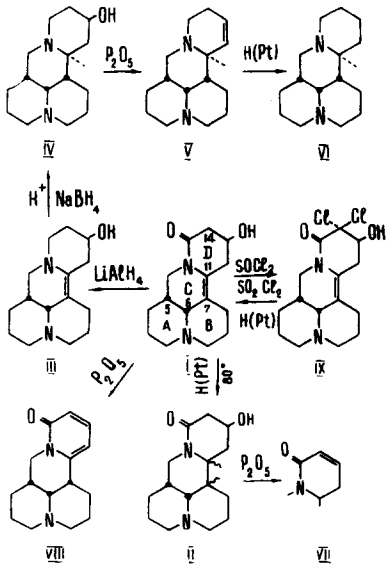
# A STUDY OF THE STRUCTURE OF ALBERTINE

S. Iskandarov, D. Dzh. Kamalitdinov, and S. Yu. Yunusov

UDC 547.944/945

Structure (I) has previously been proposed for albertine, an alkaloid isolated from the epigeal part of Leontice albertii [1, 2]. The present paper gives the results of a study of the position of the hydroxy group of the alkaloid and its configuration.

The heating of dihydroalbertine with phosphorus pentoxide gave the anhydro base (VII), the UV spectrum and the nature of the mass-spectrometric decomposition of which resemble those for sophocarpine [3, 4]. The dehydration of deoxydihydroalbertine (IV) led to an unsaturated compound (V) with a molecular mass of 232. The latter does not react with sodium tetrahydroborate, which shows that its double bond is not adjacent to the nitrogen atom. The catalytic hydrogenation of (V) in the presence of platinum black yielded matridine. Consequently, the hydrogens at $C_5$ and $C_6$ in the albertine molecule have the cis arrangement. The asymmetrical carbon atom arising as a result of the acidification of deoxoalbertine with migration of its double bond and the formation of an ammonium derivative also has the relative cis configuration. To determine the position of the hydroxy group in albertine, it was chlorinated with a mixture of thionyl and sulfuryl chlorides. Under these conditions, two hydrogen atoms in the molecule of the alkaloid were replaced by halogen, as in matrine [5]. The mass spectrum of the halogenated compound showed the peak of an ion with m/e 314 corresponding to the molecular mass of dichloroanhydroalbertine. The ions corresponding to the fragments arising by the splitting off of hydrocarbon radicals and residues from rings A and B were each displaced by 70 amu. This shows that the halogens entered at $C_{14}$. However, the NMR spectrum of dichloroalbertine (IX) lacks the signal of an olefinic proton. Consequently, the ion with m/e 314 appearing under the conditions of mass spectrometry is a product of the dehydration of dichloroalbertine. The hydrogenation of dichloroalbertine in the presence of a platinum catalyst in ethanolic solution formed albertine. These results show that the hydroxy group remains unchanged in the chlorination reaction. Thus, albertine has the structure of 13-hydroxy-7,11-dehydromatrine (I).




Institute of the Chemistry of Plant Substances, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 628-631, September-October, 1972. Original article submitted February 10, 1972.

## EXPERIMENTAL

O-Tosyl Ester of Albertine. A solution of 0.1 g of albertine in 3 ml of dry pyridine was treated with 0.15 g of toluenesulfonyl chloride, and the mixture was heated in a sealed tube at 60°C for 10 h. The residue after the evaporation of the pyridine in vacuum was dissolved in water and washed with ether; it was then made alkaline with ammonia and was extracted with ether. The residue after the distillation of the solvent was crystallized from petroleum ether and had mp 155-156°C.

Dihydroalbertine (II). A solution of 0.4 g of albertine in 10 ml of glacial acetic acid was added to a flask containing freshly reduced platinum from 0.4 g of $PtO_2$ in 10 ml of glacial acetic acid and was shaken in an atmosphere of hydrogen at 70-80°C for two days. After the catalyst had been eliminated, the solution was dried under vacuum, the residue was made alkaline with caustic soda, and the base was extracted with ether. After the ether had been distilled off, the residue was dissolved in acetone. On concentration, the solution deposited crystals of (II) with mp 170-171°C, $[\alpha]_D$ +34° (c 0.6; ethanol), $R_f$ 0.2 [TLC, silica gel–gypsum (9 : 1); chloroform–methanol (5 : 1)].

