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STRUCTURE AND CONFIGURATION OF EDPETILIDINE AND EDUARDINE

R. N. Nuriddinov and S. Yu. Yunusov

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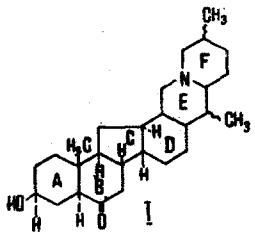
The structure of cevane-3, 6-diol has been established for edpetilidine $C_{27}H_{45}O_2N$ and that of 3-hydroxycevan-6-one for eduardine $C_{27}H_{43}O_2N$ [1]. The presence of a tertiary hydroxy grouping in these alkaloids was put forward erroneously on the basis of the stability of eduardine to oxidation with chromic acid. Tertiary hydroxy groups in C-nor-D-homosteroid alkaloids are not acetylated under the usual conditions. The acetylation of eduardine with acetic anhydride in the presence of pyridine at 20-25° C gave an O-acetyl derivative with mp 146-147° C (from acetone). In a thin layer of Al_2O_3 and $CaSO_4$ (9 : 1), R_f 0.72 [ethyl acetate-petroleum ether-methanol (5 : 5 : 1) system]. The IR spectrum had ν_{max} cm^{-1}: 1730, 1245, 1140 ($-COOCH_3$), 1710 (CO), and 2740-1750 (trans-quinolizidine) and there were no absorption bands of a hydroxyl group, and the NMR spectrum exhibited a three-proton singlet characteristic for the protons of an acetyl group.

Consequently, one oxygen atom in eduardine and both oxygen atoms in edpetilidine are present in the form of secondary hydroxyl groups. To establish the positions of the substituents in eduardine the chemical shifts of the methyl protons in the NMR spectra of eduardine (I), O-acetyleduardine (II), and edpetilidine (III) were compared with the corresponding chemical shifts of compounds of known structure: imperialine (IV), O-acetylimperialine (V), and dihydroimperialine (VI) (table).

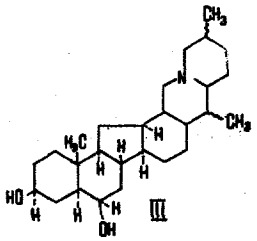
From the figures given it can be seen that the shift of the signals of the 19-CH_3 protons in the NMR spectra of I and IV after the introduction of an acetyl group are very similar. This shows the presence of a 3β hydroxyl group in I, which is confirmed by the presence in the spectrum of II and V of a one-proton multiplet. The difference in the chemical shifts of the 19-CH_3 protons in the spectra of I and III and of IV and VI is small. Consequently, the carbonyl group in I is in position 6, as in IV. The similar values of the chemical shifts of the 19-CH_3 protons in the NMR spectra of III and VI shows that in III the hydroxyl group at C_6 has the β orientation. The values of the 19-CH_3 signals in the NMR spectra of I, II, and III confirm that the linkage of the A, B, C, and D rings in I and III is the same as in IV [2]. From the values of the signals in I and III, the 21-CH_3 is equatorial and the 27-CH_3 is axial.

The presence in the IR spectra of I-III of a trans band shows the trans linkage of rings E/F.

Thus the following formulas and configurations are proposed as the most probable for eduardine (I) and edpetilidine (III):



I



III

The NMR spectra were taken on a JNM-4H-100/100 MHz instrument (with HMDS as internal standard) and the IR spectra on a UR-10 spectrometer in the form of molded tablets with KBr.

Chemical Shifts (τ)

Substance	s, 3H; C–19 CH_3	d, 3H; C–21 CH_3	s, 3H; C–21 CH_3	d, 3H; C–27 CH_3	s, 3H; $-OCOCH_3$	m, H(a); H–CO–$COCH_3$	Solvent
(I)	9.30	9.32	—	9.02	—	—	$CDCl_3$
(II)	9.27	9.30	—	8.97	8.03	5.40	$CDCl_3$
(III)	8.75	9.43	—	8.99	—	—	C_5D_5N
(IV)	9.32	—	9.01	9.01	—	—	$CDCl_3$
(V)	9.30	—	9.01	8.99	8.04	5.40	$CDCl_3$
(VI)	8.82	—	9.00	9.02	—	—	C_5D_5N

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

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ALKALOIDS OF PEDICULARIS

A. Abdusamatov and S. Yu. Yunusov

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From the epigeal part of P. rhinanthoides Schrenk., collected on July 21, 1966, in the flowering period in the gorge of the R. Nura, KirgSSR, by chloroform extraction we have obtained 0.3% of total alkaloids.

The ethereal fraction of the total alkaloids was treated with acetone, giving 0.04% of plantagonine [1]. By separating the mother liquor on a column of alumina [eluant: ether–chloroform (9 : 1)] we obtained a liquid base with R_f 0.67 [in the butan-1-ol–water–acetic acid (20 : 20 : 1) system], $[\alpha]_D^{20}$ +5.9 (c 0.508; ethanol), $C_{10}H_{13}NO$, mol. wt. 163 (mass spectroscopy). The picrate has mp 151–152° C (water). IR spectrum: λ_{max} 263, 270 mμ (log ε 2.74, 2.70).

The IR spectrum of the base has absorption bands at 3400–3200 cm^{-1} (OH), 2960 cm^{-1} (C–CH_3), 1595 cm^{-1} (pyridine ring), and 895, 850, and 815 cm^{-1}. Oxidation of the base with potassium permanganate in an alkaline medium added two oxygen atoms with the formation of an acid with mp 218–220° C (decomp.). A mixture of this acid with plantagonine showed no depression of the melting point. Thus, the base that we have isolated is the dextrorotatory form of the known alkaloid *l*-tecostidine [2].

From the epigeal part of P. olgae Rgl., collected on June 15, 1968, in the flowering period in the village of Saed, TadzhSSR, we have obtained 0.65% of total alkaloids from which we have isolated 0.11% of plantagonine.

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MALATE DEHYDROGENASE FROM COTTON SEED

K. Davranov, M. A. Kuchenkova, and P. Kh. Yuldashev

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From the seeds of the cotton plant of variety 108-F, we have isolated a fraction possessing malate dehydrogenase activity.

The seeds, freed from their coating and ground, were defatted [1]. The resulting acetonic powder (100 g) was mixed with 0.01 M phosphate buffer, pH 7.4 (1 : 10) containing 0.005 M EDTA and 0.005 β-mercaptoethanol. The extracts were centrifuged at 6000 rpm for 30 min. The supernatant liquid was fractionally precipitated with ammonium sulfate. The precipitate obtained at 20% saturation was filtered off with suction and the supernatant liquid was brought to 50% saturation. Then the precipitate was dissolved in the minimum amount of 0.1 M phosphate buffer, pH 7.4, containing EDTA and β-mercaptoethanol and was passed through a 2.5 × 45 cm column containing Sephadex G-25 equilibrated with the same buffer. The fractions containing protein were combined and the percentage protein content was