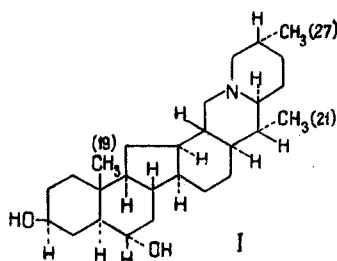


hydropetilinedione [1]. The identity of the products was shown by the melting point of mixtures and by a comparison of their IR spectra; this shows a structural relationship between petilidine and petilinine. In the mass spectrum of petilidine, as in that of petilinine, the main characteristic peaks 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 9.1τ as in $3\beta, 6\beta$ -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 9.21τ , as in the spectrum of $3\beta, 6\beta$ -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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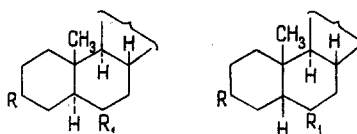
UDC 547.944/945

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

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Imperialine is a representative of the 5α H- and verticine a representative of the 5β 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 5α H-series. A comparison of the values of the signals of the 5α H-series with the corresponding values
for the 5β 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 5β H-series into the weak field (table).



5α H-series

5β H-series

- | | | |
|------------------------------------|---|--------------------------------|
| I. $R=R_1=H$; | V. $R=\beta OH$; $R_1=\alpha$ | IX. $R=\beta OH$; $R_1=O$; |
| II. $R=\beta OH$; $R_1=H$; | VI. $R=\beta OCOCH_3$; $R_1=\alpha OCOCH_3$ | X. $R=\beta OCOCH_3$; $R_1=O$ |
| III. $R=\beta OCOCH_3$; $R_1=H$; | VII. $R=\beta OH$; $R_1=\beta OH$; | XI. $R=R_1=O$; |
| IV. $R=O$; $R_1=H$; | VIII. $R=\beta OCOCH_3$; $R_1=\beta OCOCH_3$; | |

It can be seen from the table that in the NMR spectra of the 5 α H- and 5 β H-C-nor-D-homosteroids, the chemical shifts of the 19-methyl protons change regularly in accordance with the nature, position, and configuration of the substituents in rings A and B. Consequently, the values of the relative screening and descreening of the signals from the

Chemical Shifts of the Methyl Protons, τ

Substance	5 α H-Series			5 β H-Series		
	imperialine series			verticine series [2]		
	C-19 CH ₃ (C)	C-21 CH ₃ (C)	C-27 CH ₃ (D) (J)	C-19 CH ₃ (C)	C-21 CH ₃ (C)	C-27 CH ₃ (D) (J)
(I)*	9.32	9.00	9.00 (6)	9.20	9.01	8.94 (8)
(II)	9.30	9.01	9.00 (7)	9.20	8.97	8.92 (7)
(III)*	9.28	9.01	9.00 (7.5)	—	—	—
(IV)	9.10	8.99	8.99 (6.5)	9.00	9.00	8.93 (6)
(V)	9.28	9.00	9.00 (6.5)	9.19	8.98	8.93 (7)
(VI)	9.21	9.00	9.00 (6.5)	9.09	8.96	8.93 (6)
(VII)	9.07	8.99	8.98 (7)	8.96	8.96	8.91 (7)
(VIII)	9.08	8.99	8.99 (6.5)	8.99	8.99	8.91 (7)
(IX)	9.32	9.01	9.01 (6)	9.24	8.99	8.94 (6)
(X)	9.30	9.01	8.99 (6)	9.24	9.01	8.97 (7)
(XI)	9.13	9.00	8.99 (6.5)	9.07	9.01	8.96 (6)

*In the NMR spectra of these substances (5 α H) (taken in a mixture of chloroform and trifluoroacetic acid), the singlet of the C-21 CH₃ is lifted into the weak field from the C-27 CH₃ doublet by 16 and 14 Hz, respectively.

19-methyl protons can be used to establish the positions and configurations of substituents and the configurations of the A and B rings in the C-nor-D-homosteroid alkaloids. The A and B rings in the 5 α H- and 5 β H-C-nor-D-homosteroids and the 5 α H- and 5 β H-steroids are similar, but the chemical shifts of the protons of the 19-methyl groups are different. When the values of the signals given in published tables [3-5] are used, to prove the structure and configuration of the steroid molecule, it is necessary to take into account the nature, the basic skeleton, and the configuration of the compound being compared.

The conditions of recording the NMR spectra have been given previously [6]. The bases were obtained from imperialine by the methods described by Boit [7].

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DETERMINATION OF THE CONFIGURATION OF THE HYDROXY GROUPS IN STEROID ALKALOIDS

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We have studied the NMR spectra of O, N-diacetylsolasodine (I), diacetyldihydrokorsevine (II) [1], O, N-diacetylpeimisine (III) [2], acetylsewkoridine (IV) [3], acetyl-desoxoimperialine (V), diacetyldihydroimperialine (VI), acetyl-imperialine (VII), diacetylisodihydroimperialine (VIII) [4], diacetylkorseveriline (IX) [5], diacetylpetilidine (X) [6], and diacetylpetilinine (XI) [7] (table).