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A MASS SPECTROMETRIC STUDY OF DES-BASES

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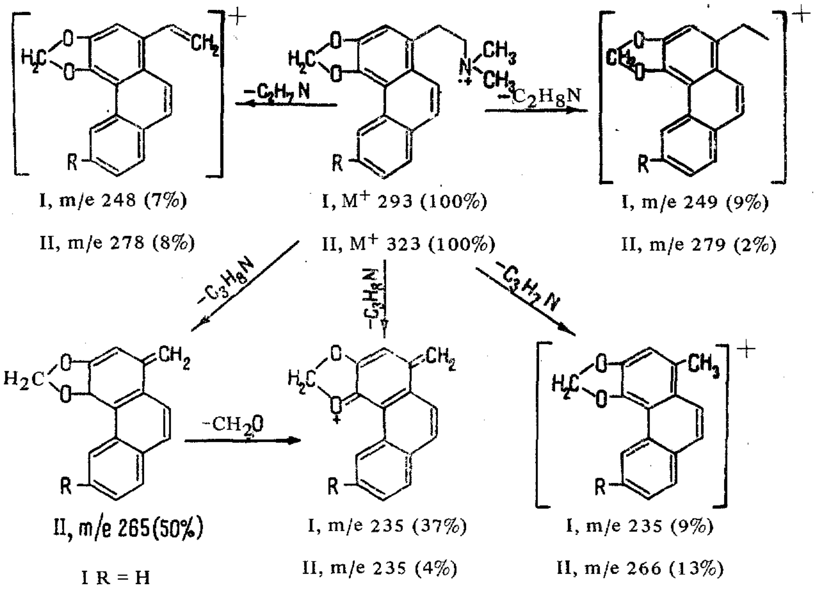
The presence of the maximum peak of the molecular ion is characteristic for the mass spectra of des-N-methyl-1-isoroemerine (I) and des-N-methyl-O-methylisofugapavine (II) [1] The spectrum has the peaks M-44, M-45, M-57, and M-58, which are formed, respectively, by the loss by the molecular ion of C_2H_6N, C_2H_7N, C_3H_7N, and C_3H_8N groups, and also the peak of the M + 1 ion. However, the spectra do not exhibit the peaks of the ions M-1 and M-15 which are characteristic of the aporphine alkaloids.

In the spectrum of des-N-methyl-O-methylisofugapavine there is a peak with m/e 235, which arises from an ion with m/e 265 by the loss of a formyl group.



I, m/e 248 (7%)
II, m/e 278 (8%)

I, M+ 293 (100%)
II, M+ 323 (100%)

I, m/e 249 (9%)
II, m/e 279 (2%)

II, m/e 265(50%)

I, m/e 235 (37%)
II, m/e 235 (4%)

I, m/e 235 (9%)
II, m/e 266 (13%)

I R = H

II R = OCH_3

The spectra were taken on an MKh-1303 mass spectrometer at an ionizing potential of 70 eV and at temperatures of 120 and 210° C, respectively.

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STRUCTURE AND CONFIGURATION OF KORSEVERINE

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The IR spectrum of korseverine $C_{27}H_{41}O_2N$ [1] has ν_{max} 3510, 3390, 1060 cm^{-1} (—OH), 2920–2870 and 1440 cm^{-1} ($-CH_3$), 2760 cm^{-1} (trans-quinolizidine), 1703 cm^{-1} (>CO), and 1650 cm^{-1} (C=C), and its UV spectrum has λ_{max} 300 mμ (log ε 2.07) (ethanol). Acetylation of the alkaloid with acetic anhydride in pyridine gives acetylkorseverine (II) with mp 185–186° C, R_f 0.9. The IR spectrum of the latter has ν_{max} 2960–2860, 1450 ($-CH_3$), 2730 (trans-quinolizidine), 1725, 1235–1270, 1040, 1025 (—$OCOCH_3$), and 1703 cm^{-1} (CO). On Kuhn-Roth oxidation, korseverine gives 3 moles of acetic acid, and on oxidation in glacial acetic acid with chromic acid it gives the ketone korseverinone (III), with mp 223–224° C (from acetone) R_f 0.85. The UV spectrum of (III) has λ_{max} 253, 298 mμ (log ε 2.61, 2.19). The Huang-Minlon reduction of korseverine gives deoxodihydrokorseverine (IV), with mp 172–174° C (from acetone) and the composition $C_{27}H_{43}ON$, R_f 0.6. The IR spectrum of (IV) lacks the absorption band of a carbonyl group. The oxidation of the reduced substance leads to the formation of a ketone (V) with mp 198–199° C. The IR spectrum of (V) has no absorption band of a hydroxy group. The reduction of korseverine in ether with lithium aluminum hydride and in aqueous methanol with $NaBH_4$ forms the dihydro base with mp 164–165° C (from acetone). The IR spectrum of this base has ν_{max} 3410, 1015–1070 (—OH), 1650 cm^{-1} (C=C) and no absorption bands of the carbonyl group. The mass spectrum of korseverine has peaks of ions with m/e 98, 111, 112, 396 (M-15), 393 (M-18), and 411 (M^+), which are characteristic for C-nor-D-homosteroid alkaloids.

The results given show that korseverine is based on the heterocyclic skeleton of imperialine.

The main features of the NMR spectra of (I)–(V) are given in the table.

From a comparison of the chemical shifts of the methyl protons in the NMR spectra of compounds (I)–(V), it can be seen that the substituents in them are located in trans-linked rings A and B.

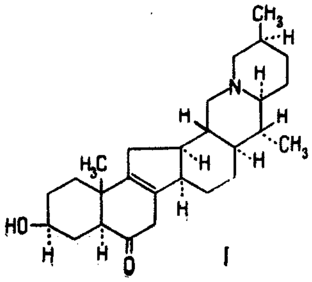
Chemical Shifts, τ

Substance	(S), 3H, C-19 CH_3	(D), 3H, C-21 CH_3	(D), 3H, C-27 CH_3	(M), H(a), $HCOCOCH_3$	(S), 3H, $-OCOCH_3$ (e)	H, (olefin)
(I)	9.27	9.13	8.96	—	—	None
(II)	9.25	9.13	9.98	5.38	8.04	
(III)	9.08	9.13	8.96	—	—	
(IV)	9.24	9.15	8.97	—	—	
(V)	9.04	9.15	8.96	—	—	

Note. S—singlet, D—doublet, M—multiplet.

The difference in the chemical shifts of the protons of the C-19 methyl groups in the NMR spectra of (I) and (II), and the multiplet with a center at 5.38τ and the singlet at 8.04τ in the spectrum of (II) make it possible to show that the hydroxy group in korseverine is located at C_3 and has the β-orientation. The signal from the 19-methyl group in the NMR spectrum of (IV) is displaced by 3 Hz as compared with the signal of (I) [2]. Consequently, in korseverine the carbonyl group is located in position 6. Hence, in korseverine and imperialine rings A and B are similar with respect to the position of the substituent groups, but in the NMR spectrum of korseverine the chemical shift of the 19-methyl group is displaced to a weaker field than in the NMR spectrum of imperialine. This shows that in korseverine the double bond is between C_8 and C_9.

In the trans-quinolizidine part of the alkaloid, the 21-methyl group is α-orientated and the 27-methyl group β-orientated. Thus, korseverine has the most probable structure and configuration (I).



I

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