

The Crystal Structure and Absolute Configuration of the Dihydrobromide of (+)-Haplophytine

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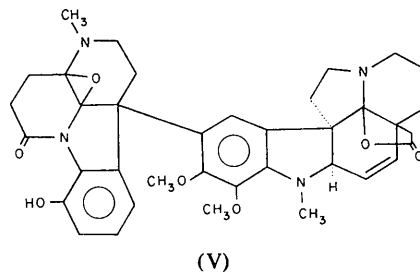
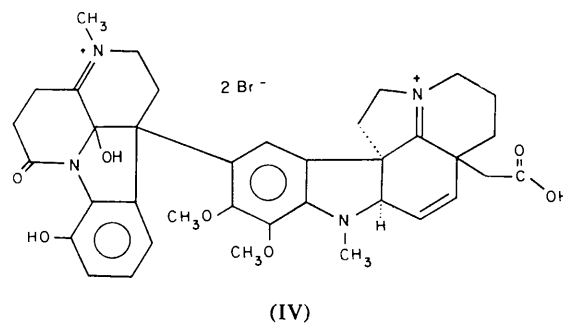
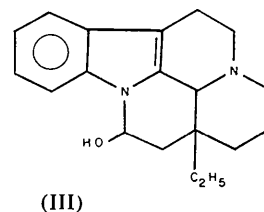
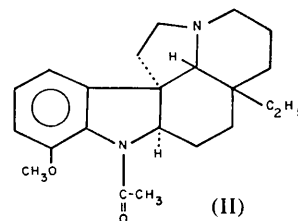
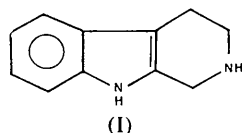
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The dihydroindole alkaloid, haplophytine, from the plant *Haplophytine cimicidum* (Apocynaceae) forms a dihydrobromide, $C_{37}H_{42}Br_2N_4O_7$, which is monoclinic, space group $C2$ with $a = 25.535$, $b = 7.490$ and $c = 18.861$ Å, $\beta = 101^\circ 19'$ with four molecules in the unit cell. Data were collected on a Picker four-circle automated diffractometer with Cu $K\alpha$ radiation. The structure was solved with the heavy-atom technique and refined anisotropically by a full-matrix least-squares procedure to a final R index of 0.071. The hydrogen atom positions were not determined. The molecular ion consists of two large residues, one having the skeleton and absolute configuration of (–)-aspidospermine and the other a tetracyclic tetrahydro- β -carboline skeleton closely resembling the alkaloid eburnamine.

Introduction

Haplophytine is the major alkaloid of the Mexican insecticidal 'Cucaracha' (cockroach) plant *Haplophyton cimicidum* A. DC. (Apocynaceae) and, together with the alkaloid cimicidine, it is responsible for the insect-killing property. When these two substances were isolated and partially characterized in the first reported chemical investigation, it was found that haplophytine possessed most of the insect-toxicity (Rogers, Snyder & Fischer, 1952; Snyder, Fischer, Walker, Els & Nussberger, 1954a, b; Snyder, Strohmayer & Mooney, 1958). More recent reports of chemical studies (Cava, Talapatra, Nomura, Weisbach, Douglas & Shoop, 1963; Cava, Talapatra, Yates, Rosenberger, Szabo, Douglas, Raffauf, Shoop & Weisbach, 1963) have described the isolation and characterization of seven minor alkaloids from this plant. Three of these, eburnamine (III), isoeburnamine, and *O*-methyleburnamine contain the tetrahydro- β -carboline skeleton (I) and the remaining four are of the aspido-spermine type (II). The occurrence of both eburnamine- and aspido-spermine-type alkaloids in this and in several other plant genera (*Hunteria*, *Vinca* (*Catharanthus*), *Pleiocarpa* and *Rhazia*) has led to the hypothesis that both arise from a common biogenetic precursor (Schnoes, Burlingame & Biemann, 1962). The chemistry of the *Haplophytine* alkaloids has been reviewed by Saxton (1965); that of the *Aspido-spermine* alkaloids by Gilbert (1965, 1968) and that of the eburnamine-type (*Hunteria*) by Taylor (1965). The absolute configuration of (–)-aspido-spermine-*N*(*b*)-methiodide has recently been determined by Craven & Zacharias (1968).



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Table 1. Atomic positional and thermal parameters and their estimated standard deviations

