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DEOXYDELSOLINE AND DIHYDROMONTICAMINE FROM *Aconitum monticola*

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The epigeal part of *Aconitum monticola* Steinb. has yielded two C_{18} diterpene alkaloids which, on the basis of the results of a study of NMR, IR, and mass spectra, and also of chemical transitions, have been shown to be identical with synthetic deoxydelsoline and dihydromonticamine. This is the first time that these alkaloids have been found in a plant.

Continuing the separation of the total alkaloids from the epigeal part of *Aconitum monticola* Steinb. [1, 2], in addition to known alkaloids — songorine, songorine N-oxide [1], songoramine, norsongoramine, monticamine, monticoline [2], and delsoline [4, 5] — we have isolated two new bases. Base (I) had the composition $C_{22}H_{35}NO_5$, mp 156–157°C. Its IR spectrum contained the broad absorption band of hydroxy group in the 3300–3600 cm^{-1} region with two maxima at 3335 and 3550 cm^{-1}. The PMR spectrum, taken in pyridine, showed the following signals (ppm); 0.92 (t, 3 H, $N-CH_2-CH_3$), 3.14 and 32.8 (singlets, 3 H each, OCH_3); 3.75 (triplet, 1 H, C_{14}-βH).

The mass spectrum of the base is characteristic for the lycoctonine alkaloids with C_1-αOH, showing the following ion peaks: M^+ 393 (13%), M — 17 (100%), M — 15 (28%), M — 31 (2%), M — 33 (20%).

The facts given, and also a direct comparison of the base with the dihydromonticamine obtained by the reduction of monticamine [2] showed their identity. This is the first time that dihydromonticamine has been found in a plant.

Base (II) had the composition $C_{25}H_{41}NO_6$, mp 134–135°C. Its IR spectrum contained absorption bands of hydroxy groups at 3400 and 3550 cm^{-1}. The NMR spectrum taken in $CDCl_3$ showed signals due to the protons of four methoxy groups at 3.10, 3.12, 3.30, and 3.16 ppm (three-proton singlets, 4 OCH_3) and one-proton triplets at 1.41 ppm ($N-CH_2-CH_3$) and 3.48 ppm (J = 5 Hz; due to the β-proton at C_{14}). The mass spectrum of the base contained the following ion peaks: M^+ 451 (45%), M — 15 (100%), M — 31 (97%), M — 33 (93%). When the base was oxidized with potassium permanganate in an aqueous acetone medium, an oxo compound $C_{25}H_{39}NO_7$ (III) with mol. wt. 465, containing a lactam carbonyl in a six-membered ring (ν_{max} 1640 cm^{-1}) was obtained. The oxidation of (III) with periodic acid yielded a product (IV), the UV spectrum of which ($\lambda_{mas}^{C_2H_5OH}$ 225, 325 mμ; log ε 4.04, 2.57) was practically identical with that of dehydromethoxyoxosecodelphatine [3]. The IR spectrum of the product obtained — with a strong absorption band at 1160 cm^{-1} having additional weak splitting and a

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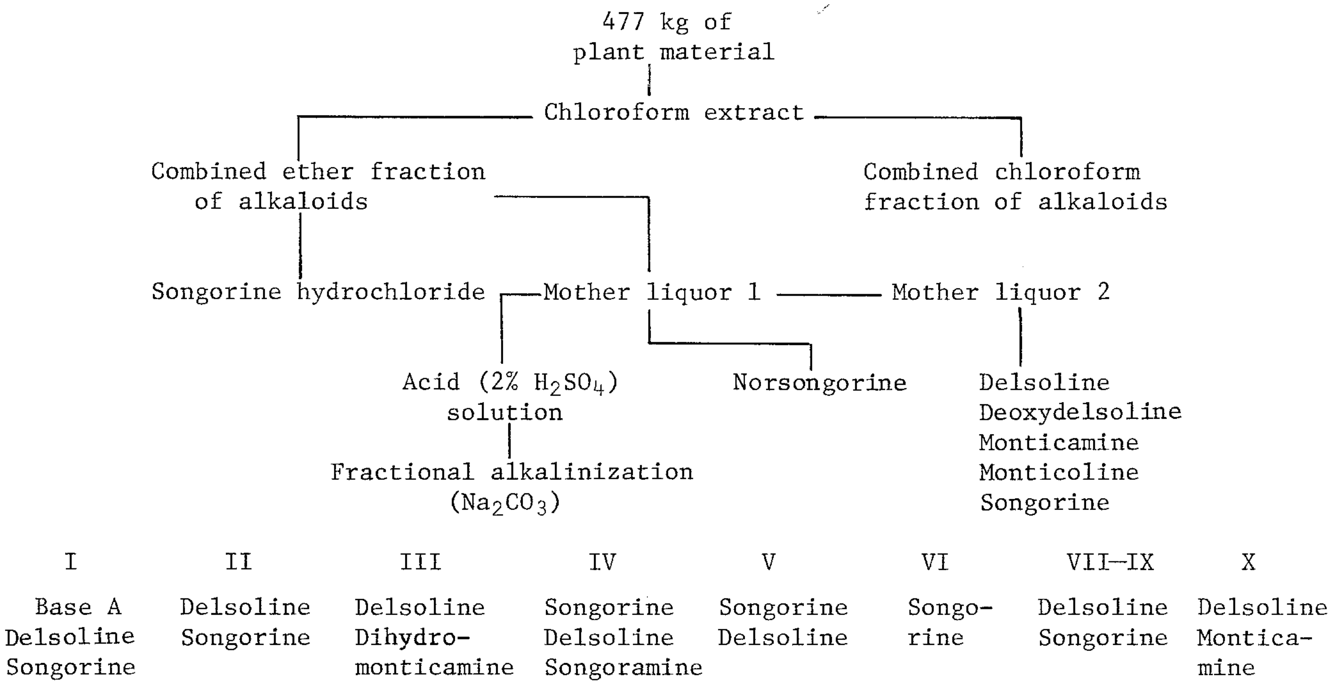
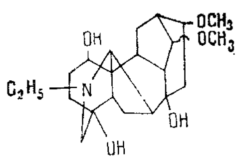
weaker band at 1757 cm^{-1} — shows the position of one carbonyl group in a five-membered ring and of the other in a six-membered or larger ring conjugated with a double bond. The NMR spectrum of the product showed three-proton singlets at 1.45 ppm ($N-CH_2-CH_3$) and 3.17, 3.27 and 3.44 ppm (3 OCH_3). In the mass spectrum, the maximum peak was that of the ion M — 28, which is characteristic for oxosecodemethanol and oxoseco derivatives of the lycoctonine alkaloids [6]. Analysis of the facts presented permitted the assumption that the base was deoxydelsoline which has been obtained previously from delsoline [4]. To confirm this we synthesized deoxydelsoline from delsoline, for which purpose we passed from the latter to anhydrodelsoline [4] which was then reduced with Raney alloy to deoxydelsoline. The product obtained in this way was identical with the material obtained from the plant.



