

**Guanine (VIIa).**—A suspension of VIa (1.5 g) in 1 *N* sodium hydroxide (40 ml) was refluxed for 3 hr. After neutralization with acetic acid to pH 6, a mixture of benzoic acid and guanine was collected by filtration, washed with water, and dried. The finely divided powder was suspended in 100 ml of hot ethanol with stirring for removing benzoic acid. The purity of the crude guanine (987 mg) was found to be 90% by measuring the ultraviolet absorbancy at 250  $\mu$ . Recrystallization from a minimum amount of 0.5 *N* sulfuric acid yielded the sulfate of VIIa: 540 mg (49%); mp over 300°. This compound was identified with an authentic sample by the comparison of infrared and ultraviolet spectra.

*Anal.* Calcd for  $C_5H_7ON_5 \cdot 0.5H_2SO_4 \cdot H_2O$ : C, 27.67; H, 3.93; N, 31.87. Found: C, 27.40; H, 3.65; N, 31.96.

Ia (5 g) was converted to the sulfate of VIIa with an over-all yield of 37–41%. In this case no effort was made to purify the intermediates, and the crude products were directly employed in the subsequent reactions.

**2',3'-O-Isopropylidene-guanosine (VIIb) from Ib.**—5-Amino-1-(2',3'-O-isopropylidene- $\beta$ -D-ribofuranosyl)-4-imidazolecarboxamide (Ib) (6.70 g, 22.48 mmoles) was dissolved in 380 ml of hot anhydrous acetone under stirring. To the solution was added portionwise benzoyl isothiocyanate (4 g, 24.53 mmoles), and the mixture was heated under reflux for 1 hr. During this period, a spot corresponding to the starting material disappeared on paper chromatogram (solvent A) and a new spot appeared. The resulting pale yellow solution was evaporated to dryness *in vacuo*. The yellow powder (11 g) thus obtained was employed in the next reaction: paper chromatography,  $R_f$  0.86 (solvent B). The ultraviolet absorption spectrum of the water extract from an excised spot ( $R_f$  0.86) showed  $\lambda_{max}^{pH 1}$  250  $\mu$ .

The benzoylthioleido compound IIb was dissolved in 200 ml of 0.2 *N* sodium hydroxide. To this solution was added portionwise dimethyl sulfate (3.21 g, 25.3 mmoles), and the mixture was stirred vigorously for 2 hr at room temperature. A yellow gummy substance separated. After acidification with glacial acetic acid to pH 6, the gummy substance was extracted four times with 100-ml portions of chloroform. The combined extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo* to afford amorphous solid (9.5 g.): paper chromatography,  $R_f$  0.93 (solvent B). The ultraviolet absorption spectrum of the extract from an excised spot ( $R_f$  0.93) showed  $\lambda_{max}^{pH 1}$  250  $\mu$ .

The S-methylthio derivative Vb, thus obtained, was dissolved in 120 ml of ethanol containing 2% ammonia and heated at 120°

for 1 hr in a sealed tube. At the end of the reaction, the odor of methyl mercaptan was recognized. The solvent was removed *in vacuo* to afford a yellow powder (8.9 g): paper chromatography,  $R_f$  0.76 (solvent B). The ultraviolet absorption spectra of the extract from an excised spot ( $R_f$  0.76) showed  $\lambda_{max}^{pH 1}$  245 and  $\lambda_{max}^{pH 13}$  262  $\mu$ .

Crude N'-benzoylguanidino compound (VIb) was added to 200 ml of 0.5 *N* sodium hydroxide and the solution was heated under reflux for 1 hr. Paper chromatography of this reaction mixture indicated the presence of three spots, 2',3'-O-isopropylidene-guanosine (VIIb), benzoic acid, and a trace of starting material. After neutralization with glacial acetic acid to pH 7, the solution was concentrated *in vacuo* to about 20 ml and the resulting mixture of VIIb and benzoic acid was collected, dried, and pulverized. After the benzoic acid was extracted three times with 200-ml portions of hot ethyl ether, the residue was treated with charcoal and crystallized from water to afford 2.8 g of pale yellow crystals. Recrystallization of the crude substance from water gave an analytically pure sample. The average isolated yield of VIIb was found to be about 35–40%. The pure sample showed mp 290–295° dec;  $[\alpha]_{D}^{25} -67.7^\circ$  (c 1, 0.1 *N* sodium hydroxide). The compound was identified with an authentic sample by comparison of ultraviolet and infrared absorption spectra and  $R_f$  values in paper chromatography.

