CRYSTAL AND MOLECULAR STRUCTURE OF THE ALKALOID

d-AMMODENDRINE (ISOAMMODENDRINE) HYDRIODIDE

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UDC 547.944/945+536.26

We give the results of an x-ray structural analysis of the crystals of the hydride of a base (VII) isolated from *Ammopiptanthus mongolicus* [1]. Analysis of the x-ray structural results showed that the base (VII) is d-ammodendrine (I) or isoammodendrine [2] (Fig. 1).

The spatial structure of the molecule of (I) is characterized by the conformation and mutual arrangements of two six-membered rings. The piperidine ring has the chair conformation, and the second six-membered ring is close to the envelope conformation: the C(1),C(3), N(4),C(5),C(6) atoms lie in one plane with an accuracy of 0.08 Å, and the C(2) atom departs from it by 0.63 Å. The orientation of the ketone group favors the conjugation of the π-electronic systems of the double bonds with the free electron pair of the N(4) atom [the angle between the planes formed by the N(4),C(1),O(14),C(15) and C(3),N(4),C(5),C(6),C(1) atoms is 7.7°]. No anomalies are observed in the valence distance (see Fig. 1). The mean-square errors in the determination of bond lengths do not exceed 0.036 Å. The small increases in the lengths of the double bonds C(13)—O(14) (1.28 Å) and C(5)—C(6) (1.34 Å), and also the decrease in the lengths of the ordinary bonds N(14)—C(15) (1.32 Å) and N(4)—C(13) (1.35 Å) can be explained by the conjugation of the π-electronic systems. The values of the valence angles are, on the whole, close to the standard values [3] within the limits of error, apart from the N(4)C(5)C(6) angle, where a substantial increase is observed — to 130° (the standard deviation in the determination of the valence angles is not greater than 2.3°).

An analysis of the intermolecular contacts in the packing of the molecules shows the possibility of intermolecular hydrogen bonds [distance between N(12) and O(14) 2.69 Å] and of a donor-acceptor bond [I(16)...N(12) distance 3.46 Å].

Colorless crystals of (I) in the form of elongated prisms were grown from ethanolic solution. The space groups and the parameters of the elementary cell were determined from rotation and Weissenberg x-ray patterns and were refined on a Sintex P2$_1$ diffractometer (Institute of Bioorganic Chemistry of the Academy of Sciences of the Uzbek SSR) using Mo-K$_\alpha$ radiation: $a = 8.240$, $b = 11.568$, $c = 15.051$ Å, $d_{calc} = 1.578$ g/cm³; space group P2$_1$2$_1$2$_1$, Z = 4 4. A three-dimensional set of intensities was obtained on the diffractometer mentioned. In the calculations 972 structural factors exceeding 2σ were used. The structure was inter-
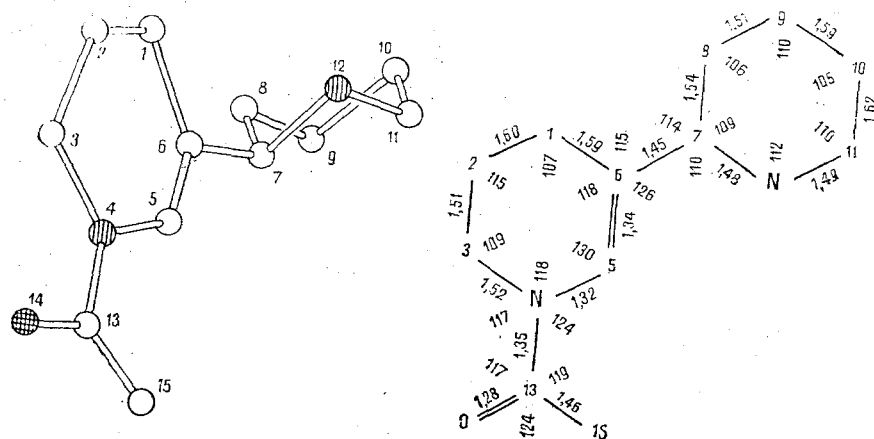

Fig. 1. Geometry of the d-ammodendrine molecule.

TABLE 1. Coordinates of the Atoms ($\times 10^3$) of the Molecule of (I)

Atom	x	y	z	Atom	x	y	z
C (1)	182 (3)	274 (2)	85 (1)	C (9)	312 (4)	521 (2)	−129 (1)
C (2)	184 (3)	203 (3)	176 (2)	C (10)	202 (3)	626 (2)	−99 (1)
C (3)	344 (3)	148 (2)	200 (2)	C (11)	259 (3)	654 (2)	1 (2)
N (4)	474 (2)	240 (1)	199 (1)	N (12)	239 (2)	549 (1)	58 (1)
C (5)	452 (2)	331 (2)	148 (2)	C (13)	600 (3)	224 (2)	255 (2)
C (6)	341 (2)	353 (2)	85 (1)	O (14)	608 (2)	127 (2)	296 (1)
C (7)	340 (2)	450 (1)	22 (1)	C (15)	720 (3)	317 (2)	264 (2)
C (8)	277 (3)	417 (2)	−71 (1)	I	−179	529	54

preted by the direct method using the Rentgen-75 program [4] and was refined by the method of least squares, initially in the isotropic (R = 0.19) and then in the anisotropic approximation (R = 0.113). The coordinates of the nonhydrogen atoms are given in Table 1.

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CHANGE IN PHYTIN UNDER THE INFLUENCE OF VARIOUS FACTORS

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UDC 615.45:615.7

Depending on the quality of rice flour, its phytin content ranges from 4.5 to 7%. Under the action of a high temperature in roasting, a considerable amount of the phytin is converted into phosphate and, consequently, the phytin content in cooked rice flour has fallen considerably.

Continuing investigations to determine the reasons for the formation of phosphate in the preparation of phytin from uncooked rice flour [1], we have directed our attention to the fact that freshly precipitated paste-like moist phytin (sample 1) and phytin dried at room temperature (sample 2) differ somewhat in color after they have been dried in the drying chest at 100-105°C for 5-6 h. Neither of the dried phytin samples gave the qualitative reaction for phosphate [2]. At the same time, if they were dissolved in 1% nitric acid and the solutions were neutralized with ammonia to pH 8.0-9.0, the precipitates that deposited were not uniformly amorphous but contained microcrystalline inclusions and this was more pronounced in sample 1. Both precipitates, after being dried at room temperature, gave the yellow coloration characteristic for phosphate with an aqueous solution of silver nitrate.

Earlier, on heating phytin at 160-200°C for three hours, we likewise observed no formation of phosphate, which led us to an erroneous conclusion [1]. It was found that this sample of phytin also contained phosphate but, for unknown reasons, this was not directly detected qualitatively but only after the reprecipitation of the phytin. The reason for this phenomenon can perhaps be explained after the structure of the phosphate has been established.

It must be mentioned that in sample 1 the amount of phosphate formed was considerably greater than in sample 2. At a high temperature, apparently, the presence of a certain amount of moisture leads to an easier cleavage of the phosphate—magnesium and phosphate—calcium bonds of the phytin molecule.