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## The Crystal and Molecular Structure of $\alpha$ -Isosparteine Monohydrate

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As a test of stereochemical formulae proposed by Marion & Leonard for the thermopsine-anagryrine family of  $C_{15}$  lupin alkaloids, the structure of  $\alpha$ -isosparteine monohydrate,  $C_{15}H_{26}N_2 \cdot H_2O$ , has been determined. The space group is  $C222_1$ ,  $a = 20.18$ ,  $b = 10.61$ ,  $c = 6.84$  Å,  $Z = 4$ . The four rings of the molecule have the 'chair' form with both outer rings *trans* to the methylene bridge that is common to the two inner rings. Bond lengths and angles have been measured. The water molecule of the monohydrate does not appear to be hydrogen bonded to the alkaloid molecule.

### Introduction

The thermopsine-anagryrine stereochemical family of  $C_{15}$  lupin alkaloids comprises thermopsine and anagryrine with composition  $C_{15}H_{20}N_2O$ , lupanine,  $\alpha$ -isolupanine, and two other (at present unknown) isomers having the composition  $C_{15}H_{24}N_2O$ , and sparteine,  $\alpha$ -isosparteine, and  $\beta$ -isosparteine of composition  $C_{15}H_{26}N_2$  (Marion & Leonard, 1951). A provisional stereochemical structure was assigned to sparteine by Leonard & Beyler in 1950. Structures for the other members of the family have recently been proposed by Marion & Leonard (1951) on the basis of that for sparteine and a study of the course of catalytic hydrogenation reactions, with the aid of Fisher-Hirschfelder-Taylor scale molecular models. The family relationships are shown in Fig. 1, where *cis* and *trans* refer to the hydrogen atoms on  $C_6$  and  $C_{11}$  relative to the  $C_{7,9}$ -methylene bridge, and the black discs represent these hydrogen atoms when in *cis*

position. The lettering (*A, B, C, D*) of the four rings and the numbering of the C and N atoms are those of Marion & Leonard (1951). The principal assumption made in the identification of the various isomers with the possible stereochemical formulae was that, in accordance with the spatial configurations of the scale molecular models, hydrogen enters the  $C_{15}H_{20}N_2O$  molecule at  $C_6$  *cis* to the methylene bridge more readily than *trans*. The validity of this assumption can be tested by a detailed X-ray structure study of almost any one of the substances concerned.

With this object in view, it seemed desirable to select a completely hydrogenated member of the family to avoid possible complications due to double bonds and carbonyl groups. Of the three compounds fulfilling this condition, sparteine (*cis-trans*) obviously is the least suitable structurally, while  $\beta$ -isosparteine had not been characterized chemically when the present investigation was undertaken. The structure of  $\alpha$ -isosparteine, however, if established as *cis-cis*, would immediately confirm that of its chemical progenitor, thermopsine, as blank-*cis* and thus indirectly those of the other isomers as represented in Fig. 1. This

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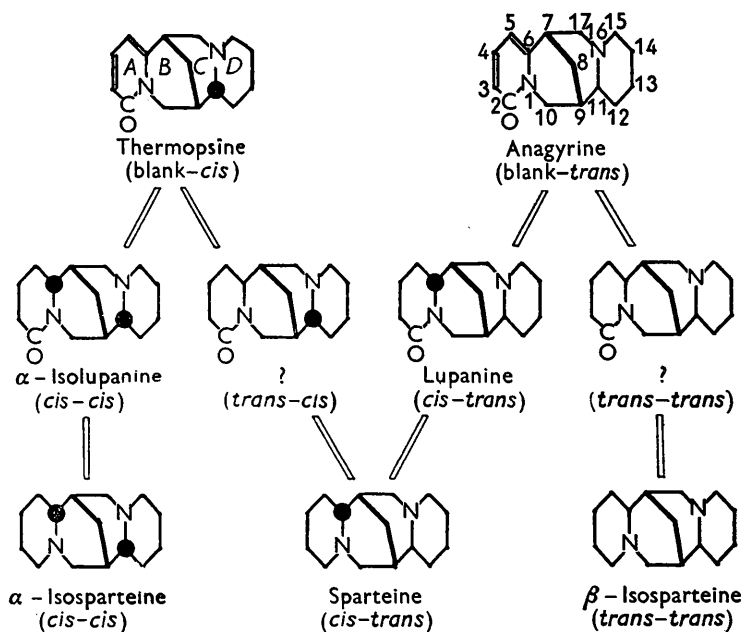


Fig. 1. The thermopsine-anagyrine family of  $C_{15}$  lupin alkaloids (after Marion & Leonard, 1951).

assumes, of course, that no reversal of *cis* and *trans* occurs during the course of the hydrogenation reactions, a contingency that is most unlikely on chemical grounds (Marion & Leonard, 1951).

To avoid possible distortion of the molecule, and undesirable overlapping effects, it was decided to attempt the structure determination of the free alkaloid without recourse to a heavy-atom derivative. Since anhydrous  $\alpha$ -isosparteine takes up water of crystallization extremely readily, however, it was necessary to use the stable monohydrate,  $C_{15}H_{26}N_2 \cdot H_2O$ .

