It can be seen from the table that in the NMR spectra of the 5αH- and 5βH-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 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 5αH- and 5βH-C-nor-D-homosteroids and the 5αH- and 5βH-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.

Chemical Shifts of the Methyl Protons, τ

Substance	5αH-Seris			5βH-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)

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*In the NMR spectra of these substances (5αH) (taken in a mixture of chloroform and trifluoroacetic acid), the singlet of the C-21 CH_3 is lifted into the weak field from the C-27 CH_3 doublet by 16 and 14 Hz, respectively.

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].

REFERENCES

1. R. N. Nuriddinov and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], no. 4, 1968.
2. S. Ito, M. Kato, K. Shibata, and T. Nosol, Chem. Pharm. Bull., **11**, 1337, 1963.
3. R. F. Zürcher, Helv. Chim. Acta., **46**, 2054, 1963.
4. T. Masamune, N. Sato, K. Kobajashi, I. Jamasaki, and J. Mori, Tetrah., **23**, 1591, 1967.
5. S. Ito, I. B. Stothers, and S. M. Kupchan, Tetrah., **20**, 913, 1964.
6. R. N. Nuriddinov, A. I. Saidkhodzhaev, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], **4**, 161, 1968.
7. H. G. Boit, Ber., **90**, 723, 1957.

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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], acetyldesoxoimperialine (V), diacetyldihydroimperialine (VI), acetylimperialine (VII), diacetylisodihydroimperialine (VIII) [4], diacetylkorseveriline (IX) [5], diacetylpetilidine (X) [6], and diacetylpetilinine (XI) [7] (table).

It can be seen from the table that in the NMR spectra of the acetyl derivatives of the steroid alcohols the values of the signals from the methyl protons of the acetyl groups in the equatorial and axial positions are very similar, frequently being found on one line. Our results are not in agreement with the conclusions of American workers [8] that the chemical shifts of the methyl protons of axial acetyl groups must always be found in a stronger field than when they are in the equatorial position. Thus, for example, in diacetyldihydrokorsevine the acetyl group at C_3 has the equatorial orientation and the one at C_6 the axial.

Chemical Shifts, τ

Substance	(S) 3H, C–19 CH_3	(S) 3 H, C–18 CH_3	(D), 3H, C–21 CH_3	(S) 3H, C–21 CH_3	(D) 3H, C–26 CH_3	(D) 3H, C–27 CH_3	(M), H (olefin)	(S) 3H N–$COCH_3$ or NCH_3	(S) $(3H)_n$ $OCOCH_3$ (a)	(S) $(3H)_n$ $OCOCH_3$ (e)	(M), H (a) $HCOCOCH_3$	(M), H (e) $HCOCOCH_3$
(I)	9.04	9.16	9.14	—	9.00	—	4.70	7.88	—	8.05	5.50	—
(II)	9.15	8.45	9.32	—	9.07	—	—	7.76	8.05	8.05	5.35	5.05
(III)	9.36	8.35	9.21	—	—	—	—	7.96	—	8.04	5.36	—
(IV)	9.04	9.49	9.22	—	—	—	4.67	7.88	—	8.04	5.40	—
(V)	9.28	—	—	9.01	—	9.00	—	—	—	8.06	5.40	—
(VI)	9.08	—	—	8.99	—	8.99	—	—	8.05	8.05	5.36	5.11
(VII)	9.32	—	—	9.01	—	9.01	—	—	—	8.05	5.36	—
(VIII)	9.21	—	—	9.00	—	9.00	—	—	—	8.05	5.40	—
(IX)	9.11	—	9.21	—	—	9.21	—	—	8.05	8.03	—	4.97 5.14
(X)	9.21	—	9.23	—	—	9.23	—	—	8.04	—	5.42	—
(XI)	9.24	—	9.23	—	—	9.23	—	—	8.05	8.02	5.42	4.97

Note: S–singlet, D–doublet, M–multiplet, (a)–axial, (e)–equatorial.

In the NMR spectrum of the latter, the signal from the methyl groups of the axial and equatorial acetyl groups is found in the form of a six-proton singlet at 8.05 τ. The situation is similar in the NMR spectra of (V), (VI), (VII), (VIII), etc. Consequently, it is difficult to use the chemical shifts of the methyl protons of the acetyl groups to establish the structure and configuration of the steroid alcohols. More important are the signals from the equatorial and axial protons attached to the carbon atoms connected to the hydroxy groups. The chemical shifts of these protons are displaced strongly into the weak field after the hydroxy groups have been acetylated. The signals from the equatorial protons are found at 4.97–5.14 τ and those from the axial protons between 5.35 and 5.5 τ (see table), which is confirmed by literature data obtained in a study of the NMR spectra of the simplest epimeric compounds [8].

Thus, from the value of the signals from the protons on a carbon atom connected with an acetyl group in the NMR spectra of steroid alcohols it is accurately possible to establish the configuration of the acetyl groups and, therefore, of the secondary hydroxy groups.

O, N-diacetylsolasodine was obtained from solasodine. The NMR spectra were recorded in deuterochloroform on a JNM-4H-100 instrument with hexamethyldisiloxane as internal standard.

REFERENCES

1. R. N. Nuriddinov and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], **3**, 398, 1967.
2. R. N. Nuriddinov, R. Shakirov, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 3, 413, 1967.
3. R. N. Nuriddinov and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], **4**, 60, 1968.
4. H. G. Boit, Ber., **90**, 723, 1957.
5. R. N. Nuriddinov and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 4, 258, 1968.
6. R. N. Nuriddinov, B. Babaev, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], this issue, p. 332.
7. R. N. Nuriddinov, B. Babaev, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 4, 261, 1968.
8. R. U. Lemieuv, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, J. Amer. Chem. Soc., **79**, 1005, 1957; **80**, 6098, 1958.

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