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EDPETINOSINE — A NEW ALKALOID FROM *Petilium eduardi* BULBS

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A new glycoalkaloid, edpetinosine, has been isolated from Petilium eduardi *bulbs, and its structure has been established on the basis of chemical transformations and spectral characteristics.*

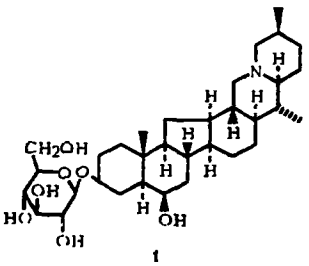
Continuing a study of the alkaloids of *Petilium eduardi* (Regel) VVed. [1], we have isolated from the bulbs, in addition to the alkaloids peimisine and edpetiline obtained previously [1, 2], the new alkaloid edpetinosine (**1**) with mp 174-176°C, composition $C_{33}H_{55}NO_7$.

The IR spectrum of (**1**) (KBr, ν, cm^{-1}) contained absorption bands at 3335 (OH), 2870-2925 ($-CH_2$, $-CH_3$), and 1024-1160 (C−O of the sugar moiety).

In the mass spectrum the main peaks were those of ions with m/z (I_{rel}, %): 98 (30), 111 (100), 112 (76), 124 (8), 125 (6), 138 (6), 139 (8), 149 (4), 150 (4), 162 (2), 164 (10), 179 (4), 272 (4), 328 (6), 358 (4), 380 (10), 386 (6), 398 (46), 415 (18), 521 (12), 548 (14), 559 (8), 562 (20), 577 (M^+, 84), which are characteristic for the *C*-nor, *D*-homosteroid alkaloids edpetilidine (**2**) and eduardinine [3, 4].

The PMR spectrum of (**1**) (100 MHz, $CDCl_3$ + CD_3OD, δ, ppm, J, Hz) showed signals of protons at 0.69 (3H, d, CH_3-21), 0.95 (3H, s, CH_3-19), 1.03 (3H, d, CH_3-27), 4.36 (1H, d, J = 6.7), and 3.32 and 3.74 (4H, m, gem-protons).

The acetylation of (**1**) formed a pentaacetyl derivative (**3**) the PMR spectrum of which showed signals from five acetoxy groups at 1.97-2.03 ppm.



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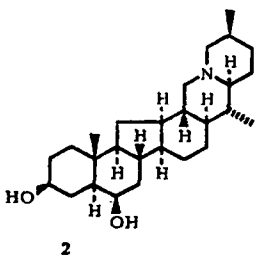

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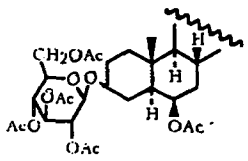

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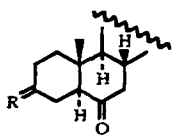

4. R = 

5. R=O

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The acid hydrolysis of (1) gave an aglycon identical with edpetilidine (2) [5, 6]. After the separation of the aglycon from the hydrolysate, *D*-glucose was detected in the carbohydrate moiety by paper chromatography (PC). In addition to this, oxidation of the aglycon with chromium trioxide led to a monoketone identical with eduardine (4) [5, 6] and a diketone identical with a diketone, edpetilidone (5) [4], obtained from edpetilidine (2).

On the basis of the facts given above, edpetinosine is a glycoalkaloid of edpetilidine. It was established by GLC that (1) contained one *D*-glucose residue [7]. The *D*-glucose residue could be located at C-3 or C-6 in the edpetinosine molecule. In the PMR spectrum of (3) the resonance signals of the geminal and acetyl groups of protons of the sugar and aglycon moieties were observed in a weaker field at 4.95 and 5.12 ppm. This showed that one of the acetyl residues was present at C-6 in edpetinosine pentaacetate. Consequently, the *D*-glucose residue in (1) was located at C-3.

The SSCC of the anomeric proton, which resonated in the form of a doublet at 4.53 ppm with ^3J = 6.5 Hz, showed the C1 conformation and a β-glycosidic bond of the *D*-glucopyranoside residue in edpetinosine.

Thus, edpetinosine has the structure of edpetilidine 3β-*D*-glucopyranoside.

EXPERIMENTAL

IR spectra were obtained on a Perkin-Elmer model 2000 Fourier IR spectrometer; ^1H NMR spectra on a Tesla BS 567 A instrument at 100 MHz ($CDCl_3$; internal standard HMDS, δ); and mass spectra on an MKh-1310 instrument at an ionizing energy of 60-70 eV, 100-170°C.

