In the PMR spectrum taken in $CDCl_3$ signals were observed from a methoxy group at (ppm) 3.75 (3H, s), from a methylenedioxy group at 5.98 (2H, s), from methylene protons at 3.00 (2H, t) and 4.30 (2H, t), each with J = 7 Hz, and from six aromatic protons at 6.12 (1H, d, J = 8.5 Hz), 7.13 (1H, d, J = 8.5 Hz, 6.77 (1H, s), 7.12 (1H, s), 7.47 (1H, s), and 9.11 (1H, s). When (II) was reduced with $NaBH_4$ in methanolic solution, a crystalline base was obtained with mp 179-180°C, M^+ 325, whichwas identified as (±)-tetrahydroberberrubine. From the facts given above, base (II) was identified as berberrubine [10].

Thus, from young shoots of B. iliensis Pop., together with bases known previously, we have isolated magnoflorine, obaberine, berbamunine, N-methylcoclaurine, and berberrubine, and also (+)-β-N-methylcorypalmine, which is a new alkaloid, found in Nature for the first time.

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ATIDINE AND ATISINE AZOMETHINE FROM Aconitum zeravschanicum

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Continuing a study of the alkaloids of Aconitum zeravschanicum, from the epigeal part of the plant gathered in the environs of the village of Dzhirgatal' (Tadzhikistan, Peter I Range) at the beginning of vegetation, together with the heteratisine [1], atisine, isoatisine, nominine [2], and zeravshanisine [3] found previously, we have isolated base (I) with mp 179-180°C (acetone), M 359 (mass spectrometry) and base (II) with mp 180-182°C (hexane–acetone) M 299 (mass spectrometry).

The IR, PMR, and ^{13}C NMR spectra showed that (I) belonged to the C_{20}-diterpene alkaloids of the type of dihydroatisine; they were identical with those of atidine [4-6], found previously in Aconitum heterophyllum [7].

Base (II) dissolved readily in chloroform, methanol, and ethanol, moderately well in acetone, and sparingly in hexane. Its IR spectrum (tablet with KBr) contained absorption bands at (cm^{-1}) 3340 (OH group), 3080, 900 ($C{=}CH_2$), and 1650 (N=C bond). In its PMR spectrum (100 MHz, $CDCl_3$, 0 – HMDS) signals were observed at δ (ppm) 0.77 (3H, s, $C18{-}H_3$), 3.35 (2H, d, J ≈ 3.0 Hz, $C19{-}H_2$), 3.61 (1H, br. s, C15–αH), 4.98, 5.03 (1H, d, J ≈ 2.0 Hz; 1H, s, $C17{-}H_2$), and 7.83 (1H, br. s, C20–H). The mass spectrum of (II) showed the peaks of ions with m/z 299 (M^+, 100%), 284, and 256.

The spectral results permitted (II) to be assigned to the C_{20}-diterpene alkaloids and were close to those of the azomethine derivatives of the alkaloids atisine [5, 8] and veatchine [5]. The heating of (II) in 10% HCl for 10 h gave a keto derivative (III) with

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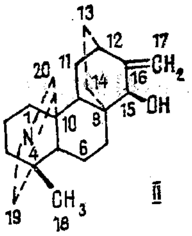

II

M 299, containing a carbonyl group in a six-membered ring (1700 cm^{-1}). The results of acid-catalytic isomerization, showing the presence of a C15−βOH group in (II) [9], permitted the assumption that (II) was atisine azomethine, which had been obtained previously from atisine [8]. To confirm this, we performed the passage from atisine to atisine azomethine by the procedure of [8]. A direct comparison showed the identity of (II) and atisine azomethine.

This is the first time that atisine azomethine has been isolated from plants.

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ALKALOIDS OF Aconitum firmum AND A. tokii

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Continuing a systematic investigation of alkaloids from plants of the genus Aconitum L. collected in various growth sites [1], we have studied the epigeal part and roots of Aconitum firmum Reichb., gathered in the Transcarpathian province (Tyachev region, left bank of the R. Luzhanki). Aconitine has been isolated from this plant previously [2].

The air-dry comminuted epigeal part (1000 g) and roots (350 g) were first treated with sodium carbonate solution and then the alkaloids were isolated by extraction with chloroform and subsequent treatment of the concentrated chloroform extracts with sulfuric acid. After being made alkaline, the acid solutions yielded ether (3.1 g, A) and chloroform (0.67 g, B) fractions of alkaloids from the epigeal part and hexane (1.47 g, C), ether (3.14 g, D), and chloroform (0.76 g, E) fractions from the roots (the total amounts of alkaloids being 0.38% of the weight of the air-dry epigeal part and 1.53% of the weight of the roots).

When fraction A was treated with acetone a crystalline mixture (0.55 g) separated out the chromatography of which on alumina gave hypaconitine with mp 190-191°C, mesaconitine with mp 207-208°C, 3-deoxyaconitine with mp 174-176°C, and songorine with mp 201-202°C. From the mother solution (2.50 g) after the separation of the crystalline mixture of alkaloids we isolated similarly not only the alkaloids mentioned above but also taurenine with mp 100-102°C. All these susbtances were identified by direct comparison with authentic samples of the alkaloids [1, 3, 4].

By chromatographing the chloroform fraction B of the alkaloids on silica gel we obtained an amorphous base with the composition $C_{23}H_{37}NO_6$ (M^+ 423). A comparative analysis of the

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