

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 μ A 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].

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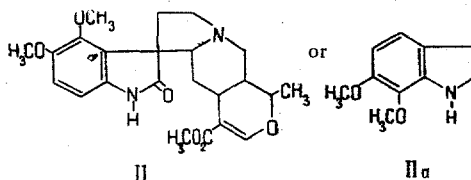
UDC 547.944.1

THE STRUCTURE OF MAJDINE

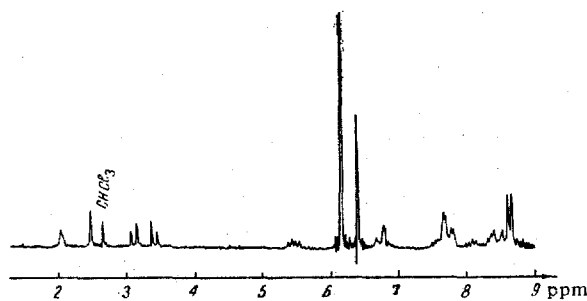
M. R. Yagudaev, N. Abdurakhimova, and S. Yu. Yunusov

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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].



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



NMR spectrum of majdine in CDCl_3 .

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.

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 spagazzidine [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].

The NMR spectrum of isomajdine also shows the identity of the position of the OCH_3 substituents in the aromatic ring of isomajdine and majdine.

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THE ALKALOIDS OF HAPLOPHYLLUM BUCCHARICUM

S. M. Sharafutdinova and S. Yu. Yunusov

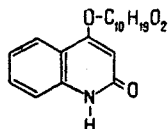
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From the plant H. bucharicum Litv. (family Rutaceae) collected in the flowering stage in the Kashka-Dar'inskaya Oblast we have isolated skimmianine [1], folifine [2], haplopine [3], and a new base bucharaine.

Bucharaine, with mp $151-152^\circ\text{C}$ (from methanol) has the composition $\text{C}_{19}\text{H}_{25}\text{O}_4\text{N}_4$, mol. wt. 331 (mass spectrometry). It gives a dibromo derivative with mp $145-146^\circ\text{C}$ (from acetone), an O-acetyl derivative with mp $168-169^\circ\text{C}$ (from acetone), and a N-methyl derivative with mp $142-143^\circ\text{C}$. The IR spectrum of the alkaloid has absorption bands at 3310 cm^{-1} (hydroxy group), 2955 (NH group), and 1657 cm^{-1} (amide carbonyl). The UV spectrum has the three maxima that are characteristic for 2-quinolone: λ_{max} 226, 266, and $276\text{ m}\mu$ ($\log \epsilon$ 2.76, 2.26, and 2.24, respectively).

The Adams hydrogenation of bucharaine gave a substance (A) with mp $354-356^\circ\text{C}$, with the composition $\text{C}_9\text{H}_7\text{O}_2\text{N}$, and a nitrogen-free oily substance (B) with the composition $\text{C}_{10}\text{H}_{22}\text{O}_2$. A direct comparison of substance (A) and its nitroso and O-methyl derivatives with 2,4-dihydroxyquinoline [4] and its nitro and O-methyl derivatives showed that they were identical.

Consequently the basic skeleton of bucharaine is 2,4-dihydroxyquinolone, with a $\text{C}_{10}\text{H}_{19}\text{O}_2$ residue attached in the γ position.



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