The temperature factor expression used is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.
 The estimated standard deviations in parentheses refer to the last decimal digits of the respective values.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	0.2286 (1)	0.0000 (0)	0.1546 (1)	0.0012 (0)	0.0182 (5)	0.0040 (1)	-0.0002 (1)	0.0000 (0)	0.0003 (2)
Br(2)	0.4452 (1)	0.5349 (5)	0.1161 (1)	0.0013 (0)	0.0216 (6)	0.0032 (1)	-0.0006 (1)	0.0006 (0)	0.0009 (2)
O(1)	0.3335 (4)	0.2725 (20)	0.3902 (5)	0.0005 (2)	0.0267 (33)	0.0015 (4)	0.0010 (8)	0.0001 (2)	0.0012 (11)
O(2)	0.2421 (5)	0.1463 (22)	0.4331 (7)	0.0014 (3)	0.0295 (37)	0.0023 (4)	0.0025 (9)	0.0008 (3)	0.0047 (13)
O(3)	0.1569 (6)	0.3537 (23)	0.0048 (7)	0.0024 (3)	0.0254 (43)	0.0030 (5)	-0.0021 (10)	0.0005 (4)	-0.0005 (13)
O(4)	0.0854 (6)	0.2281 (20)	0.0350 (7)	0.0021 (3)	0.0172 (34)	0.0031 (5)	-0.0016 (8)	0.0011 (3)	0.0002 (11)
O(5)	0.3330 (4)	0.1343 (18)	0.2614 (6)	0.0009 (2)	0.0168 (29)	0.0019 (4)	0.0006 (8)	0.0004 (2)	0.0009 (11)
O(6)	0.4948 (5)	0.1823 (26)	0.2770 (9)	0.0011 (3)	0.0307 (48)	0.0066 (8)	0.0032 (10)	0.0004 (4)	-0.0046 (16)
O(7)	0.5186 (5)	0.4398 (27)	0.3635 (9)	0.0008 (2)	0.0458 (64)	0.0066 (7)	0.0000 (10)	0.0000 (3)	-0.0078 (18)
N(1)	0.1386 (6)	0.3107 (26)	0.3633 (8)	0.0009 (3)	0.0254 (47)	0.0025 (6)	0.0025 (10)	0.0006 (3)	0.0050 (14)
N(2)	0.1079 (5)	0.7896 (21)	0.2017 (8)	0.0006 (2)	0.0104 (39)	0.0034 (6)	0.0006 (8)	0.0009 (3)	0.0014 (13)
N(3)	0.3165 (5)	0.3490 (23)	0.1092 (8)	0.0010 (3)	0.0214 (43)	0.0026 (6)	-0.0004 (10)	0.0005 (3)	0.0024 (13)
N(4)	0.4112 (5)	0.3033 (24)	0.2709 (7)	0.0003 (2)	0.0240 (40)	0.0016 (5)	-0.0010 (9)	0.0001 (3)	-0.0019 (13)
C(1)	0.0989 (6)	0.4217 (26)	0.3148 (10)	0.0007 (3)	0.0097 (38)	0.0033 (7)	0.0008 (8)	0.0006 (4)	0.0021 (15)
C(2)	0.1328 (6)	0.5694 (28)	0.2862 (10)	0.0002 (3)	0.0185 (51)	0.0031 (7)	0.0000 (10)	0.0002 (3)	-0.0007 (15)
C(3)	0.2306 (6)	0.5231 (30)	0.2670 (8)	0.0007 (3)	0.0132 (41)	0.0028 (6)	-0.0003 (12)	0.0001 (3)	-0.0014 (17)
C(4)	0.2804 (6)	0.4424 (26)	0.2946 (8)	0.0005 (3)	0.0174 (42)	0.0011 (5)	0.0005 (9)	0.0001 (3)	-0.0015 (13)
C(5)	0.2392 (6)	0.3266 (26)	0.3792 (8)	0.0008 (3)	0.0093 (37)	0.0032 (6)	0.0012 (9)	0.0006 (3)	0.0000 (17)
C(6)	0.1893 (6)	0.3502 (28)	0.3481 (9)	0.0009 (3)	0.0284 (59)	0.0008 (4)	0.0023 (12)	0.0001 (3)	0.0027 (15)
C(7)	0.1885 (6)	0.4767 (24)	0.2978 (8)	0.0006 (3)	0.0068 (38)	0.0025 (6)	0.0020 (11)	0.0004 (4)	0.0043 (16)
C(8)	0.2672 (8)	0.0251 (34)	0.4223 (12)	0.0018 (5)	0.0178 (60)	0.0051 (10)	0.0017 (16)	0.0008 (6)	-0.0007 (22)
C(9)	0.3509 (8)	0.3436 (34)	0.4603 (9)	0.0020 (4)	0.0291 (60)	0.0006 (4)	0.0001 (15)	0.0001 (4)	-0.0018 (18)
C(10)	0.1305 (9)	0.2495 (37)	0.4314 (11)	0.0022 (4)	0.0320 (65)	0.0030 (6)	0.0008 (8)	0.0005 (4)	0.0025 (21)
C(11)	0.0661 (7)	0.3131 (29)	0.2570 (10)	0.0011 (3)	0.0169 (49)	0.0030 (8)	0.0020 (12)	0.0005 (5)	0.0023 (17)
C(12)	0.0615 (6)	0.3428 (27)	0.1836 (11)	0.0003 (3)	0.0116 (41)	0.0047 (9)	0.0009 (2)	0.0010 (4)	0.0015 (16)
C(13)	0.0891 (6)	0.4922 (32)	0.2106 (9)	0.0007 (3)	0.0188 (48)	0.0019 (6)	-0.0018 (12)	0.0001 (3)	0.0005 (17)
C(14)	0.1098 (6)	0.6204 (25)	0.2106 (9)	0.0004 (3)	0.0125 (46)	0.0019 (6)	0.0005 (9)	0.0002 (3)	0.0009 (14)
C(15)	0.1287 (8)	0.8962 (30)	0.2696 (10)	0.0021 (5)	0.0171 (50)	0.0020 (7)	0.0007 (13)	0.0004 (4)	-0.0007 (16)
C(16)	0.0845 (8)	0.8823 (29)	0.1309 (10)	0.0022 (4)	0.0157 (50)	0.0020 (7)	0.0011 (12)	0.0001 (4)	0.0029 (16)
C(17)	0.0707 (8)	0.7617 (40)	0.0707 (10)	0.0015 (4)	0.0354 (68)	0.0022 (6)	0.0017 (16)	0.0002 (4)	0.0014 (21)
C(18)	0.0469 (7)	0.5938 (29)	0.0919 (11)	0.0010 (3)	0.0185 (48)	0.0042 (8)	-0.0009 (11)	0.0007 (4)	0.0037 (17)
C(19)	0.1388 (6)	0.4241 (26)	0.1195 (9)	0.0007 (3)	0.0149 (43)	0.0021 (6)	0.0017 (10)	0.0001 (3)	-0.0009 (14)
C(20)	0.1263 (7)	0.3358 (30)	0.0474 (9)	0.0017 (4)	0.0182 (51)	0.0015 (5)	0.0009 (13)	0.0009 (4)	-0.0001 (16)
C(21)	0.1360 (8)	0.7544 (31)	0.3302 (9)	0.0014 (3)	0.0198 (53)	0.0013 (6)	0.0007 (13)	0.0001 (4)	0.0002 (16)
C(22)	0.3181 (7)	0.5978 (30)	0.1955 (8)	0.0015 (3)	0.0288 (59)	0.0006 (5)	0.0002 (12)	0.0000 (3)	-0.0002 (16)
C(23)	0.2874 (6)	0.5068 (36)	0.1278 (8)	0.0010 (3)	0.0223 (48)	0.0020 (6)	0.0020 (14)	0.0000 (3)	0.0017 (14)
C(24)	0.3301 (6)	0.4803 (29)	0.2603 (9)	0.0010 (3)	0.0160 (47)	0.0027 (6)	0.0004 (11)	0.0010 (3)	0.0039 (18)
C(25)	0.3498 (6)	0.2612 (25)	0.1570 (8)	0.0010 (4)	0.0123 (39)	0.0016 (5)	-0.0018 (10)	0.0000 (5)	0.0016 (13)
C(26)	0.4213 (6)	0.0393 (25)	0.2014 (9)	0.0013 (3)	0.0079 (38)	0.0031 (6)	0.0026 (11)	0.0002 (4)	-0.0002 (20)
C(27)	0.3537 (7)	0.2945 (27)	0.2395 (9)	0.0011 (3)	0.0120 (37)	0.0015 (6)	0.0001 (11)	-0.0004 (4)	0.0007 (15)
C(28)	0.3813 (7)	0.1045 (26)	0.1380 (10)	0.0013 (3)	0.0129 (49)	0.0028 (6)	0.0008 (12)	0.0008 (4)	-0.0010 (15)
C(29)	0.3745 (7)	0.7082 (33)	0.3517 (11)	0.0012 (4)	0.0235 (48)	0.0033 (8)	-0.0023 (14)	-0.0002 (5)	0.0052 (21)
C(30)	0.3029 (7)	0.2967 (36)	0.0331 (9)	0.0017 (4)	0.0370 (69)	0.0008 (5)	0.0021 (14)	0.0003 (3)	-0.0009 (19)
C(31)	0.4449 (8)	0.1756 (31)	0.2524 (11)	0.0014 (3)	0.0203 (53)	0.0027 (7)	0.0023 (13)	0.0010 (4)	0.0002 (16)
C(32)	0.4235 (9)	0.7756 (41)	0.3947 (11)	0.0020 (5)	0.0350 (67)	0.0025 (8)	-0.0011 (19)	0.0011 (5)	-0.0034 (32)
C(33)	0.3764 (6)	0.5510 (26)	0.3144 (9)	0.0012 (4)	0.0126 (48)	0.0026 (7)	-0.0006 (12)	0.0011 (4)	0.0030 (16)
C(34)	0.4704 (6)	0.5300 (37)	0.3595 (9)	0.0005 (3)	0.0272 (65)	0.0023 (6)	0.0003 (4)	-0.0002 (4)	-0.0015 (23)
C(35)	0.4326 (6)	0.4591 (27)	0.3162 (8)	0.0008 (3)	0.0186 (53)	0.0010 (5)	0.0014 (12)	0.0003 (3)	-0.0017 (15)
C(36)	0.4684 (8)	0.6820 (31)	0.3963 (11)	0.0014 (5)	0.0206 (46)	0.0031 (9)	-0.0019 (14)	0.0002 (5)	-0.0047 (19)

