QUINOLIZIDINE ALKALOIDS FROM THE SEEDS

OF Leontice smirnovii

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The ripe seeds of <u>Leontice smirnovii</u> Trautv. are rich in quinolizidine alkaloids. The maximum amount of total alkaloids in them is 2.3%. By chromatography in a thin layer of silica gel [chloroform-methanol (2:1) system] and on paper [isobutanol-conc. HCl-water (7.5:13.5:5:50)* system] we detected seven bases in the combined alkaloid fraction. In their qualitative composition, the combined alkaloids of the seeds of <u>Leontice</u> smirnovii are identical with those obtained from the epigeal part.

To study the alkaloids, 45.0 g of the comminuted seeds after defatting with petroleum ether, were made alkaline with an 8% solution of ammonia. The alkaloids were extracted with chloroform, and the extract was concentrated and treated with 2% sulfuric acid. With cooling, the acid solution was made alkaline with 25% ammonia. The bases were extracted with chloroform. The solvent was distilled off to give 1.068 g of combined alkaloids, and these were treated in ethanol with a 54% solution of perchloric acid. After recrystallization from acetone, 0.6 g of a perchlorate was isolated. The base from the perchlorate had the composition $C_{12}H_{16}ON_2$, mp 134-135°C (from petroleum ether) and formed a crystalline hydrochloride with mp 253-254°C, R_f 0.23 (PC). The IR and UV spectra of the base coincided completely with those of N-methylcytisine [1].

After the isolation of N-methylcytisine perchlorate, the mother solution was fractionated according to solubilities. The chloroform-soluble fraction yielded a crystalline perchlorate with mp 165°C. The base obtained from it melted at 152-153°C $[\alpha]_D$ + 218° (c 2.11; ethanol). This alkaloid was identical with the D-argemonine that we isolated previously from the tubers and epigeal part of the <u>Leontice smirnovii</u> [2-3].

From the mother liquor remaining after the separation of the D-argemonine, recrystallization from ethanol gave a perchlorate with mp 210-211°C. The base from it was optically active, had $[\alpha]_D = 75.3^\circ$ (c 1.4; ethanol) and formed a methiodide with mp 95-96°C and a picrate with mp 178-180°C. A comparison of the physicochemical properties of this alkaloid with those of *l*-lupanine showed their identity.

The remaining mother solutions were combined, converted into the bases, and chromatographed on a column of silica gel $(100 \times 2.5 \text{ cm})$, the column being washed successively with chloroform, chloroform-ethanol in various ratios, and pure methanol. The first eluates yielded a crystalline alkaloid with mp 116-118 °C, $[\alpha]_D$ -198° (ethanol). A mixture with leontidine gave no depression of the melting point. The following eluates gave a mixture of two bases which could not be separated from one another. Thus, from the seeds of Leontice smirnovii we have isolated four individual alkaloids: N-methylcytisine, d-argemonine, *l*-lupanine, and leontidine

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