*Anal.* Calcd for  $C_{13}H_{17}O_5N_5$ : C, 47.88; H, 5.60; N, 21.52. Found: C, 48.30; H, 5.26; N, 21.67.

When VIIb was synthesized from Ib by the series of reactions described above without isolation of the intermediates, the yield estimated paper chromatographically was 60–65%.

**Registry No.**—IIa, 10333-86-5; III, 10333-87-6; IV, 10333-88-7; Va, 10333-89-8; VIa, 10333-90-1; sulfate of VIIa, 10333-92-3; VIIb, 362-76-5; benzoyl isothiocyanate, 532-55-8; 5-amino-1- $\beta$ -D-ribofuranosyl-4-imidazolecarboxamide, 2627-69-2; guanosine, 85-30-3.

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## The Crystal and Molecular Structure of the Alkaloid 7-Hydroxy- $\beta$ -isosparteine Perchlorate

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The structure of an hydroxy- $\beta$ -isosparteine perchlorate salt has been determined from three-dimensional data collected by an automated diffractometer. The structure was solved by straightforward heavy atom methods and refined by least squares to give unequivocal positions for all of the structural atoms and most of the hydrogen atoms. The hydroxyl group was found to be on the C-7 position, and the proton from the perchloric acid was found on the N-16 position.

The structure of hydroxy- $\beta$ -isosparteine (Figure 1) is of interest because of its place in the biosynthesis scheme of the *Spartium scoparium* Lupine family of *Leguminosae*, because of the similarity of pharmacological activity of this class of compound to the hormone oxytocin, and because of the unusual pK values of the two tertiary nitrogen atoms. The pK values of the two nitrogen atoms have been determined to be 2.61 and 11.26 in a similar compound,  $\alpha$ -isosparteine.<sup>1</sup> In addition we were interested to see whether the perchlo-

rate group could be used conveniently as a heavy atom group for the determination of a crystal structure.

### Crystal Data

Small needle crystals of the perchlorate salt were given to us by Dr. Marvin Carmack, Department of Chemistry, Indiana University, Bloomington, Ind. The space group and unit cell parameters were obtained from rotation and Weissenberg photographs using Cu K $\alpha$  radiation. The crystals are orthorhombic with space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. The unit cell dimensions, with the estimated error in the last figure, are  $a = 13.04$

(1) P. Baranowski, J. Skolik, and M. Wiewioroski, *Tetrahedron*, **20**, 2383 (1964).

(2)  $A, b = 13.19$  (2)  $A, c = 9.59$  (1)  $A$ . The number of molecules in the unit cell is four, and one molecule of the alkaloid and one perchlorate group are in the asymmetric unit. The density from flotation in benzene-bromobenzene mixture is  $1.41$  (1)  $\text{g/cc}$ , giving an observed molecular weight of  $351 \pm 3$ ; that expected from  $\text{C}_{15}\text{N}_2\text{H}_{27}\text{O}_5\text{Cl}$  would be  $350.4$ .

The unique set of three-dimensional data was taken around the  $c$  axis on the Supper-Pace autodiffractometer using filtered  $\text{Mo K}\alpha$  radiation and a scintillation counter. The size and composition of the crystal used were such that corrections for absorption and for anomalous scattering were negligible. Each reflection was scanned using the stationary counter and moving crystal technique. Owing to the Weissenberg geometry, extension of the inner reflections of the upper levels occurs. For these the usual  $2^\circ$  scan was expanded in increments of  $0.5^\circ$  to a maximum of  $9^\circ$ . The scan was routinely divided into six equal segments, and the count for each segment was recorded. For each reflection the first processing of the raw data divided the six segments into the reflection peak, background, and some of the more obvious errors such as the white radiation streaks from nearby reflections. In all 1032 of a possible 1063 reflections within  $1.0 \text{ \AA}$  resolution were above background. The second processing of the data applied the usual Lorentz and polarization factors. The scale factor for each level was assumed to be 1. The data levels were later scaled to the calculated structure factors.

