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The crystal structure and the absolute configuration of schelhammerine hydrobromide

By **C. Kowala** and **J. A. Wunderlich**

Division of Applied Chemistry, C.S.I.R.O., Chemical Research Laboratories, Melbourne*

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Auszug

Die Struktur von Schelhammerin, einem Alkaloid, isoliert aus *Schelhammera pedunculata* F. Muell., wurde als deren Hydrobromidsalz mittels röntgenographischer Analyse bestimmt. Die Kristalle sind rhombisch und gehören der Raumgruppe $P2_12_12_1$ an. Die Elementarzelle enthält vier Moleküle. Die Gitterkonstanten, bei Zimmertemperatur gemessen, betragen $a = 21{,}22$, $b = 9{,}64$, $c = 8{,}92$ Å. Die Analyse stützte sich auf 818 Reflexen, von welchen 636 beobachtet wurden.

Der Ort des Bromions wurde mittels der dreidimensionalen Pattersonfunktion bestimmt. Für die Bestimmung der Orte der C-, N- und O-Atome wurden Fourier-Synthesen sowie Differenz-Synthesen angewandt. Die vollständige Struktur wurde dann mit Hilfe der Vollmatrix nach dem Prinzip der kleinsten Quadrate bis zum Endwert $R = 0{,}147$ verfeinert. Die absolute Konfiguration wurde nach der Methode von Bijvoet ermittelt.

Abstract

The structure of schelhammerine, an alkaloid isolated from *Schelhammera pedunculata* F. Muell., has been determined as its hydrobromide salt by x-ray diffraction analysis. The crystals are orthorhombic, space group $P2_12_12_1$ with four molecules in the unit cell. The cell dimensions are $a = 21.22$, $b = 9.64$, $c = 8.92$ Å taken at room temperature. The analysis was based on 818 reflections, 636 of which were observed.

The site of the bromide ion was determined from the three-dimensional Patterson function. The sites of C, N and O atoms were determined from electron density and difference maps. The complete structure was then refined by the full-matrix least-squares method to a final R value of 0.147.

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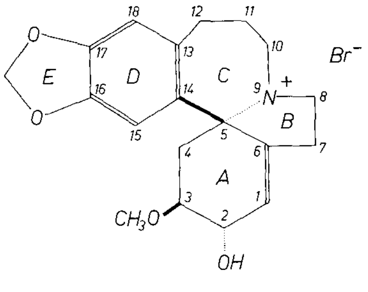
* Box 4331 G.P.O., Melbourne, Victoria 3001, Australia.

The absolute configuration was determined by Bijvoet's method and is shown below:



Introduction

Preliminary chemical and spectroscopic examination of a group of related alkaloids extracted from the rare northern Queensland plant *Schelhammera pedunculata*, F. Muell. (family Liliaceae) indicated these to have a new ring system. Since one base, named schelhammerine, appeared to possess as many as three asymmetric centres, it was chosen for the crystallographic determination of its molecular structure and absolute configuration. The analysis was carried out on the hydrobromide salt and a preliminary communication describing the chemical, spectroscopic and x-ray crystallographic work has been published elsewhere (Johns, Kowala, Lamberton, Sioumis and Wunderlich, 1968).

Experimental

Schelhammerine hydrobromide crystallizes from ethanol in the orthorhombic system as colourless prisms elongated in the *c* direction though a few crystals were found with their elongation along the *b* axis. The x-ray analysis required several crystals because of the gradual decomposition of the compound in the x-ray beam (Cu$K\alpha$ radiation). The unit-cell dimensions were measured at room temperature from Weissenberg patterns, with the crystals mounted about the *b* and *c* axes (Co$K\alpha$ radiation). The powder lines of silicon ($a = 5.4305$ Å at 25 °C) were used to calibrate all films. The density of crystals was determined by flotation, suspension occurring in bromobenzene at 19.8 °C (Wunderlich, 1957).

Crystal data—Schelhammerine hydrobromide, $C_{19}H_{23}NO_4 \cdot HBr$, M.W. 410.32. Orthorhombic, $a = 21.22 \pm 0.03$, $b = 9.64 \pm 0.03$, $c = 8.92 \pm 0.02$ Å. $V = 1825 \pm 12$ Å^3, $D_m = 1.495$, $D_x = 1.49 \pm 0.01$;

$Z = 4$, $F(000) = 848$, $\mu = 36\ \mathrm{cm}^{-1}$ for Cu$K\alpha$ radiation, $\Sigma f^2(\mathrm{Br})/\Sigma f^2(\mathrm{C,H,N,O}) = 1.24$ at $(\sin\theta)/\lambda = 0$.

