STRUCTURE AND CONFIGURATION OF PETILINE

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Continuing a study of the structure of petiline (I) [1], it was found that the absorption in its UV spectrum at 240 and 290 mμ (log ε 2.66 and 1.99) is not the absorption of an α,β-unsaturated ketone, as was considered previously, but corresponds to the absorption of a —N═C chromophore and an isolated carbonyl group [2]. The mass spectrum of I has peaks with m/e 110 (8%), 111 (84%), 112 (17%), 125 (100%), 150 (7%), 151 (16%), 164 (12%) 165 (18%), $(M - H_2O)^+$, $(M - CH_3)^+$, and 413 (54%) (M^+), and the mass spectrum of tetrahydropetiline (II) the peak of an ion with m/e 98 (100%) with a series of weak peaks $(M - H_2O)^+$, $(M - CH_3)^+$, and 417 (M^+). A comparison of the mass spectra of I and II clearly shows that the double bond in petiline is in the form of a —C═N bond.

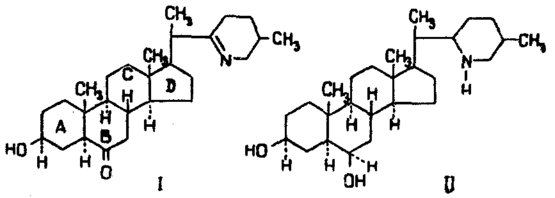
Substance	Chemical shifts, τ							
	s, 3H; 19–CH_3	s, 3H; 18–CH_3	d, 3H; 21–CH_3	d, 3H 26–CH_3	s, 3H $OCOCH_3$	s, $NCOCH_3$	m, H, $HCOCOCH_3$	m, H, Olefin
I	9.32	9.37	9.17	8.99	—	—	—	—
II	9.03	9.38	9.27	9.10	—	—	—	—
III	9.31	9.43	9.11	8.86	8.05	7.94	5.40	4.90

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

The formation of O, N-diacetylpetiline (III) by the acetylation of I is explained in the following way: in I, on acetylation, as in verazine, there is a displacement of the double bond from the $-C_{(22)}{=}N-$position to the $C_{(22)}-C_{(23)}$ position with the formation of substance III. The NMR spectra of I, II, and III, which are given in the table, confirm the information given above.

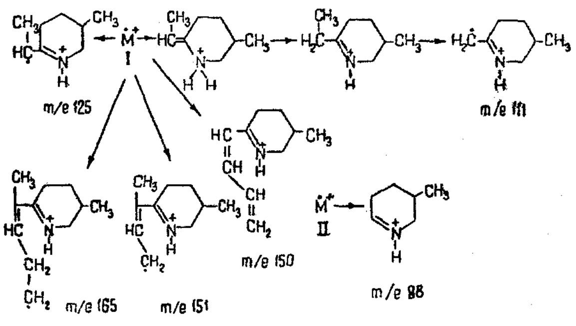
In the NMR spectra of I, II, and III, the characteristic chemical shifts of the 18-CH_3 and 19-CH_3 protons show trans A/B, B/C, and C/D ring linkages. The displacements of the signals in the NMR spectra of I, II, and III show that in I the β-oriented hydroxyl group is present at $C_{(3)}$ and the carbonyl group is in position 6. From the value of its signal, the methyl group at $C_{(25)}$ is axial [3, 4].

On the basis of what has been said, the following structural formulas with partial configurations are proposed:



I II

In addition, we give a scheme of the fragmentation of I and II.



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