THE STRUCTURE OF EDPETISIDINE

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Continuing an investigation of the alkaloids of the epigeal part of *Petilium eduardi* (Rgl.) Vved [1, 2], the mixture of bases from the pH 8 fraction was chromatographed on a column of silica gel. A benzene–methanol (9:1) eluate yielded the new alkaloid edpetisidine with mp 257-259°C (acetone), $[\alpha]_D$ −33.63° (c 1.87; methanol). $C_{27}H_{43}NO_3$ (I), M^+ 429, IR spectrum of (I), λ_{max}, cm^{-1}: 3400 (OH), 2760 (trans-quinolizidine), 1670 (>C=C<).

The Adams hydrogenation of (I) yielded dihydroedpetisidine (II), M^+ 431. The acetylation of (II) led to diacetyldihydroedpetisidine (III), M^+ 515, the IR spectrum of which showed the adsorption bands of an ester carbonyl (1740, 1245 cm^{-1}) with the retention of the hydroxyl band (3500 cm^{-1}).

The mass spectrum of (I) had the peaks of ions with m/e 98, 111, 112 (100%), 124, 125, 149, 154, 155, 156, 358, 368, 374, 386, 388, $(M-18)^+$, $(M-15)^+$, 429 M^+, which are characteristic for the C-nor-D-homosteroid alkaloids imperialine, isodihydroimperialine, and edpetisinine [2-5].

Below we give the chemical shifts (CSs) of the protons of compounds (I), (III), and (IV) (CD_3OD, JNM-4H-100, HMDS, δ scale):

Substance	19-CH_3, s	21-CH_3, s	27-CH_3, d	6H, $-OCOCH_3$, s	2H, $HC-OCOCH_3$, m
I	0.97	1.03	0.85		
III	1.00	1.06	0.81	1.95; 1.98	4.73; 4.94
IV	1.00	0.87 (doublet)	0.87	1.97; 1.99	4.77; 5.05

Thus, edpetisidine is a C-nor-D-homosteroid alkaloid and is based on the heterocyclic skeleton of cevanine [6] with two secondary and one tertiary hydroxy groups and a tetrasubstituted double bond [the NMR spectra of (I) and (III) lack the signals of olefinic protons].

A comparison of the CSs of the protons of the 19-CH_3 group in (III) and those of diacetylkorseveriline (IV) [7] shows that in (III) the linkages of rings A/B and B/C are trans and of C/D cis, and in (I) the two hydroxyls are present at C_3 and C_6 [8].

In the NMR spectrum of (III) the protons geminal to the acetoxy groups resonate in a weaker field (4.94 and 4.73 ppm) and are oriented equatorially [9]. Consequently, in (I) the C_3–OH group has the α-axial and the C_6–OH group the β orientation. In the NMR spectrum of (I), the CS of the 19-CH_3 protons are shifted downfield by 0.05 ppm as compared with those of edpetisinine [2]. This shows that the double bond (I) is between C_8 and C_9.

The formation in the mass spectrometric decomposition of edpetisidine of an ion with m/e 112 as the maximum peak and of fragments with m/e 154, 155, and 156 [3], and also the singlet nature of the signals from the 21-CH_3 group show that the tertiary hydroxy group is located at C_{20}.

The presence of a Bohlmann band in the IR spectrum of (I) shows the trans linkage of rings E/F [10]. According to their CS values, the secondary and tertiary (at C_{20}) methyl groups 27-CH_3 and 21-CH_3 have the α-equatorial orientation [11]. The CS value of the 21-CH_3 group shows that rings D/E are probably trans-linked.

On the basis of the facts given, the most probable structure and configuration of edpetisidine are cevan-8-ene-3α,6β,20β-triol (I):

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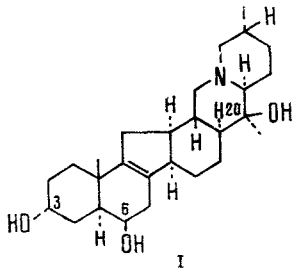

I

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THE STRUCTURE OF ARENINE

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From the phenolic fraction of the total alkaloids of *Papaver arenarium* M. B. we have isolated a new amorphous base $[\alpha]_D$ −31° (c 1.03; CH_3OH) which we have called arenine (I) [1]. UV spectrum: λ_{max} 244, 291, 319, 333 nm (log ε 4.49, 3.78, 3.57, 3.57). The IR spectrum shows absorption bands at (cm^{-1}) 930, 1040, (CH_2O_2), 1495, 1510 (aromatic ring), and 3300 (OH). In the mass spectrum there are the peak of the molecular ion with m/e 392 and also the peaks of ions with m/e 377, 363, 349, 135, and 84 (100%). The NMR spectrum of the base taken in deuterochloroform showed the signals of three-proton singlets at 2.19 ppm from a N-methyl group and at 3.94 ppm from a methoxy group, and of two-proton singlets at 5.47 ppm from a methylenedioxy group and at 4.32 ppm from a methylene group. Six aromatic protons are represented by signals at 6.53-6.60 (3H), 7.47 (1H), 7.74 (1H), and 8.30 ppm (1H). Methylene and methine protons appear in the form of multiplets at 1.90-3.50 ppm.

The UV, NMR, and mass spectra of arenine are close to the spectra of macrostomine [2]. On the basis of the facts obtained the following developed formula may be suggested for (I): $C_{20}H_{15}N$ (N—CH_3) (CH_2O_2) (OCH_3) (OH).

A comparison of the developed formulas of macrostomine and arenine shows that the latter contains a hydroxy group in place of a methoxy group in macrostomine. When arenine was methylated with diazomethane, O-methylarenine (II) was obtained, which was identical according to TLC with macrostomine. A mixture of the hydrochlorides of (II) and of macrostomine gave no depression of the melting point. The hydroxy group in arenine may be present in ring A at C_6

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