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STRUCTURE AND CONFIGURATION OF PETILININE

R. N. Nuriddinov, B. Babaev, and S. Yu. Yunusov

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From the methanolic mother liquor of the hydrochloride of petiline [1], after the usual treatment, we have isolated a new alkaloid petilinine with mp 277-278° C (from methanol), $[\alpha]_D - 9.6^\circ$ [c 1.25; methanol-chloroform (1:1)] with the composition $C_{27}H_{45}O_2N$, mol. wt. 415 (mass spectrum). The hydrochloride has mp 296-297° C and the hydrobromide mp 281-283° C. IR spectrum of petilinine; ν_{\max} 3410, 3140, 1053 (OH), 2980-2860, 1455, 1435 ($-\text{CH}_3$), 2785 cm^{-1} (trans-quinolizidine). The base contains two secondary hydroxy groups, as is shown by the production of diacetylpetilinine (I) with mp 193-194° C (ν_{\max} 1730, 1250, 1025 cm^{-1}) and petilinedione (II) with mp 226-228° C (ν_{\max} 1710 cm^{-1}). The latter, on Huang-Minlon reduction, forms desdioxotetrahydropetilinedione (III) with mp 150-151° C. Petilinine is not oxidized by periodic acid.

Chemical Shifts (τ)

Sub- stance	(S), 3H, C-19 CH_3	(D), 3H, C-21 CH_3	(D), 3H, C-27 CH_3	(S), 3H, 3 α - OCOCH_3	(S), 3H, 6 α - OCOCH_3	(M) βH , at C_3	(M), βH at C_6
(I)	9.24	9.23	9.23	8.05	8.02	4.97	5.42
(II)	9.13	9.21	9.21	—	—	—	—
(III)	9.34	9.22	9.22	—	—	—	—

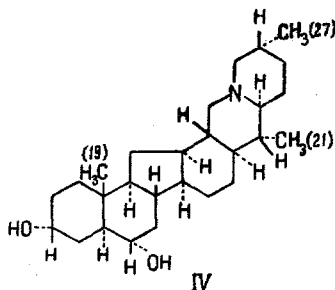
Note: S—singlet, D—doublet, M—multiplet.

The NMR spectra of substances (I), (II), and (III) have signals from methyl protons (in each case two in the form of a doublet and one in the form of a singlet) and the mass spectrum of petilinine has characteristic peaks of the ions with m/e 97 (24%), 98 (10%), 111 (100%) and 112 (33%), 415 (M^+) (32%) [2].

The information given shows that petilinine has the heterocyclic skeleton of imperialine [2]. It can be seen from the table that in petilinine rings A and B have a trans-linkage and the hydroxy groups are located at C_3 and C_6 [3]. The presence in the IR spectrum of petilinine of a band with ν_{\max} 1053 cm^{-1} and the appearance after acetylation of one with ν_{\max} 1025 cm^{-1} shows that one of the hydroxy groups in the substance is located at C_3 and has the α -orientation [4]. This position is confirmed by the fact that the NMR spectrum of (I) has a signal from a $3\beta\text{-H}$.

The difference in the chemical shifts from the C-19 methyl protons of (I) and (III) is characteristic for C-3 α - OCOCH_3 and C-6 α - OCOCH_3 . Consequently, the hydroxy group at C_6 is in the α -position. Rings A and B and the trans-quinolizidine part of the molecule in petilinine are connected in the same way as in the alkaloid cervine. The difference in the values of the signals from the C-21 and C-27 methyl protons in compounds (I), (II), and (III) shows the angular

configuration of petilinine. From the value of their chemical shifts, the C-21 and C-27 methyl groups have the α -orientation [5]. Thus, configuration (IV) may be put forward for petilinine.



The NMR spectra were taken in deuteriochloroform on a JNM-4H-100 instrument (with hexamethyldisiloxane as internal standard), the IR spectra (compressed tablets with KBr) on a UR-10 instrument, and the mass spectra on an MKh-1303 instrument with a glass inlet system.

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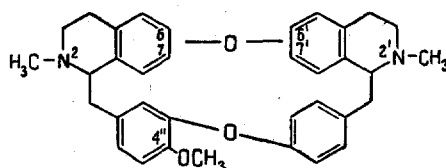
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THE NMR SPECTRA OF THALMINE, O-METHYLTHALICBERINE, THALSIMINE, AND FOETIDINE

Z. F. Ismailov, M. R. Yagudaev, and S. Yu. Yunusov

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In the NMR spectrum of thalmine (I) [1], two three-proton signals of N-CH₃ clearly appear at 7.90 ppm in position 2 and at 7.45 ppm in position 2'. The positions of these signals in O-methyl-I are, respectively, 7.90 and 7.43 ppm. The singlet at 6.23 ppm in substance (I) relates to the OCH₃ group in position 6 and the six-proton signal at 6.17 ppm corresponds to two OCH₃ groups at 7' and 4". In the spectrum of O-methyl-I, in addition to those mentioned, there is an additional signal of the 6'-OCH₃ group at 6.37 ppm. The signals of the ten aromatic protons in (I) and in O-methyl-I are in the 4.15-3.10 ppm region. The signal of the proton of the hydroxy group in (I) appears at 5.00 ppm.



The values of the chemical shifts (CS) of the signals of the methoxy groups in O-methylthalicberine (II) are 6.20, 6.23, 6.31, and 6.44 ppm. The N-CH₃ group in (II) resonates at 7.52 and 7.99 ppm.

The absence of a methyl group on the nitrogen in position 2' in thalsimine (III) [2] substantially affects the nature of its NMR spectrum, namely: the methoxy groups resonate in a narrow region at 6.16-6.26 ppm and the signal of the N-CH₃ in position 2 appears in the form of a three-proton doublet at 7.80 ppm (J = 10.0 Hz).