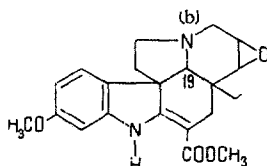


The reduction of ervincinine with zinc in methanolic sulfuric acid gave dihydroervincinine $C_{22}H_{28}O_4N_2$, mol. wt. 384 (by mass spectrometry), mp 206.5° – 207.5° C (ether). UV spectrum: λ_{max} (ethanol), 245, 304 m μ ($\log \epsilon$ 4.06, 4.02), which is characteristic of indoline bases.

The NMR spectrum of ervincinine exhibited signals of an ethyl group (δ = 0.61 ppm), of the six protons of two methoxy groups (δ = 3.71 ppm, singlet), of three aromatic protons (δ = 6.34–7.01 ppm), and of an NH group (δ = 8.89 ppm, singlet). The mass spectrum of ervincinine is very similar to that of lochnerinine [4], differing only by the low intensity of the peaks with m/e 138 and 108. The IR spectra of the base lacks a band in the 2700–2800 cm^{-1} region, showing cis-orientation of the hydrogen in relation to the unshared pair of electrons of the nitrogen atom N(b).

On the basis of the data presented, a structure is proposed for ervincinine which differs from that of lochnerinine by the configuration of the hydrogen at C₁₉.



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STRUCTURE AND CONFIGURATION OF PETILIDINE

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From the acetic mother liquors from petilinine [1] we have isolated a new alkaloid, petilidine (I), with mp 265° – 266° C (acetone–methanol (2:1)), $[\alpha]_D -15.5^{\circ}$ (c 1.2; methanol), composition $C_{27}H_{45}O_2N$, mol. wt. 415 (mass spectrum). In a thin layer of Al_2O_3 and $CaSO_4$ (9:1), R_f 0.19 in the chloroform–benzene–methanol (10:5:0.5) system. The alkaloid forms a hydrochloride with mp 273° – 274° C and a hydrobromide with mp 310° – 312° C. IR spectrum of petilidine: ν_{max} 3300, 1055 (–OH), 2950–2860, 1450 (–CH₃), 2750 cm^{-1} (trans-quinolizidine). A mixture of petilidine with petilinine melted at 235° – 246° C.

Chemical Shifts, τ

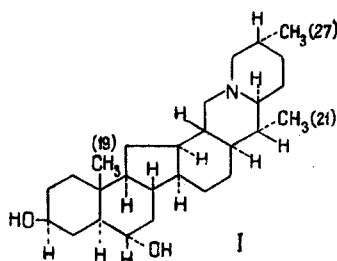
Substance	(S), 3H, C–19 CH ₃	(D), 3H, C–21 CH ₃	(D), 3H, C–27 CH ₃	(S) 6H, 2 COOCH ₃	(M) 2H, 2 HCO COCH ₃
(I)	9.29	9.23	9.23	—	—
(II)	9.21	9.23	9.23	8.04	5.42
(III)	9.13	9.22	9.22	—	—

The action of acetic anhydride on petilidine in pyridine forms the difficultly crystallizing diacetylpetilidine (II). In a thin layer of Al_2O_3 and $CaSO_4$ (9:1), R_f = 0.82 in the butyl acetate–petroleum ether–methanol (20:20:5) system. IR spectrum: ν_{max} 1730, 1245, 1030 cm^{-1} . The NMR spectrum exhibited a 6-proton singlet at 8.04 τ . Oxidation of the alkaloid with chromic acid gave a diketone with mp 226° – 228° C (III) (ν_{max} 1708 cm^{-1}), identical with petilinedione. Reduction of the latter by the Huang-Minlon method led to an oxygen-free base which was identical with desdioxotetra-

hydropetilinedione [1]. The identity of the products was shown by the melting point of mixtures and by a comparison of their IR spectra; this shows a structural relationship between petilidine and petilinine. In the mass spectrum of petilidine, as in that of petilinine, the main characteristic peaks are those of the ions with m/e 97, 98, 111, 112, 397, $(M-18)^+$, 400 $(M-15)^+$, and 415 (M^+) .

Consequently, petilidine differs from petilinine only by the configuration of the substituting groups, which was established by a study of the NMR spectra of substances (I), (II), and (II) (table).

The values of the signals of the protons of the 19-methyl group and the two acetyl groups in diacetylpetilidine and diacetylpetilinine are different. This shows a difference in the configurations of the hydroxy groups in petilidine and petilinine. In diacetylpetilidine, unlike diacetylpetilinine, the acetyl group could be present in the β -position at C_6 . Then the signal from the 19-methyl protons should be found at approximately 9.1 τ as in 3 β , 6 β -diacetyldihydroimperialine. However, this is not the case. Thus, in diacetylpetilidine the acetyl group at C_3 has the β -orientation. This is confirmed by the presence in the NMR spectrum of diacetylpetilidine of a singlet of the 19-methyl group at 9.21 τ , as in the spectrum of 3 β , 6 β -diacetyldihydroimperialine [2]. In addition, the difference in the chemical shifts of the 19-methyl protons in diacetylpetilidine and diacetylpetilinine is 3 Hz. In analogous steroid compounds this difference is 2.5 Hz. [3]. Consequently, the structural formula and configuration (I) may be put forward for petilidine.



The conditions for recording the spectra have been reported previously [1].

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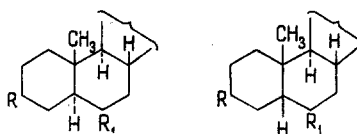
UDC 547.944/945

NUCLEAR MAGNETIC RESONANCE SPECTRA OF 5 α H-C-NOR-D-HOMOSTEROIDS

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Imperialine is a representative of the 5 α H- and verticine a representative of the 5 β H-C-nor-D-homosteroid alka-
loids [1]. In this paper we give the values of the signals from the C-19, C-21, and C-27 methyl protons found in the
NMR spectra of the 5 α H-series. A comparison of the values of the signals of the 5 α H-series with the corresponding values
for the 5 β H-series [2] has in many cases enabled us to establish a relative displacement of the chemical shifts from the
C-19 methyl group in the 5 β H-series into the weak field (table).



5 α H-series

5 β H-series

- | | | |
|---|---|--|
| I. R=R ₁ =H; | V. R= β OH; R= α | IX. R= β OH; R ₁ =O; |
| II. R= β OH; R ₁ =H; | VI. R= β OCOCH ₃ ; R ₁ = α OCOCH ₃ | X. R= β OCOCH ₃ ; R ₁ =O |
| III. R= β OCOCH ₃ ; R ₁ =H; | VII. R= β OH; R ₁ = β OH; | XI. R=R ₁ =O; |
| IV. R=O; R ₁ =H; | VIII. R= β OCOCH ₃ ; R ₁ = β OCOCH ₃ ; | |