The immediate object of the present study has been to establish the form of the  $\alpha$ -isosparteine rings and whether the outer ones (*A*, *D*, Fig. 1) are directed upwards (*cis*) or downwards (*trans*) with respect to the methylene bridge, i.e. whether the hydrogen atoms on  $C_6$  and  $C_{11}$  are in *trans-trans* or in *cis-cis* positions. In subsequent papers from this laboratory it is hoped to report on the X-ray crystallography of other members of this family of alkaloids and their derivatives.

### Crystal data

The crystals of  $\alpha$ -isosparteine monohydrate were colourless, m.p. (corr.)  $96^\circ$ – $117^\circ$  C.,  $[\alpha]_D^{22} = -51.3^\circ$  (ethanol), and had been isolated from natural sources by Marion, Turcotte & Ouellet (1951). They crystallized from aqueous ethanol in thin striated plates but better specimens were obtained from acetone. The predominant habit of the latter was prismatic with elongation in the direction of the *c* axis. The crystals showed the apparent symmetry of the orthorhombic bipyramidal class with the side pinacoid (100) and two domes, (110), (201), prominently developed. The

*a* axis was one of pseudo fourfold symmetry owing to the closeness of the angles ( $54^\circ$ ,  $56^\circ$ ) between the pinacoid and the domes. The crystals were soft and sublimed readily.

### Unit cell and space group

The unit-cell dimensions and space group were determined with a Buerger precession instrument using Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Measurements were corrected for film shrinkage (Barnes, Przybylska & Shore, 1951). The unit cell is orthorhombic, with

$$a = 20.18 \pm 0.04, \quad b = 10.61 \pm 0.02, \quad c = 6.84 \pm 0.02 \text{ \AA},$$

and volume  $1464.5 \text{ \AA}^3$ . The molecular weight is 252.23 so that there are 4 molecules of  $C_{15}H_{26}N_2 \cdot H_2O$  per cell. The calculated density is  $1.1438 \text{ g.ml.}^{-1}$ ; that measured by flotation in aqueous KI solution was  $1.14 \text{ g.ml.}^{-1}$  at room temperature. The number of electrons per unit cell,  $F(000)$ , is 560. The absorption coefficient for Cu  $K\alpha$  radiation is  $6.44 \text{ cm.}^{-1}$ .

Direct comparison of upper-level with zero-level precession photographs showed the diffraction symbol to be  $mmmC - - 2_1$ . The space group, therefore, is uniquely established as  $C222_1 - D_2^2$  and the orthorhombic class as bisphenoidal. Space-group extinctions are  $\{hkl\}$  when  $h+k = 2n+1$  and  $\{00l\}$  when  $l = 2n+1$ .

### Structure determination

#### Experimental

Intensity data were collected by means of Weissenberg photographs with Cu  $K\alpha$  radiation. Crystals were cut to approximately cubical shape with sides

parallel to the crystallographic axes, edges less than 0.3 mm. in length and differences in edge lengths of less than 0.03 mm. Absorption corrections were negligibly small and were not applied. Of the possible reflections, 81% were observed for the  $\{hk0\}$  zone, 71% for the  $\{h0l\}$  zone, and 60% for the  $\{0kl\}$  zone. Multiple-film technique was employed with two lots of three Kodak 'Industrex' films exposed for different lengths of time for each of the  $\{hk0\}$  and  $\{h0l\}$  zones and one lot of three films for the  $\{0kl\}$  zone. In all cases the films were interleaved with double sheets of black paper and the absorption factor was 3.0. Intensities were estimated visually, standard formulae and correction factors for mosaic crystals were used, and the absolute scale of  $F$  was obtained by correlation with the calculated structure factors.

Geometrical structure factor formulae were derived from the equivalent points of  $C222_1$  as given in the *Internationale Tabellen* (1935). The simplified forms differ from the corresponding ones of Lonsdale (1936) by an interchange of  $hx$  and  $ky$ .

For the electron-density projection on (010) it was convenient to shift the origin from 0, 0, 0 to the centre of symmetry at 0, 0,  $\frac{1}{4}$ .

Bevers & Lipson strips were used for all Fourier syntheses, the  $a$  axis being divided into 120 intervals, the  $b$  into 60, and the  $c$  into 30. Projections were made on (001) and (010), but, owing to overlapping on (100), the  $\{0kl\}$  structure factors were used only for corroborative purposes.

During the early stages of the work the atomic scattering curve for carbon given in the *Internationale Tabellen* (1935) was employed for all atoms, modified by a rough temperature factor as refinement progressed. The curve finally adopted for carbon was obtained by plotting  $F_0/S$  (where  $S$  is the geometrical structure factor) against  $\sin \theta$  and drawing a smooth curve through the greatest density of points. Values for points on this curve are given in Table 1.

Table 1.  $f$  values for C ( $\lambda = 1.5418 \text{ \AA}$ )

$\sin \theta$	0.0	0.1	0.2	0.3	0.4	0.5
$f$	6.00	5.28	4.20	2.91	1.72	1.04
$\sin \theta$	0.6	0.7	0.8	0.9	1.0	
$f$	0.76	0.58	0.45	0.34	0.29	

The same atomic scattering curve was used for nitrogen and for oxygen after multiplication of the  $f$  values by 1.17 and 1.33, respectively (C:N:O=6:7:8).

