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IMPERIAZINE, A NEW ALKALOID FROM *Petilium eduardi*

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The new C-nor-D-homosteroidal alkaloid imperiazine was isolated from the bulbous plant Petilium eduardi *Rgl. (Liliaceae). The structure was established using spectral data.*

Key words: *Petilium eduardi*, alkaloid, IR, mass and PMR spectra.

We isolated imperialine (**1**) [1-3] and the new alkaloid imperiazine (**2**), $C_{27}H_{43}NO_3$, mp 214-216°C from the aerial part of *Petilium eduardi* Rgl. collected in Babatag of Surkhandar′ya district during a study of alkaloids from plants of the *Petilium* (Liliaceae) genus [1].

Imperiazine (**2**) is a saturated tertiary base. The IR spectrum (KBr, ν, cm^{-1}) contains absorption bands at 3502 (OH), 2870-2943 ($–CH_2–$ and $–CH_3$), 2787 (*trans*-quinolizidine), 1703 (C=O). The fingerprint region of **2** (<1500 cm^{-1}) is similar to that of the C-nor-D-homosteroid alkaloid **1** [3-5].

The mass spectrum of **2** has principal peaks for ions with *m/z* $[M]^+$ 429, 412 $[M - 17]^+$, 386, 384, 372, 358, 316, 289, 260, 236, 204, 180, 164, 162, 156, 155, 154, 152, 150, 140, 125, 124, 112 (100%), 111, and 98, which are characteristic of the mass spectrometric decomposition of imperialine [6].

The PMR spectrum of **2** has signals for protons of two tertiary and one secondary methyl and a multiplet for a proton geminal to a hydroxyl, like for **1** [2, 5]. However, the chemical shifts of the 27-CH_3 protons are at stronger field by 0.21 ppm compared with **1**. Other signals for methyls and the proton geminal to the hydroxyl are identical to **1** (Table 1).

The *trans*-quinolizidine band in the IR spectrum of **2** indicates that the ring is E and F *trans*-fused [7]. A comparison of the chemical shifts for the 19-CH_3 and 21-CH_3 protons of imperiazine and those for **1** [2, 5] indicates that rings A/B and B/C are *trans*-fused whereas C/D and D/E are *cis*-fused, like for imperialine [3]. The secondary hydroxyl is located on C-3; the carbonyl, on C-6. The presence in the mass spectrum of **2** of peaks for ions with *m/z* 156, 155, and 154, which are formed by cleavage of the C-13–C-18 and C-17–C-20 bonds of ring E, and the appearance of a signal for the 21-CH_3 protons as a singlet and its chemical shift indicate that the tertiary hydroxyl is located on C-20 and has the β-axial orientation [6, 8].

Comparison of the half-width $W_{1/2}$ of signals for the geminal hydroxyl and the chemical shifts of the 19-CH_3 with those for isoverticine, imperialine, and petine prove that the secondary hydroxyl is located on C-3 and has the β-equatorial orientation. The chemical shifts indicate that the 21-CH_3 and 27-CH_3 have the α-equatorial orientation [5, 9-11].

The elemental composition, number of functional groups, and heterocyclic skeleton of imperiazine are identical to those of **1** [3, 4]. These alkaloids differ in melting point, R_f, and orientation of the C-27 methyl.

Therefore, the data indicate that **2** is a C-nor-D-homosteroid alkaloid of the imperialine group and has the structure and configuration 3β,20β-dihydroxy-19β,21α,27α-trimethylcevaninone-6.

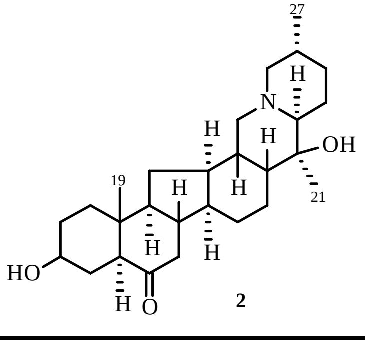

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TABLE 1. Proton Chemical Shifts ($CDCl_3$, δ, ppm) and Spin—Spin Coupling Constants (J/Hz)

Compound	$19\text{-}CH_3$ s	$21\text{-}CH_3$ s	$27\text{-}CH_3$ d	3-H m
(**2**)	0.68	1.01	0.77 (J=7)	3.51 ($W_{1/2}$=24)
(**1**)	0.67	0.99	0.98 (J=7)	3.45 ($W_{1/2}$=24)

EXPERIMENTAL

Silica gel (KSK) and $CHCl_3$—C_2H_5OH—NH_4OH (25:1:0.2) were used for column (125-250 μm) and thin-layer (50-80 μm) chromatography.

IR spectra were recorded on a Perkin—Elmer System 2000 Fourier-IR spectrometer; PMR, on a Tesla BS-567A instrument at working frequency 100 MHz (in $CDCl_3$, HMDS internal standard, δ); mass spectra, in a Kratos MS 25RF mass spectrometer.

Imperialine (1) and Imperiazine (2). Treatment of the total alkaloids (50 g) with ether precipitates crystals of crude imperialine. Crude **1** was purified by recrystallization from methanol. The resulting methanol mother liquor was condensed to a small volume and dried. The solid was dissolved in $CHCl_3$ and separated on a silica-gel column with elution by $CHCl_3$ and then a $CHCl_3$—C_2H_5OH—NH_4OH (25:1:0.2) mixture. Thus, we also isolated from the initial fractions **1**, mp 263-265°C (methanol), R_f 0.45; and from the next fractions, crude **2**, which was purified by chromatography over a silica-gel column with elution by $CHCl_3$—C_2H_5OH (10:1). The eluate was dried. The solid was treated with acetone to precipitate crystals of pure **2**, mp 214-216°C, R_f 0.37, 0.1 g.

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