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.

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NMR SPECTRA OF THALICMINE, THALICSIMIDINE, AND THALICMIDINE

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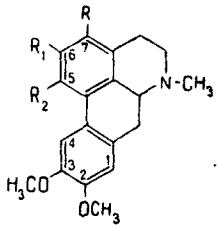
We have studied the NMR spectra of thalicmine (I) [1], thalicsimidine (II) [2], thalicmidine (III), and O-acetylthalicmidine (IV). The spectra were obtained on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard, its signal being taken as 10 (τ scale).



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

are completely identical. When the specific rotation of thalicmidine was redetermined, we found $[\alpha]_D^{17}$ + 44° (c 0.97; ethanol); + 41° (c 1.0; chloroform).

Thus, the assignment of the signals of the protons in the NMR spectra confirm the structures proposed previously for thalicmine (I) and thalicsimidine (II), and for thalicmidine it makes it possible to establish the structure 2,3,6-trimethoxy-5-hydroxyporphine (III).

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LETTER TO THE EDITOR

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In the paper "Alkaloids of Glaucium flavum" published in the journal Khimiya Prirodnykh Soedinenii [Chemistry of Natural Compounds], 3, no. 4, 285, 1967, the text of the summary was changed and it is therefore necessary to give the following explanation.

As a result of the investigations carried out, we consider that the base $C_{19}H_{21}NO_4$ and the alkaloid isolated by J. Slavik and L. Slavikova from G. flavum and described as d-aurotensine is actually bis-O,O-desmethylglaucine. Aurotensine is 2,9-dihydroxy-3,10-dimethoxytetrahydroprotoberberine. J. Slavik and L. Slavikova erroneously considered that the base $C_{19}H_{21}NO_4$ that they isolated from G. flavum was d-aurotensine. We have shown that this compound belongs not to the protoberberine group, but to the aporphine group of alkaloids.