Glycoside I is hederagenin 3-O-[O-β-D-glucopyranosyl-(1 → 2)-α-L-arabinoside] 28-O-[O-α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside].

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ALKALOIDS OF Aconitum barbatum.

STRUCTURE OF BATACONINE

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The epigeal part of Aconitum barbatum gathered in the early vegetation period in the environs of Ulan-Bator has yielded delcosine, lycoctonine, songorine, and the new base bataconine. The structure of bataconine has been shown on the basis of spectral characteristics (IR, NMR, and mass spectra) and also of a correlation with the known alkaloid neoline.

We have investigated the alkaloids of the epigeal part of Aconitum barbatum Pers gathered in the early vegetation period in the environs of Ulan Bator (Mongolian People's Republic). The amount of combined alkaloids was 1.5% on the weight of the air-dry plant. By separating the combined alkaloids, we isolated delcosine, lycoctonine, songorine, and a new base with the composition $C_{23}H_{37}NO_6$, which has been named cataconine (I).

The IR spectrum of the alkaloid had absorption bands of hydroxy groups at 3525, 3480, and 3365 cm^{-1} and of ether bonds at 1120 and 1090 cm^{-1}. According to its PMR spectrum, the alkaloid contained one N-ethyl and two methoxy groups. The mass spectrum of the alkaloid was characteristic for the spectra of C_{19} diterpene alkaloids and contained the peak of the $M^+ - 17$ ion (100%), which is due to a hydroxy group at C-1 [1]. The presence in the mass spectrum of the peaks of the ions $M^+ - 15$ (26%), $M^+ - 17$ (100%), $M^+ - 56$ (4.5%), and $M^+ - 87$ (7%) showed that it belonged to the alkaloids of the aconitine type, containing hydroxy groups at C-1 and C-8 and a methoxymethyl group at C-4 [2].

When the alkaloid was acetylated with acetic anhydride in pyridine a triacetyl derivative (II) was obtained, which indicated the presence of three secondary hydroxy groups in the alkaloid. The PMR spectrum of the triacetate had the signals of one N-ethyl, three acetoxy, and two methoxy groups and the signals of protons geminal to the three acetoxy groups: a one-proton doublet with a splitting constant of 7 Hz at 5.93 ppm assigned to H-6; a quartet at 4.93 ppm with splitting constants of 10 and 7 Hz assigned to 1-β-H; and a triplet with a spin–spin coupling constant of 5 Hz, assigned to 14-β-H [4, 5].

The facts given permit structure (I) to be proposed for bataconine. To confirm this hypothesis we methylated (I) with methyl iodide in the presence of sodium hydride, and obtained the 6,14-dimethyl derivative (I), which proved to be identical with the product of the methylation of neoline (III) under similar conditions. Consequently, bataconine has the structure (I).

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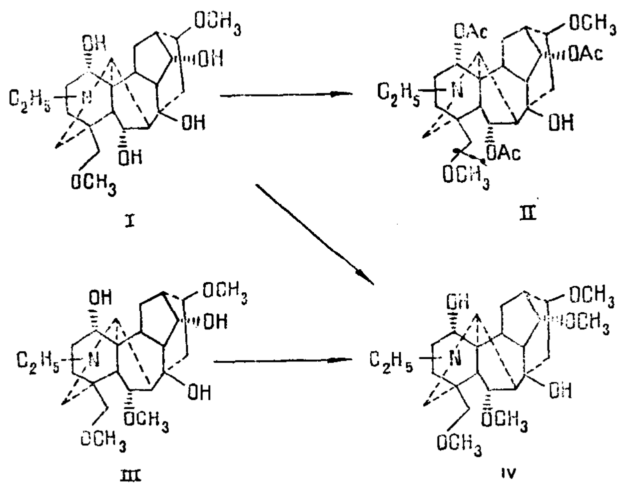

Bataconine has the same elementary and functional composition as senbusine A [6]. The latter is described as an amorphous substance, while bataconine crystallizes from acetone. There are also some differences in the spectral characteristics of the bases. The structure suggested for bataconine coincides with that put forward for senbusine A. The two compounds are possibly identical.

EXPERIMENTAL

Mass spectra were taken on MKh-1303 and MKh-1310 instruments fitted with a system for the direct introduction into the ion source, PMR spectra on HNM-4H-100/100 MHz and Tesla BS-567 A instruments in dueterochloroform and deuteropyridine with HMDS as internal standard (values given on the δ scale), and IR spectra on a UR-20 spectrophotometer with the substances in tablets with KBr and also in the form of oils. Type KSK silica gel and alumina (Brockmann activity grade II, neutral) were used for chromatography.

Bataconine (I). $C_{23}H_{37}NO_6$ (HRMS), mp 96-99°C (acetone). PMR spectrum ($CDCl_3$; ppm): 1.05 (3H, t); 3.25 (6H, s); 4.65 (1H, d, J = 7 Hz).

Bataconine Triacetate (II). A solution of 0.1 g of bataconine in 3 ml of acetic anhydride and 0.2 ml of pyridine was kept at room temperature for 48 h. The excess of acetic anhydride was evaporated off, the residue was dissolved in water, the solution was made alkaline with sodium carbonate, and the product was extracted with ether. After elimination of the solvent the product was purified on a column of alumina. Elution with hexane—chloroform (50:1) gave 0.05 g of the amorphous triacetate. IR spectrum (cm^{-1}); 3455 (OH group); 1735 (ester carbonyl). PMR spectrum (C_5D_5N; ppm): 1.00 (3H, t), 1.90 (6H, s), 1.92 (3H, s), 3.12 (3H, s), 3.16 (3H, s), 4.81, (1H, t, J = 5 Hz), 4.93 (1H, q, J_1 = 10 Hz, J_2 = 7 Hz), 5.93 (1H, d, J = 7 Hz). Mass spectrum: M^+ 549.

6,14-Dimethylbataconine (III). A solution of 0.07 g of bataconine in 25 ml of dioxane was treated with 0.03 g of sodium hydride, and the mixture was stirred for 1 h. Then 1 ml of methyl iodide was added and stirring was continued at room temperature for 6 h. The precipitate was filtered off and was washed with chloroform. The residue after elimination of the solvent was dissolved in 5% sulfuric acid. The acid solution was washed with ether, made alkaline with sodium carbonate, and extracted with chloroform. The extract was dried over sodium sulfate and distilled. The product was purified on a column of alumina with elution by hexane—chloroform. This gave 0.05 g of homogeneous oily 6,14-dimethylbataconine. IR spectrum (cm^{-1}): 3560 (OH group); 1120 (C—O—C bonds). PMR spectrum (ppm): 1.07 (3H, t): 3.28 (9H, c); 3.35 (2H, s); 4.09 (1H, d, J = 7 Hz). Mass spectrum: M^+ 451.

Methylation of Neoline. A solution of 0.27 g of neoline in 40 ml of dioxane was treated with 0.19 g of sodium hydride, and the mixture was stirred for an hour. Then 2 ml of methyl iodide was added to the reaction mixture, and stirring was continued for 5 h at room temperature. The product, isolated as described above, was identical with 6,14-dimethylbataconine according to TLC and to IR, PMR, and mass spectra.

SUMMARY

Delcosine, lycoctonine, songorine, and the new alkaloid bataconine have been isolated form the epigeal part of Aconitum barbatum Pers gathered in the early vegetation period.

The structure of bataconine has been established on the basis of spectral characteristics and of correlation with the known alkaloid neoline.

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