dimensional Patterson function. The space group origin was fixed by arbitrarily setting the y coordinate of one bromine atom equal to zero. Using the phases of only the two heavy atoms, all of the light atoms excepting hydrogen were located after three cycles of structure factor calculations and three-dimensional electron density syntheses.

The structure was refined by a full-matrix least-squares procedure using isotropic temperature factors until convergence at $R=0.103$. The atomic scattering factors and the dispersion corrections for the bromine atoms ($\Delta f' = -0.95$, $\Delta f'' = 1.6$ for Cu $K\alpha$ radiation) were those in *International Tables for X-ray Crystallography*, (1962). The estimated standard deviation in an observed structure amplitude $|F|$ was taken as $\sigma(F) = |F_{\min}| + 0.07|F|$, where $|F_{\min}|$ is the average value for the structure amplitude assigned to the unobservable reflections. The structure factors were then calculated reversing the sign of the imaginary contribution $\Delta f''$, for the bromine atoms. The resulting $R=0.108$ gave an initial indication that the assumed absolute configuration was correct. Three further refinement cycles of all positional parameters and anisotropic temperature factors for bromine converged with $R=0.084$. The correctness of the assumed absolute configuration was again tested by a structure factor calculation using these refined positional parameters with the sign of the y coordinate reversed for all atoms. The higher disagreement index of 0.094 again supported the assumed model. Finally, all atoms were refined anisotropically until the shift-to-error ratio was less than 0.1 for all parameters refined. Owing to the limitation of computer memory, it was necessary to refine the atoms of the molecule in four groups, as follows:

Atomic groups for full-matrix anisotropic refinement:

- (1) O: 5, 6, 7; N: 3, 4; C: 3, 4, 5, 23 through 32, 34, 36.
- (2) Br: 1, 2; O: 1, 2; N: 4;
C: 3, 4, 6 through 10, 25, 28, 30, 33 through 37.
- (3) N: 1, 2; C: 1 through 8, 11 through 16, 20, 22, 25.
- (4) O: 3, 4; N: 1, 2; C: 1, 2, 12 through 22.

The final disagreement factors are as follows:

	Unweighted R	Weighted R
All data	0.086	0.096
Omitting unobserved reflections	0.071	0.083

where

$$R = \frac{\sum |\Delta|}{\sum |F_o|} \quad \text{Weighted } R = \frac{\sqrt{\sum (W\Delta^2)}}{\sqrt{\sum (W|F_o|^2)}}$$

$$W = [1/\sigma(F)]^2 \quad \Delta = |F_o| - |F_c|$$

The final atomic parameters with e.s.d.'s are given in Table 1. The corresponding observed and calculated structure factors are listed in Table 2. The comparison of the observed and calculated values using these positional parameters referred to a right-handed crystal axial system for the intensities $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ is made in Table 3. The hydrogen atom positions were not determined.

