was separated according to their basicities into 10 fractions. and from the 10-th fraction we obtained thalisopyrine. isolated previously from Th. isopyroides [3]. From a comparison of the UV and IR spectra, paper chromatography, and the melting point of a mixture, thalisopyrine was identical with an authentic sample of cryptopine kindly provided by Dr. J. Slavik (Czechoslovakia).

After chloroform extraction, the raw material was dried and covered with methanol. Six decantations were performed. The methanolic extract was evaporated and the residue was dissolved in 5% hydrochloric acid. The acid solution was washed with chloroform, and 0.03% of berberine chloride was isolated from it. Potassium iodide was added to the solution and the white crystals that deposited were separated off and identified as magnoflorine iodide. Yield 1.04%.

REFERENCES

1. S. T. Kholodkov, K. L. Lutfullin, and Z. F. Ismailov, DAN UzSSR, no. 4, 39, 1965.
2. Z. F. Ismailov, S. Kh. Maekh, and S. Yu. Yunusov, DAN UzSSR, no. 7, 32, 1959.
3. Z. F. Ismailov, A. U. Rakhmatkariev, and S. Yu. Yunusov, DAN UzSSR, no. 5, 34, 1959.

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NMR SPECTRUM OF FOLIOSIDINE

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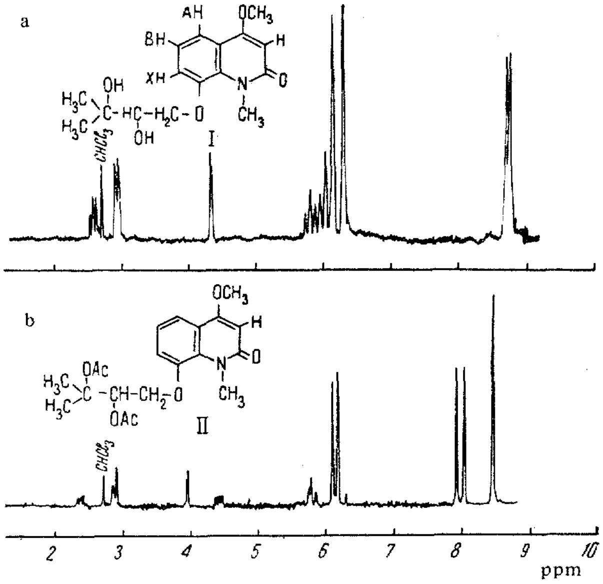
We have studied the NMR spectrum of foliosidine (I) [1] and O,O-diacetylfoliosidine (II) obtained on a JNM-4H-100/100 MHz instrument (internal standard HMDS, the signal of which was taken as 10 on the τ scale).



NMR spectra of foliosidine (a) and O,O-diacetylfoliosidine (b) in $CDCl_3$.

In the NMR spectrum of (I) (figure, a) the signals of three aromatic protons forming an ABX system appear clearly, but because of the closeness of the chemical shifts (CS) many peaks coincide. Consequently the proton X forms a distorted quartet with a center at $\tau = 2.60$ pmm; the two-proton doublet at 2.97 ppm, $J = 6.0$ Hz, relates to the AB protons. The one-proton singlet at 4.35 ppm corresponds to a β proton.

The molecule of (I) contains four CH_3 groups giving rise to four singlets in the NMR spectrum: $OCH_3-6.15$, $N-CH_3-6.30$ ppm and two CH_3 groups on quaternary carbon atoms—a doublet at 8.68 and 8.76 ppm which shows their nonequivalence, evidently because of the influence on them of the oxygen atom of the OH group. This is also shown by the CS of the protons metioned, which are shifted slightly to the weak-field region. The total intensity of the signals of the multiplet at 5.90 ppm in (I) (see figure, a) is five proton units. Consequently, in this region the signals of the protons of a CH_2-O group, two OH groups, and a methine proton coincide. The latter assumption is justified by the fact that in the spectrum of (II) (figure, b) in this region the signals of the two OH groups are completely absent and the signal of the HCOH proton undergoes a paramagnetic shift on acetylation and appears at 4.45 ppm, i.e., in the 5.80 ppm region. The signal of the remaining two-proton quartet corresponds to CH_2-O.