#### Determination of the Structure

A three-dimensional unsharpened Patterson synthesis was calculated, and from the Harker sections the coordinates of the center of the perchlorate group were obtained readily. From these a heavy atom synthesis was calculated, and a fourfold minimum function was performed on the Patterson shifted to each of the positions of the four perchlorate groups in the unit cell. Since the  $x$  coordinate of the perchlorate group was very near 0, both the heavy atom synthesis and the Patterson superposition contained a pseudo-mirror plane at  $x = 0$ . However, by employing peaks that were common to both, the positions of ten atoms were obtained. These were now used in the phasing and a second electron-density synthesis enabled six more atoms to be placed. Yet another cycle of Fourier analysis gave the complete molecule and showed that three of the atoms, one from the second cycle and two from the third, were incorrect.

Refinement of the 23 structural atoms by block diagonal least squares on the 32K IBM 7040 was now started with isotropic temperature factors for all atoms. All reflections were weighted as 1. After five cycles, the levels were rescaled to the calculated structure factors, a difference synthesis indicated the need for anisotropic temperature factors for the chlorine and oxygen atoms, and six more cycles of least-squares were run. Finally, a difference synthesis was calculated from which the contributions of all atoms except hydrogen had been subtracted. Except for a pair of peaks near the perchlorate, the only peaks of greater than 0.2 electron were at positions where hydrogen atoms were expected. With the aid of these peaks, positions were assigned to 26 of the 27 hydrogen atoms

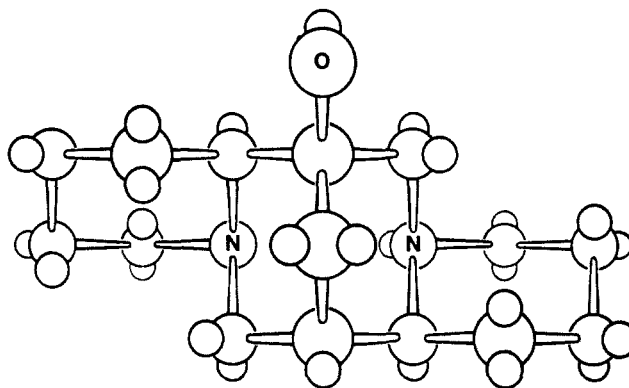


Figure 1.—A ball and stick drawing of the molecule looking down the pseudo-twofold rotation axis.

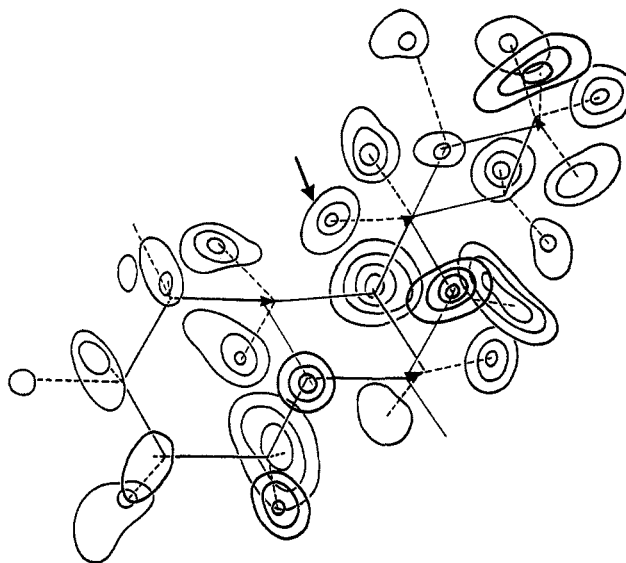


Figure 2.—A difference electron density synthesis in which the chlorine, oxygen, nitrogen, and carbon atoms have been subtracted, leaving only the hydrogen atoms. Contours at 0.2 electron per  $\text{\AA}^3$ , zero and negative contours omitted. The skeleton of the molecule is drawn in solid lines; the bonds to the hydrogen atoms are dashed. The molecule is tilted to the side with respect to Figure 1.

