2. It has been established that the N-oxide forms of the alkaloids are reduced during the dialysis process.

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ALKALOIDS OF *Corydalis gortschakovii*

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Continuing the separation of the combined alkaloids of *Corydalis gortschakovii* collected in the upper reaches of the R. Pskem in the flowering period, by chloroform extraction we have obtained 0.66% (0.59% of ether fraction and 0.07% of chloroform fraction) of combined alkaloids. Protopine, d-bicuculline, *l*-adlumine, sendaverine, and isocorydine have previously been isolated from this plant collected at the same site [1]. The combined ether-soluble alkaloids were separated into phenolic and nonphenolic fractions. The nonphenolic fraction of the total alkaloids yielded isocorydine, corydine, *l*-adlumidine, and d-bicuculline. The mother liquor after the separation of these alkaloids was chromatographed on a column of silica gel. Elution with benzene and with benzene–methanol yielded isocorydine, d-bicuculline, stylopine, protopine, *l*-adlumine, and gortschakoine [2].

The combined ether-soluble phenolic bases were separated according to basic strength into 13 fractions. The first fraction by chromatography on a column of silica gel yielded juziphine [3] and a base with mp 215-216°C, and the second fraction gave a base with mp 197-198°C; fractions 6-10 yielded sendaverine. The phenolic chloroform-soluble alkaloids were chromatographed on a column of silica gel, and domesticine and isoboldine were isolated. On treatment with methanol, the combined chloroform-soluble bases yielded corytuberine.

The base with mp 215-216°C, composition $C_{18}H_{21}NO_4$, is sparingly soluble in organic solvents. UV spectrum: λ_{max} 232, 284 nm (log ε 4.28, 4.04). The mass spectrum shows a weak peak of the molecular ion with m/e 315, and also the peaks of ions with m/e 299, 298, 297, 178, 150, 135, 121 (100%), and 107. The NMR spectrum of the base has the following signals: two three-proton singlets at 3.50 and 3.55 ppm from two methoxy groups, one-proton singlets at 6.29 and 6.43 ppm (para aromatic protons), and two-proton doublets at 6.70 and 7.09 ppm (J = 8 Hz, two pairs of equivalent ortho aromatic protons). There are a two-proton singlet at 4.41 ppm, one-proton doublets at 4.15 and 4.35 ppm (J = 14 Hz), and also two two-proton multiplets at 3.61 and 2.93 ppm. The spectral characteristics given permit this base to be assigned to the benzyltetrahydroisoquinoline alkaloids of the sendaverine type. The poor solubility of the base in organic solvents, the low intensity of the peak of the molecular

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ion of the base, and the difference by 16 mass units in comparison with the mass spectrum of sendaverine permitted the assumption that the base was an N-oxide. By reduction with zinc dust in sulfuric acid we obtained a substance with mp 136-137°C which was identical with sendaverine. Thus, the base isolated is sendaverine N-oxide.

The base with mp 197-198°C had the composition $C_{18}H_{21}NO_4$. UV spectrum: λ_{max} 228, 281 nm (log ε 4.36, 3.73). The mass spectrum contained the peaks of ions with m/e 315 (M^+), 299, 298, 297, 192 (100%), 178, 150, 135, 121, 107. The NMR spectrum of the base contained the signals of an N-methyl group (3 H, doublet, 3.03 ppm) and a methoxy group (3 H, singlet, 3.53 ppm) and a one-proton multiplet at 5.04 ppm, and in the 6.30-6.80 ppm region there were the signals from six aromatic protons. These spectral features are characteristic for the benzyltetrahydroisoquinoline alkaloids. The difference by 16 mass units in comparison with the mass spectrum of juziphine permitted the assumption that the base was its N-oxide. Reduction of the base with zinc in sulfuric acid yielded a substance with mp 158-159°C identical with juziphine. Thus, the base with mp 197-198°C is juziphine N-oxide.

EXPERIMENTAL

For chromatography we used type KSK silica gel. The UV spectra were taken on a Hitachi spectrometer (in ethanol), the mass spectra on an MKh-1303 spectrometer, and the NMR spectra on a JNM-4H 100/100 MHz instrument (with hexamethyldisilane as the internal standard, δ scale, CF_3COOH).

Isolation and Separation of the Combined Alkaloids. The air-dry epigeal part of the plant *C. gortschakovii* (10 kg) was wetted with a 7% solution of ammonia and extracted with chloroform (8 times). The alkaloids were extracted from the combined chloroform solution with 5% sulfuric acid. The acid solution was made alkaline by 25% ammonia and extracted first with ether and then with chloroform. After the solvents had been distilled off, 58.8 g of ether-extracted and 7.2 g of chloroform-extracted alkaloids were obtained. The combined ether-extracted alkaloids were separated into phenolic (16.7 g of ether-extractable and 5.2 g of chloroform-extractable bases) and nonphenolic (36.9) fractions. The nonphenolic fraction was treated with methanol and the resulting crystalline mixture of bases (11.98 g) was separated off. The fractional crystallization of this mixture from methanol yielded isocorydine (8.2 g), corydine (0.8 g), *l*-adlumidine (0.9 g), and d-bicuculline (1.3 g). The methanolic mother solution (24.8 g) was chromatographed on a column of silica gel. The alkaloids were eluted with benzene, benzene—methanol, and methanol. A benzene—methanol (99:1) eluate yielded stylopine (0.9 g), d-bicuculline (3.9 g), isocorydine (10.2 g), and gortschakoine (60 mg). A benzene—methanol (97:3) eluate yielded protopine (4 g) and a (95:5) eluate gave *l*-adlumine (2.5 g).