### Analysis

With four molecules of  $\alpha$ -isosparteine monohydrate per cell in space group  $C222_1$ , each must possess a twofold axis of symmetry and the asymmetric structural unit is one-half of the molecule. It follows, therefore, that the twofold axes of the cell parallel to either the  $a$  or  $b$  axis must pass through the oxygen atoms of the water molecules and must coincide with

the twofold axes of the alkaloid molecules. It is also clear from Fig. 1 that the molecular twofold axis must go through  $C_8$  of the methylene bridge, and hence that the outer rings,  $A$  and  $D$ , must both be either *cis* or *trans*. Thus a *cis-trans* configuration for isosparteine can be eliminated entirely on the basis of the unit cell and space-group data alone.

However, in addition to the possibility that rings  $A$  and  $D$  may both be either up or down relative to  $C_7-C_8-C_9$ , they may have the 'chair' form or either of two 'boat' forms, the last two depending on whether  $N_1-C_2$  and  $C_4-C_5$ , or  $C_2-C_3$  and  $C_5-C_6$ , are parallel. Similarly, the pair of inner rings,  $B$  and  $C$ , may be of the 'chair' or of either of the 'boat' types. In view of the structure of cyclohexane and those of its chloro and bromo derivatives (Pauling & Brockway, 1937; Halmøy & Hassel, 1939; Hassel & Lund, 1949; van Vloten, Kruissink, Strijk & Bijvoet, 1950; Haak, de Vries & MacGillavry, 1952), the 'chair' form was considered to be the most probable for both pairs of rings. Accordingly, one set of four molecules ( $Z = 4$  mols./cell) was assembled from Fisher-Hirschfelder-Taylor atom models with inner rings of a 'boat' form, and six sets were constructed with inner rings of 'chair' form. Three of the latter were arranged with outer rings of the 'chair' and the two 'boat' types, respectively, *trans* to the methylene bridge, while the other three were given the same modifications of the outer rings but in *cis* orientation.

Packing considerations and observed intensities showed that a 'boat' form of the inner rings was most unlikely and no further models of this type were examined. The only promising structure was that in which all rings of the molecules were of 'chair' form with the outer ones *trans* to the methylene bridge, and in which the molecular twofold axes were parallel to the  $a$  axis of the unit cell. Furthermore, it was possible to estimate the angle between a line joining  $C_8$  to  $N_1$  and the  $b$  axis in the projection of this structure on (100) as between  $15^\circ$  and  $30^\circ$ , with the lines joining  $C_8$  to  $N_1$  and to  $C_6$ , respectively, on opposite sides of the (001) plane. Finally, a projection on (001), assuming C-C and C-N bond lengths of 1.54 and 1.47  $\text{\AA}$ , respectively, with approximately tetrahedral angles, led to sufficiently close agreement between calculated and observed structure factors to permit an immediate Fourier synthesis.

Refinement of the  $x$  and  $y$  coordinates by five successive double Fourier  $\{hk0\}$  syntheses gave a discrepancy factor  $(\sum |F_o| - |F_c|) \div \sum |F_o|$  of about 0.30. Four applications of the simplified method of steepest descents (Qurashi, 1949) using a weighting factor  $W = 1/\xi^2 f$ , reduced it to 0.22. Two  $(F_o - F_c)$  syntheses (Cochran, 1951), the first of which led to appreciable changes in the  $x$  coordinates of four atoms, brought it down to 0.16.

To establish the  $z$  coordinates, one double Fourier and several  $(F_o - F_c)$  syntheses for the  $\{h0l\}$  zone were completed with a final discrepancy again of 0.16. The