which were included, but not refined, in the last cycles of least squares. A projection of this synthesis is shown in Figure 2. The progress of  $R$ , the reliability index, in the various stages of refinement is given in Table I. A list of the final structure factors may be obtained on request. The final positional and temperature parameters are given in Table II. The final bond distances

TABLE I

Cycle	No. of atoms used in phasing	Value of $R^a$	Comments
1	1	64.8	Perchlorate ion as one atom
2	11	45.9	
3	17	37.6	
4	23	29.3	All perchlorate atoms in place
5	23	17.7	Levels rescaled
6	23	15.9	Cl, O anisotropic from now on
9	23	12.5	13 bad reflections removed
12	39	10.7	16 hydrogen atoms included
13	49	9.8	26 hydrogen atoms

<sup>a</sup>  $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$  where  $F_o$  is the observed value of the structure factor and  $F_c$  is the calculated value. The summation is over all reflections.

TABLE II  
FRACTIONAL ATOMIC COORDINATES AND TEMPERATURE FACTORS WITH STANDARD DEVIATIONS

Atom	$x/a$ ( $\sigma \times 10^4$ )	$y/b$ ( $\sigma \times 10^4$ )	$z/c$ ( $\sigma \times 10^4$ )	$B$ ( $\text{Å}^2$ ) ( $\sigma \times 10^3$ )		
N-1	0.4123 (3)	0.3497 (3)	0.5122 (4)	2.05 (7)		
C-2	0.4002 (3)	0.2411 (3)	0.5502 (4)	3.03 (7)		
C-3	0.2955 (4)	0.1998 (4)	0.5182 (6)	3.01 (14)		
C-4	0.2062 (4)	0.2652 (4)	0.5734 (6)	3.98 (10)		
C-5	0.2231 (4)	0.3739 (4)	0.5372 (7)	3.04 (13)		
C-6	0.3301 (4)	0.4125 (4)	0.5768 (5)	2.43 (10)		
C-7	0.3499 (3)	0.5224 (3)	0.5463 (5)	3.22 (9)		
C-8	0.3562 (4)	0.5419 (4)	0.3861 (6)	1.88 (11)		
C-9	0.4442 (3)	0.4759 (3)	0.3284 (5)	1.96 (9)		
C-10	0.4194 (4)	0.3630 (4)	0.3608 (5)	3.05 (10)		
C-11	0.5487 (3)	0.5087 (3)	0.3928 (5)	2.48 (9)		
C-12	0.5830 (4)	0.6114 (4)	0.3383 (6)	2.52 (10)		
C-13	0.6883 (4)	0.6331 (4)	0.4076 (5)	4.22 (9)		
C-14	0.6775 (4)	0.6380 (4)	0.5638 (6)	2.77 (10)		
C-15	0.6395 (4)	0.5336 (4)	0.6156 (7)	3.55 (12)		
N-16	0.5407 (4)	0.5056 (4)	0.5509 (6)	2.38 (11)		
C-17	0.4489 (4)	0.5624 (4)	0.6108 (6)	1.87 (10)		
O-18	0.2725 (2)	0.5862 (2)	0.6089 (3)	<i>a</i>		
Perchlorate ion	$x/a$ ( $\sigma \times 10^4$ )	$y/b$ ( $\sigma \times 10^4$ )	$z/c$ ( $\sigma \times 10^4$ )	$B$ ( $\text{Å}^2$ ) ( $\sigma \times 10^3$ )		
O-19	0.4431 (4)	0.9866 (3)	0.5278 (5)	<i>a</i>		
O-20	0.4451 (3)	0.8239 (3)	0.4548 (5)	<i>a</i>		
