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ALKALOIDS OF *Delphinium tamarae*

L. V. Beshitaishvili, M. N. Sultankhodzhaev, K. S. Mudzhiri, and M. S. Yunusov

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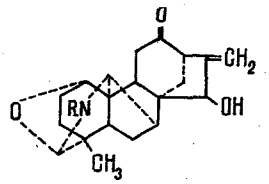
The roots of *Delphinium tamarae* Kem. Nath., collected in the period of the withering of the epigeal part of the environs of the village Bakuriani (Georgian SSR) have yielded 2.02% of combined alkaloids. When the combined material was separated, methyllycaconitine, lycoctonine, and anthranoyllycoctonine were isolated, together with a new base having mp 286°C which has been called norsongoramine. The structure of norsongoramine has been shown on the basis of its spectral characteristics and conversion to songoramine.

We have investigated the roots of *Delphinium tamarae* Kem. Nath., collected in the period of the withering of the epigeal part in the environs of the village of Bakuriani, Georgian SSR. The combined alkaloids amounted to 2.02% of the weight of the dry plant. When the combined alkaloids were separated, methyllycaconitine, lycoctonine, anthranoyllycoctonine, and a new base with the composition $C_{20}H_{25}NO_3$, mp 286°C (acetone), were isolated. The NMR spectrum of the new alkaloid contains the signals of tertiary C-methyl group (three-proton singlet at 1.12 ppm) and of a terminal methylene group (broadened one-proton singlets at 4.63 and 4.85 ppm). In the IR spectrum there are the absorption bands of hydroxy groups at 3450 and 3530 cm^{-1} and of a carbonyl in a 6-membered ring at 1710 cm^{-1}.

The mass spectrum of the compound is characteristic for the alkaloids of the songorine group and is similar to that songoramine [1]. In addition to the peak of the molecular ion (M^+ 327), there is a peak of the $M^+ - 56$ ion, showing the presence of the grouping of an internal ether of an α-carbinolamine [1].



I. R=H
II. R=C_2H_5

The difference in the molecular weights of the alkaloid and of songoramine of 28 amu, the absence of the signal of N-ethyl group from the NMR spectrum, and the presence of an internal α-carbinolamine ether grouping have permitted the assumption that the alkaloid is

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norsongoramine (I). This hypothesis has been confirmed by the production of songoramine (II) on the N-ethylation of the alkaloid with ethyl iodide in the presence of potassium carbonate.

EXPERIMENTAL

The mass spectra were recorded on MKh-1303 and MKh-1310 instruments fitted with systems for direct introduction into the ion sources, the NMR spectra on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard (the values are given in the δ scale), and the IR spectra on a UR-20 spectrophotometer in tablets with KBr. Type KSK silica gel and alumina (activity grade II) were used for chromatography.

Isolation and Separation of the Combined Alkaloids. The air-dry cominuted roots of *Delphinium tamarae* (4 kg) were moistened with a 5% solution of sodium carbonate, and the alkaloids were extracted with chloroform. The chloroform extract was shaken with 5% sulfuric acid solution. With cooling, the acid solution was made alkaline with sodium carbonate, and the alkaloids were extracted first with ether and then with chloroform. Distillation of the ether yielded 62 g, and of the chloroform 19 g, of combined alkaloids. A methanolic solution of the combined alkaloids yielded 22.4 g of methyllycaconitine perchlorate.

The mother liquor after the elimination of the methanol was dissolved in water, and the solution was washed with chloroform and was made alkaline with sodium carbonate, and the alkaloids were extracted with ether and chloroform. With the aid of acetone, the washed chloroform fraction yielded 2.4 g of lycoctonine. The ether-extracted fraction was chromatographed on a column of alumina, and elution with ether–methanol (1:1) gave 0.8 g of lycoctonine, and with methanol alone 0.9 g of anthranoyllycoctonine was obtained.

The chloroform-extracted part of the combined alkaloids was treated with acetone, which gave 9 g of lycoctonine. The acetone was evaporated off from the mother solution and the residue was dissolved in 5% sulfuric acid; the acid solution was washed with chloroform and was made alkaline with sodium carbonate, and the alkaloids were extracted with ether and chloroform. The ether fraction yielded 4.4 g of methyllycaconitine perchlorate. The chloroform fraction was chromatographed on a column of alumina, and elution with chloroform–methanol (50:1) yielded 30 mg of norsongoramine.

Norsongoramine, mp 286-288°C (acetone). Mass spectrum: M^+ 327 (28%), 310 (23%), 299 (7%), 281 (100%), 271 (29%).

N-Ethylation of Norsongoramine. To 15 mg of the alkaloid in 3 ml of dry acetone were added 50 mg of K_2CO_3 and two drops of ethyl iodide. The mixture was boiled for 90 min, the solvent was evaporated off, the residue was dissolved in water, the solution was made alkaline with sodium carbonate, and the reaction product was extracted with ether. After the ether had been distilled off, 8 mg of a product was obtained which was identified as songoramine (by TLC and mass spectroscopy).

SUMMARY

From the roots of *Delphinium tamarae* have been isolated methyllycaconitine, lycoctonine, anthranoyllycoctonine, and the new base norsongoramine, the structure of which has been demonstrated.

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