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

B. T. Ibragimov, G. N. Tishchenko,
Yu. K. Kushmuradov, T. F. Aripov,
and A. S. Sadykov

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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

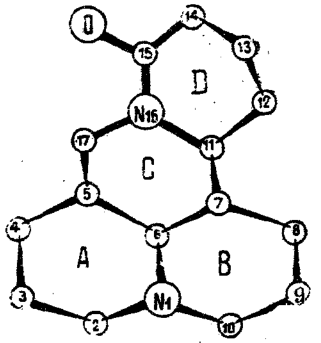

Fig. 1

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linkages in the molecule are trans and are made by bonds equatorial in relation to one another. The angles between the mean-square planes of rings A, B, and C differ little from zero. It is just with such a geometry of the molecule that the minimum interatomic nonbond interactions in the molecule are observed, while all the other possible linkages of four chair-shaped rings lead to more or less strained structures. The C(15)—O interatomic distance is 1.22(6) Å. The coordination of the N(1) nitrogen atom is pyramidal and that of the N(16) is plane-trigonal because of conjugation in the lactam fragment of the molecule.

The oxidation of allomatrine to its N-oxide does not lead to appreciable change in the conformation of the molecule. The chair conformation of the rings and the type of their linkages do not change. The coordination of the N(1) atom becomes tetrahedral. There are no special packing features in the crystal structure of allomatrine, and all the intermolecular contacts are normal from the point of view of intermolecular radii. In the crystal of the N-oxide, the molecules are joined into infinite layers connected with one another through molecules of water of crystallization by hydrogen bonds.

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TETRAHYDROPROTOBERBERINE ALKALOIDS OF *Corydalis ledebouriana*

I. A. Israilov, M. S. Yunusov,
and S. Yu. Yunusov

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From the nonphenolic ether-soluble compounds of *C. ledebouriana* collected in the period of the end of flowering to the beginning of fruit-bearing at Baraldaisae we have isolated bases (I) and (II).

Base (I) has mp 139-140°C, $[\alpha]_D$ —105° (c 0.7; CH_3OH). UV spectrum. λ_{max}, nm: 288 (log ε 3.85). The IR spectrum shows absorption bands at (cm^{-1}) 935 and 1050 (CH_2O_2), 1515 and 1605 (aromatic ring), and 2760 (trans-quinolizidine). The mass spectrum contains the peaks of the molecular ion with m/e 353, and also those of ions with m/e 338, 192, 190, 162 (100%), and 176.5 (M^{2+}). The NMR spectrum of (I) taken in $CDCl_3$ shows signals from a $>CH-\underline{CH_3}$ group in the form of a doublet at 0.88 ppm (J = 7 Hz), a signal from two methoxy groups at 3.82 ppm, and one from a methylenedioxy group at 5.87 ppm (quadruplet). Aromatic protons give signals at 6.62 ppm (3 H) and 6.54 ppm (4 H). There are two one-proton doublets at 3.42 and 4.01 ppm (J = 15 Hz), and the signals of the remaining protons appear in the 2.5-3.5 ppm region.

The facts presented permit base (I) to be assigned to the tetrahydroprotoberberine alkaloids containing a methyl group at C_{13}. All the spectral characteristics of base (I) coincide completely with those of *dl*-cavidine, isolated from *C. thalictrifolia* [1, 2].

Thus, base (I) is *l*-cavidine, which has not previously been described in the literature.

Base (II), with mp 199-200°C (from methanol), $[\alpha]_D$ +300° (c 0.23; CH_3OH). The UV spectra of (II) and of *l*-cavidine are similar. The mass spectrum contains the peaks of ions with m/e 337 (M^+), 332, 176, 174, 162 (100%), and 168.5 (M^{++}). The NMR spectrum of (II) shows signals from two methylenedioxy groups at 5.86 ppm, while the remainder of the spectrum coin-

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