O-21	0.5926 (3)	0.8899 (4)	0.5454 (6)	<i>a</i>		
O-22	0.4531 (3)	0.8548 (3)	0.6891 (4)	<i>a</i>		
Cl-23	0.4839 (0.9)	0.8903 (0.9)	0.5543 (1.4)	<i>a</i>		
Atom	$\beta_{11}$ ( $\sigma$ ) ( $B_{11}$ )	$\beta_{22}$ ( $\sigma$ ) ( $B_{22}$ )	$\beta_{33}$ ( $\sigma$ ) ( $B_{33}$ )	$\beta_{12}$ ( $\sigma$ ) ( $B_{12}$ )	$\beta_{13}$ ( $\sigma$ ) ( $B_{13}$ )	$\beta_{23}$ ( $\sigma$ ) ( $B_{23}$ )
O-18	44 (2) (3.0)	29 (2) (2.0)	76 (4) (2.8)	32 (3) (2.2)	48 (5) (2.4)	-25 (5) (-1.3)
O-18	181 (5) (12.3)	36 (2) (2.5)	18 (7) (0.6)	89 (6) (6.1)	37 (12) (1.8)	34 (8) (1.7)
O-20	88 (3) (4.5)	77 (3) (5.4)	155 (6) (5.7)	-55 (5) (-3.8)	-39 (9) (-1.9)	-74 (8) (-4.1)
O-21	66 (3) (6.0)	119 (4) (8.3)	227 (8) (8.3)	-16 (6) (-1.1)	59 (10) (2.9)	59 (13) (3.0)
O-22	91 (3) (6.2)	76 (3) (5.3)	109 (5) (4.0)	-43 (6) (-3.0)	-28 (8) (-1.4)	46 (7) (2.4)
Cl-23	44 (0.7) (3.0)	42 (0.7) (2.9)	70 (1) (2.6)	1 (1) (0.7)	15 (2) (0.7)	-1 (2) (-0.5)
Hydrogen atoms <sup>a</sup>	$x/a$	$y/b$	$z/c$	$B^c$		
H-24	0.47	0.20	0.49			
H-25	0.42	0.22	0.67			
H-26	0.29	0.19	0.45			
H-27	0.29	0.13	0.54			
H-28	0.15	0.23	0.54			
H-29	0.20	0.24	0.68			
H-30	0.20	0.39	0.45			
H-31	0.15	0.41	0.57			
H-32	0.35	0.42	0.66			
H-33	0.26	0.50	0.35			
H-34	0.38	0.62	0.37			
H-35	0.42	0.49	0.24			
H-36	0.37	0.35	0.31			
H-37	0.44	0.30	0.33			
H-38	0.63	0.46	0.36			
H-39	0.52	0.68	0.38			
H-40	0.62	0.61	0.25			
H-41	0.72	0.70	0.37			
H-42	0.76	0.61	0.37			
H-43	0.63	0.70	0.62			
H-44	0.74	0.65	0.60			
H-45	0.69	0.48	0.63			
H-46	0.63	0.53	0.70			
H-47	0.52	0.45	0.58			
H-48	0.47	0.63	0.59			
H-49	0.45	0.57	0.72			
H-50	Not located					

<sup>a</sup> Anisotropic temperature factors and standard deviations of the form  $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$  and conversion to approximately the same scale as the isotropic temperature factors by  $B_{ii} = 4\beta_{ii}/a^{*2}$ .  $\beta$  and  $\sigma$  have been multiplied by  $10^4$ . <sup>b</sup> The hydrogen atoms were included in the last structure factor calculation, but were not refined. Standard deviations are estimated to be at least ten times those for the nonhydrogen atoms. <sup>c</sup> Given the value  $3.0 \text{ Å}^2$  for each hydrogen atom.

and angles are given in Figure 3. The standard deviations, as obtained from the least-squares calculation, are between 0.008 and 0.015 Å for the C-C bonds.