Table 3. Determination of absolute configuration

h	k	l	$(I_{hkl} - I_{\bar{h}\bar{k}\bar{l}})/(I_{hkl} + I_{\bar{h}\bar{k}\bar{l}})$	Calc.*	Obs.
1	1	13	+0.02	+0.04	
1	1	-13	+0.06	+0.21	
5	1	7	+0.04	+0.02	
5	1	-7	+0.06	+0.04	
5	1	14	-0.20	-0.18	
5	1	-14	+0.05	-0.01	
9	1	6	-0.05	-0.05	
9	1	-6	-0.15	-0.11	
13	1	6	+0.05	+0.03	
13	1	-6	-0.02	0.00	

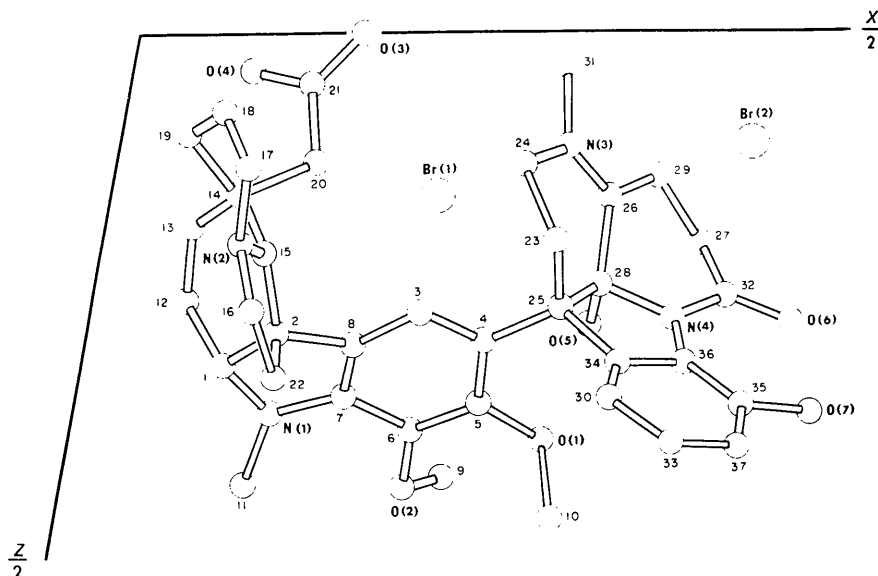


Fig. 1. The absolute configuration of haplophytine dihydrobromide. The positive sense of y is towards the viewer.

Table 3 (cont.)

9	1	-11	+0.12	+0.11
6	2	15	-0.20	-0.30
6	2	-15	+0.08	0.00

* These values are calculated with the atomic parameters listed in Table 1, referred to a right-handed crystal axial system.

Description and discussion of the structure

The absolute atomic configuration of the molecular ion is shown in Fig. 1. It consists of two structural units: part *A*, on the left, has the framework and absolute configuration of (-)-aspidospermine as confirmed by Craven & Zacharias (1968); part *B*, on the right, possesses the β -carboline skeleton and resembles eburnamine. The bond lengths are shown in Fig. 2(a) and (b) and are listed in Table 4. The bond angles are given in Table 5. Conformation data are presented in Table 6. In part *A*, the carboxyl group and C(20) to which it is attached are nearly coplanar. O(2) lies in the same plane as that formed by the benzene ring but the other atoms attached to the ring, C(2), C(25), O(1) and N(1) are considerably out of the plane. Both the six-membered rings, C(1), C(2), C(15), C(14), C(13), C(12) and N(2), C(15), C(14), C(19), C(18), C(17) have the boat conformation but are distorted owing to the rigidity imposed by the quaternary N(2) atom and adjacent double bond to C(15). The planarity of the least-squares plane through N(2), C(15) and their associated atoms C(2), C(14), C(16) and C(17) is comparable with that of the benzene ring.

Table 4. Intramolecular bond lengths and distances and their estimated standard deviations

The e.s.d.'s are in parentheses and refer to the last decimal digits of the respective values.

Bond	Length	Bond	Length
O(1)-C(10)	1.41 (2) Å	C(4)-C(5)	1.42 (2) Å
O(1)-C(5)	1.39 (2)	C(4)-C(25)	1.56 (2)
O(2)-C(9)	1.47 (3)	C(5)-C(6)	1.35 (2)
O(2)-C(6)	1.39 (2)	C(6)-C(7)	1.42 (2)
O(3)-C(21)	1.23 (2)	C(7)-C(8)	1.34 (2)
O(4)-C(21)	1.30 (2)	C(12)-C(13)	1.38 (2)
O(5)-C(28)	1.41 (2)	C(13)-C(14)	1.51 (2)
O(6)-C(32)	1.27 (3)	C(14)-C(15)	1.48 (3)
O(7)-C(35)	1.39 (3)	C(14)-C(19)	1.60 (2)
N(1)-C(1)	1.48 (2)	C(14)-C(20)	1.60 (3)
N(1)-C(7)	1.41 (2)	C(16)-C(22)	1.54 (3)
N(1)-C(11)	1.42 (2)	C(17)-C(18)	1.44 (3)
N(2)-C(15)	1.28 (2)	C(18)-C(19)	1.48 (2)
N(2)-C(16)	1.51 (2)	C(20)-C(21)	1.49 (3)
N(2)-C(17)	1.52 (3)	C(23)-C(24)	1.52 (3)
N(3)-C(24)	1.48 (2)	C(23)-C(25)	1.49 (2)
N(3)-C(26)	1.29 (2)	C(25)-C(28)	1.60 (2)
N(3)-C(31)	1.46 (3)	C(25)-C(34)	1.50 (3)
N(4)-C(28)	1.47 (2)	C(26)-C(28)	1.56 (2)
N(4)-C(32)	1.38 (2)	C(26)-C(29)	1.51 (3)
N(4)-C(36)	1.44 (2)	C(27)-C(29)	1.49 (3)
C(1)-C(2)	1.56 (2)	C(27)-C(32)	1.45 (3)
C(1)-C(12)	1.48 (2)	C(30)-C(33)	1.44 (2)
C(2)-C(8)	1.56 (2)	C(30)-C(34)	1.38 (2)
C(2)-C(15)	1.48 (2)	C(33)-C(37)	1.34 (2)
C(2)-C(22)	1.61 (2)	C(34)-C(36)	1.38 (2)
C(3)-C(4)	1.41 (2)	C(35)-C(36)	1.41 (2)
C(3)-C(8)	1.36 (2)	C(35)-C(37)	1.34 (3)

Table 4 (cont.)

