C-7), 28.38 (t, C-15), 27.62 (q, C-29), 26.21 (t, C-21), 25.68 (t, C-16), 24.86 (t, C-27), 23.88 (t, C-11), 18.11 (t, C-6), 17.60 (q, C-25), 16.91 (q, C-26), 16.78 (q, C-24), 16.29 (q, C-30). Methyl 2α, 3α, 19α, 23-tetrahydroxyurs-12-en-28-oate was acetylated (pyridine-Ac_2O, 1:1) at room temperature to give a triacetate, mp 207-209°, identified as methyl 2α, 3α, 23-triacetoxy, 19α-hydroxyurs-12-en-28-oate from its ir, ms, and ^{1}H nmr data (6,7).

Full details of the isolation and spectral identification of the compounds are available on request to the authors.

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ISOLATION OF PETASITENINE, A CARCINOGENIC PYRROLIZIDINE ALKALOID FROM *FARFUGIUM JAPONICUM*

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Farfugium japonicum Kitam. (Compositae) is used in Japan as a medicinal herb and foodstuff, and the carcinogenic activity of this plant has recently been reported (1). Isolation of two alkaloids, senkirkine (2) and farfugine (3), from this plant was previously reported. As part of our continuing studies on carcinogenic compounds in the edible plants, we describe here the isolation of petasitenine, a carcinogenic pyrrolizidine alkaloid from *F. japonicum*. Petasitenine was previously isolated from *Petasites japonicus* Maxim. (4,5) and proved to be the carcinogenic principle of this plant (6). The result of the present study provides the first example of the isolation of petasitenine from a plant other than *P. japonicus*.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded on the following instruments: ir, JASCO Model IRS; ^{1}H nmr, JEOL JNM-FX90QE; ms, Hitachi RMU-6C. Optical rotation was measured with a JASCO DIP-181 digital polarimeter. Adsorbents for cc and preparative tlc were Aluminiumoxid 90 (Activity II-III) and Alumina 150 F_{254} Type T obtained from E. Merck.

PLANT MATERIAL.—Plants of *F. japonicum* were collected in Nagoya, Japan in June 1980 and were identified by a botanist, H. Wakita. A voucher specimen (no. HN-FJK-1) is deposited at the Herbarium of the Laboratory of Organic Chemistry, Faculty of Science, Nagoya University.

EXTRACTION AND ISOLATION OF PETASITENINE.—The dried and pulverized plant materials (400 g) were extracted with EtOH (4 liters) for 20 days at room temperature. The EtOH extracts, after concentration, gave a residue, which was diluted with H_2O (50 ml). The mixture was acidified (pH 2) with 0.5M H_2SO_4 and extracted with Et_2O (4×200 ml). The aqueous phase was made basic (pH 10) with NH_4OH and extracted with $CHCl_3$ (4×300 ml). Concentration of the $CHCl_3$ extracts gave an alkaloidal mixture (147 mg), which was chromatographed on alumina (10 g) with $CHCl_3$-MeOH (100:1) to afford a fraction (80 mg) containing petasitenine and senkirkine. Further separation and purification by preparative tlc on alumina with $CHCl_3$-MeOH (100:1) gave petasitenine (5.4 mg, 0.001%), mp 127-128°, $[\alpha]^{23}D$ +51° (c=1.00, EtOH) and senkirkine (23.9 mg, 0.006%). Identification of petasitenine and senkirkine was performed by comparison of the spectral (ir, ^{1}H nmr, and ms) data with those of the authentic specimens, respectively.

Full details of the isolaton and identification of petasitenine are available on request to the senior author.

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