The molecule is called by convention<sup>2</sup> *trans,trans* (while  $\alpha$ -isosparteine is called *cis,cis* and sparteine is *cis,trans*), and all four of the six-membered rings are found to be in the chair conformation. The packing of the four molecules in the full unit cell is shown in Figure 4. Przybylska<sup>3</sup> also has found the chair conformation in  $\alpha$ -isosparteine monohydrate, which she investigated with two-dimensional data.

### Discussion

In spite of the perchlorate group being very near to a special position, the determination of the structure was not seriously hampered, and we conclude that the perchlorate ion is quite useful as a heavy atom. However, the oxygen atoms of the perchlorate ion were among the very last to be found, and two of these first appeared on the wrong side of the pseudo-mirror plane at  $x = 0$ . Since the oxygen atoms of the perchlorate group were not distinguishable in either the superposition or the first heavy atom synthesis, the group could be represented only by a single atom at the center. In an effort to account partially for the scattering of the oxygen atoms, particularly for the lower order reflections, the group was represented by a single bromine atom during the next few cycles of refinement. We feel that some of the difficulty with the oxygen atoms can be attributed to the nearness to  $x = 0$ .

The molecule of  $\alpha$ -isosparteine<sup>3</sup> was found to have a twofold rotational axis which was incorporated into the crystallographic symmetry. In the present work there is no rotational axis in the crystallographic symmetry, and any suspected molecular symmetry must be found by other means. As seen in Figure 1 the molecule, except for the OH group, can be turned into itself by rotating 180° about C-8, in which case the midpoint of a line joining any atom with its equivalent on the other half of the molecule will by necessity lie on the molecular twofold rotational axis. Thus, a plot of the midpoints should define the twofold axis, which is not otherwise defined by the crystallographic symmetry. The average deviations of these points from a straight line in three dimensions was found to be only 0.028 Å. Therefore, except for the OH group, the molecule retains a twofold rotational axis of molecular symmetry to within experimental error.

The OH group is not attached to the bridge atom C-8 as was previously thought from chemical evidence, but is instead attached to C-7. As was expected, the two nitrogen atoms are quite close to each other (2.68 Å). This is enough to explain the difference in  $pK$  for the two groups, which, when both protonated, should be identical except for the presence of the distant OH group. Not only would there be electrostatic repulsion if both nitrogen atoms were charged, but also there would not be room for the second proton unless the molecule were to undergo a considerable opening up, perhaps one of the rings becoming a boat. Since this structure is of the monobasic salt there must be only one proton involved with the two nitrogen atoms, and it becomes a question of how this proton

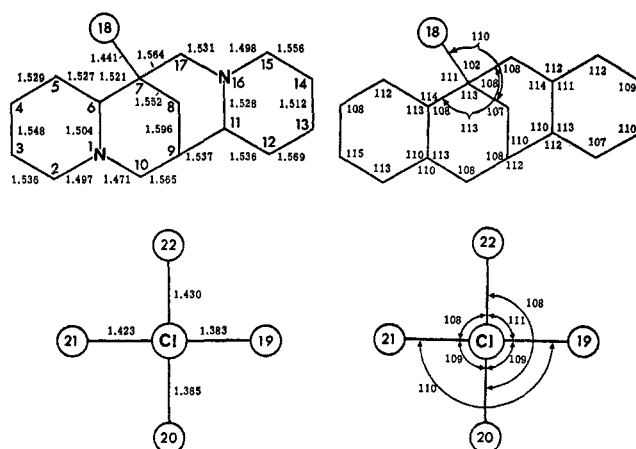


Figure 3.—Interatomic bond distances in angstrom units and bond angles in degrees.