Table 2. *Observed and calculated structure factors*

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
200	32.5	-31.0	401	13.0	1.5	110	58.5	65.0
400	96.0	-100.0	402	63.5	-60.0	130	33.0	31.5
600	12.0	13.0	403	19.5	-19.5	150	2.5	-3.5
800	24.0	23.5	404	9.0	10.5	170	2.0	1.0
10,0,0	10.5	14.5	405	10.5	9.5	190	12.0	9.0
12,0,0	2.0	1.0	406	14.0	-15.0	1,11,0	8.5	-7.5
14,0,0	3.5	-4.0	407	9.0	-10.5	1,13,0	3.0	6.0
16,0,0	9.5	10.5	408	< 1.5	3.0	220	53.5	-57.5
18,0,0	10.5	10.0	601	< 1.0	-4.0	240	11.5	11.5
20,0,0	2.5	2.0	602	3.5	4.0	260	11.0	7.0
22,0,0	6.5	7.5	603	12.5	-12.0	280	6.5	5.0
24,0,0	5.0	4.0	604	< 2.0	7.5	2,10,0	7.5	8.5
020	33.5	-39.0	605	6.5	6.5	2,12,0	< 2.0	1.5
040	15.0	22.5	606	19.0	17.0	310	76.5	-85.5
060	14.5	17.5	607	3.5	-6.0	330	71.0	67.0
080	5.0	1.5	608	< 1.5	0	350	8.0	3.5
0,10,0	11.5	-9.5	801	6.5	-2.5	370	13.0	14.5
0,12,0	< 2.0	3.5	802	< 1.5	0.5	390	6.0	7.5
002	20.5	-1.5	803	31.5	-27.5	3,11,0	8.5	10.5
004	10.0	14.5	804	2.0	2.5	3,13,0	< 1.5	-1.0
006	4.5	-4.5	805	6.0	-4.5	420	112.0	116.5
008	2.5	4.0	806	2.0	1.5	440	36.5	33.5
			807	8.0	8.5	460	12.0	14.0
021	27.0	-32.0	808	< 1.5	1.5	480	7.0	-4.0
022	15.0	13.0	10,0,1	< 1.5	-3.0	4,10,0	10.0	12.0
023	< 3.0	5.5	10,0,2	18.5	16.0	4,12,0	< 2.0	1.0
024	4.0	8.0	10,0,3	8.5	8.5	510	82.0	82.5
025	< 4.5	-2.5	10,0,4	14.0	-16.5	530	7.0	8.5
026	< 5.0	5.5	10,0,5	3.0	-3.0	550	11.0	10.0
027	< 4.5	-1.5	10,0,6	11.0	-9.5	570	9.5	7.5
028	< 3.5	-1.0	10,0,7	< 2.0	-0.5	590	19.5	-18.0
041	14.0	-5.5	10,0,8	4.0	-3.0	5,11,0	5.0	5.5
042	11.0	-4.0	12,0,1	2.0	1.5	5,13,0	< 1.5	1.0
043	6.5	10.0	12,0,2	2.5	-6.0	620	36.0	42.0
044	16.5	12.5	12,0,3	13.5	16.0	640	9.0	-15.5
045	21.0	-18.0	12,0,4	< 2.0	6.5	660	< 2.0	-1.5
046	10.5	12.0	12,0,5	3.0	-2.0	680	2.5	-3.0
047	11.0	9.0	12,0,6	< 2.0	-2.0	6,10,0	2.5	-1.5
048	6.0	10.0	12,0,7	2.5	-0.5	6,12,0	< 2.0	0
061	20.5	16.0	14,0,1	10.0	-10.0	710	40.0	39.5
062	30.0	29.0	14,0,2	6.5	-6.0	730	31.5	-41.0
063	10.5	3.0	14,0,3	11.0	11.0	750	14.5	16.0
064	4.5	3.5	14,0,4	< 2.5	5.5	770	10.0	6.0
065	< 5.0	1.5	14,0,5	< 2.0	-0.5	790	7.0	9.5
066	< 4.5	5.0	14,0,6	< 2.0	-2.0	7,11,0	< 2.5	2.0
067	< 3.5	1.5	14,0,7	< 1.5	1.0	7,13,0	< 1.0	4.0
081	< 4.5	-2.5	16,0,1	2.0	-3.5	820	7.0	-1.0
082	8.0	10.0	16,0,2	14.5	-16.5	840	19.0	18.0
083	8.5	9.0	16,0,3	3.0	-3.0	860	2.0	0
084	9.5	-4.5	16,0,4	10.0	12.5	880	22.5	24.5
085	< 4.5	-4.0	16,0,5	< 2.0	-1.0	8,10,0	< 2.5	2.5
086	< 3.5	-1.0	16,0,6	8.0	4.5	8,12,0	< 2.0	0.5
087	< 2.0	-0.5	18,0,1	2.5	1.0	910	10.0	5.5
0,10,1	< 5.0	5.5	18,0,2	2.5	-1.0	930	10.0	10.0
0,10,2	9.5	11.0	18,0,3	8.0	-9.0	950	13.5	16.5
0,10,3	12.0	-14.0	18,0,4	< 2.0	2.5	970	6.0	-6.5
0,10,4	7.0	12.0	18,0,5	6.5	-5.0	990	13.5	13.0
0,10,5	< 3.5	1.5	18,0,6	2.5	-6.0	9,11,0	3.0	-3.0
0,12,1	< 4.0	2.5	20,0,1	4.0	3.0	10,2,0	3.0	3.5
0,12,2	< 3.5	1.5	20,0,2	2.0	-5.0	10,4,0	12.5	8.0
0,12,3	< 3.0	1.0	20,0,3	< 2.0	0.5	10,6,0	3.5	0
0,12,4	< 2.0	0	20,0,4	< 2.0	-0.5	10,8,0	6.5	4.0
			20,0,5	5.5	5.5	10,10,0	10.5	-9.5
201	144.0	149.0	22,0,1	3.5	0	10,12,0	6.5	5.5
202	34.5	-38.0	22,0,2	< 2.0	-1.0	11,1,0	7.5	5.0
203	29.5	37.5	22,0,3	< 1.5	-0.5	11,3,0	17.0	13.5
204	7.5	9.5	22,0,4	< 1.5	1.0	11,5,0	10.5	8.0
205	< 2.0	4.5	24,0,1	9.5	9.0	11,7,0	2.5	-2.5
206	6.5	-8.0	24,0,2	< 1.5	2.0	11,9,0	3.5	-1.5
207	5.0	4.0	24,0,3	< 1.0	1.0	11,11,0	7.0	9.0
208	< 1.5	3.0				12,2,0	12.0	15.0

Table 2 (cont.)

