STRUCTURE AND CONFIGURATION OF EDPETINE

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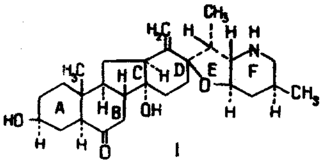
Together with R. Shakirov, we have isolated from the chloroform fraction of the total alkaloids of the epigeal part of Petilium Edwardi the new alkaloid edpetine (I), $C_{27}H_{41}O_4N$, with mp 314–315° C (from ethanol), mol. wt. 443 (mass spectrum). The IR spectrum of I has absorption bands at (cm^{-1}): 3460, 3260 (OH), 3120 (>N—H), 2980–2850, 1470–1430 (—CH_3), 1690 (CO), and 1640–1650 (C═C). The acetylation of I in pyridine with acetic anhydride yielded O, N-diacetyledpetine (II), with R_f 0.3 on Al_2O_3 and $CaSO_4$ (9 : 1) in the toluene–petroleum ether–methanol (5 : 5 : 0.5) system. The IR spectrum of II has absorption bands at (cm^{-1}): 3450 (OH), 2960–2850, 1470–1420 (CH_3), 1725, 1240 ($COOCH_3$), 1700 (CO), and 1650–1640 (N—$COCH_3$). In the mass spectrum of I, of peumisine (III) [1] and of jervine (IV) [2, 3] there are similar characteristic peaks of ions, showing the identity of the structure and configurations of rings E and F in I, III, and IV. In the mass spectrum of I there are peaks of ions with m/e 97 (5%); 110 (12%); 113 (14%); 114 (10%); 124 (100%); 125 (24%); $(M - 33)^+$ $(M - 29)^+$; $(M - 15)^+$, and 443 (M^+). The differences observed in the intensities of the peaks are caused by the nature of the double bond. In IV, the double bond is conjugated with a carbonyl group, and in III there is no such conjugation, while in I it exists between other carbon atoms. This difference could be caused to some extent by the conditions of recording the spectra. This conclusion is confirmed by the practically identical values of the signals from 21-CH_3 and 26-CH_3 in the NMR spectrum of II, of O, N-diacetylpeumisidine (V), and of derivatives of IV [4].

Substance	Chemical shift, τ								
	s, 3H; 19-CH_3	s, 3H; 18—CH_3	d, 3H; 21—CH_3	d, 3H; 26—CH_3	s, 3H; $OCOCH_3$	s, 3H; $NCOCH_3$	м, H; C_3—H	s, H; Olefin	s, H; Olefin
II	9.40	—	9.19	9.04	8.08	8.03	5.40	4.67	4.82
V	9.36	8.35	9.21	9.03	8.04	7.96	5.36	—	—
III	9.38	8.44	9.15	9.14	—	—	—	—	—

A comparison of the NMR spectra of II and V shows that in I and III the structure of rings A, B, and C differ by the absence from I of a double bond between $C_{(12)}$ and $C_{(13)}$ [4]. In both I and III there are β-oriented secondary hydroxyl groups at $C_{(3)}$ and a carbonyl group in position 6. The tertiary hydroxyl group at $C_{(14)}$ in I has the α-orientation. In the NMR spectrum of II, the presence of two signals from olefinic protons and the absence of a signal from 18-CH_3 shows that the double bond in I is between $C_{(13)}$ and $C_{(18)}$ [4–7]. The NMR spectra of II, III, and V are given in the table.

On the basis of the information presented, the following structure and configuration are proposed for edpetine (I):



I

The schemes of fragmentation of I and IV are similar [2].

The conditions of recording the spectra have been reported previously [8].

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