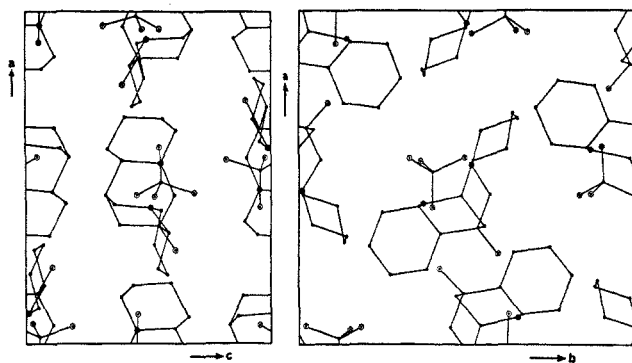


Figure 4.—Packing diagram for the full unit cell.

is situated. It could be on only one of the nitrogen atoms, it could be halfway between the two, or it could divide its time equally between the two positions. Fortunately, this hydrogen atom appears clearly in Figure 2, as marked by the arrow, and is situated in one position only, 1.04 Å from one nitrogen atom and 1.84 Å from the other. Thus, the hydrogen atom is covalently bonded to N-16 and probably hydrogen bonded to N-1 (making an N-H-N angle of 163°).

The only other hydrogen bond in the structure is that from the hydroxyl group of O-22 of the perchlorate group, which would have a hydrogen bond distance of 2.96 Å. The hydrogen atom in this hydrogen bond did not appear in Figure 2, probably owing to the vibration of the perchlorate group. Also, the hydrogen atoms do not appear clearly in the lower numbered end of the alkaloid molecule. This, too, is probably due to a slightly higher vibration in this part of the molecule, as well as some anisotropic vibration for which no correction has been made. Hydrogen positions have been assigned from Figure 2; the resulting carbon-hydrogen bond lengths are given in Table III. With two exceptions these are reasonable. The distances involving C-8 and C-15 are probably the result of our data, which cannot be expected to give highly accurate hydrogen positions.

The bonds around the two nitrogen atoms are significantly shorter than the C-C bonds, resulting in a slight bend in the middle of the molecule. This bend, which causes the bonds in the two ends of the molecule to be no longer parallel, can be seen in Figure 2.

(2) L. Marion and N. J. Leonard, *Can. J. Chem.*, **29**, 355 (1951).

(3) M. Przybylska and W. H. Barnes, *Acta Cryst.*, **6**, 377 (1953).

TABLE III  
BOND LENGTHS INVOLVING HYDROGEN ATOMS

Atoms	Bond length (Å)	Atoms	Bond length (Å)
N-1	None		
C-2-H-24	1.09	C-2-H-25	1.19
C-3-H-26	0.91	C-3-H-27	1.08
C-4-H-28	1.10	C-4-H-29	1.09
C-5-H-30	1.05	C-5-H-31	1.03
C-6-H-32	0.97		
C-7	None		
C-8-H-33	1.71	C-8-H-34	1.06
C-9-H-35	0.97		
C-10-H-36	1.20	C-10-H-37	0.78
C-11-H-38	1.25		
C-12-H-39	1.20	C-12-H-40	1.08
C-13-H-41	1.06	C-13-H-42	1.28
C-14-H-43	1.14	C-14-H-44	1.10
C-15-H-45	1.11	C-15-H-46	1.90
N-16-H-47	1.04		
C-17-H-48	0.98	C-17-H-49	1.11
O-18	Not located		
	Estd std dev -0.1 Å		

The perchlorate ion, whenever found in crystal structures, seems to have associated with it an unusual

amount of vibration and rotation. This can range from wide amplitudes of vibration<sup>4</sup> to disorder<sup>5</sup> to free rotation.<sup>6</sup> In the present structure the vibration is somewhat less, but present all the same. Correction for the rotational-vibrational effect<sup>7</sup> would lengthen the Cl-O bonds and result in better agreement with the accepted value<sup>8</sup> of  $1.45 \pm 0.01$  Å.

**Registry No.**—7-Hydroxy- $\beta$ -isosparteine perchlorate, 10257-17-7.

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(4) M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **88**, 198 (1966).

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(6) R. J. Prosen and K. N. Trueblood, *Acta Cryst.*, **9**, 741 (1956).