The nature of the splitting of the HCOAc proton at 4.45 ppm—a quartet with $J_1 = 7.5$ Hz and $J_2 = 3.0$ Hz—shows the nonequivalence of the CH_2 protons. The signals at 7.94 and 8.06 ppm relate to 2 $OCOCH_3$ and to the two CH_3 groups, since on acetylation a deshielding action of the C=O group and a shift of the signal of the two CH_3 groups into the weak field by $\Delta\tau = 0.32$ ppm is found. The position of the signals of the β proton of the ring B and the X proton show that the side chain of (I) and (II) is located above or below the plane of the ring: on acetylation the β

proton undergoes a considerable paramagnetic shift by 0.35 ppm as a result of the deshielding of the C=O of the acetate. The nature of the splitting of these three ABX protons also changes (see figure, b).

Thus, the results of a study of the NMR spectra of (I) and (II) confirm the structure proposed previously for these substances and enables the arrangement of their side chains to be deduced.

REFERENCE

1. V. I. Pastukhova, G. P. Sidyakin, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 1, 27, 1965.

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NMR SPECTRA OF THALICMINE, THALICSIMIDINE, AND THALICMIDINE

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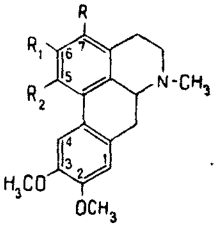
We have studied the NMR spectra of thalicmine (I) [1], thalicsimidine (II) [2], thalicmidine (III), and O-acetylthalicmidine (IV). The spectra were obtained on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard, its signal being taken as 10 (τ scale).



I $R = OCH_3$; R_1 u $R_2 = O_2CH_2$

II $R = R_1 = R_2 = OCH_3$

III $R = H$; $R_1 = OCH_3$; $R_2 = OH$

IV $R = H$; $R_1 = OCH_3$; $R_2 = OCOCH_3$

The NMR spectrum of substance (I) clearly shows two one-proton signals at 2.47 ppm (H-4) and 3.30 ppm (H-1). Because of their nonequivalence, the two protons of the methylenedioxy group form an AB system and give a quadruplet at 4.10 ppm with a geminal interaction constant $J_{AB} = 2.0$ Hz. At 6.10, 6.18, 6.21 ppm there are sharp signals of the three methyl groups of aromatic methoxyls. The 3-proton singlet in the strong field at 7.58 ppm relates to the $N-CH_3$ protons. In the 6.80–7.70 ppm region there is a multiplet due to three methylene and one methine protons.

The NMR spectrum of (II) has two one-proton signals at 2.11 ppm (H-4) and 3.30 ppm (H-1). The five OCH_3 groups give rise to four sharp signals at 6.11, 6.15, 6.18, and 6.35 ppm with a total intensity of 15 proton units. The signals of the OCH_3 group in position 7 are located in the very strong field at 6.35 ppm. The signal of the $N-CH_3$ group in (II) is found at 7.35 ppm.

In the NMR spectrum of (III) the three aromatic protons appear at 1.98 ppm (H-4), 3.30 ppm (H-1) and 3.56 ppm (H-7). The OCH_3 signals are found at 6.16, 6.18, and 6.28 ppm and the $N-CH_3$ at 7.55 ppm. In the spectrum of (IV), the signal of the aromatic proton in position 4 undergoes a considerable diamagnetic shift by 0.57 ppm, and at the same time the signal of the proton in position 1 undergoes a weak paramagnetic shift by 0.12 ppm. We have attempted to replace H-7 by deuterium [3]. When the PMR spectrum of the product was taken, it was found that H-7 had not disappeared. Consequently, the OH group in (III) is at position 5 and the OCH_3 group at position 6. The fact that H-4 in (IV) undergoes a marked shift in the strong-field direction is explained by the fact that H-4 is affected by the diamagnetic anisotropy of the carbonyl group of $OCOCH_3$. The spectrum of IV clearly shows the $OCOCH_3$ signal at 7.76 ppm. From a comparison of the spectra of (III) and (IV) it can be seen that in the 7.0 ppm region the intensity of the multiplet increases in (IV). This shows the presence of a signal of the OH group in this region in the spectrum of (III). The results of a direct comparison of thalicmidine with 2-O-methylisoboldine has shown that these substances