

STRUCTURE OF EDPETISININE

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We have previously reported the isolation of crystals with mp 253-257°C from *Petilium eduardi* [1]. A further investigation showed that they consisted of bases with mp 247-248°C (methanol) [α]_D -45.63° (c 0.71; (methanol), composition C₂₇H₄₅NO₃ (I), and with mp 263-265°C. Alkaloid (I) is new and we have called it edpetisinine.

IR spectra of (I); λ_{\max} 3420 cm⁻¹ (OH), 2770 cm⁻¹ (trans-quinolizidine). We prepared the triacetate of (I) with mp 199-201°C (II), M⁺ 557, λ_{\max} 1745, 1250 cm⁻¹ (O-acetyl). Oxidation of (I) with chromium trioxide formed the diketone etpetisininedione with mp 200-202°C (III), M⁺ 427, and two isomeric monoketones with mp 154-156°C (IV), M⁺ 429, and mp 204-206°C (V), M⁺ 429. An attempt to prepare a triketone from (I) was unsuccessful, since the molecule underwent far-reaching changes.

The IR spectra of (III)-(V) showed absorption bands of an OH group and of a C = O in a six-membered ring. The UV spectrum of (V) [λ_{\max} 305 (log ϵ 1.63)] was similar to that of imperialine [1].

The mass spectrum of (I) contained the peaks of ions with m/e 98, 111 (100%), 112, 124, 125, 138, 139, 149, 150, 164, 178, 179, 218, 258, 260, 361, 375, (M-29)⁺, (M-18)⁺, (M-15)⁺, 431 M⁺, which are characteristic for the C-nor-D-homosteroid alkaloids Korseveriline and korseveridine [2, 3]. Consequently, (I) contains a cevanine skeleton [4], and the three oxygen atoms are present in the form of secondary OH groups. Details of the NMR spectra of (I)-(III) are given in Table 1 (compound (I) in a mixture of CDCl₃ and CD₃OD, and (II) and (III) in CDCl₃; JNM-4H-100/100 MHz, HMDS). The values of the chemical shifts (CSs) from the 19-CH₃ and 21-CH₃ groups in the NMR spectra of (I)-(III) show that the linkages of rings A/B, B/C, and D/E are trans and of C/D cis, just as for imperialine and for korseveriline [2, 5]. The presence of a Bohlmann band in the IR spectrum of (I) shows the trans linkage of rings E/F, and the presence of peaks of ions with m/e 111 and 112 in the mass spectra of (I-III) shows the absence of OH groups from rings E and F.

A comparison of the CSs of the protons of the 19-CH₃ groups in (II) and (III) with those of diacetylkorseveriline and korseverilinedione [2] shows that in (I) the two hydroxyls and in (III) the two carbonyls are present at C₃ and C₆, and it also excludes C₁ and C₁₁ as positions for hydroxy groups [6].

Edpetisidine is not oxidized by periodic acid, which means that the third OH group cannot be located at C₂, C₄, or C₇ and the only position remaining for it C₁₅ or C₁₆. The impossibility of obtaining a triketone from (I) and the presence in the mass spectra of ions with m/e 111, 112, 164, and 179 formed by a published scheme [3, 7, 8] shows that the third OH group is located at C₁₅.

TABLE 1

Substance	Chemical shifts (δ , ppm; J, Hz)						
	19-CH ₃ s	21-CH ₃ d	27-CH ₃ d	6H, OCOCH ₃ s	3H, OCOCH ₃ s	H-C- ² H-OCOCH ₃ m	H-C- ² H-OCOCH ₃ m
I	0,92	0,84(6)	1,03(7)				
II	0,90	0,76(6)	1,00(7)	1,97	2,00	5,00	4,73
III	0,86	0,77(6)	0,99(7)				

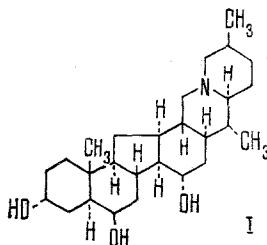
Note. s) singlet; d) doublet; m) multiplet.

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In the NMR spectrum of (II), the protons geminal to the acetoxy groups resonate in a weaker field (see Table 1) and are oriented equatorially [9]. Consequently, the OH groups at C₃ and C₁₅ are α -axially and that at C₆ β -axially oriented. According to the values of the CS of the protons of the secondary methyl groups [10], the 21-CH₃ group has the α -equatorial and the 27-CH₃ group the β -axial orientation.

The facts presented permit the structure and configuration of 3 α , 16 β , 15 α -trihydroxycevanine (I) to be put forward as the most probable for edpetisinine:



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ALKALOIDS OF *Heliotropium eichwaldi*

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We have studied the alkaloid composition of *Heliotropium eichwaldi* Steud. — which is morphologically close to *H. lasiocarpum* Fisch et Mey. [1] — growing in the environs of Erevan. The comminuted raw material collected in the flowering phase was extracted with methanol in the usual way to give the total tertiary alkaloids (yield 0.44% of the weight of the raw material) and N-oxide alkaloids (0.5% — after reduction). By TLC [nonfixed layer of alumina (activity grade III): chloroform-ethanol (20:1) system] it was shown that the two fractions of the combined alkaloids have the same qualitative composition (R_f 0.82 and 0.2). By chromatography on a column of alumina, both fractions of the combined material were separated quantitatively into individual alkaloids which were identified by IR, NMR, and mass spectroscopy and mixed melting points as lasiocarpine (R_f 0.82) (I) and heliotrine (R_f 0.2) (II). The amount of (I) in the fraction of tertiary bases from the combined alkaloids was 64% and of (II) 36%, and the amount of the N-oxide of (I) in the N-oxide fraction was 15% and of the N-oxide of (II) 85%.

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