(7) D. W. J. Cruickshank, *ibid.*, **9**, 757 (1956); **14**, 896 (1961).

(8) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

## Leguminosae Alkaloids. V. Chemistry and Stereochemistry of Multiflorine<sup>1</sup>

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Lithium aluminum hydride reduction of the alkaloid, multiflorine, proceeds *via* the metal enolate of 4-oxosparteine stereospecifically to 4 $\alpha$ -hydroxysparteine. The same alcohol is the sole product of hydride reduction of 4-oxosparteine. The intermediacy of 4-oxosparteine was also demonstrated in the catalytic hydrogenation of multiflorine. It was shown that the saturated ketone is both the source of 4 $\alpha$ -hydroxysparteine and the source of the over reduction product, sparteine. Analysis of the ORD curve determined from 4-oxosparteine was found to be consistent with previous absolute configurational correlation work. The possibility that multiflorine actually possesses the  $\beta$ -isosparteine skeleton which undergoes isomerization to the more favorable sparteine arrangement during the reactions discussed was found to be inconsistent with the ORD curve determined from the plant alkaloid.

In 1955, Crow and Riggs<sup>3</sup> reported isolation of an alkaloid (C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O) from the seeds and tops of *Lupinus varius* L. (now *Lupinus digitatus* Forsk.<sup>4</sup>) which they called Base LV-1. Preliminary structural information was determined in 1957,<sup>5</sup> followed by a complete structure assignment in 1959.<sup>6</sup> In the meantime Comin and Deulofeu,<sup>7</sup> studying the Argentine plant, *Lupinus multiflorus* Lam., isolated an alkaloid (C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O) which they named multiflorine. The similarity of properties determined from multiflorine with those reported for Base LV-1 led to a direct comparison which established the identity of the two plant products.<sup>6-8</sup>

Examination of the spectral data determined from

multiflorine led<sup>6</sup> to the conclusion that a vinylogous amide (I) must be present in the alkaloid. This information combined with the fact that both hydride reduction<sup>6</sup> and catalytic hydrogenation<sup>6,7</sup> of an acid solution of multiflorine were reported to result in production of sparteine (II) was taken to mean that multiflorine possesses the sparteine skeleton, and that the vinylogous amide (I) may be accommodated within II in only two ways: III and IV. Structure III was favored<sup>6</sup> mainly because partial reduction of multiflorine gave rise to a saturated ketone that did not possess properties of an amide, while the properties of its oxime were clearly different from those exhibited by the oxime of 13-oxosparteine.

Recent phytochemical investigations of *Lupinus diffusus*<sup>9</sup> and of *L. westianus*<sup>10</sup> in this laboratory established the presence of multiflorine in these plants and provided a source of the alkaloid for further study.

In contradistinction to the report by Crow,<sup>6</sup> we have been unable to observe the formation of sparteine by treatment of multiflorine with lithium aluminum hydride. The only compound formed on complete reduc-

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(2) Taken in part from the doctoral dissertation submitted in April 1966 by R. F. M. to the Graduate School, University of South Carolina, in partial fulfillment of the requirements for the Ph.D. degree.

(3) W. D. Crow and N. V. Riggs, *Australian J. Chem.*, **8**, 136 (1955).

(4) J. S. Gladstones, *J. Roy. Soc. W. Australia*, **41**, 29 (1958).

(5) W. D. Crow and M. Michael, *Australian J. Chem.*, **10**, 177 (1957).

(6) W. D. Crow, *ibid.*, **12**, 474 (1959).

(7) J. Comin and V. Deulofeu, *ibid.*, **12**, 468 (1959).

(8) Despite its obvious priority, the designation Base LV-1, which is inconsistent with traditional nomenclature practice, is avoided here in favor of the name, multiflorine, which does reflect the customary practice of relating an alkaloid to an original natural source.

(9) S. I. Goldberg and R. F. Moates, *Phytochemistry*, **6**, 137 (1967).

(10) S. I. Goldberg and M. S. Sahli, *J. Med. Chem.*, **10**, 124 (1967).