Dehydration of Dihydroalbertine. Dihydroalbertine (0.05 g) was mixed with purified sand and heated with 0.2 g of $P_2O_5$ at 200°C for 4 h. Then the mixture was decomposed with ice and was made alkaline with 25% caustic soda solution, and the bases were extracted with ether. The residue consisted of an oil with $R_f$ 0.1 (VII) and 0.2 (starting material). UV spectrum: $\lambda_{max}$ 262 nm.

Deoxoalbertine (III). A solution of 0.8 g of albertine in 200 ml of absolute ether was treated with 1.5 g of $LiAlH_4$, and the mixture was boiled for 4 h. The excess of reagent was decomposed with water, and the reaction product was exhaustively extracted with ether. The solvent was distilled off to give 0.71 g of a light-colored oil with $R_f$ 0.35.

Perchlorate. A solution of 0.7 g of the reduction product in ethanol was acidified with 54% perchloric acid. The crystalline perchlorate of (III) deposited with mp 190-192°C, $[\alpha]_D$ +66° (c 0.9; ethanol).

Deoxodihydroalbertine. A solution of 0.4 g of deoxoalbertine perchlorate in 50 ml of methanol was treated with 0.7 g of $NaBH_4$ in portions. The mixture was heated on the water bath for 20 min, cooled, acidified with ethanolic hydrogen chloride, and evaporated under vacuum. The residue was dissolved in water, the solution was made alkaline with caustic soda, and the base was extracted with ether. The base (IV) (0.26 g) crystallized from acetone with mp 214-215°C, $[\alpha]_D$ −24.7° (c 0.6; ethanol), $R_f$ 0.25.

Dehydration of Deoxodihydroalbertine. Under similar conditions to the dehydration of dihydroalbertine, 0.2 g of deoxodihydroalbertine yielded 0.13 g of a product with $R_f$ 0.25; 0.15.

Matridine. The catalytic hydrogenation of 0.1 g of the mixture with $R_f$ 0.25 and 0.15 over the platinum from 0.1 g of $PtO_2$ in 10 ml of ethanol yielded 0.1 g of a base with $R_f$ 0.25; 0.3 (VI).

Hydriodide of (VI). A solution of the reaction product in ethanol was acidified with hydriodic acid. On the addition of acetone, crystals formed with mp 310-312°C. A mixture with matridine hydriodide melted at the same temperature.

*l*-Sophoramine (VIII). Albertine (0.3 g) was mixed with purified sand and with 0.5 g of $P_2O_5$ and was heated at 200-210°C for 5 h. This gave 0.2 g of a base from an ethereal solution of which crystals of (VIII) were isolated with mp 163-164°C, $[\alpha]_D$ −90° (c 0.6; ethanol). A mixture with a sample of *l*-sophoramine gave no depression of the melting point, and their IR spectra were identical.

Dichloroalbertine (IX). To 0.4 g of albertine were added 1 ml of $SOCl_2$ and 1 ml of $SO_2Cl_2$, and the mixture was left for 20 h. Then the solvents were distilled off, the residue was dried and dissolved in a 1% solution of hydrochloric acid, and this solution was made alkaline with caustic soda and was exhaustively extracted with ether. On concentration of the ethereal solution, an amorphous precipitate of dichloroalbertine deposited (0.18 g) with $R_f$ 0.9, $[\alpha]_D$ −96° (c, 0.46; ethanol).

Albertine. The catalytic hydrogenation of 0.1 g of dichloroalbertine over the platinum black from 0.1 g of $PtO_2$ in 10 ml of ethanol gave 0.06 of albertine with mp 161°C.

## SUMMARY

Albertine, isolated from the epigeal part of Leontice albertii, is the first hydroxyl-containing unsaturated alkaloid of the matrine series. On the basis of a study of its mass and NMR spectra and its conversion into sophoramine and matridine, its structure has been established as 13e-hydroxy-7,11-dehydromatrine.

## LITERATURE CITED


1. S. Iskandarov, R. N. Nuriddinov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 26 (1967).
2. S. Iskandarov and S. Yu. Yunusov, Khim. Prirodn. Soedin., 137 (1968).
3. S. Iskandarov and S. Yu. Yunusov, Khim. Prirodn. Soedin., 106 (1968).
4. N. A. Proskurnina and A. D. Kuzovkov, Dokl. Akad. Nauk SSSR, 91, 1145 (1953).
5. S. Iskandarov, D. Dzh. Kamalitdinov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 174 (1971).