THE STRUCTURE OF THE ALKALOID K-13 FROM Colchicum kesselringii

Kh. Turdikulov, M. K. Yusupov, and A. S. Sadykov

UDC 547.944.6

In a preceding paper [1] we have reported the isolation of alkaloids from the corms of Colchicum kesselringii Rgl. A study of the unknown phenolic substance with R_f 0.31 which we called alkaloid K-13 has shown that it belongs to the series of photochemical isomers of the tropolone alkaloids.

Alkaloid K-13 has the composition $C_{21}H_{23}O_6N$, mp 287-288°C, $[\alpha]_D$ −420° (c 0.40; chloroform). Its UV spectrum (Fig. 1) has three absorption maxima – at 226, 266, and 340 nm. The IR spectrum (Fig. 2) shows the absorption bands of a hydroxy group (3310 cm^{-1}), a conjugated carbonyl group (1710 cm^{-1}), and an amide carbonyl group (1635 cm^{-1}).

The NMR spectrum of the alkaloid K-13 (Fig. 3) shows the signals of one three-proton singlet at δ 2.04 ppm (N-acetyl group) and of three three-proton singlets at 3.72, 3.92, and 3.98 ppm (three O-methyl groups).

The above facts and functional analysis shows that alkaloid K-13 corresponds to the developed formula $C_{15}H_9(OCH_3)_3(OH)(CO)(NHCOCH_3)$.

Its molecular weight is 385 (low-intensity molecular ion in the mass spectrum). The mass-spectrometric decomposition of the alkaloid takes place with the formation of an intense peak of an ion with m/e 342. This is due to the splitting off of an acetyl group from a nitrogen atom, which is characteristic of the lumi derivatives of the tropolone alkaloids [2].

In view of the fact that in alkaloid K-13 the sign of the specific rotation is negative, it can be assigned to the lumi compounds of the γ series, and partial formula (I) may be proposed for it.

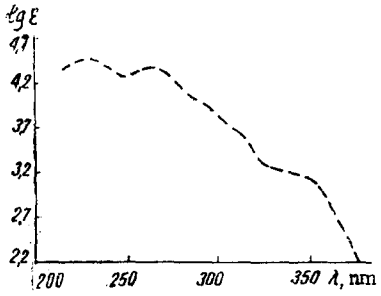


Fig. 1

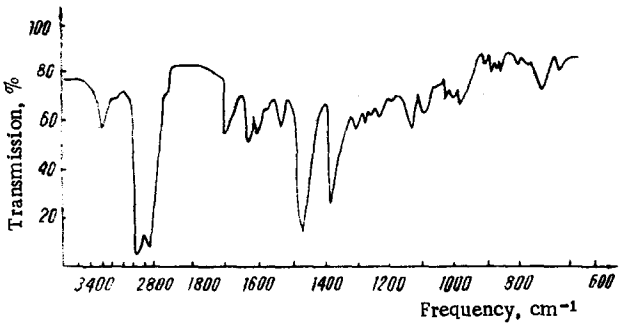


Fig. 2

Fig. 1. UV spectrum of alkaloid K-13 (methanol).

Fig. 2. IR spectrum of alkaloid K-13 (paraffin oil).

V. I. Lenin Tashkent State University. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 502-505, July-August, 1972. Original article submitted February 17, 1972.

TABLE 1

Phenophase	Date of collection	Weight of raw material, kg	Total alkaloids		Phenolic alkaloids	
			g	%	g	%
Flowering	3/23-26 1957	3,4	5,78	0,17	2,72	0,08
	3/1-5 1958	3,0	5,42	0,18	2,39	0,08
Setting of the fruit	4/18-20 1957	9,0	13,50	0,15	6,30	0,07
Fruit-bearing	4/20-26 1958	10,0	13,15	0,13	5,33	0,05

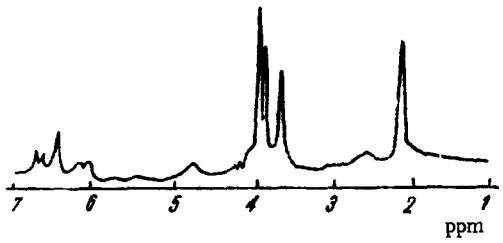
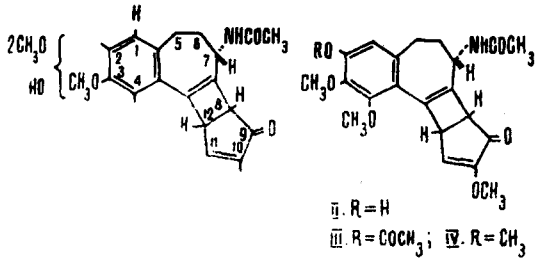


Fig. 3. NMR spectrum of alkaloid K-13 ($CHCl_3$).