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
12,4,0	5.0	1.0	15,9,0	7.5	5.0	19,9,0	< 1.0	1.0
12,6,0	12.0	9.0	15,11,0	4.5	— 3.5	20,2,0	< 2.5	0.5
12,8,0	< 2.5	— 0.5	16,2,0	< 2.5	— 2.5	20,4,0	8.5	7.5
12,10,0	< 2.0	2.0	16,4,0	< 2.5	3.0	20,6,0	2.0	4.0
12,12,0	6.0	11.0	16,6,0	7.0	7.0	20,8,0	< 1.5	3.5
13,1,0	5.0	3.0	16,8,0	3.0	4.5	21,1,0	6.5	— 6.5
13,3,0	7.0	8.0	16,10,0	6.0	8.0	21,3,0	< 2.5	1.5
13,5,0	3.5	— 0.5	17,1,0	2.5	4.0	21,5,0	< 2.0	0.5
13,7,0	3.5	2.5	17,3,0	2.5	— 2.5	21,7,0	< 1.5	2.5
13,9,0	< 2.5	— 0.5	17,5,0	3.5	— 1.5	22,2,0	< 2.0	— 4.0
13,11,0	1.5	3.0	17,7,0	3.5	5.0	22,4,0	3.5	— 4.5
14,2,0	10.5	9.5	17,9,0	2.5	— 2.0	22,6,0	< 1.5	4.5
14,4,0	2.5	3.0	18,2,0	< 2.5	0.5	23,1,0	10.0	11.0
14,6,0	2.5	0	18,4,0	6.5	5.0	23,3,0	2.0	— 2.5
14,8,0	2.5	0.5	18,6,0	2.5	— 1.0	23,5,0	2.5	3.5
14,10,0	6.5	5.0	18,8,0	7.0	— 6.0	24,2,0	6.5	9.0
15,1,0	10.5	9.0	19,1,0	2.5	0.5	24,4,0	< 1.5	1.5
15,3,0	2.5	— 1.0	19,3,0	16.5	20.0	25,1,0	2.0	0
15,5,0	2.5	3.5	19,5,0	3.5	— 0.5	25,3,0	< 1.0	0
15,7,0	10.5	11.5	19,7,0	2.0	— 1.5			

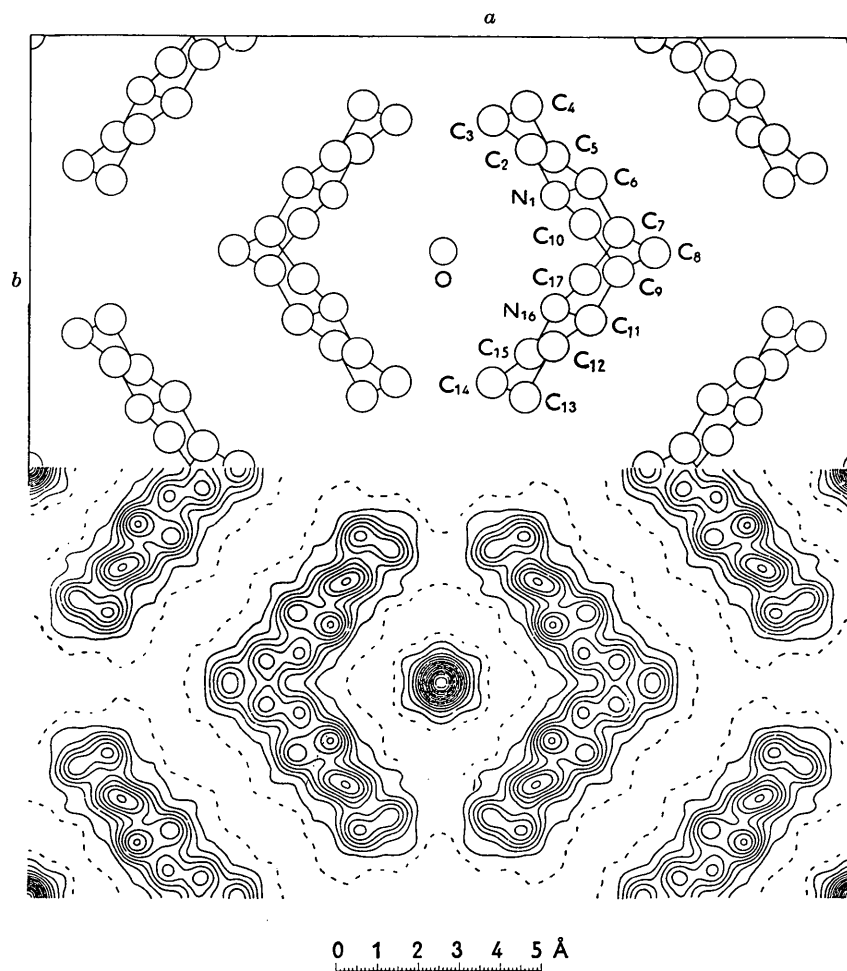


Fig. 2. Structure and electron density of  $\alpha$ -isosparteine monohydrate projected on (001); contour lines are at intervals of 1 e.Å<sup>-2</sup>, the first being broken.

