(CuK_α radiation, graphite monochromator, $\theta/2\theta$ scanning). The crystals were monoclinic: a = 9.196(2), b = 14.711(3), c = 17.792(5) Å; β = 91.87(3); d_{calc} = 1.508 g/cm³; space group $P2_1/n$; Z = 4. In the calculations we used 2619 reflections with $|F| > 4\sigma(|F|)$. The structure was interpreted by the direct method in the full-matrix isotropic-anisotropic approximation using the XTL-SM program to R = 0.064. All the H atoms, located in the calculated positions, were refined isotropically. The coordinates of the nonhydrogen atoms are given in Table 1.

The crystal structure of the complex $2C_{11}H_{13}N^{2+}\cdot[ZnCl_4]^{2-}$ is shown in Fig. 1. The crystallographically independent part of the structure consists of the complex anion $[ZnCl_4]^{2-}$ and two cations of deoxypeganine protonated at the N1 atoms, $2[DOP + H]^+$. The coordination environment of the Zn is a slightly distorted tetrahedron. The crystal is constructed of cation–anion–cation triads formed by the H-bonds Cl4...N1(Ia) (3.13 Å), Cl1... N1(Ib) (3.43 Å), and Cl3...N1(Ib) (3.34 Å).

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ALKALOIDS OF Aconitum orientale

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Caucasian monkshood Aconitum orientale, family Ranunculaceae, is an annual herbaceous plant growing in the mountain-forest and subalpine zones of the Caucasus [1, 2]. It is used in folk medicine as a wound-healing agent [3]. Alkaloids have been isolated from the herbage and roots of this plant collected in Azerbaidzhan and Georgia: avadharine and lappaconitine [4], and also acetyllappaconitine, gigactonine, cammaconine, lycoctonine, and ranaconitine [5].

Lappaconitine hydrobromide is known as the antiarrhythmic drug Allapinin. An expansion of the raw materials base for the drug will provide the possibility of an increase in the volume of its production and a more rational approach to the preservation of plant resources.

We have studied the alkaloids of Caucasian monkshood, the sole representtive of the Lycoctonum D. C. section of the genus Aconitum in the Northern Caucasus, for which the presence of lappaconitine is the main chemotaxonomic characteristic. The specimens for investigation were collected in the Northern Caucasus (Arkhyz, Karachaevo-Cherkessk Autonomous Province).

The total alkaloids (8.3 g, 0.55%) were obtained by chloroform extraction and, from these, lappaconitine and gigactonine were isolated by crystallization from methanol. After the separation of the crystals, the mother liquor was chromatographed on a column of alumina (2.0 × 75 cm). Hexane and also mixtures of diethyl ether and hexane in various proportions were used as eluents. In this way, six alkaloids were isolated: lappaconitine, corydine, lappaconine, gigactonine, N-deacetyllappaconitine, and lycoctonine [5, 6].

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The amount of lappaconitine in the total alkaloids was determined by a gravimetric method at the stage of treating the total ether-soluble alkaloids with methanol and on column chromatography of the mother solution on alumina [diethyl ether–hexane (1:1)]. Lappaconitine made up about 25% of the total alkaloids, i.e., 0.12-0.15% on the weight of the raw material.

Thus, for the first time, six alkaloids have been isolated from the epigeal part of Caucasian monkshood collected in the Northern Caucasus in the incipient vegetation phase, five of which were diterpene alkaloids (lappaconitine, lappaconine, N-deacetyllappaconitine, lycoctonine, and gigactonine), while one belonged to the isoquinoline group – corydine. Lappaconine and corydine have not previously been isolated from this species.

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SYNTHESIS OF THE DIBENZYL ESTER OF tert-BUTOXYCARBONYL-L-ALANYL-D-GLUTAMIC ACID FROM RACEMIC GLUTAMIC ACID

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The synthesis has been effected of the dibenzyl ester of Boc-L-alanyl-D-glutamic acid by the esterification of D,L-glutamic acid, condensation of the racemic diester with the p-nitrophenyl ester of Boc-L-alanine, and separation of the mixture of diastereomers.

The dipeptide L-alanyl-D-glutamic acid (L-Ala-D-Glu) is a component part of a number of immunoactive glycopeptides [1-3]. Methods are known for obtaining the dibenzyl ester (DBE) of Z-Ala-D-Glu [2], the DBE of Boc-L-Ala-D-Glu (I) [1, 4, 5], and the dimethyl ester of Boc-L-Ala-D-Glu [6] in which D-glutamic acid was used. We have developed a synthesis of (I) from the cheap and readily available racemic glutamic acid which includes the stage of the azeotropic esterification of D,L-glutamic acid with benzyl alcohol and the condensation of the racemic diester with the p-nitrophenyl ester of Boc-L-alanine [7], with the subsequent separation of the mixture of diasteromers by crystallization from ether.

A mixture of 3.0 g (20.4 mmoles) of D,L-glutamic acid, 4.26 g (24.8 mmoles) of TsOH, 25 ml of benzyl alcohol, and 40 ml of benzene was boiled with a Dean–Stark trap until the evolution of water ceased. The solution was evaporated, and the DBE of D,L-Glu was precipitated with ether in an amount of 5.56 g (90%). A solution of 3.0 g (9.2 mmoles) of the diester in 5 ml of DMFA was treated with 3.0 g (9.7 mmoles) of the p-nitrophenyl ester of Boc-L-Ala and 1.3 ml of Et_3N, and the mixture was stirred at 40°C for 2 days. The resulting solution was evaporated and the residue was dissolved in EtOAc and was washed free from p-nitrophenol with 1 N aqueous ammonia. The organic layer was dried and evaporated. The residue (3.84 g; 84%) was crystallized from ether, to give 1.77 g (39%) of dipeptide (I) with mp 105-107°C and $[\alpha]_{546}^{20}$ −2.0° (c 2.0; MeOH). The mother solution was evaporated, giving a product crystallizing with difficulty from hexane (the DBE of Boc-L-Ala-L-Glu, II) with $[\alpha]_{546}^{20}$ −33° (c 2.0; MeOH).

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