Distances less than the sum of the van der Waals radii			
	Distance		Distance
O(1)-O(5)	2.64 (2) Å	Br(1)-O(5)	3.17 (1) Å
O(6)-O(7)	2.52 (2)	Br(2)-C(26)	3.39 (2)
Close approaches less than 4 Å			
	Distance		Distance
Br(1)-C(26)	3.65 (2) Å	Br(2)-N(3)	3.55 (2) Å
-N(3)	3.66 (2)	-N(4)	3.64 (2)
-C(20)	3.90 (2)	-C(29)	3.67 (2)
-C(21)	3.90 (2)	-C(32)	3.72 (2)
-C(31)	3.94 (2)	-C(23)	3.86 (2)
-C(28)	3.95 (2)	-C(36)	3.96 (2)

Bond lengths averaged according to bond type
Trigonally and tetrahedrally bonded atoms are denoted by 'trig' and 'tetr' respectively.

Type	No. of bonds	Average bond length	R.m.s. deviation
C(tetr)-C(tetr)	11	1.54 Å	0.017 Å
C(tetr)-C(trig)	11	1.51	0.011

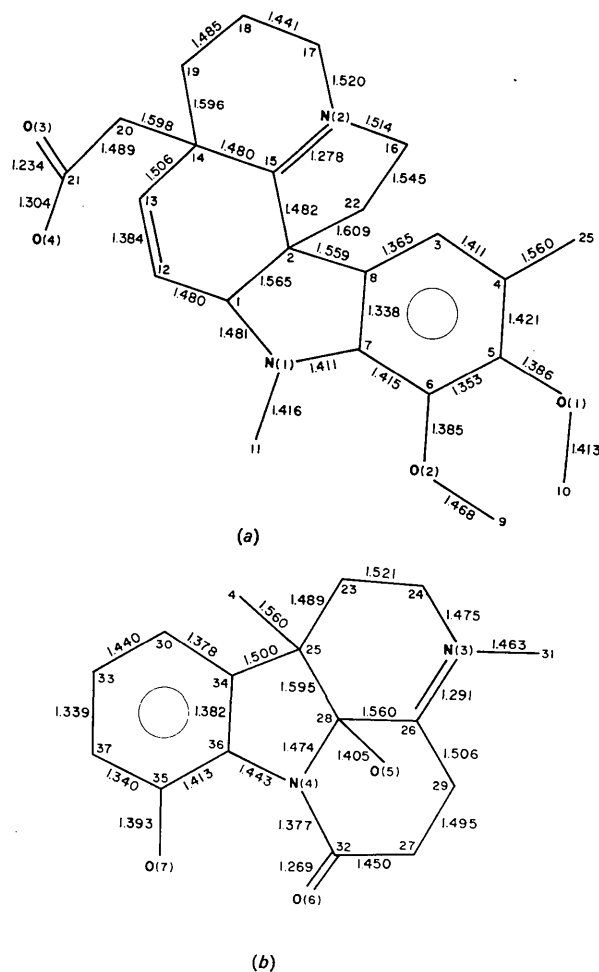


Fig. 2. Intramolecular distances in haplophytine dihydrobromide.

Table 4 (*cont.*)

C(tetr)-N(tetr)	3	1.46	0.030
C(tetr)-N(trig)	4	1.49	0.028
C(trig)-C(trig)	13	1.38	0.010
C(trig)-N(tetr)	3	1.41	0.027
C(trig)-N(trig)	2	1.29	0.003

In the *B* part of the molecular ion, the benzene ring is more nearly planar and the adjacent atoms N(4) and O(7) lie within this plane (*cf.* planes 4 and 5 in Table 6). Both the aliphatic six-membered rings also have the boat conformation, again somewhat distorted by the double bond between N(3) and C(26). The junctions

Table 5. *Molecular bond angles and their estimated standard deviations*

The e.s.d.'s are in parentheses and refer to the corresponding decimal digits of the respective values.