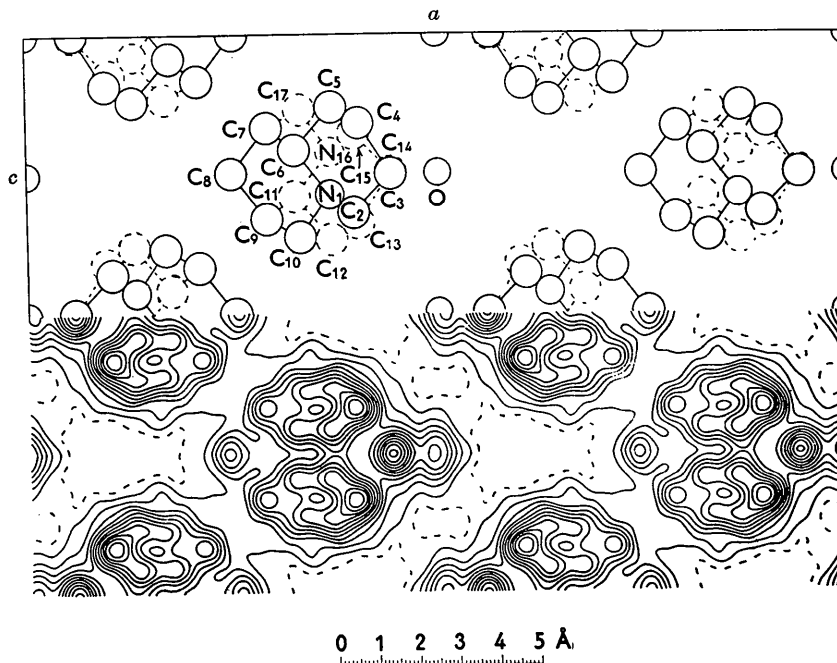


Fig. 3. Structure and electron density of  $\alpha$ -isopartine monohydrate projected on (010); contour lines are at intervals of  $1 \text{ e.}\text{\AA}^{-2}$ , the first being broken, as are the circles representing the atoms of the lower half of each molecule.

Table 3. Atomic coordinates

	$x/a$	$x$ (Å)	$y/b$	$y$ (Å)	$z/c$	$z$ (Å)
$N_{16}$	+0.133	+2.684	+0.133	+1.411	+0.077	+0.527
$C_{17}$	+0.104	+2.099	+0.240	+2.546	+0.142	+0.971
$C_{15}$	+0.058	+1.170	+0.306	+3.247	+0.003	+0.021
$C_{14}$	+0.098	+1.978	+0.340	+3.607	-0.180	-1.231
$C_{13}$	+0.131	+2.644	+0.222	+2.355	-0.238	-1.628
$C_{12}$	+0.177	+3.572	+0.161	+1.708	-0.084	-0.575
$C_{11}$	+0.211	+4.258	+0.047	+0.499	-0.164	-1.122
$C_{10}$	+0.255	+5.146	0	0	0	0
$C_9$	+0.170	+3.431	+0.067	+0.711	+0.229	+1.566
$O$	0	0	0	0	0	0

( $F_o - F_c$ ) syntheses for this zone were troublesome owing to overlapping of  $C_2$  and  $C_{13}$ . Two additional Fourier projections were made but the coordinates obtained from them were not in very good agreement with those from the ( $F_o - F_c$ ) syntheses. Apparently, errors due to termination of the series play a more important role in this projection. The coordinates given by the last ( $F_o - F_c$ ) synthesis, therefore, were adopted.

In none of these procedures were the hydrogen atoms included.

Observed and calculated structure factors are tabulated in Table 2 for  $\sin \theta \leq 0.990$ .

There was some uncertainty in the phase constants of eighteen planes of large spacings, owing to the omission of hydrogen terms from the computation of the structure factors given in Table 2. Assuming a C-H bond length of 1.1 Å, and tetrahedral angles, the  $F$  values for these planes were recalculated using the scattering curve for the hydrogen atom employed

by Morrison & Robertson (1949). Changes in sign from those given in Table 2 were obtained for (12,0,0), (150), (820), (002), and (602); the signs of ten were unaffected, and those of three remained doubtful. The changed signs were used in the final Fourier synthesis but the three reflections whose signs remained in doubt were omitted.

#### Results

Projections of the structure on (001) and on (010), with the corresponding electron-density maps, are shown in Figs. 2 and 3.

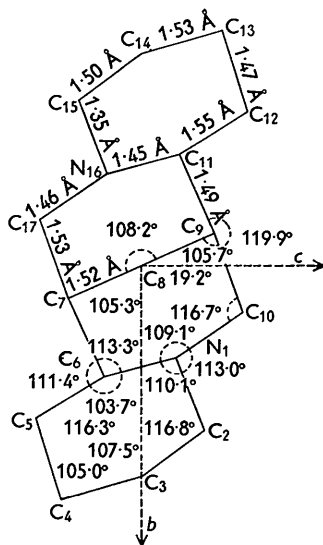
The coordinates of the atoms of the asymmetric unit and those of the oxygen atom of the water molecule are given in Table 3.

