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STRUCTURE OF EDPETISIDININE

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We have previously reported the isolation from *Petilium eduardi* (Rgl.) Vved. of a base with mp 263-265°C (methanol) $[\alpha]_D$ −15.3° (c 0.39; methanol—chloroform (9:1)) [1], composition $C_{27}H_{43}NO_3$ (I). The alkaloid is new and we have called it edpetisidinine. IR spectrum of (I), ν_{max}, cm^{-1}: 3300 (OH), 2770 (trans-quinolizidine) [2], 1670 $(\rangle C{=}C\langle)$. The acetylation of (I) with acetic anhydride in pyridine gave a triacetyl derivative (I), M^+ 555. IR spectrum of (II), ν_{max}, cm^{-1}: 1745, 1255 (ester C=O). The oxidation of (I) with chromium trioxide gave edpetisidininedione (III), with mp 216-218°C (benzene—petroleum ether), M^+ 425. It was impossible to obtain a triketone derivative of edpetisidinine. An acid solution of (I) instantaneously decolorized a solution of potassium permanganate. However, it was impossible to reduce edpetisidinine by the Adams method under various conditions.

The mass spectrum of (I) had the peaks of ions with m/e 98, 111, 112, 123, 124, 125, 149, 164, 178, 373, 400, 414 $(M-15)^+$, and 429 M^+ (100%), which are characteristic for the decomposition of the C-nor,D-homosteroid alkaloids of the cevine group [3-5].

The NMR spectrum of (I) showed the signals from one tertiary methyl group at 0.90 ppm (19-CH_3) and from two secondary methyl groups at 0.87 and 0.79 ppm (21-CH_3, 27-CH_3) (in CD_3OD + $CDCl_3$). The difficulty in the reduction of the double bond and the absence of the signal of an olefinic proton in the NMR spectrum of edpetisidinine show that the double bond in the molecule of (I) is tetrasubstituted. The NMR spectrum of (II) contained singlets at 0.90 ppm (19-CH_3) and 1.95, 1.98, and 2.0 ppm (9 H, $OCOCH_3$), doublets from secondary methyl groups at 0.86 and 0.79 ppm, and multiplets from protons geminal to acetoxy groups at 5.07 ppm (2 H, $\underline{H}C{-}OCOCH_3$) and 4.78 ppm (1 H, $\underline{H}C{-}OCOCH_3$) ($CDCl_3$).

Judging from the facts given above, (I) has the heterocyclic skeleton of cevanine and contains three secondary hydroxy groups and one doublet bond.

A comparison of the chemical shifts (CSs) of the protons of the 19-CH_3 group in the NMR spectra of (I) and (II) with those of edpetisinine, triacetyledpetisinine [1], and diacetylkorseveriline [6] showed that two of the OH groups in (I) were present at C_3 and C_6, while positions of the double bonds between C_8 and C_9 and between C_8 and C_{14} and of the third OH group at C_1 and C_{11} were excluded. Edpetisidinine is not oxidized by periodic acid. This means that the third OH group cannot be located at C_2, C_4, or C_7. In the mass spectrum of (I), the peaks of ions with m/e 111, 112, 164, and 178, which are formed by a known pathway [3, 5, 8], exclude the possibility that the OH group and the double bond are located on the carbon atoms of rings E/F. The impossibility of obtaining a triketone by the oxidation of (I) and the presence in the mass spectrum of (I) of the peaks of an ion with m/e 178 [6] show that the third OH group is located at C_{15}.

The close values of the CSs of the protons of the 19-CH_3 group in the NMR spectra of edpetisidinine and edpetisinine [1] show that the double bond is probably between C_{12} and C_{13}, since the presence of a double bond in this position in the C-nor,D-homosteroid alkaloids does not affect the CSs of the protons of the 19-CH_3 group [7]. According to the CSs of the protons of the 19-CH_3 group in the NMR spectrum of (I), rings A/B and B/C are trans-

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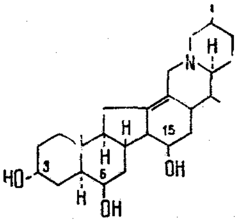
linked [1, 6], and the CSs of the 21-CH_3 and 27-CH_3 groups show that they have the α-equatorial orientation [8].

In the NMR spectrum of (II), the protons geminal to the acetoxy groups resonate in a weaker field. Consequently, the hydroxy group at C_3 has the α-axial orientation and that at C_6 the β-axial orientation [9, 10].

Thus, the facts given permit us to put forward for edpetisidinine the most probable stru-ture and partial configuration of 3α,6β,15-trihydroxycevan-12-ene (I).



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UNGVEDINE — A NEW ALKALOID FROM *Ungernia vvedenskyi*

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Continuing a study of the alkaloid composition of various organs of the plant *Ungernia vvedenskyi* S. Khamidh., family Amaryllidaceae [1, 2], we have investigated the flowers with peduncles collected in August 1976 in the Chimkent oblast of KazSSR. Chloroform extraction yielded 0.36% of combined alkaloids, which were separated on a column of silica gel. A benzene—methanol (99:1) eluate yielded a new base (0.024% of the weight of the dry plant) with mp 148-150°C, $[\alpha]_D$ +12.5° (c 0.528; chloroform), with the composition $C_{19}H_{25}NO_5$, which we have called ungvedine (I). The subsequent eluates gave tazettine and lycorine.

The UV spectrum of (I) showed absorption maxima at 206, 235 (inflection) and 295 nm (log ε 4.50, 3.66, 3.62).

The IR spectrum showed absorption bands characteristic for a benzene ring with a methylenedioxy group (1255, 1035, 935 cm^{-1}) [3, 4].

The mass spectrum had the peaks of ions with m/e 70, 71, 104, 115, 159, 181, 201, 229, 231, 247, 260, 298, 316, 332, and M^+ 347, which are characteristic for alkaloids of the tazettine type [5].

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