The C_3 position of the hydroxy group is excluded since it is characteristic for a known substance – 3-demethyl-γ-lumicolchicine [3]. According to the NMR spectrum, the hydroxy group cannot occupy the C_{10} position, because the signal of one of the O-methyl groups is located in a stronger field (3.72 ppm) and corresponds to a C_{10} methoxy [4]. It is not characterized by the C_4 position, either: no alkaloid with the hydroxy group in this position has been found in colchicine-containing plants.

Thus, the only possible position for the phenolic hydroxy group is the C_2 atom; i.e., alkaloid K-13 corresponds to the structure of 2-demethyl-γ-lumicolchicine (II).



The acetylation of alkaloid K-13 with acetic anhydride gave a nonoacetyl derivative (III). Methylation of the alkaloid with diazomethane formed an O-methyl derivative (IV) identical with γ-lumicolchicine [2].

EXPERIMENTAL

Isolation of Fractions of Alkaloids. The corms of Colchicum kesselringii were gathered on the banks of the R. Syrdar'ya in the flowering and fruit-bearing period. The dried and comminuted raw material was extracted repeatedly with methanol. Details of the treatment of the extracts by the procedure described previously [5] are given in Table 1.

Isolation of Individual Compounds. The fraction of alkaloids with a phenolic nature isolated from the corms gathered in 1957 (9.0 g) was chromatographed on a column containing 180 g of alumina. Elution from the adsorbent with mixture of ether and chloroform in various proportions [1] led to the isolation of 3-demethyl-β-lumicolchicine, 2-demethyl-β-lumicolchicine, and 2-demethylcochicine. The subsequent elution of the adsorbent with chloroform gave 67 mg of alkaloid K-13.

Alkaloid K-13 (II) formed a white crystalline substance sparingly soluble in methanol and acetone, insoluble in ether and petroleum ether, and soluble in chloroform and in solutions of alkalis. The solutions gave no color with ferric chloride and the Oberlin–Zeisel reaction for the tropolone ring was negative. The substance dissolved in conc. sulfuric acid giving an orange solution.

Found %: C 65.22; H 6.23; N 3.40. $C_{21}H_{23}O_6N$. Calculated %: C 65.44; H 6.02; N 3.64.

Acetyl Derivative of (II) – (III). A mixture of 40 mg of (II), 100 mg of freshly fused anhydrous sodium acetate, and 0.7 ml of acetic anhydride was left at 45-50°C for a day. The completeness of the formation of the acetyl derivative was checked by thin-layer chromatography [alumina; chloroform–methanol (24 : 1), R_f 0.42; alkaloid K-13 with R_f 0.21]. After cooling, the mixture was diluted with methanol. The residue after the evaporation of the solvent was extracted with chloroform. This gave (III) with mp 274-276°C (from ethyl acetate and ether).

Methyl Ether of (II) – (IV). An ethereal solution of diazomethane was added to a solution of 10 mg of (II) in methanol. The mixture was left at room temperature until the following day. Then the solvent was distilled off, and the residual substance was shown by thin-layer chromatography to be identical with γ-lumicolchicine. The two compounds proved to be identical in their R_f values (0.64) and in the coloration of the spots with iodine vapor (gray).

SUMMARY

A new alkaloid, K-13, with the composition $C_{21}H_{23}O_6N$, mp 287-288°C, $[\alpha]_D$ −420°, has been isolated from the corms of Colchicum kesselringii Rgl.

On the basis of UV, IR, NMR, and mass spectroscopy and its conversion into γ-lumicolchicine, the structure of 2-demethyl-γ-lumicolchicine has been proposed for alkaloid K-13.

LITERATURE CITED

1. Kh. Turdikulov, M. K. Yusupov, and A. S. Sadykov, Khim. Prirodn. Soedin., 541 (1971).
2. J. M. Wilson, M. Ohashi, H. Budzikiewicz, F. Santavy, and C. Djerassi, Tetrahedron, 19, 2225 (1963).
3. B. Chommadov, M. K. Yusupov, F. G. Kamaev, and A. S. Sadykov, Izv. Akad. Nauk Turkmen. SSR, Seriya Fiziko-tekhn., Khim. i Geol. Nauk, III (1970).
4. V. Delaroff and P. Rathle, Bull. Soc. Chim. France, 1965, 1621.
5. M. K. Yusupov and A. S. Sadykov, Nauchn. Tr. TashGU im. V. I. Lenina, Khimiya Rast. V-v, II, No. 286, 56 (1966).