	Angle		Angle
C(5)—O(1)—C(10)	115.5 (1.4) ^o	C(2)—C(8)—C(3)	126.9 (1.5) ^o
C(6)—O(2)—C(9)	117.4 (1.5)	C(2)—C(8)—C(7)	107.6 (1.5)
C(1)—N(1)—C(7)	107.6 (1.5)	C(3)—C(8)—C(7)	125.3 (1.6)
C(1)—N(1)—C(11)	122.5 (1.7)	C(1)—C(12)—C(13)	124.9 (1.7)
C(7)—N(1)—C(11)	123.6 (1.7)	C(12)—C(13)—C(14)	124.0 (1.7)
C(15)—N(2)—C(16)	114.4 (1.5)	C(13)—C(14)—C(15)	108.3 (1.5)
C(15)—N(2)—C(17)	124.5 (1.5)	C(13)—C(14)—C(19)	109.4 (1.5)
C(16)—N(2)—C(17)	120.9 (1.5)	C(13)—C(14)—C(20)	112.6 (1.5)
C(24)—N(3)—C(26)	122.4 (1.5)	C(15)—C(14)—C(19)	108.3 (1.5)
C(24)—N(3)—C(31)	114.4 (1.5)	C(15)—C(14)—C(20)	107.4 (1.4)
C(26)—N(3)—C(31)	123.1 (1.5)	C(19)—C(14)—C(20)	110.7 (1.4)
C(28)—N(4)—C(32)	119.3 (1.5)	N(2)—C(15)—C(2)	112.3 (1.5)
C(28)—N(4)—C(36)	111.1 (1.4)	N(2)—C(15)—C(14)	123.1 (1.6)
C(32)—N(4)—C(36)	129.5 (1.6)	C(2)—C(15)—C(14)	124.5 (1.5)
C(2)—C(1)—N(1)	104.5 (1.4)	N(2)—C(16)—C(22)	103.4 (1.5)
C(12)—C(1)—N(1)	111.5 (1.5)	N(2)—C(17)—C(18)	113.5 (1.7)
C(2)—C(1)—C(12)	114.0 (1.5)	C(17)—C(18)—C(19)	111.6 (1.9)
C(1)—C(2)—C(8)	100.8 (1.4)	C(14)—C(19)—C(18)	110.0 (1.7)
C(1)—C(2)—C(15)	111.8 (1.5)	C(14)—C(20)—C(21)	116.7 (1.5)
C(1)—C(2)—C(22)	114.0 (1.5)	O(3)—C(21)—O(4)	122.5 (1.8)
C(8)—C(2)—C(15)	115.3 (1.5)	O(3)—C(21)—C(20)	119.7 (1.7)
C(8)—C(2)—C(22)	111.1 (1.4)	O(4)—C(21)—C(20)	117.4 (1.6)
C(15)—C(2)—C(22)	104.2 (1.5)	C(2)—C(22)—C(16)	102.9 (1.5)
C(4)—C(3)—C(8)	117.5 (1.6)	C(24)—C(23)—C(25)	114.4 (1.5)
C(3)—C(4)—C(5)	117.1 (1.5)	N(3)—C(24)—C(23)	110.9 (1.5)
C(3)—C(4)—C(25)	121.0 (1.5)	C(4)—C(25)—C(23)	113.3 (1.5)
C(5)—C(4)—C(25)	121.8 (1.5)	C(4)—C(25)—C(28)	108.6 (1.4)
O(1)—C(5)—C(4)	117.3 (1.5)	C(4)—C(25)—C(34)	112.3 (1.4)
C(4)—C(5)—C(6)	120.2 (1.5)	C(23)—C(25)—C(28)	109.9 (1.5)
O(1)—C(5)—C(4)	122.4 (1.6)	C(23)—C(25)—C(34)	111.0 (1.5)
O(2)—C(6)—C(5)	121.5 (1.6)	C(28)—C(25)—C(34)	100.9 (1.4)
O(2)—C(6)—C(7)	119.8 (1.6)	N(3)—C(26)—C(28)	121.3 (1.5)
C(5)—C(6)—C(7)	118.7 (1.6)	N(3)—C(26)—C(29)	122.6 (1.5)
N(1)—C(7)—C(6)	128.2 (1.6)	C(28)—C(26)—C(29)	115.5 (1.4)
N(1)—C(7)—C(8)	113.9 (1.6)	C(29)—C(27)—C(32)	115.5 (1.6)
C(6)—C(7)—C(8)	118.0 (1.6)	O(5)—C(28)—N(4)	108.8 (1.4)
O(5)—C(28)—C(25)	119.4 (1.4)	C(25)—C(34)—C(30)	123.2 (1.6)
O(5)—C(28)—C(26)	101.7 (1.3)	C(25)—C(34)—C(36)	114.1 (1.5)
N(4)—C(28)—C(25)	104.9 (1.4)	C(30)—C(34)—C(36)	122.1 (1.7)
N(4)—C(28)—C(26)	105.7 (1.4)	O(7)—C(35)—C(36)	119.1 (1.7)
C(25)—C(28)—C(26)	115.5 (1.4)	O(7)—C(35)—C(37)	120.5 (1.9)
C(26)—C(29)—C(27)	112.1 (1.5)	C(36)—C(35)—C(37)	120.3 (1.8)
C(33)—C(30)—C(34)	118.2 (1.9)	N(4)—C(36)—C(34)	107.4 (1.4)
O(6)—C(32)—N(4)	120.8 (1.9)	N(4)—C(36)—C(35)	135.2 (1.6)
O(6)—C(32)—C(27)	121.8 (1.9)	C(34)—C(36)—C(35)	117.5 (1.6)
N(4)—C(32)—C(27)	117.3 (1.7)	C(33)—C(37)—C(35)	123.5 (2.1)
C(30)—C(33)—C(37)	118.3 (2.2)		

Table 6. *Conformation data*

(a) Equations of the best least-squares planes

The equations of these planes are in the form $Ax + By + Cz = D$ and are referred to the crystallographic axes with x, y, z in Å. Planes 1–3 are in part *A* of the molecule, 4 and 5 in part *B* and 6–9 are those used to calculate the conformation of the atoms about the C(4)–C(25) bond.

- 1 Atoms of the benzene ring (*A* part)
- 2 Atoms of the carboxyl group and C(20)
- 3 Atoms N(2), C(2), C(14), C(16), C(15), C(17)
- 4 Atoms of the benzene ring (*B* part)
- 5 Atoms of the benzene ring (*B* part), O(7) and N(4)

Table 6 (cont.)

Plane	A	B	C	D
1	0.05834	0.74034	0.64524	6.49951
2	-0.49093	0.77544	-0.29305	0.07274
3	0.97185	-0.01598	-0.42118	0.95860
4	0.33300	0.52156	-0.78542	0.40942
5	0.33473	0.52201	-0.83494	0.43100
6	0.12933	0.77405	0.58236	6.72694
7	0.10227	0.80471	0.55337	6.47363
8	0.42136	-0.04447	0.80552	7.34597
9	-0.28686	0.93420	-0.15170	0.19845

(b) Distances of atoms from the planes

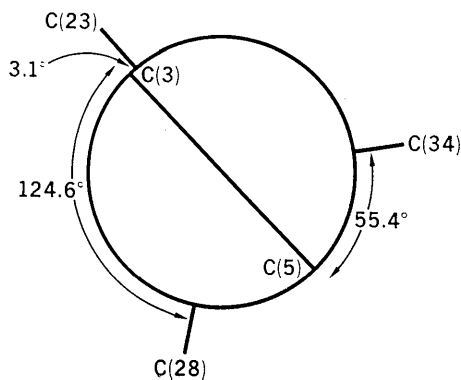
For each plane, column (i) lists the distances in Å from the plane of atoms forming the plane and column (ii) lists the distances in Å above or below (-) the plane for atoms not forming the plane. With reference to Fig. 1, the positive side of each plane (above) is that side which is furthest from the coordinate origin (*i.e.* closest to the viewer).

