a picrate with mp 127–128° C (water), $C_{14}H_{23}ON \cdot C_6H_8O_7N_3$ the properties of which agreed with those of the picrate of indicamine from Plantago indica [2].

From the chloroform fraction by treatment with a mixture of ethanol and petroleum ether (1 : 5) was isolated a base with mp 136–138° C, $[\alpha]_D^{25}$ −168.2° (c 0.215; ethanol). By comparative paper chromatograms and a mixed melting point, this alkaloid was shown to be identical with an authentic sample of N-methylcytisine [1].

REFERENCES

1. Kh. Ubaev, P. Kh. Yuldashev, and S. Yu. Yunusov, Uzb. khim. zh., no. 3, 33, 1963.
2. A. V. Danilova and R. A. Konovalova, ZhOKh, 22, 2237, 1952.

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MASS SPECTROMETRIC DATA FOR THALICMINE, THALICMIDINE, AND THALICSIMIDINE

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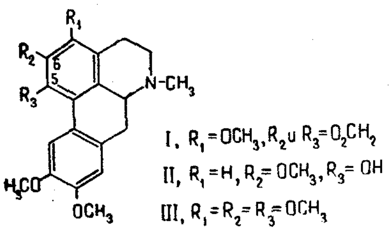
We have studied the mass spectra of the alkaloids thalicmine (I), thalicmidine, (II), and thalicsimidine (III).



I, $R_1 = OCH_3$, R_2 и $R_3 = O_2CH_2$
II, $R_1 = H$, $R_2 = OCH_3$, $R_3 = OH$
III, $R_1 = R_2 = R_3 = OCH_3$

Characteristic features of these alkaloids are the maximum intensities of the peaks of the molecular ions and the considerable intensities of the peaks of the $(M - 1)^+$ ions.

Substance	m/e and relative intensity, %							
	M^+	a	b	c	d	$(M-1)^+$	$(M-15)^+$	$(M-31)^+$
(I)	369(100)	326(15)	311(16)	295(21)	—	368(94)	354(22)	338(21)
(II)	341(100)	298(50)	283(11)	267(57)	236(21)	340(92)	326(36)	310(28)
(III)	385(100)	342(33)	327(17)	311(33)	280(26)	384(74)	370(50)	354(21)

The results of the fragmentation of the molecular ions of the alkaloids (I)–(III) agree mainly with literature data [1]. The mass spectra of these alkaloids contain fragments with m/e 43 ($H_2C{=}N{-}CH_3$) and *a* $(M - 43)^+$. The intensity of the ion *a* is from 15 to 50% of the maximum peak. When the ion *a* loses a methyl group, ion b is formed, and when it loses a methoxy group it forms ion c. The further loss of a methoxy group by ion c in the alkaloids (II) and (III) leads to the appearance of ion d.

The peaks of the ions $(M - 1)^+$, $(M - 15)^+$, and $(M - 31)^+$ are found in the spectra of all three compounds and are formed by the loss of hydrogen, methyl, and methoxy radicals from the molecular ion. The results of our study of the mass spectra of (I)–(III) are given in the table.

The transitions $a \rightarrow b$, $a \rightarrow c \rightarrow d$ are shown by the presence of the following metastable peaks in the mass spectra:

(I), $m^* = 311^2/326 = 296$ (calc. 296.6); $m^* = 295^2/326 = 267$ (calc. 266.9);
(II), $m^* = 283^2/298 = 269$ (calc. 268.7); $m^* = 267^2/298 = 239$ (calc. 239.2); $m^* = 236^2/267 = 208$ (calc. 208.5);
(III), $m^* = 327^2/342 = 312$ (calc. 312.6); $m^* = 311^2/342 = 283$ (calc. 282.8); $m^* = 280^2/311 = 252$ (calc. 252).

The mass spectra were recorded on an MKh-1303 mass spectrometer with an energy of the ionizing electrons of 34 eV, an ionizing current of 150 μA at 150° C (I), 185° C (II), and 130° C (III). The mass spectrometric data obtained confirm the structures proposed previously for the alkaloids (I) and (III) [2–4].

REFERENCES

1. M. Ohashi, J. M. Wilson, H. Budzikiewicz, M. Shamma, W. A. Slusarchyk, and C. Djerassi, J. Am. Chem. Soc., 85, 2807, 1963.
2. N. N. Progressov and S. Yu. Yunusov, DAN UzSSR, no. 10, 24, 1953.
3. Kh. G. Pulatova, Z. F. Ismailov, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 3, 67, 1967.
4. Z. F. Ismailov, M. V. Telezhenetskaya, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 4, 136, 1968.

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THE STRUCTURE OF MAJDINE

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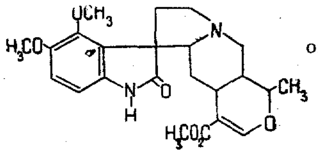
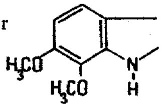
A structure (I), in which the OCH_3 substituents were allocated to the aromatic ring on the basis of an assignment of the proton signals of the NMR spectra taken on an instrument with a working frequency of 60 MHz was previously proposed for majdine [1].



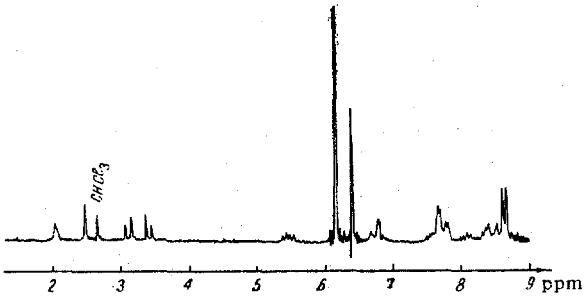
II

or



IIa

On considering the NMR spectrum of majdine obtained on a JNM-4H-100 instrument with a working frequency of 100 MHz (figure), it can clearly be seen that in the weak-field region there is a two-proton quadruplet at $\tau = 3.33$ ppm, J = 8.0 Hz, and $\tau = 3.53$ ppm, J = 8.0 Hz, corresponding to the ortho protons of an aromatic ring (the latter form a system of the AB type). Consequently, in majdine the two OCH_3 groups may be located at C_9 and C_{12}, at C_9 and C_{10}, or at C_{11} and C_{12} of the phenyl nucleus. The C_9, C_{12} positions can apparently be excluded since the protons at C_{10} and C_{11} would be equivalent.



NMR spectrum of majdine in $CDCl_3$.

To make a choice between the C_9, C_{10} and C_{11}, C_{12} positions, we compared the region of the AB quartet of majdine with that of the indoline alkaloid spegazzidine [2], in the NMR spectrum of which the protons at C_9, C_{10} form a quartet with a center at $\tau = 3.43$ ppm, J = 8.0 Hz, while in our case we have a quadruplet with the center at $\tau = 3.38$ ppm, J = 8.0 Hz. On the basis of this, we place the OCH_3 groups in majdine at C_9 and C_{10} or at C_{11} and C_{12}, as is shown by structures (II) and (IIa). Thus, an analysis of the NMR spectrum shows that majdine is the new hydroxyindole (II) or (IIa) and not an isomer of carapanaubine as was assumed previously [1].