

ALKALOIDS OF THE EPIGEAL PART OF Thalictrum minus AND

Th. foetidum

D. A. Murav'eva, O. N. Tolkachev,
and A. A. Akopov

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In studying the alkaloid compositions of Thalictrum minus and Th. foetidum L. - representatives of the flora of the Northern Caucasus - we have considered the epigeal parts of both species, while incidently studying the number of chromosomes, which is particularly important in relation to the highly polyploid species Th. minus.

To obtain the total alkaloids from the raw material we used the method of chloroform extraction followed by the isolation of the individual bases with the aid of column and preparative thin-layer chromatography.

The chromosomes were calculated in preparations of young rootlets and buds of the plants fixed with Carnoy's fluid [1]. The results of the investigation are given below:

Site and data of collecting <u>Th. minus</u> 2n = 42	Plant organ and vegetation phase	Total alkaloids, % on the absolutely dry raw material	Alkaloid
SO ASSR,* Terskaya, Mozdokskii region, May 28, 1983.	Herbage Budding	0.66	Thalicberine O-Methylthalicberine α -Allocryptopine Palmatine Base I Base II
<u>Th. foetidum</u> 2n = 14			
KChAO,† Daut, Karachaevskii region, July 10, 1983	Herbage Fruit-bearing	0.31	Thalflavine Magnoflorine Berberine

*Severo-Osetinskaya Autonomous Soviet Socialist Republic.

†Karachaero-Cherkesskaya Autonomous Province.

The bases isolated were identified from the results of a comparison of their physico-chemical characteristics, UV, IR, NMR, and mass spectra, and literature information [2-5].

The bases α -allocryptopine, palmatine, magnoflorine, and berberine were identified additionally in comparison with authentic samples. The properties of base(I), isolated in the form of the hydroxide, were compared with the properties of N-methylcanadine hydroxide, obtained from berberine, and their identity was established [6].

The fraction of quaternary iodides yielded the base (II) with mp 125-128°C (ethanol). UV spectrum, $\lambda_{\max}^{\text{ethanol}}$: 287 nm. NMR spectrum of the base (II) (CF₃COOH, ppm, TMS = 0); 3.43 (s, 3 H, N-CH₃); 3.98 and 4.05 (s, 2-OCH₃); 4.98 (s, 2 H); 6.01 (s, 2 H, CH₂-O₂); 6.8 and 7.15 (s, 4ArH). The mass spectrum showed with peaks of ions with m/z 354 (M⁺), 353, 339, 174, 164, 149, 142, and 127.

In the PMR spectrum the presence of a broad singlet in the 4.98 ppm region of two aliphatic protons in the base (II), in contrast to the quartet in the 4.79 ppm region of N-methylcanadine, permitted us to draw the conclusion that base (II) was a 10,11-substituted N-methyl derivative of tetrahydroprotoberberine [7].

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Thus, we have isolated six bases from Th. minus, of which base (II) is new for the genus [8, 9].

Three bases have been isolated from Th. foetidum of which thalflavine is new for this species [4].

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SPECIOSAMINE - A NEW BASE FROM Colchicum speciosum

B. Chomnadov, M. K. Yusupov,
and Kh. A. Aslanov

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The combined alkaloids of Colchicum speciosum Stev. (showy autumn crocus), obtained from the corms, were separated into fractions of strongly basic, weakly basic, and neutral substances. Then a chloroform extract of the weakly basic compounds was treated successively with 3% caustic soda solution and with water and was dried over sodium sulfate, and after the solvent had been distilled off the mixture of substances was separated by chromatography on a column of alumina. By eluting the substances with mixtures of ether and chloroform in ratios of 9:1, 3:1, 2:1, 1:1, and 1:2 and with chloroform, four individual compounds were isolated with R_f 0.86, 0.83, 0.76, and 0.68 (TLC on type LS 5/40 silica gel with 13% of gypsum; methanol-chloroform-benzene-acetone-25% aqueous ammonia (8:10:3:6:3) system). We have established the structure of one of them, with R_f 0.83, composition $C_{28}H_{31}O_5N$, mp 192-294°C, $[\alpha]_D^{25} -42^\circ$ (c 0.26; chloroform), mol. wt. 461 (mass spectrum), and have called it speciosamine (I).

From its color reactions [1, 2] and spectral characteristics, (I) was assigned to the group of tropolone alkaloids of the autumn crocuses. Its UV spectrum had absorption maxima at 248 and 350 nm, and its IR spectrum had eight absorption bands in the 1400-843 cm^{-1} region that were characteristic for the tricyclic system of the colchicine alkaloids [3], and those of a tropolone ring (1588 cm^{-1}) and of a tropolone carbonyl (1616 cm^{-1}) [3, 4]. The PMR spectrum of (I) exhibited the signals of four methoxy groups (3.83, 3.80, 3.76, and 3.54 ppm), of nine aromatic protons - H_8 (7.90 ppm, s), H_{12} (6.95 ppm, d, $J_{12,11} = 11$ Hz), H_{11} (6.52 ppm, d, $J_{11,12} = 11$ Hz), and H_4 (6.37 ppm, s) of a tropolone ring [5], a five-proton singlet at 7.14 ppm, and a three-proton singlet at 2.00 ppm, obviously due to the presence in the structure of the base of a monosubstituted benzene ring and of a N-methyl or N-acetyl group. In view of the absence from the IR spectrum of the absorption band of an amide carbonyl, the last of the signals mentioned can be assigned to a N-methyl group. The absence of the signals of a NH group from the spectrum was also noted.

The elementary composition and the PMR spectrum of the alkaloid permitted the assumption that it was an analogue of speciosine (II) [6, 7], isolated from the same plant previously. A comparison of their developed formulas showed that in (I), unlike (II), there was no hydroxy group. The closeness of the structures of these two compounds was also confirmed by the

V. I. Lenin Tashkent State University. M. I. Kalinin Turkmen Agricultural Institute, Ashkhabad. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 417-418, May-June, 1985. Original article submitted January 8, 1985.