THE STRUCTURE OF CODONOPSININE

S. F. Matkhalikova, V. M. Malikov,
M. R. Yagudaev, and S. Yu. Yunusov

UDC 547.944/945

Previously, on the basis of preliminary results, the structure of 3,4-dihydroxy-5-(m-methoxyphenyl)-1,2-dimethylpyrrolidine was proposed for codonopsinine (I) [1].

The oxidation of (I) with potassium permanganate in acetone led to an acid with mp 179-180° C (sublimed) giving no depression of the melting point with a sample of anisic acid.

A study of the NMR spectrum of the diacetyl derivative of (I) (Fig. 1), taken in carbon tetrachloride, showed that there were two two-proton doublets at τ 2.82 and 3.24 ppm with an ortho coupling constant J = 8.5 Hz in the aromatic region.

This shows that the four aromatic protons form a four-spin system of the A_2B_2 type. It follows from this that the methoxy group in the aromatic ring is present in the para position to the pyrrolidine ring.

The results of a comparison of the mass spectra of codonopsine and (I) show that the main peaks in the latter differ from the corresponding peaks of codonopsine by 30 m/e (Table 1). This additionally shows the structural similarity of the alkaloids considered.

The mass-spectrometric fragmentation of (I) takes place with α-cleavages of C–C bonds [2]. Characteristic for it, as for codonopsine, is the loss by the molecular ion of 60 m/e, corresponding to the loss of ethylene glycol, which unambiguously shows the position of the hydroxy groups. This leads to the appearance of an ion with m/e 177 (a), from which, by the splitting off of a proton, the maximum ion in the spectrum with m/e 176 (b), corresponding to the ion with m/e 206 in the spectrum of codonopsine, is formed. The loss of 15 mass units by the ion with m/e 177 leads to an ion with m/e 162 (c). This corresponds to the ion with m/e 192 in the case of codonopsine [3].

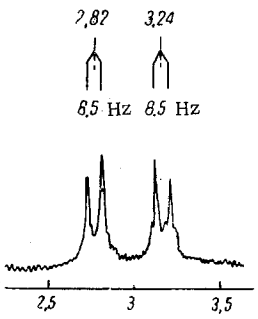
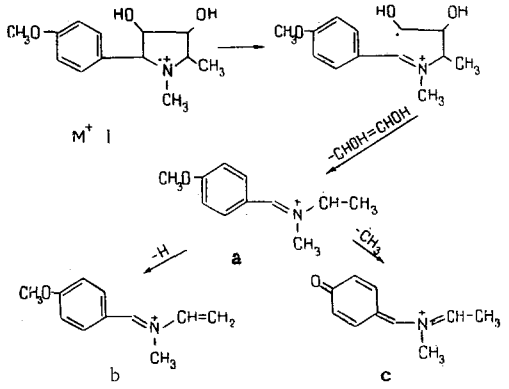


Fig. 1.

TABLE 1

Substance	Relative intensities, %			
	M^+	$(M-60)^+$	$(M-60-1)^+$	$(M-60-15)^+$
Codonopsine	267 (50)	207 (92)	206 (100)	192 (60)
Codonopsinine	237 (29)	177 (81)	176 (100)	162 (43)

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 210-211, March, 1971. Original article submitted January 13, 1971.



LITERATURE CITED

1. S. F. Matkhalikova, V. M. Malikov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 5, 607 (1969).
2. A. M. Duffield, H. Budzikiewicz, and C. Djerassi, J. Amer. Chem. Soc., No. 13, 87, 2926 (1965).
3. S. F. Matkhalikova, V. M. Malikov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 5, 606 (1969).