Berberis ALKALOIDS.

XX. INVESTIGATION OF THE ALKALOIDS OF *Berberis iliensis*

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A number of known alkaloids [1-3] have previously been isolated from the roots of *Berberis iliensis*. Continuing an investigation of alkaloids from plants of the genus *Berberis*, we have studied the alkaloid composition of young shoots of this plant gathered in the flowering phase in the Kegen region near the settlement of Dzhalanash (Alma-Ata province).

The comminuted young shoots were extracted with ethanol in a Soxhlet apparatus until the reaction for alkaloids was negative. The extract was evaporated and the residue was dissolved in 5% hydrochloric acid; the addition of potassium iodide then led to the precipitation of quaternary alkaloids in the form of their iodides [4]. The acid filtrate was made alkaline with ammonia to pH 9, and alkaloids were extracted successively with ether and chloroform. This gave 0.35% of quaternary iodides, 0.37% of a chloroform fraction, and 0.23% of an ethereal fraction of alkaloids.

By separating the total quaternary iodides according to solubility and by chromatography on a silica gel column we isolated berberine (0.12%), magnoflorine (0.05%), palmatine, jatrorrhizine, columbamine [5], and base (I) in the form of iodides.

By chromatography on a silica gel column, the chloroform fraction yielded oxyacanthine, berbamine, obaberine, berbamunine, and N-methylcoclaurine [6], which were identified from their physicochemical constants and spectral characteristics, and also by comparison with authentic samples. In addition, on the separation of the chloroform fraction we isolated base (II) with mp 285-286°C, in the form of the iodide.

Base (I), with mp 230-231°C, $[\alpha]_D$ +127.3°C (C 0.14; CH_3OH), was isolated from the total quaternary bases in the form of the iodide. The IR spectrum of (I) showed absorption bands at (cm^{-1}) 3400 (OH) and 2840 (trans-quinolizidine). The UV spectrum of (I) had absorption maxima at $\lambda_{max}^{C_2H_5OH}$, nm: 224 and 285 ($\log \varepsilon$ 4.17, 3.94), which are characteristic for the tetrahydroprotoberberines [11]. The mass spectrum of (I) showed the peaks of ions with m/z 355 (M − HI), 341 ($M - CH_3I$), 178, 104, 149, 142, and 127, which are characteristic for N-methyltetrahydroberberines having methoxy substituents in positions 9 and 10 [12]. The PMR spectrum of (I), taken in DMSO-d_6 (δ scale, ppm) had signals from three methoxyls at 3.75 (9H, br. s), from a $\overset{+}{N}-CH_3$ group at 3.35 (3H, s), from methylene protons at 4.01 (1H, d, J = 15 Hz), 3.08 (1H, d, J = 15 Hz), 2.75 (2H, m), 4.76 (2H, m), from aromatic protons at 6.75 (1H, s), 6.87 (1H, s), and 7.05 (2H, s). The methylation of (I) with methyl iodide in the presence of K_2CO_3 gave (+)-N-methyltetrahydropalmatine iodide, which was identical with (±)-tetrahydropalmatine methiodide according to TLC and IR spectroscopy. On the basis of the facts given, base (I) was a quaternary N-methyltetrahydroprotoberberine alkaloid having methoxy substituents at C_9 and C_{10} and hydroxy and methoxy substituents in the C_2 and C_3 positions. Consequently, the alkaloid isolated could have been (+)-N-methylcorypalmine or (+)-N-methylisocorypalmine. The choice between them was made from a comparison of the physicochemical constants of base (I) with the literature [13] and also on the basis of the identity of its TLC characteristics and IR spectrum with those of (±)-N-methylcorypalmine.

From the facts presented, base (I) was (+)-β-N-methylcorypalmine.

The UV spectrum of base (II), taken in ethanol, showed absorption maxima at (nm) 235, 276, 354, and 450 ($\log \varepsilon$ 4.3, 4.1, 3.91, and 3.78), while in the spectrum taken with the addition of alkali the bathochromic shifts characteristic for berberrubine [7] and other phenolic protoberberine salts [8, 9] were observed.

The IR spectrum of (II) contained the absorption band of a hydroxy group at 3350 cm^{-1}.

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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, $C15{-}\alpha H$), 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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