Systematic extinctions ($h00$, $0k0$ and $00l$ reflections absent only for h, k and l odd, respectively) uniquely determined the space group to be $P2_12_12_1$. The intensity data were obtained by the multiple-film Weissenberg equi-inclination technique with visual estimation against a calibrated scale. From five b-axis and five c-axis levels a total of 818 independent reflections were obtained, of which 182 (22.2 %) were too weak to be observed. The diffraction patterns on most films faded at about $\theta = 45°$ due to apparent strong thermal motion. The intensities were corrected for the Lorentz and polarization factors and for the splitting of the $\alpha_1\alpha_2$ doublet (Rae and Barker, 1961).

Since the dimensions of the crystals used were about one-tenth of the "optimum size" $(2/\mu)$ (Buerger, 1942), no absorption correction was applied. Correlation factors between sets of films were determined and the data placed on the absolute scale by a least-squares fit of Wilson's plot (Wilson, 1942).

Structure determination

The bromide-ion position was determined from the three-dimensional sharpened Patterson map using structure factors modified by the expression $(1/\hat{f}^2)\cosh[2a(\sin\theta)/\lambda)\ \exp[-(4\pi^2/p)(\sin^2\theta)/\lambda^2]$ where $a = 4$ Å and $p = 3.3$ Å^{-2} (Wunderlich, 1965).

The x coordinate of the bromide ion was indistinguishable from zero so that the electron-density map based on bromide ion only contained a mirror plane at $x = 0$. In addition to the "real" and "ghost" peaks in this map there was a number of spurious peaks presumably due to the poor data and to abrupt series termination.

It was possible to identify eleven atoms making up a planar system of fused 5 and 6-membered rings with two ortho-substituent atoms on the 6-membered ring, but the electron density map based on these and the Br atom did not afford any new information regarding the rest of the molecule. It was clear, however, that a shift of the bromide ion away from $x = 0$ was necessary. Successive difference maps, in which x_{Br} was progressively varied and least-squares refinement, in which only the Br parameters were varied, both gave $x_{\mathrm{Br}} = -0.009$. Further Fourier syntheses using the refined Br parameters were calculated but it became evident that a complete structure would not be found on the basis of the differentiation of "real" and "ghost" atoms according to peak height even when taken in conjunction with stereochemical criteria. Furthermore, the overall R factor remained over 0.40 during these trials. In retrospect, part of the reason for this failure was obvious: no peak appeared for three of the carbon atoms, and of the two pairs of atoms falling on both "real" and "ghost" sites, only one such pair was identifiable from its higher than average peak.

It was decided at this stage to proceed in the manner suggested by HANSON (1963) for structures in which the heavy atom when taken alone generates a mirror plane. Either the A or the B component of F is a cosine function of the parameter perpendicular to this mirror plane and is therefore independent of the choice of "real" or "ghost" atom site. HANSON found that when these components only were used as Fourier coefficients, clearer and more informative maps were obtained.

With $x_{\text{heavy}} \sim 0$ in $P2_12_12_1$, these invariant components are A when $h + k = 2n$ and B when $h + k = 2n + 1$ and they result in Fourier syntheses containing a mirror plane at $x = 0$. In the present analysis, the maps were not significantly improved probably because of the inadequate data but at least it was no longer possible to be misled by the relative heights of peaks related by the "real"-"ghost" relationship. However, the advantages of this approach were immediately obvious in another direction. A dissection of R factors was made for reflections for which F is made up of the invariant ($\sum_i f_i \cos 2\pi h x_i$) component only ($h0l$ and $hk0$ when $h + l = 2n$ and $k = 2n$ respectively and all $0kl$) and of the variant ($\sum_i f_i \sin 2\pi h x_i$) component only ($h0l$ and $hk0$ when $h + l = 2n + 1$ and $k = 2n + 1$ respectively). The first column in Table 1 shows the break-down of R factors derived from a structure-factor calculation in which the Br atom and 21 light atoms were included. It was obvious at this stage that a number of "ghost" atoms had been chosen (five, in fact) and as well, two were spurious. From this point on, the complete structure gradually emerged from considerations of:

(a) stereochemistry—in particular, the quaternary nitrogen atom site was characterised on the basis of N—H $\cdots$ Br bond formation,

(b) van der Waals contacts—several "ghost" atoms were eliminated on these criteria and the methoxyl C atom site was adjusted for best van der Waals contacts before refinement,

(c) high-temperature parameter values—least-squares refinement of one trial structure indicated that two atoms were incorrectly placed,

(d) inspection of dissected R factors as outlined above,

(e) and of course peaks on the symmetric electron density and difference maps.