The combined ether-extracted phenolic bases (16.7 g) were separated according to basic strength into 13 fractions. The first fraction (1 g) was chromatographed on a column of silica gel and the alkaloids were eluted with benzene—methanol (4:1) to give juziphine (58 mg) and sendaverine N-oxide (72 mg). The second fraction (1.2 g) was chromatographed on a column of silica gel and eluted with benzene—methanol (4:1); this yielded juziphine N-oxide (120 mg). When fractions 6-10 were treated with methanol, 3.5 g of sendaverine separated out. The combined chloroform-extracted phenolic bases (5.2 g) were chromatographed on a column of silica gel, and the alkaloids were eluted with benzene and with benzene—methanol. The benzene—methanol eluate (98:2) yielded domesticine (0.6 g) and isoboldine (0.6 g). The combined chloroform-extracted bases (7.2 g) were treated with methanol, to give corytuberine (4 g).

Reduction of Sendaverine N-Oxide. Zinc was added to a solution of 27 mg of sendaverine N-oxide in 3 ml of 5% sulfuric acid and the mixture was left at room temperature for three days. The acid solution was made alkaline with 25% ammonia, and the base was extracted with ether. This gave a base with mp 136-137°C, identical with sendaverine.

Reduction of Juziphine N-Oxide. Juziphine N-oxide (30 mg) was reduced in a similar way to sendaverine N-oxide, and a base was obtained with mp 158-159°C, identical with juziphine.

SUMMARY

Isocorydine, corydine, protopine, *l*-adlumine, d-bicuculline, *l*-adlumidine, gortschakoine,

juziphine, domesticine, isoboldine, corytuberine, stylopine, sendaverine, and the new alkaloids sendaverine N-oxide and juziphine N-oxide have been isolated from the epigeal part of *Corydalis gortschakovii* growing in the upper regions of the R. Pskem.

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ALKALOIDS OF *Delphinium iliense*

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We have investigated the epigeal part of *Delphinium iliense* Huth collected in the budding and incipient flowering stage in the Trans-Ili Ala-Tau on the R. Purgen'. An unidentified alkaloid with mp 192.5-193°C has been isolated from this plant previously [1].

Chloroform extraction of the epigeal part of *D. iliense* yielded 0.24% of combined alkaloids, from which we isolated delcorine, lycoctonine, eldeline, a base (I), and a base with mp 141-143°C (II).

The mass spectrum of (I) was characteristic for diterpene alkaloids with a lycoctonine skeleton and had the maximum peak M — 31 [2]. The IR spectrum of (I) contained an absorption band at 1750 cm^{-1} due to a carbonyl group in a five-membered ring, and the NMR spectrum contained the signals from an N-ethyl group (1.03 ppm, 3 H, triplet), from four methoxy groups (3.23, 3.26, 3.30, 3.35; 3 H each, singlets), and from a methylenedioxy group (5.03 and 5.46 ppm; one-proton doublets, J = 1.5 Hz). Such a difference in the chemical shifts of the protons of a methylenedioxy group is observed in lycoctonine alkaloids for a C_7—C_8 methylenedioxy group when a keto group is present at C_6 [3].

A comparison of (I) with dehydrodelcorine [3] showed that these compounds were identical. Because of the small amount of (I) it was impossible to obtain it in the crystalline form. This is the first time that dehydrodelcorine has been isolated from a plant.

The base (II), having the composition $C_{25}H_{37}NO_7$, proved to be new and we have called it ilidine.

Its spectral characteristics enable (II) to be assigned to the lycoctonine group of alkaloids. The presence in the mass spectrum of the maximum ion M — 31 shows that there is a methoxy group at C-1 [2]. The IR spectrum of (II) shows the absorption bands of a hydroxy group (3445 cm^{-1}) and of a carbonyl group (1745 cm^{-1}). According to its NMR spectrum, (II) contains an N-ethyl group (1.02 ppm, triplet, J = 7 Hz), three methoxy groups (3.25, 3.27, 3.31 ppm, 3 H each, singlets), and a methylenedioxy group (5.07 and 5.53 ppm, poorly resolved one-proton doublets, J = 1.5 Hz). Consequently, the developed formula of ilidine can be given in the following form: $C_{18}H_{20}$ $(N{-}C_2H_5)$ (OH) (CO) $(OCH_3)_3$ (CH_2O_2).

In its spectral characteristics (II) is similar to dehydrodelcorine, and its composition differs from that of dehydrodelcorine by a methylene group. The methylation of the base with methyl iodide in the presence of sodium hydride gave O-methylilidine, which was identical with dehydrodelcorine.

In order to determine the position of the hydroxy group, ilidine was acetylated with acetic anhydride in the presence of pyridine, which gave a monoacetyl derivative (III), the NMR spectrum of which contained the signal of an acetyl group (1.99 ppm, 3 H, singlet), and

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