The bond lengths and angles for the asymmetric unit are listed in Table 4 and are shown in Fig. 4.

In the projection on (100), a line through  $C_8$  and  $N_1$  makes an angle of  $20.5^\circ$  with the  $b$  axis while one through  $C_8$  and  $C_9$  is at  $19.2^\circ$  to the  $c$  axis.

Table 4. Bond lengths and angles

Lengths (Å)		Angles (°)	
C <sub>2</sub> -C <sub>3</sub>	1.50	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	107.5
C <sub>3</sub> -C <sub>4</sub>	1.53	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	105.0
C <sub>4</sub> -C <sub>5</sub>	1.47	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	116.3
C <sub>5</sub> -C <sub>6</sub>	1.55	C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	111.4
C <sub>6</sub> -C <sub>7</sub>	1.49	C <sub>6</sub> -C <sub>7</sub> -C <sub>8</sub>	105.3
C <sub>7</sub> -C <sub>8</sub>	1.52	C <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub>	108.2
C <sub>8</sub> -C <sub>9</sub>	1.53	C <sub>8</sub> -C <sub>9</sub> -C <sub>10</sub>	105.7
		C <sub>11</sub> -C <sub>9</sub> -C <sub>10</sub>	119.9
C <sub>6</sub> -N <sub>1</sub>	1.45	C <sub>6</sub> -N <sub>1</sub> -C <sub>10</sub>	109.1
N <sub>1</sub> -C <sub>10</sub>	1.46	C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub>	110.1
N <sub>1</sub> -C <sub>2</sub>	1.35	C <sub>10</sub> -N <sub>1</sub> -C <sub>2</sub>	113.0
		N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	116.8
		N <sub>1</sub> -C <sub>10</sub> -C <sub>9</sub>	116.7
		N <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub>	103.7
		N <sub>1</sub> -C <sub>6</sub> -C <sub>7</sub>	113.3

Fig. 4. Bond lengths and angles in the molecule of  $\alpha$ -isosparteine.

Finally, the shortest intermolecular C-C distances between one molecule and its four nearest neighbours lie between 3.97 Å and 4.20 Å, while the distances between the oxygens of the water molecules at 0, 0, 0 and at 0, 0,  $\frac{1}{2}$  and the nearest nitrogen are 3.08 and 3.26 Å, respectively, with closest oxygen to carbon distances of 3.44 and 3.38 Å.

### Discussion

Although the average discrepancy between the observed and calculated values of  $F$  in Table 2 is only 16%, some of the individual differences are appreciably larger. It will be noted, however, that the majority of these are among reflections from planes of low indices where the omission of hydrogen contributions and neglect of extinction corrections would have the greatest effect.

The mean standard deviation (Cochran & Penfold, 1952, p. 648) in the bond lengths is 0.023 Å, which corresponds to a probable error of  $\pm 0.016$  Å. Owing

to the overlapping of C<sub>13</sub> and C<sub>2</sub> in the projection on (010), however, the values for C<sub>4</sub>-C<sub>5</sub> and N<sub>1</sub>-C<sub>2</sub> are less precise. Since the greatest uncertainty is in the  $z$  coordinates, the error in each of these two bonds probably does not exceed  $\pm 0.04$  Å. It is possible that the  $z$  coordinate of C<sub>2</sub> should have a larger value, which would make C<sub>2</sub>-C<sub>3</sub> more nearly equal to C<sub>3</sub>-C<sub>4</sub>, and would reduce the angles N<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> and C<sub>10</sub>-N<sub>1</sub>-C<sub>2</sub>. The decreased length (1.35 to 1.40 Å) of the N<sub>1</sub>-C<sub>2</sub> bond, however, is significant because its difference from the normal N-C bond is more than three times the standard deviation (Cruickshank, 1949, p. 67). It is probably the cause of the reduced length of the parallel bond, C<sub>4</sub>-C<sub>5</sub>. Although the sum of carbon and nitrogen single bond covalent radii is normally 1.47 Å (Pauling, 1945, p. 164) appreciably shorter distances have been found in several structures (Brown, 1949, Table 3, p. 231). If the length of the C<sub>4</sub>-C<sub>5</sub> bond be omitted, the average C-C distance in the  $\alpha$ -isosparteine molecule is 1.52 Å, only slightly less than the sum (1.54 Å) of the single bond covalent radii (Pauling, 1945).

The mean standard deviation in the bond angles is 1.5°. Within the limits of experimental error, tetrahedral angles have been found for C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub>, C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub>, C<sub>6</sub>-N<sub>1</sub>-C<sub>2</sub>, C<sub>7</sub>-C<sub>8</sub>-C<sub>9</sub>, and C<sub>6</sub>-N<sub>1</sub>-C<sub>10</sub>. An outstanding departure is shown by C<sub>11</sub>-C<sub>9</sub>-C<sub>10</sub>, the value of which is almost 120°. It is clear from Fig. 4, however, that this is dependent primarily on the distance apart of the two nitrogen atoms, N<sub>1</sub> and N<sub>16</sub>. These atoms are separated by a length of 3.01 Å, which, it is interesting to note, is virtually the same as the sum of the van der Waals radii (3.0 Å). An N<sub>1</sub>-N<sub>16</sub> distance of 2.5 Å would be required to reduce the angle C<sub>11</sub>-C<sub>9</sub>-C<sub>10</sub> to 109.5°. The other departures from the tetrahedral angle (see Fig. 4) appear to be due to the effect of the difference in length between carbon-nitrogen and carbon-carbon single bonds coupled with the nitrogen-nitrogen separation requirement.