Column 2 in Table 1 shows the R factors when the complete structure had been found, the indication being clearly given by the now acceptable values of R for "variant only" terms.

Table 1. *Analysis of* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ *at various stages of the determination*

Stage of determination	1*	2	3	4
F independent of sign of x coordinates—invariant terms				
$h0l$ $h + l = 2n$	0.277	0.168	0.123	0.095
$hk0$ $k = 2n$	0.252	0.204	0.244	0.153
$0kl$ all	0.298	0.195	0.193	0.132
F dependent on sign of x coordinates—variant terms				
$h0l$ $h + l = 2n + 1$	0.522	0.261	0.169	0.126
$hk0$ $k = 2n + 1$	0.568	0.292	0.187	0.183
F composite of invariant and variant terms				
hkl all	0.361	0.227	0.189	0.147
$h0l$ all	0.356	0.180	0.139	0.106
$hk0$ all	0.399	0.239	0.217	0.167

* Each stage is described in the text.

Table 2. *Analysis of* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

	R	Range of $\sin\theta$	R	Number of reflections
All planes	0.147	0.00—0.40	0.141	171
h odd	0.153	0.40—0.50	0.155	129
k odd	0.159	0.50—0.60	0.146	163
l odd	0.165	0.60—0.70	0.201	187
$k + l$ odd	0.144	0.70—0.75	0.287	65
$h + l$ odd	0.161	0.75—0.80	0.254	45
$h + k$ odd	0.155	0.80—0.85	0.272	23
All $0kl$	0.132	0.85—0.90	0.197	14
All $h0l$	0.107	0.90—0.95	0.296	19
All $hk0$	0.167			

Table 3. *Observed and calculated structure factors and phase angles* (in millicycles)
Unobserved reflections are starred

