STRUCTURE OF EDUARDININE

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UDC 547.944/945

Continuing an investigation of the alkaloids of the epigeal part of *Petilium eduardi* [1], we have separated the combined ether-soluble fraction by means of a citrate–phosphate buffer solution. The alkaloids from the pH 6 fractions in chloroform were chromatographed on a column of alumina. The later eluates yielded the new alkaloid eduardine (I), $C_{27}H_{45}NO_2$ with mp 255-257°C (acetone), $[\alpha]_D + 7.4°$ (c 0.875; $CHCl_3$) ν_{max} 3360 cm^{-1} (OH), 2930-2860, 1460 cm^{-1} ($-CH_2$, $-CH_3$), 2750 cm^{-1} (trans-quinolizidine). With acetic anhydride in pyridine, (I) formed an amorphous diacetate (II), ν_{max} 1740, 1250 cm^{-1} (O-acetyl). The oxidation of (I) with chromium trioxide yielded eduardininedione (III) with mp 238-240°C (acetone), ν_{max} 1710 cm^{-1} (carbonyl in a 6-membered ring).

The mass spectrum of (I) has the peaks of ions with m/e 98, 111, (100%), 112, 124, 125, 139, 149, 150, 178, 218, 358, 360, 386, 397, (M–18), 400 (M–15), 415 M^+, which are characteristic for the C-nor-D-homosteroid alkaloids of the cevine group [2-6]. Consequently, compound (I) contains the cevanine skeleton [7]. Characterisitcs of the NMR spectra of (I-III) are given in Table 1 ($CDCl_3$, JNM-4H-100, HMDS).

The differences in the chemical shifts (CSs) of the 19-CH_3 protons in (I) and in (II) and (III) show that the two hydroxy groups in (I) are present in rings A and B at C_3 and C_6 [8]. The results of a comparison of the CSs of 19-CH_3 with those of edpetilidine and petilidine [3, 4] showed that rings A/B, B/C and C/D are trans-linked [9]. The 21-CH_3 protons in (I) undergo a diamagnetic shift by 0.33 ppm as compared with those of isodihydroimperialine [5] because of the absence from (I) of a tertiary hydroxy group at C_{20} [10]. It follows from the CSs of the 21-CH_3 protons that rings D/E are trans-linked just as in imperialine [1, 9].

In the NMR spectrum of (II), the protons geminal to the acetyl groups resonate in a stronger field (4.60 ppm). This shows the 3β,6α-equatorial orientations of the hydroxy groups in (I) [9]. The CSs of the protons of the secondary methyl groups show that in (I) 21-CH_3 possesses the α-equatorial and 27-CH_3 the β-axial orientation [11].

Another confirmation of the basic heterocyclic skeleton (I) is the fact that the oxidation of edpetilidine [1] under the conditions of the oxidation of (I) gave eduardine [1, 2]

TABLE 1. Chemical Shifts (δ, ppm)

Substance	19-CH_3 s	21-CH_3 d	27-CH_3 d	6H, $OCOCH_3$ s.	2H, H-C-O-$COCH_3$ m
I	0,76	0,67	0,99	—	—
II	0,84	0,70	1,02	1,99	4,60
III	0,92	0,68	1,00	—	—

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

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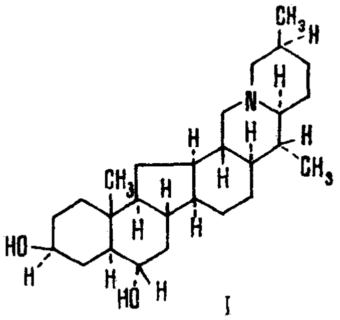
Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 535-536, July-August, 1975. Original article submitted March 25, 1975.

and a diketone with mp 238-240°C (acetone), identical with (III) but not identical with petilidinedione [4].

On the basis of the facts given, eduardine has the most probable structure and configuration of 3β, 6α-dihydroxycevanine (I).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LITERATURE CITED

1. R. Shakirov, R. N. Nuriddinov, and S. Yu. Yunusov, Dokl. Akad. Nauk UzSSR, No. 9, 23 (1963); Khim. Prirodn. Soedin., 384 (1967).
2. R. N. Nuriddinov, R. Shakirov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 316 (1967).
3. R. N. Nuriddinov and S. Yu. Yunusov, Khim. Prirodn. Soedin., 333 (1969).
4. R. N. Nuriddinov, B. Babaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 261, 332 (1968).
5. R. N. Nuriddinov and S. Yu. Yunusov, Khim. Prirodn. Soedin., 458, 767 (1971).
6. H. Budzikiewicz, Tetrahedron, 20, 2267 (1964).
7. IUPAC-IUB Revised Tentative Rules for the Nomenclature of Steroids, J. Org. Chem., 34, 1517 (1969).
8. R. F. Zürcher, Helv. Chim. Acta, 46, 2054 (1963).
9. R. N. Nuriddinov and S. Yu. Yunusov, Khim. Prirodn. Soedin., 260, 333, 334 (1968).
10. R. Shakirov, M. R. Yagudaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 639 (1972).
11. T. M. Moynehan, K. Schofied, R. A. Y. Jones, and A. R. Katritzky, J. Chem. Soc., 2637 (1962).