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ALKALOIDS OF THE MONGOLIAN FLORA.

IV. TURCOSINE — A NEW ALKALOID FROM Aconitum turczaninowi

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As the result of a further study of the total alkaloids from the epigeal part of Aconitum turczaninowi we have isolated beiwutine and delcaroline and also a new alkaloid, which has been called turcosine. The structure of turcosine as 6β,16β-dimethoxy-4β-methoxymethyl-1α,7β,8β,10β,14α-pentahydroxy-N-ethylaconitane has been shown from a study of the IR, mass, PMR, and ^{13}C NMR spectra of the alkaloid and of the triacetate obtained from it.

In the preceding communication [1] we described the isolation from the epigeal part of Aconitum turczaninowi Worosch of aconitine, delsoline, delcosine, and lepenine and the new alkaloid tursoline. Continuing the study of the alkaloid composition of this plant, we have obtained beiwutine and delcaroline and a new alkaloid, which we have called turcosine (I).

Turcosine (I) has the composition $C_{24}H_{39}NO_8$ (M^+ 469.26664, HRMS). In the IR spectrum of alkaloid there were absorption bands of hydroxy groups at 3300-3530 cm^{-1} and of ether bonds at 1090 and 1100 cm^{-1}. The PMR spectrum of turcosine contained the signals of a N-ethyl group and of three methoxy groups and also the signals of a C-6-α proton at 3.99 ppm in the form of a doublet (J = 2 Hz) [2] and of a C-14-β proton in the form of a doublet of doublets at 4.62 ppm ($J_1 = J_2 = 5$ HZ). The mass spectrum of the alkaloid was close to that of delcosine, but differed from it by 16 m.u., i.e., by the presence of an additional hydroxy group. In the mass spectrum of turcosine, just as in the case of delcosine, the maximum peak was that of the $M^+ - 15$ ion, and there were also the ions $M^+ - 17$ (41%) and $M^+ - 33$ (38%), showing the presence of a hydroxy group at C-1 and a methoxy group at C-6 and of a 7,8-diol system [3].

In a comparison of the PMR spectra of turcosine (I) and delcosine (III) it was observed that the signal of the C-14-β proton was shifted downfield by 0.52 ppm (in the PMR spectrum of delosine the signal appears at 4.10 ppm), which is connected with the presence of a hydroxy group at C-10 [4].

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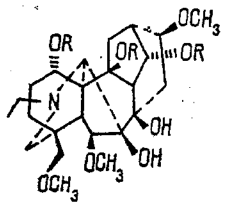
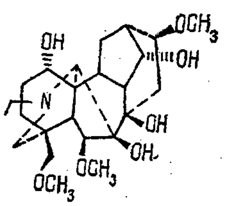
TABLE 1. Chemical Shifts of the Carbon Nuclei of Turcosine (I), Delcosine (III) and Delcaroline (IV)

Carbon	I	III	IV	Carbon	I	III	IV
1	69,7	72,7	79,4	13	39,9	45,3	37,0
2	27,3	27,5	25,5	14	74,2	75,8	73,6
3	30,5	29,4	32,2	15	35,3	34,5	33,9
4	37,3	37,6	38,1	16	81,2	82,0	81,3
5	41,2	44,0	45,1	17	66,9	66,3	66,1
6	90,5	90,1	90,8	18	77,3	77,4	77,2
7	87,1	87,9	88,0	19	57,1	57,1	52,5
8	76,4	78,1	75,1	N–CH$_2$	50,4	50,4	51,3
9	54,8	45,3	54,0	CH$_3$	13,3	13,7	14,3
10	81,8	39,4	79,9	6′	57,6	57,4	57,7
11	53,6	48,9	53,8	16′	56,3	56,4	56,3
12	39,9	29,4	37,6	18′	59,1	59,1	59,1

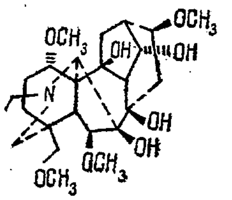
The acetylation of turcosine with acetic anhydride in the presence of pyridine for 48 h gave the triacetyl derivative (II). The PMR spectrum of turcosine triacetate revealed downfield shifts of the signal of the C-1-β proton (5.20 ppm, 1H, q, J_1 = 10 Hz, J_2 = 7 Hz) and of that of the C-14-β proton (5.10 ppm, t, J = 5 Hz), showing that the hydroxy groups at C-1 and C-14 had been acetylated. The third acetyl group was obviously located at C-10, since the hydroxy groups of diol systems are not acetylated under these conditions. It is possible that cooperation on the part of the 1,3-located hydroxy groups at C-1 and C-14 has an effect here.