For column and thin-layer chromatographies we used type KSK silica gel (125-250 μm and 50 μm, respectively) with the solvent systems chloroform–methanol (5:1) (1) and (95:5) (2).

For detecting the sugar we performed PC on FN-11 paper in the *n*-butanol–pyridine–water (6:4:3) system, with the revealing agent acid aniline phthalate.

The GLC of the monosaccharide in the form of aldononitrile acetates [7] was conducted on a Chrom-5 chromatograph with a flame-ionization detector, steel column (0.3 × 200 cm) filled with 5% of Silicone XE-60 on Chromaton N-AW-DMCS (0.200-0.250 mm), column temperature 210°C, carrier gas helium at 60 ml/min.

Isolation of Edpetinosine and Edpetiline. A solution of 61.44 g of the total alkaloids of the bulbs of the plant in 600 ml of chloroform was extracted with 50-ml portions of 0.1% sulfuric acid. Then the aqueous acid solutions obtained were separately made alkaline with ammonia and extracted with chloroform. Five fractions were obtained. The combined fractions 1-3 and combined fractions 4 and 5 were each separated on a column of silica gel with elution by system 2 and the collection of the eluate in amounts of 10-15 ml. The combined fractions 1-3 gave 15 eluates, and fractions 4 and 5 gave 20 eluates. From the initial eluates 4-7 of fractions 1-3 we isolated edpetiline (0.05 g) with mp 260-265°C, and from eluates 9-12 edpetinosine (0.35 g) with mp 174-176°C (acetone–methanol), R_f 0.17 in system 1. The combined eluates 4-6 from fractions 4 and 5 yielded peimisine with mp 230-232°C (from acetone), R_f 0.64 in system 1.

The known alkaloids were identified by direct comparison with authentic specimens.

Edpetinosine Pentaacetate (3). Edpetinosine (1) (0.2 g) was acetylated with 5 ml of acetic anhydride in 4 ml of pyridine at room temperature for 48 h. After elimination of the solvent in vacuum, the residue was treated with ammoniacal chloroform. The chloroform was distilled off, and the residue was treated with a mixture of methanol and acetone. This gave the pentaacetate with mp 217-220°C, R_f 0.70 in system 1, M^+ 787 (MS).

IR spectrum (KBr, ν, cm^{-1}): 2851-2928 ($-CH_2$, $-CH_3$), 1754, 1737, 1251, 1232 (ester grouping).

The PMR spectrum of (3) contained the signals of protons at (ppm) 0.71 (3H, d, CH_3-21, J = 6.5 Hz), 0.92 (3H, s, CH_3-19), 1.02 (3H, d, CH_3-27, J = 7 Hz), 1.97, 1.99, 2.03 (15H, s, $OCOCH_3$), of a gem-proton at 4.14 (CH-5 of the sugar residue), of an anomeric proton at 4.53 (1H, d, ^3J = 6.5 Hz), and gem-protons to acetyl groups at 4.95 and 5.12 (6H, m, $CH-OCOCH_3$).

Hydrolysis of Edpetinosine (1). A solution of 0.1 g of edpetinosine in 10 ml of ethyl alcohol was treated with 10 ml of 10% hydrochloric acid, and the mixture was heated for 5 h. Then the ethanol was distilled off in vacuum, and the residue was made alkaline with ammonia and extracted with chloroform. After the chloroform had been distilled off, the residue was treated with acetone, giving an aglycon with mp 210-212°C (acetone), identical with edpetilidine (2), R_f 0.35 in system 1.

After the removal of the aglycon from the alkaline solution, *D*-glucose was determined by PC and GLC.

Oxidation of the Aglycon. A solution of 0.1 g of the aglycon in 5 ml of acetic acid was treated with 2 ml of a 0.3% solution of chromium trioxide in aqueous acetic acid, and the reaction mixture was heated at 70-80°C for 30 min. Then it was evaporated in vacuum to an oily consistency and the precipitate was dissolved in water acidified with 5% sulfuric acid. The acid solution was made alkaline with ammonia and was extracted with chloroform. The residue from the distillation of the chloroform was treated with acetone. This gave eduardine (**4**) and edpetilidone (**5**), respectively, with R_f 0.58 and 0.42 in system 1.

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