The distance between C<sub>10</sub> and C<sub>11</sub> is 2.62 Å, which is appreciably shorter than the sum of the van der Waals radii. Some decrease, however, is to be expected since the line joining the non-bonded atoms, C<sub>10</sub> and C<sub>11</sub>, makes small angles with the bonded pairs C<sub>9</sub>-C<sub>10</sub> and C<sub>9</sub>-C<sub>11</sub> (Pauling, 1945, p. 193).

It is of interest to note that all intermolecular carbon-carbon distances are greater than about 4.0 Å, thus indicating that only van der Waals forces are involved in maintaining the structure, and accounting for the ease with which the solid sublimes. Furthermore, Figs. 2 and 3 show that the structure of  $\alpha$ -isosparteine monohydrate is consistent with the observed preferential growth of the crystals along the  $c$  axis and the predominance of the faces (100), (110) and (201).

In the later stages of the structure analysis some evidence was obtained that the water molecule is not hydrogen bonded to the alkaloid molecule.

Small peaks, apparently due to the hydrogen atoms

of the water molecule, occur in the electron-density maps based on the  $(F_o - F_c)$  syntheses for the  $\{h0l\}$  zone. Their heights are slightly greater than three times the mean standard deviation of the electron density for this zone. One of these maps is shown in Fig. 5, where the atomic positions of one of the water

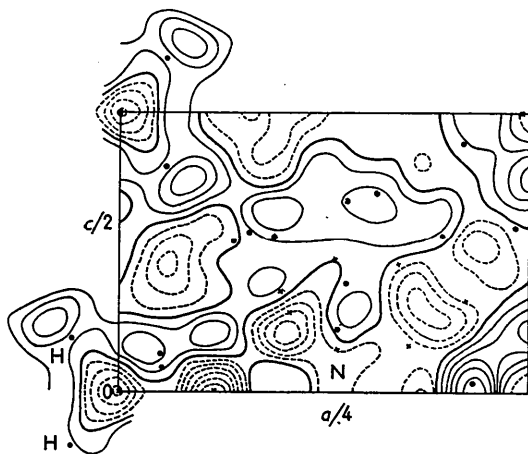


Fig. 5.  $(F_o - F_c)$  synthesis for the  $\{h0l\}$  zone; the centres of C, N and O atoms are shown by crosses; the probable positions of the hydrogen atoms are indicated by dots. Contour lines are at intervals of  $0.2 \text{ e.}\text{\AA}^{-2}$  with the zero line heavy and negative contours broken.

molecules and the nearest nitrogen atom are designated H, H, O, N, respectively. The coordinates of the hydrogen atoms are  $x \simeq -0.59 \text{ \AA}$ ,  $z \simeq +0.66 \text{ \AA}$ , for that attached to the oxygen atom at 0, 0, 0, and  $x \simeq +0.59 \text{ \AA}$ ,  $z \simeq +2.76 \text{ \AA}$ , for that attached to the oxygen atom at 0, 0,  $\frac{1}{2}$ . Taking the O-H bond length as  $0.97 \text{ \AA}$  (Pauling, 1945, p. 168) and the angle H-O-H as  $105^\circ$ , the  $y$  coordinate of each is  $\pm 0.40 \text{ \AA}$ . On this basis, not one of the hydrogen-nitrogen distances is less than  $2.7 \text{ \AA}$ , the sum of the van der Waals radii (N,  $1.5 \text{ \AA}$ ; H,  $1.2 \text{ \AA}$ ). Furthermore, it appears from Fig. 5 that the hydrogen atoms of the water molecule are on the opposite side of the oxygen atom from the nearest atom of nitrogen. Thus, if the positions of the hydrogen atoms of the water molecules have indeed been located, it is clear that the latter do not form hydrogen bonds with the nitrogen atoms of the  $\alpha$ -isosparteine molecule. This is somewhat unexpected in view of the marked hygroscopic nature of the anhydrous compound.

In so far as the  $\alpha$ -isosparteine molecule is concerned,

the crystal structure investigation has fully confirmed the stereochemical configuration proposed by Marion & Leonard (1951). It thus provides strong support for their assumption that during the hydrogenation of either thermopsine or anagyrene, the hydrogen atom preferentially attaches itself to C<sub>6</sub> *cis* to the methylene bridge. Thus, indirectly, it upholds the stereochemical arrangements deduced for all members of the thermopsine-anagyrene family of C<sub>15</sub> lupin alkaloids.

Grateful acknowledgment is made to Dr L. Marion for stimulating our interest in the lupin alkaloids, for helpful discussions, and for providing the authenticated crystals of *l*- $\alpha$ -isosparteine monohydrate for the structure determination. The use of the simplified method of steepest descents was expedited by assistance from Dr M. M. Qurashi.

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