I. R=H
II. R=Ac



III



IV

The facts given above permitted the conclusion that turcosine differed from delcosine by the presence of a hydroxy group at C-10. This conclusion was confirmed by a study of the ^{13}C NMR spectrum of turcosine. The multiplicities of the signals were found with the aid of the INEPT technique. Assignments were made in a comparison with the spectra of delcosine (III) and delcaroline (IV) [5, 6].

Consequently, turcosine is 6β,16β-dimethoxy-4β-methoxymethyl-1α,7β,8β,10β,14α-pentahydroxy-N-ethylaconitane.

EXPERIMENTAL

We used KSK silica gel and alumina (activity grade I) for chromatography.

Mass spectra were recorded on a MKh-1310 instrument with a system for direct introduction into the ion source, IR spectra on a UR-20 spectrometer (KBr), and PMR and ^{13}C NMR spectra on a Bruker AM-300 MHz spectrometer in deuterochloroform at frequencies of 300 and 75 MHz, respectively.

Isolation of the Total Alkaloids. The air-dry epigeal part of Aconitum turczaninowi gathered in the budding period in the Central aimak of Mongolia (17 kg) was wetted with a 5% solution of sodium carbonate and was extracted five times with chloroform. The chloroform extracts were concentrated to a volume of 10 liters and the alkaloids were extracted with 5% sulfuric acid (5 liters). With cooling, the acid solution was made alkaline with sodium carbonate, and the alkaloids were exhaustively extracted with chloroform. The chloroform extract was evaporated and, after elimination of the solvent, 130 g of total alkaloids was obtained, which corresponds to 0.76% of the weight of the dry plant.

Separation of the Total Alkaloids. The total alkaloids (50 g) were chromatographed on a column of alumina (ratio of sorbent to substance 200:1) using gradient elution (hexane, chloroform, methanol). The fractions obtained on elution with hexane–chloroform (4:1) were rechromatographed on a column of alumina with elution by hexane–chloroform (1:1), and, with the aid of ether, 0.05 g of aconitine was isolated.

Acetone treatment of the fractions obtained on elution with hexane–chloroform (7:3) gave 0.1 g of delsonine.

The fractions obtained on elution with hexane–chloroform (1:1) yielded 0.15 g of lepenine (acetone) and 0.17 g of delcosine.

With the aid of acetone, 1.0 g of turcosine was isolated from the hexane–chloroform (1:4) eluates.

The fractions obtained on elution with hexane–chloroform (3:2) were rechromatographed on a column of alumina, and, by elution with hexane–chloroform (2:1), 0.2 g of tursoline was isolated (acetone).

The fractions obtained on the further elution by hexane–chloroform (3:2) were rechromatographed on a column of silica gel. After elution with benzene–methanol (50:1), 0.3 g of delcaroline was isolated with the aid of acetone, and on further elution 0.02 g of beiwutine was obatinbed (ether).

Turcosine (I), mp 206-208°C (acetone). IR spectrum (ν_{max}^{KBr}, cm^{-1}): 3300-3530, 1090, 1100. PMR spectrum ($CDCl_3$, δ, ppm): 1.08 (3H, s, J = 7 Hz, $N-CH_2-CH_3$), 3.33, 3.35, 3.38 (each 3H, s, 3 × OCH_3), 4.62 (1H, dd, J = 5 Hz, C-14–β-H), 3.99 (1H, d, J = 2 Hz, C-6–α-H). Mass spectrum, m/z (%): M^+ 469(14), 454(100), 452(41), 438(12), 436(38), 424(3), 420(7), 418(12), 413(2), 398(5), 382(5).

Turcosine Triacetate (II). A mixture of 0.12 g of turcosine in 5 ml of acetic anhydride and 0.2 ml of pyridine was kept at room temperature for 48 h. The excess of acetic anhydride was eliminated by evaporation, the residue was dissolved in water, and the solution was made alkaline with sodium carbonate and was extracted with ether. After evaporation and the elimination of the ether, the product was purified on a column of deactivated alumina. Elution with ether–methanol (50:1) gave 0.06 g of homogeneous amorphous turcosine triacetate. IR spectrum (ν_{max}^{KBr}, cm^{-1}): 1720. PMR spectrum ($CDCl_3$, δ, ppm): 1.02 (3H, t, J = 7 Hz), 1.95, 1.97, 2.09 (each 3H, s, 3 × $OCOCH_3$), 3.20, 3.21, 3.32 (each 3H, s, 3 × OCH_3), 3.87 (1H, d, J = 2 Hz, C-6–α-H), 5.10 (1H, t, J = 5 Hz), 5.20 (1H, q, J_1 = 10 Hz; J_2 = 7 Hz). Mass spectrum m/z, (%): M^+ 595(7), 536(100).

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