STRUCTURES OF DECORINE AND DELCORIDINE

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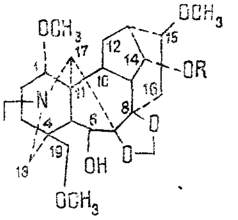
UDC 547.944/945

In order to confirm the structures of the alkaloids delcorine and delcoridine (O-demethyldelcorine) suggested previously, a direct passage has been performed from delcoridine to delcorine and from delcorine to delphatine. It has been shown that the α configuration of C_1-OCH_3 previously suggested for delcorine and delcoridine is incorrect — it should be β.

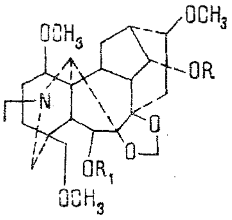
The alkaloid delcorine $C_{26}H_{41}NO_7$ was first detected in the plant *Delphinium corymbosum* Rgl., and structure (I) was put forward for it [1]. The alkaloid delcoridine, $C_{25}H_{39}NO_7$ found in *Delphinium iliense* Huth., proved to be O-demethyldelcorine, and structure (II) was proposed for it [2].

In order to confirm the structures of the two alkaloids, we have made a direct transition from delcoridine to delcorine and from delcorine to delphatine. Delcorine was methylated in dioxane with methyl iodide in the presence of sodium hydride. This gave 6-methyldelcorine (III) [2]. Heating (III) with 10% sulfuric acid for 10 h led to the known alkaloid delphatine (IV) [3]. The methylation of delcoridine in dioxane by the calculated amount of methyl iodide and sodium hydride gave delcorine. The correlation performed confirmed the assignment of delcorine and delcoridine to the lycoctonine alkaloids and the positions of all the substituents in them. On the other hand, it is obvious that the α configuration of the C_1-OCH_3 group previously suggested for delcorine and delcoridine is erroneous — it sould be β. Consequently, structures (V) and (VI) correspond to delcorine and delcoridine, respectively.



I. R = CH_3

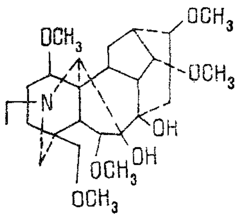
II. R = H



III. R = R_1 = CH_3

V. R = CH_3; R_1 = H

VI. R = R_1 = H



IV

It must be mentioned that the configuration of the methoxy group at C_1 was previously determined on the basis of the ratio of the M-15 and M-31 peaks in the mass spectra of the alkaloids [4]. The results obtained show that this characteristic feature of the mass spectra of the lycoctonine alkaloids deduced previously must be treated with caution; it is apparently necessary to take into account the nature of the substitution at carbon atoms 7 and 8.

EXPERIMENTAL

The homogeneity of the substances was checked by chromatography in a thin layer of KSK silica gel in the benzene—methanol (4 : 1) and chloroform—methanol (20 : 1) systems and in "for chromatography" alumina in the chloroform—methanol (50 : 1) system. IR spectra were taken on a UR-20 instrument in tablets with KBr.

Institute of the Chemistry of Plant Substances of the Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 621-623, September-October, 1981. Original article submitted March 25, 1981.

Methylation of Delcorine. A mixture of 2.0 g of delcorine, 75 ml of dioxane, 20 ml of methyl iodide, and 0.5 g of sodium hydride was boiled with stirring for 8 h. The sodium hydride was separated off, and the filtrate was evaporated to dryness. The residue was dissolved in 5% sulfuric acid, the acid solution was washed with ether and made alkaline with sodium carbonate, and the reaction product was extracted with ether. The solvent was evaporated off, the residue was dissolved in ethanol, and the solution was acidified with 10% ethanolic perchloric acid, which led to the separation of 1.96 g of 6-methyldelcorine perchlorate with mp 199-200°C (with foaming; ethanol).

Hydrolysis of 6-Methyldelcorine. A solution of 0.7 g of 6-methyldelcorine in 30 ml of 10% sulfuric acid was boiled for 10 h. The acid solution was brought to room temperature, washed with ether, made alkaline with sodium carbonate, and shaken with ether. The ethereal extracts were dried over sodium sulfate. The residue after the evaporation of the ether was dissolved in ethanol and the solution was acidified with a 10% ethanolic solution of perchloric acid. This led to the separation of 0.64 g of delphatine perchlorate with mp 204-205.5°C (foaming), shown to be identical with an authentic sample by TLC, a mixed melting point, and IR spectroscopy.

Methylation of Delcoridine. A mixture of 0.2 g of delcoridine, 20 ml of dioxane, 0.03 ml of methyl iodide, and 0.01 g of sodium hydride was boiled with stirring for 6 h. After the working up described above, 0.04 g of delcorine was obtained with mp 192-195°C (methanol), which was shown to be identical with an authentic sample by TLC and a mixed melting point.

SUMMARY

A direct transition has been made from delcoridine to delcorine and from delcorine to delphatine. It has been established that the α configuration of C_1-OCH_3 suggested previously for delcorine and delcoridine is erroneous, it should be β.

LITERATURE CITED

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