STRUCTURE AND CONFIGURATION OF EDPETISINE

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Continuing an investigation of the alkaloids of the epigeal part of Petilium eduardi [1, 2], the pH 4 fraction obtained by the citrate-phosphate buffer separation of the combined ether-soluble alkaloids was chromatographed on a column of alumina. From the initial ethereal eluates we have isolated a new alkaloid, edpetisine, with mp 169-171°C (acetone), $[\alpha]_D + 5.31°$ (c 1.6; chloroform), $C_{27}H_{41}NO_2$ (I).

The IR spectrum of (I) [λ_{max} 282 nm (log ε 2.16)] is characteristic for a nonconjugated carbonyl group. In the IR spectrum of (I) there are the absorption bands ν_{max} 3530 cm^{-1} (OH), 1685 cm^{-1} (C=O in a six-membered ring), 2790 cm^{-1} (trans-quinolizidine), and the region of the bands of the skeletal vibrations is similar to that of the IR spectrum of deoxodihydroimperialone (II) [3, 4]. An acid solution of (I) instantaneously decolorizes a solution of potassium permanganate, which shows the presence in (I) of a double bond, and since in the NMR spectrum of (I) there is no signal from an olefinic proton, the double bond is tetrasubstituted.

The mass spectrum of (I) has the peaks of ions with m/e 98, 111, 112 (100%), 124, 125, 140, 154, 155, 156, 164, 354, 355, 366, 368, 378, 393 (M−18), 396 (M−15), 411 M^+, which are characteristic for the C-nor-D-homosteroid alkaloids of the imperialine series [5, 6].

In (I), the hydroxy group has a tertiary nature (it is not acetylated and is not oxidized by chromium trioxide). The Huang-Minlon reduction of (I) gave deoxodihydroedpetisine with mp 126-128°C (acetone), $C_{27}H_{43}NO$ (III), M^+ 397. The IR spectrum of (III) lacked the absorption band of the C=O group.

A comparison of the mass spectra of (I) and (II), and also of (III) and of deoxotetrahydroimperialone (IV) [3, 4] showed that in the region of high masses there is a difference of two units. Consequently, (I) has one double bond.

The facts given show that (I) contains the cevanine skeleton [6, 7]. The characteristics of the NMR spectra of (I-IV) are given below (chemical shifts, δ ppm):

Substance	19-CH_3, s	21-CH_3, s	27-CH_3, d (J, Hz)
I	0.95	1.04	1.03 (7)
II	0.91	1.03	1.02 (7)
III	0.85	1.04	1.03 (7,5)
IV	0.68	1.00	1.00 (6)

s-singlet; d-doublet.

The presence in the mass spectrum of (I) of the peaks of ions with m/e 154, 155, and 156 shows that the tertiary hydroxy group is located at C_{20} [5]. This is confirmed by the resonance of the signal of the protons from 21-CH_3 at 1.04 ppm in the NMR spectrum of (I) in the form of a singlet. The double bond in (I) may be present between carbon atoms C_8-C_9, C_8-C_{14}, $C_{12}-C_{13}$, $C_{12}-C_{14}$, or $C_{13}-C_{17}$. In the NMR spectra of (I) and (III), the chemical shifts of the proton (CSP) of 19-CH_3 are shifted downfield by 4 and 17 Hz, respectively, as compared with the NMR spectra of (II) and (IV); hence the position between C_8 and C_9 remains for the double bond [8]. The signal from the 19-CH_3 protons is shifted 10 Hz downfield in the NMR spectrum of (I) as compared with that of (III). This shows that the carbonyl group in (I) is located at C_3 [8]. From the values of the CSP of the 19-CH_3 and 21-CH_3 groups, rings A/B and D/E are trans linked, and C/D are cis [4, 9]. The presence of Bohlman bands [10] in the IR spectrum of (I) shows the trans linkage of rings E/F, and from the CSP of the methyl groups 27-CH_3 has the β-axial and 21-CH_3 the α-equatorial orientation, and the hydroxy group at C_{20} is β-axial, as in imperialine and its transformation products (II, IV) [4, 5, 9].

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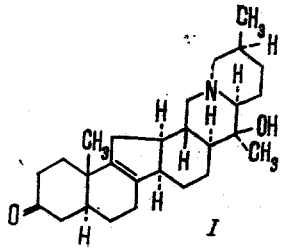
On the basis of the facts given, edpetisine has the most probable structure and configuration of 20 β-hydroxycevan-8-en-3-one (I):



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POLYBUFFER SEPARATION OF THE COMBINED ALKALOIDS OF *Peganum harmala*

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The mother solution from the combined alkaloids of *Peganum harmala* (the plant was collected in May, 1973 in the building stage), after the isolation of the peganine and deoxypeganine [1, 2] was separated according to basicities on an apparatus for automatic liquid extraction [3] between buffer solutions of various pH values and chloroform.

The chloroform mother solution (4 liters) contained 400 g of combined alkaloids. The solution of the combined alkaloids, and also the washing chloroform, was passed through the column of the apparatus at the rate of 1000-1200 ml/h, and then the buffer solutions were washed with pure chloroform. Each buffer solution was decanted off separately and made alkaline with concentrated ammonia to pH 8-9, and the alkaloids were extracted with chloroform. Then the chloroform was evaporated to dryness. The fractions of alkaloids obtained in this way were analyzed to TLC [nonfixed alumina; chloroform–methanol–benzene (5 : 1 : 4)], and the fractions with identical chromatograms were combined. The alkaloids were isolated according to their solubilities, by recrystallization, by the preparation of salts, by precipitation, etc. [2]:

Thus, the total alkaloids of *Peganum harmala* contain strongly basic (pH of the extracting buffer 6.5-7.0), moderately basic (pH 3-6.5), and weakly basic (pH 2 and 10% H_2SO_4) alkaloids, additional amounts of which can be obtained by using polybuffer separation.

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