ALKALOIDS OF *Delphinium iliense*

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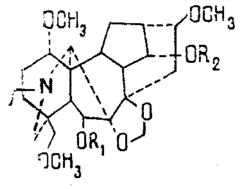
Together with delcorine, lycoctonine, eldeline, dehydrodelcorine, ilidine, browniine, and dictyocarpinine, we have isolated a new alkaloid, delcoridine, from the epigeal part of *Delphinium iliense* Huth. Its structure has been established on the basis of the results of a study of the chemical transformations and spectra characteristics. This is the first time that the alkaloid dictyocarpinine has been isolated from this plant.

Continuing a study of the epigeal part of *Delphinium iliense* Huth., collected in the budding and incipient flowering stage in the Trans-Ili Ala-Tau along the R. Turgen', in addition to the alkaloids delcorine, lycoctonine, eldine, dehydrodelcorine, and ilidine obtained previously [1], we have isolated browniine [2], dictyocarpinine [3] (the first time this has been isolated from the plant), and a new base with composition $C_{25}H_{39}NO_7$, which we have called delcoridine (I).

The IR spectrum of the base has absorption bands characteristic for a hydroxy group (3400 cm^{-1}) and for ether—C—O— bonds (1100 cm^{-1}). The NMR spectrum shows the signals of an N-ethyl group (1.0 ppm, 3 H, triplet), three methoxy groups (3.15, 3.20, 3.25 ppm, 3 H each, singlet), and a methylenedioxy group (5.0 and 5.1 ppm, 1 H each, singlets). The mass spectrum of (I) is characteristic for diterpene alkaloids with the lycoctonine skeleton and has the maximum peak M — 31 showing the presence of a methoxy group at C-1 [4].

The methylation of (I) with methyl iodide in dioxane in the presence of sodium hydride led to 6-O-methyldelcorine (II), also obtained from delcorine [5]. The correlation made confirms the presence of the lycoctonine skeleton in the base and shows the position of the substituents, including their configurations. The mutual positions of the substituents was established in the following way. The acetylation of (I) with acetic anhydride in pyridine gave delcoridine diacetate (III), the NMR spectrum of which contained a signal from two acetyl groups (1.97 ppm, 6 H, singlet) and a singlet with a one-proton intensity at 5.37 nm corresponding to a proton at C_6 geminal to an acetoxy group [3]. Consequently, in delcoridine one of the hydroxy groups is located at C_6.

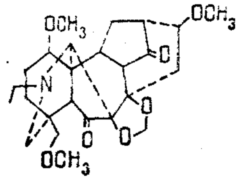
Compound (I) was oxidized with chromium trioxide in acetone. This gave a diketone (IV). The IR spectrum of (IV) in the region of absorption of the carbonyl groups has a strong absorption band at 1740 cm^{-1} characteristic for a carbonyl in a five-membered ring, and no absorption band for a carbonyl in a six-membered ring. Thus, both hydroxy groups are present in five-membered rings, at C_6 and C_{14}, and the ketone obtained has the structure (IV), that of delcoridine itself being shown by formula (I).



I. $R_1 = R_2 = H$

II. $R_1 = R_2 = CH_3$

III. $R_1 = R_2 = COCH_3$



IV

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EXPERIMENTAL

The homogeneity of the substances was checked by chromatography in a thin layer of KSK silica gel in the benzene—ethanol (4:1 and chloroform—methanol 20:1 and 50:1) systems. The IR spectrum was taken on a UR-20 instrument in KBr tablets and in chloroform, and the NMR spectra (in deuterochloroform) on a C-60-HL instrument with DMDS as internal standard (figures given on the δ scale), and mass spectra on a MKh-1310 instrument fitted with a system for direct introduction into the ion source.

Isolation of the Alkaloids. The mother liquor from a total ethereal extract of *D. iliense* [1] (2.5 g) was chromatographed on a column of silica gel, and elution with chloroform yielded 0.3 g of delcorine, 0.8 g of eldeline, 0.2 g of dehydrodelcorine, 0.06 g of browniine, 0.04 g of dictyocarpinine, minor amounts of ilidine, and 0.5 g of delcoridine, M^+ 465.

Delcoridine Acetate. A mixture of 50 mg of the base with 3 ml of acetic anhydride and 0.5 ml of pyridine was kept at room temperature for 72 h. The excess of acetic anhydride was evaporated off in a rotary evaporator, the residue was distilled in ice-cooled water, the solution was made alkaline, and the reaction product was extracted with ether. This gave delcoridine diacetate, M^+ 549.

Di-O-methyldelcoridine. A mixture of 60 mg of delcoridine, 5 ml of dioxane, 0.04 g of sodium hydride, and 1 ml of methyl iodide was boiled for 7 h. After cooling, the precipitate was separated off and the solvent was evaporated, the residue then being dissolved in 5% sulfuric acid. The acid solution was washed with ether, made alkaline with sodium carbonate, with cooling, and the reaction product was extracted with ether. This yielded di-O-methyldelcoridine, M^+ 493.

O-Methyldelcoridine. A mixture of 200 mg of delcoridine, 7 ml of dioxane, 0.1 g of sodium hydride, and 2 ml of methyl iodine was boiled for 7 h. After cooling, the precipitate was separated off and the solvent was evaporated, the residue then being dissolved in 5% sulfuric acid. The acid solution was washed with ether, made alkaline with sodium carbonate, with cooling, and the reaction product was extracted with ether. This yielded O-methyldelcoridine, M^+ 493.

Didehydrodelcoridine. A mixture of 0.15 g of delcoridine and 0.25 g of chromium trioxide in 31 ml of acetone was left at room temperature for three days. The acetone was distilled off. The residue was dissolved in 5% sulfuric acid, and the excess of chromium trioxide was decomposed with sodium sulfite. The solution was made alkaline and the reaction products were extracted with ether. The residue after the solvent had been distilled off was chromatographed on a column of silica gel, the reaction product being eluted with chloroform. This gave didehydrodelcoridine, M^+ 461.

SUMMARY

In addition of alkaloids isolated previously, the plant *Delphinium iliense* Huth. has yielded browniine, dictyocarpinine, and the new base delcoridine (I).

On the basis of the results of a study of chemical transformations and spectral characteristics, structure (I) has been established for delcoridine. This is the first time that dictyocarpinine has been isolated from this plant.

LITERATURE CITED

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