STRUCTURES OF GLAUNINE AND GLAUNIDINE

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UDC 547.943

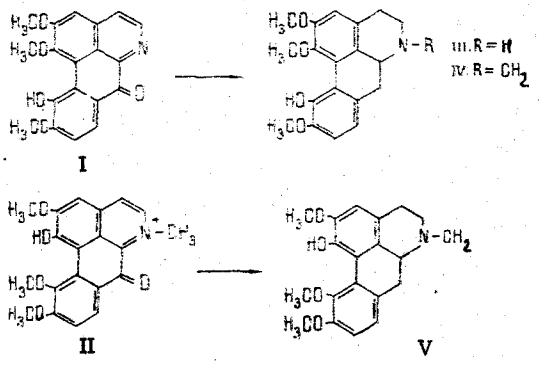
Continuing the separation of the total alkaloids of *Glaucium fimbrilligerum* [1], from the chloroform-soluble material we have isolated two new bases which we have called glaunine (I) and glaunidine (II).

Glaunine is an optically inactive base with a green coloration. UV spectrum, $\lambda_{max}^{ethanol}$, nm: 250, 272, 310 (inflection), 348, 406, 600 (log ε 4.40, 4.22, 3.97, 3.87, 2.75, 2.68). It changes on acidification $\lambda_{max}^{ethanol+H^+}$, nm: 248, 263 (inflection), 385, 320 (inflection), 375, 470 (inflection) (log ε 4.46, 4.41, 4.32, 3.88, 2.94, 2.60). The IR spectrum of (I) shows absorption bands at 1590, 1660, and 3410 cm^{-1}. The NMR spectrum taken in $CDCl_3$ contained the signals from three methoxy groups at 3.78, 4.03, and 4.04 ppm and in the aromatic region there were doublets at 7.18 and 8.50 ppm (J = 8 Hz, o-aromatic protons) and 7.72 and 8.77 ppm (J = 5 Hz), and also a singlet at 7.17 ppm.

The facts given above permit glaunine to be assigned to the exoaporphine alkaloids with a carbonyl group at C_7 [2]. When (I) was reduced with zinc in sulfuric acid, norisocorydine (III) was obtained. Methylation of the latter by Craig's method gave a product identical with isocorydine (IV) (melting point, IR spectrum). Consequently, glaunine has the structure (I).

Glaunidine is an optically inactive base which crystallizes from chloroform in the form of blue-green plates with mp 230-232°C. Its UV spectrum showed maxima at $\lambda_{max}^{ethanol}$ (nm) 235, 315, 410, 620 (log ε 4.53, 4.46, 3.72, 3.59); $\lambda_{max}^{ethanol+H^+}$ 250, 290 (inflection), 380, 450 (log ε 4.54, 4.36, 3.87, 3.55). The NMR spectrum showed absorption bands at 1585, 1625, and 3500 cm^{-1}. The NMR spectrum had signals at 3.65, 3.94, and 4.03 ppm from three methoxy groups, a three-proton singlet at 4.49 ppm, and also one-proton doublets at 7.02 and 8.09 ppm (J = 9 Hz, o-aromatic proton) and at 7.12 and 7.45 ppm (J = 6 Hz), and a singlet at 6.52 ppm.

In view of the fact that the 7-oxoaporphine alkaloids with hydroxy groups at C_1 and C_{11} have a green color which changes in an acid medium, and also in view of the downfield displacement of the signal of the N-methyl group (4.49 ppm) in the NMR spectrum [3], it was assumed that glaunidine is a N-methyl 7-oxoaporphine alkaloid. In actual fact, when it was reduced with zinc and sulfuric acid a product was obtained which was identical with corydine (V) in melting point and IR and mass spectra. Thus, glaunidine has the structure (II).



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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 415-416, May-June, 1979. Original article submitted February 16, 1979.

0009-3130/79/1503-0367$07.50

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X-RAY STRUCTURAL INVESTIGATION OF ALLOMATRINE AND ITS N-OXIDE

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UDC 548.737

For a long time, allomatrine, obtained by the isomerization of matrine [1], was not considered to be a natural base, and only recently was it isolated by Japanese workers from *Sophora flavescens* [2]. In order to determine the physiological function of matrine and its stereoisomers, and also their N-oxides, in the plant organism, it is important to know the three-dimensional structures of these compounds. With this aim, we have investigated the spatial structures of sophoridine, matrine, and allomatrine and their N-oxides by the x-ray method. The results of the investigation of the structure of sophoridine have been reported previously [3], and the investigations of the structure of matrine itself and of matrine N-oxide and of sophoridine are in the concluding stages. We give the main structural characteristics obtained in a study of the conformations of the molecules of allomatrine and its N-oxide.

The crystals of allomatrine, $C_{15}H_{24}ON_2$, have an elementary cell with the parameters a = 6.764, b = 13.026, c = 8.045 Å; γ = 102.50°; V = 692.05 Å^3; Z = 2; space group $P2_1$; and the N-oxide $C_{15}H_{24}O_2N_2$ crystallizes in the form of the monohydrate with a primitive elementary cell having the dimensions a = 6.825, b = 10.596, c = 20.151 Å; V = 1457.28 Å^3; Z = 4; space group $P2_12_12_1$. Three-dimensional sets of intensities were obtained on a Sinteks-$P2_1$ automatic diffractometer. Structures were interpreted by the direct method using the "Rentgen-75" system of programs [4] and were refined in the anisotropic approximation taking the hydrogen atoms into account to R = 0.061 (allomatrine) and R = 0.068 (N-oxide) with the aid of the "Kristall" complex of programs [5]. The geometry of the allomatrine molecule is shown in Fig. 1.

Rings A, B, and C have the chair conformation. In these rings the deviation of the corner atoms are not equal to one another and amount to 0.73±0.02 Å for the C(5), C(6), and C(10) atoms, and 0.62, 0.67, and 0.68 Å for the N(16), C(7), and C(2) atoms, respectively. The shape of ring D is close to the half-chair. The C(12) and C(13) depart from the plane of the other atoms by 0.14 and 0.56 Å, respectively, in opposite directions. All the ring

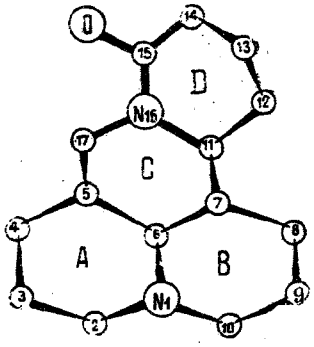

Fig. 1

Institute of Bioorganic Chemistry, Academy of Sciences of the Uzbek SSR, Tashkent. Institute of Crystallography, Academy of Sciences of the USSR, Moscow. V. I. Lenin Tashkent State University. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 416-417, May-June, 1979. Original article submitted February 22, 1979.

 0009-3130/79/1503-0368$07.50