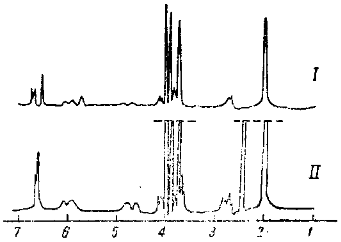
ALKALOID L-6–A $C_{(3)}$ HYDROXYLATED DERIVATIVE OF γ-LUMICOLCHICINE

B. Chommadov, M. K. Yusupov, and A. S. Sadykov

Khimiya Prirodnykh Soedinenii, Vol. 6, No. 2, p. 275, 1970

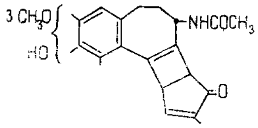
UDC 547.944.6

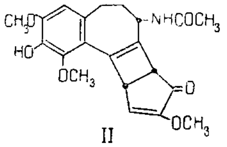
The isolation from Colchicum luteum Baker of two new alkaloids, L-5 and L-6, and the determination of the structure of L-5 as 2-desmethylcolchiceine has been reported previously [1]. The second alkaloid, L-6, with mp 291–293° C $[\alpha]_D^{20}-410°$, has a UV spectrum (λ_{max} 228, 264, 282, and 342 mμ) resembling those of β- and γ-lumicolchicines. On the basis of its IR and NMR spectra, the developed formula $C_{15}H_9(OH(OCH_3)_3(CO)(NHCOCH_3)$ was found for it. In addition, the NMR spectrum of the alkaloid L-6 (figure) shows signals (δ-scale) of the protons of methylene groups (2.65 and 1.98 ppm), an aromatic proton (singlet, 6.50 ppm), an olefinic proton (doublet at 6.70 ppm), and an imide proton (6.00 ppm), and a methine proton adjacent to nitrogen (4.60 ppm), and also a hydrogen bond (4.08 ppm), which is characteristic for the lumicolchicines [3].



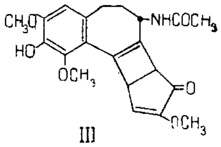
NMR spectrum of alkaloid L-6 (I) and its acetyl derivative (II) (in $CDCl_3$).

The mass spectrum of the alkaloid has the peak of the molecular ion (M^+), m/e 385 (moderate intensity) and a peak at 342 (very intense). The formation of the second peak is due to the splitting off of an acetyl group from the nitrogen atom, which is characteristic of lumicolchicines [4]. The results of a comparison of the mass spectra of the methyl ether of alkaloid L-6 (mp 275–276° C) and of γ-lumicolchicine shows that they are identical; a mixture gave no depression of the melting point (275–276° C). Consequently, alkaloid L-6 is a previously undescribed derivative of γ-lumicolchicine with a free hydroxyl (I).





II



III

In the NMR spectra of alkaloid L-6 and 3-desmethyl-β-lumicolchicine (II) the signals of the aromatic protons of ring A are identical, which shows their low sensitivity to changes in the configurations of rings C and D. It is known [5] that a O-acetyl group in the $C_{(3)}$ position of ring A, in contrast to positions $C_{(2)}$ and $C_{(4)}$ shifts the signal of the proton on the $C_{(1)}$ atom in the weak-field direction to a relatively small extent. The similar small (~0.10 ppm) shift of this signal into the weak field in acetyl derivatives of II and of the alkaloid L-6 shows that in the latter the hydroxyl group is also present on the $C_{(3)}$ atom. On the basis of these facts, for the alkaloid L-6 we propose the structure of 3-desmethyl-γ-lumicolchicine (III).

REFERENCES

1. B. Chommadov, M. K. Yusupov, and A. S. Sadykov, KhPS [Chemistry of Natural Compounds], 6, 82, 1970.
2. A. Sangster and K. Stuart, Chem. rev., 65, 69, 1965.
3. O. L. Chapman, H. G. Smith, and K. W. King, J. Am. Chem. Soc., 85, 803, 1963.
4. I. M. Wilson, M. Ohashi, H. Budzikewicz, F. Santavy, and C. Djerassi, Tetrah., 19, 2225, 1963.
5. V. Delaroff and P. Rathle, Bull. Soc. chim. France, 6, 1621, 1965.