(i)		(ii)		(i)		(ii)	
Plane 1				Plane 4			
C(3)	-0.006	O(1)	0.257	C(30)	0.002	O(6)	0.148
C(4)	-0.043	O(2)	-0.056	C(33)	0.005	O(7)	-0.006
C(5)	0.053	N(1)	-0.150	C(34)	-0.007	N(4)	0.005
C(6)	-0.013	C(2)	0.339	C(35)	-0.001	C(25)	0.174
C(7)	-0.039	C(25)	-0.177	C(36)	0.007	C(28)	0.024
C(8)	0.049			C(37)	-0.005	C(32)	0.086
Plane 2				Plane 5			
O(3)	-0.012			O(7)	-0.003	O(6)	0.149
O(4)	-0.011			N(4)	0.003	C(25)	0.169
C(20)	-0.010			C(30)	0.000	C(28)	-0.029
C(21)	0.033			C(33)	0.006	C(32)	0.084
				C(34)	-0.010		
Plane 3							
N(2)	0.023	C(18)	0.143	C(35)	0.000		
C(2)	-0.005	C(22)	-0.298	C(36)	0.006		
C(14)	-0.014			C(37)	-0.002		
C(15)	0.019						
C(16)	-0.015						
C(17)	-0.008						

(c) Dihedral angles between planes

Planes	Angle
1, 4	97.0°
3, 2	65.6
3, 1	82.3

(d) Conformation of atoms about the C(4)-C(25) bond



between all the aliphatic rings in the structure are *cis*. The dihedral angle between the planes of the benzene rings of parts *A* and *B* is 97° . There is a short distance of 2.52 \AA between the phenolic O(7) atom and the carbonyl O(6) atom of the cyclic amide which is presump-

tive evidence of an intramolecular hydrogen bond. A second intramolecular hydrogen bond is indicated by the distance 2.64 \AA between the tertiary alcoholic O(5) atom in part *B* and the methoxyl O(1) atom in part *A*.

Table 7. $\frac{1}{2}$ Intermolecular distances less than 4 \AA

Space group: *C*2

General equivalent positions: (*A*) x, y, z ; (*B*) $-x, y, -z$; (*D*) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (*E*) $\frac{1}{2}+x, \frac{1}{2}+y, z$

In this Table, the numerical subscripts of the symmetry type designator indicate the relationship of the atom not in the unit cell to the indicated atom of the reference molecule in the unit cell and refer, respectively, to the x, y and z coordinates.

The reference molecule is designated (*A*)₅₅₅ and its atoms are listed first in each pair. To derive the coordinates of an atom designated (*D*)₅₄₆, the symmetry operation (*D*) is first applied to the coordinates of the corresponding reference atom listed in Table 1. The resulting x, y, z are then added to the whole number difference between the subscript of the transformed atom and the reference atom; in this case $(5-5)+x, (4-5)+y, (6-5)+z$ or $x, -1+y, 1+z$. 'v' denotes distance less than the sum of the van der Waals radii of the two atoms.

	Distance		Distance		Distance
Br(2)—O(4) (<i>D</i>)	3.15, <i>v</i> Å	O(5)—C(30) (<i>A</i>) ₅₄₅	3.67 Å	C(7)—C(16) (<i>A</i>) ₅₄₅	3.91 Å
Br(1)—N(2) (<i>A</i>) ₅₄₅	3.72	O(6)—N(2) (<i>E</i>) ₅₄₅	3.55	C(9)—C(11) (<i>D</i>) ₅₄₆	3.80
—C(16) (<i>A</i>) ₅₄₅	3.74	—C(2) (<i>E</i>) ₅₄₅	3.26	—C(22) (<i>A</i>) ₅₄₅	3.83
—C(17) (<i>A</i>) ₅₄₅	3.72	—C(3) (<i>E</i>) ₅₄₅	3.59	—C(30) (<i>A</i>) ₅₄₅	3.83
—C(23) (<i>A</i>) ₅₄₅	3.77	—C(12) (<i>E</i>) ₅₄₅	3.37	C(10)—C(11) (<i>D</i>) ₅₅₆	3.64
—C(31) (<i>D</i>) ₅₃₅	3.79	—C(13) (<i>E</i>) ₅₄₅	3.69	—C(22) (<i>D</i>) ₅₄₆	3.96
Br(2)—O(3) (<i>D</i>)	3.92	—C(14) (<i>E</i>) ₅₄₅	3.44	C(11)—C(33) (<i>D</i>) ₅₄₆	3.81
—C(13) (<i>E</i>)	3.78	—C(16) (<i>E</i>) ₅₄₅	3.80	C(12)—C(16) (<i>A</i>) ₅₄₅	3.49
—C(17) (<i>E</i>) ₅₄₅	3.69	—C(22) (<i>E</i>) ₅₄₅	3.59	C(13)—C(16) (<i>A</i>) ₅₄₅	3.96
—C(21) (<i>D</i>)	3.96	O(7)—C(11) (<i>E</i>)	3.71	—C(17) (<i>A</i>) ₅₄₅	3.67
O(2)—C(9) (<i>D</i>) ₅₅₆	3.72	—C(12) (<i>E</i>)	3.78	—C(27) (<i>E</i>) ₄₅₅	3.94
O(3)—C(29) (<i>D</i>)	3.27	—C(16) (<i>E</i>) ₅₄₅	3.62	C(17)—C(21) (<i>A</i>) ₅₆₅	3.98
—C(31) (<i>D</i>)	3.59	—C(22) (<i>E</i>) ₅₄₅	3.47	C(19)—C(19) (<i>B</i>)	3.81
O(4)—C(17) (<i>A</i>) ₅₄₅	3.16	N(1)—C(16) (<i>A</i>) ₅₄₅	3.56	C(37)—C(37) (<i>B</i>) ₆₅₆	3.93
—C(18) (<i>A</i>) ₅₄₅	3.59				