Scheme of the separation of the alkaloids of *Aconitum monticola* (epigeal part).



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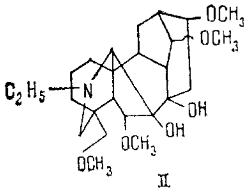
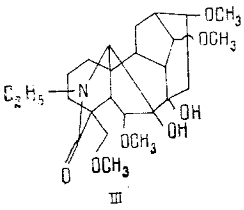
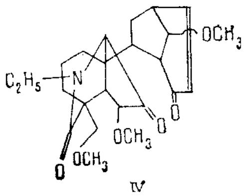


II



III



IV

It must be mentioned that deoxydelsoline is the first diterpene alkaloid with no substituent at C_1.

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument (tablets with KBr), mass spectra on MKh-1303 and MS-3301 mass spectrometers, and PMR spectra on a JNM-4H-100 MHz spectrometer (0 — HMDS, δ scale). For TLC we used Woelm DC silica and the solvent system chloroform—methanol (20:1) and for column chromatography deactivated "alumina for chromatography."

Dihydromonticamine (I). Fraction (III) (see the scheme of separation) (10 g) was chromtographed on a column of deactivated alumina (1:150). Elution was performed with ether (200-ml fractions) and with chloroform and chloroform—methanol (20:1) (50-ml fractions). The material from the chloroform—methanol fractions (2.5 g) was rechromatographed on a column of deactivated alumina (1:70) with elution by ether and by chloroform, and the chloroform fractions yielded 100 mg of (I) with mp 156—157°C (ether—acetone).

Deoxydelsoline (II). The mother liquor (see scheme) (15 g) was chromatographed on a column of deactivated alumina (1:150). Elution was performed with hexane and ether, and the ethereal fractions yielded 120 mg of (II) with mp 134—135°C (acetone).

Oxodeoxydelsoline (III). A solution of 0.25 g of deoxydelsoline in 20 ml of 80% aqueous acetone was added to 0.25 g of potassium permanganate in 200 ml of 50% aqueous acetone. The reaction mixture was shaken for 10 min. Then the excess of potassium permanganate was decomposed with sodium sulfite and the manganese dioxide was separated off. The acetone was distilled off on the water bath and the residual aqueous solution was acidified with sulfuric acid and extracted repeatedly with chloroform. The residue after the chloroform had been evaporated off was chromatographed on a column of deactivated alumina. Elution with ether gave 0.1 g of (III) with mp 196—197°C (ether—acetone).

Oxidation of (III) with Periodic Acid. A mixture of 80 mg of (III) and 80 mg of periodic acid in 5 ml of methanol—water (1:5) was left at room temperature for 4 days. Then the reaction product was extracted with chloroform. After the solvent had been driven off, the residue was chromatographed on a column of deactivated alumina, with elution by hexane and ether. The ethereal fractions yielded 30 mg of (IV) with mp 198—199°C (ether—acetone).

Reduction of Anhydrodelsoline with Raney Alloy. A solution of 100 mg of anhydrodelsoline in 100 ml of ethanol was treated with 100 ml of 10% KOH and 150 mg of Raney alloy. The mixture was heated under reflux on the water bath for 8 h. The ethanol was distilled off in a rotary evaporator, the residual aqueous solution was exhaustively extracted with chloroform and the chloroform was distilled off. This gave 35 mg of (II) with mp 134—135°C (acetone).

SUMMARY

Dihydromonticamine and deoxydelsoline have been found in a plant for the first time.

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