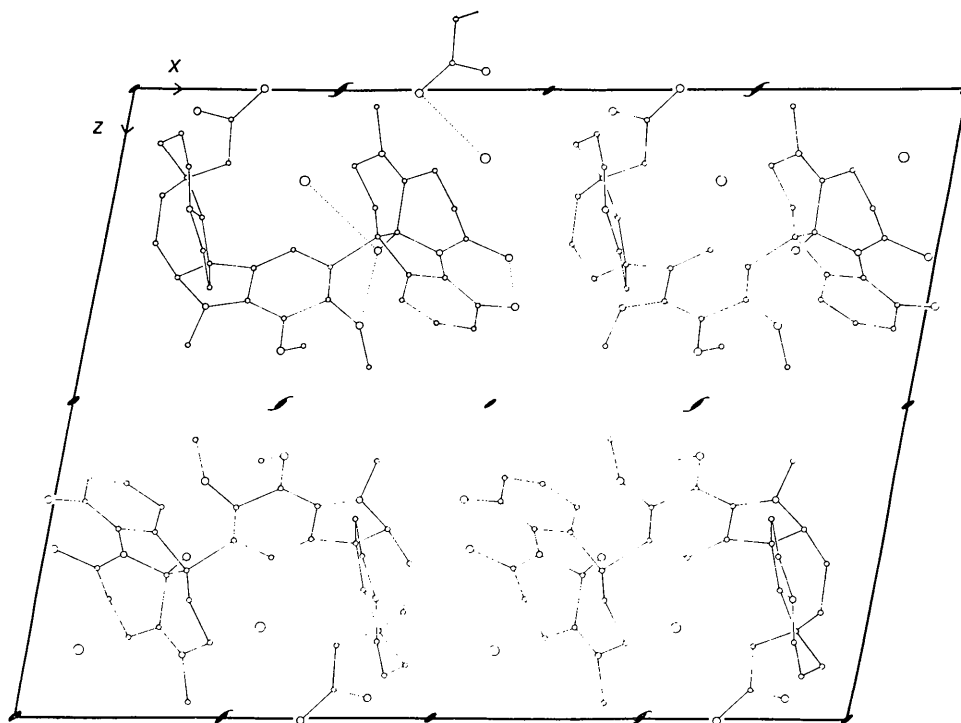


Fig. 3. Molecular packing in haplophytine dihydrobromide.

While parts *A* and *B* consist mainly of rigid fused-ring systems, different conformers of comparable energy are possible by rotation about the linking bond C(4)–C(25). The conformation about this bond observed in the crystal structure is shown in the Newman diagram in Table 6. This is most likely determined by the intramolecular hydrogen bond O(1)···H–O(5), the interactions Br(1)···O(5), 3.17 Å, and Br(2)···O(4), 3.15 Å, both of which may be hydrogen bonds, and the close approach Br(2)···C(26), 3.39 Å. These Br–O distances and the intramolecular hydrogen bonds are shown in Fig. 3 which is a diagram of the molecular packing in the unit cell. There are no other bromine distances shorter than 3.55 Å, but each bromide ion is within 4.75 Å of 29 C, N and O atoms from three different molecular cations. The intermolecular distances less than 4 Å are listed in Table 7.

It is notable that the bromide ions occupy positions which indicate participation in hydrogen bonding in preference to positions which would imply pure ionic interactions with the formally positively-charged quaternary N(2) and N(3) atoms; the shortest Br–N distance is 3.55 Å. The short Br(2)–C(26) distance may be indicative of some localization of positive charge on the carbon atom adjacent to the quaternary nitrogen atom rather than at the nitrogen atom itself.

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References

- CAVA, M. P., TALAPATRA, S. K., NOMURA, K., WEISBACH, J. A., DOUGLAS, B. & SHOOP, E. C. (1963). *Chem. & Ind.* p. 1242.
- CAVA, M. P., TALAPATRA, S. K., YATES, P., ROSENBERGER, M., SZABO, A. G., DOUGLAS, B., RAFFAUF, R. F., SHOOP, E. C. & WEISBACH, J. A. (1963). *Chem. & Ind.* p. 1875.
- CRAVEN, B. M. & ZACHARIAS, D. E. (1968). *Experientia*, **24**, 770.
- GILBERT, B. (1965). In *The Alkaloids*, Vol. 8, Ch. 14. Edited by R. H. F. MANSKE. New York: Academic Press.
- GILBERT, B. (1968). In *The Alkaloids*. Vol. 11, Ch. 9. Edited by R. H. F. MANSKE. New York: Academic Press.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- RAE, I. D., ROSENBERGER, M., SZABO, A. G., WILLIS, C. R., YATES, P., ZACHARIAS, D. E., JEFFREY, G. A., DOUGLAS, B., KIRKPATRICK, J. L. & WEISBACH, J. A. (1967). *J. Amer. Chem. Soc.* **89**, 3061.
- ROGERS, E. F., SNYDER, H. R. & FISCHER, R. F. (1952). *J. Amer. Chem. Soc.* **74**, 1987.
- SAXTON, J. E. (1965). In *The Alkaloids*, Vol. 8, Ch. 18. Edited by R. H. F. MANSKE. New York: Academic Press.
- SCHNOES, H. K., BURLINGAME, A. L. & BIEMANN, K. (1962). *Tetrahedron Letters*, p. 993.
- SNYDER, H. R., FISCHER, R. F., WALKER, J. F., ELS, H. E. & NUSSBERGER, G. A. (1954a). *J. Amer. Chem. Soc.* **76** 2819.
- SNYDER, H. R., FISCHER, R. F., WALKER, J. F., ELS, H. E. & NUSSBERGER, G. A. (1954b). *J. Amer. Chem. Soc.* **76**, 4601.
- SNYDER, H. R., STROMAYER, H. F. & MOONEY, R. A. (1958). *J. Amer. Chem. Soc.* **80**, 3708.
- TAYLOR, W. I. (1965). In *The Alkaloids*, Vol. 8, Ch. 11. Edited by R. H. F. MANSKE. New York: Academic Press.

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Structures of Ferrimagnetic Fluorides of ABF_3 Type.

I. $RbNiF_3$

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The crystal structure of $RbNiF_3$ has been determined from a least-squares refinement of three-dimensional X-ray data. Intensity data were acquired with the CCXD, a computer controlled X-ray diffractometer, operating in a time shared environment on an IBM 1800 Controller System. The space group is $P6_3/mmc$. The lattice constants of the unit cell, which contains six formula units of $RbNiF_3$, are $a = 5.840 \pm 0.002$ and $c = 14.308 \pm 0.004$ Å. All of the ions in this structure occupy special positions. The nickel ions occupy two non-equivalent sites, each the center of a fluorine octahedron. Two-thirds of the NiF_6 octahedra occur in face-sharing pairs to form Ni_2F_9 polyhedra. The remaining NiF_6 octahedra are linked to the Ni_2F_9 polyhedra by sharing of corners. The average Ni–F distance is 2.028 ± 0.008 Å.

Introduction

A great deal of attention has been directed to studies of the interesting magnetic and optical properties of ABF_3 -type ferrimagnetic fluorides with the hexagonal

$BaTiO_3$ structure. $RbNiF_3$, an unusually transparent material, has been one of the most extensively studied compounds of this group, at these Laboratories and elsewhere. Rudorff, Kandler & Babel (1962) first synthesized the compound, reported it as a probable ferri-