h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α_c
2 0 0	32.2	30.8	0
4	12.7	10.1	500
6	132.0	156.0	0
8	66.3	59.9	0
10	57.2	44.8	0
12	71.7	86.8	0
14	46.0	46.5	0
16	29.8	28.4	0
18	15.5	16.9	0
20	8.1*	11.2	0
0 1 0	27.7	30.4	500
1	58.9	72.7	250
2	85.9	110.3	500
3	90.9	109.0	250
4	97.1	103.3	500
5	88.4	83.1	250
6	54.6	42.3	500
7	94.0	98.8	250
8	71.2	65.9	500
9	53.3	35.3	250
10	40.1	36.1	500
11	5.4*	7.7	250
12	45.7	53.2	500
13	33.7	33.5	250
14	28.2	24.8	500
15	43.5	35.2	250
16	7.3*	4.0	0
17	7.6*	4.8	250
18	29.3	31.5	500
19	20.0	12.4	250
1 2 0	59.8	34.1	250
2	62.3	45.8	0
3	83.8	77.3	250
4	61.7	47.9	0
5	101.5	86.0	750
6	93.6	71.0	0
7	40.8	32.5	750
8	15.4	21.0	0
9	14.9	18.1	750
10	46.4	34.4	0
11	17.4	19.3	750
12	46.1	41.1	0
13	10.5	9.2	750
14	10.0	14.4	0
15	11.3	9.2	750
16	26.3	23.9	0
17	15.2	14.8	750
18	32.0	29.4	0
1 3 0	28.5	11.5	750
2	66.7	72.9	0
3	36.4	33.8	250
4	66.3	48.8	0
5	4.1*	0.9	751
6	40.8	28.5	0
7	38.9	27.6	250
8	68.2	60.0	500
9	47.6	56.5	250
10	30.2	29.9	500
11	20.6	18.9	250
12	20.6	20.1	0
13	25.7	18.0	250
14	6.8*	11.7	500
15	25.6	26.1	250
16	7.5*	2.8	500
17	22.2	21.1	250
18	8.1*	10.0	0
0 4 0	4.3*	2.0	500
1	77.9	76.5	750
2	77.6	67.3	500
3	83.9	91.9	750
4	4.6*	1.0	0
5	29.1	26.3	750
6	23.8	19.0	0
7	55.1	70.1	750
8	18.5	10.4	500
9	46.8	51.5	750
10	6.0*	2.8	0
11	49.7	51.1	750
12	6.6*	3.5	0
13	28.8	23.4	750
14	7.2*	4.2	500
15	41.1	36.2	750
16	7.8*	4.8	500
1 5 0	5.1*	7.4	750
2	7.3	9.4	500
3	5.2*	3.2	750
4	44.5	48.3	500
5	22.5	16.9	750
6	22.7	11.0	0
7	5.8*	4.3	250
8	18.5	14.5	500
9	19.7	18.3	250
10	35.6	31.8	500
11	16.9	15.2	750
12	7.1*	9.8	500
13	30.5	21.4	750
14	15.4	11.0	500
15	7.9*	1.6	250
16	12.4	14.8	500
0 6 0	38.5	45.0	0
1	5.9*	11.5	250
2	13.9	18.6	0
3 6 0	32.6	31.8	250
4	37.3	43.9	0
5	6.3*	10.9	750
6	64.0	69.5	0
7	6.6*	7.0	250
8	37.8	38.1	0
9	37.0	33.7	250
10	17.8	16.1	0
11	18.4	19.5	250
12	7.7*	9.6	0
13	7.9*	0.3	750
14	19.9	17.8	0
15	25.0	23.1	250
16	19.7	16.9	0
1 7 0	6.8*	7.3	250
2	13.7	13.0	500
3	6.9*	1.4	750
4	17.2	17.1	500
5	21.9	21.1	750
6	31.2	30.0	0
7	14.8	10.5	750
8	7.5*	5.4	0
9	7.7*	1.8	250
10	7.9*	0.7	499
11	27.4	21.2	750
12	27.8	25.1	0
13	8.1*	12.4	750
0 8 0	7.6*	9.3	500
1	35.9	35.9	250
2	7.7*	13.0	500
3	7.7*	3.5	750
4	46.8	41.2	500
5	19.3	8.7	250
6	7.9*	17.5	500
7	29.4	22.5	250
8	29.8	16.7	500
9	29.8	15.2	250
10	29.7	23.9	500
11	8.0*	2.8	750
12	15.8	17.1	500
1 9 0	16.3	10.2	250
2	8.1*	3.5	500
3	16.3	12.6	250
4	11.5	10.1	500
5	8.1*	0.5	250
6	16.1	12.6	0
0 10 0	7.7*	4.8	0
1	10.8	11.8	750
2	7.6*	3.6	0
3	28.5	22.2	750
4	7.5*	0.2	0
5	10.5	13.9	750
1 0 1	37.7	32.5	750
2	69.9	70.1	250
3	86.6	86.0	250
4	54.4	55.2	250
5	68.2	63.6	250
6	31.0	38.6	750
7	35.0	30.8	250
8	5.1*	10.4	750
9	31.3	17.9	250
10	20.6	18.2	750
11	6.4*	0.6	751
12	80.9	61.0	750
13	7.3*	12.3	250
14	13.5	11.8	750
15	8.3*	3.7	750
16	17.6	19.9	750
17	9.2*	4.4	250
18	33.4	27.5	750
19	19.9	23.2	250
0 1 1	37.0	26.7	750
1	75.2	84.9	944
2	94.4	109.3	172
3	53.9	55.5	224
4	83.8	94.6	306
5	33.7	31.4	68
6	104.0	97.7	242
7	64.4	65.3	964
8	58.7	52.1	232
9	37.7	30.1	0
10	85.5	78.3	231
11	21.4	23.5	160
12	43.5	42.0	213
13	49.9	44.7	25
14	41.1	26.7	277
15	11.8	10.7	157
16	40.4	31.9	211
17	5.0*	3.7	250
18	5.2*	12.5	157
19	15.6	21.2	985
20	16.8	17.7	272
0 2 1	44.9	31.3	0
1	58.4	50.5	536
2	37.1	32.1	428
3	44.5	38.0	896
4	61.3	58.9	479
5	70.2	57.7	910
6	4.5*	12.0	552
7	25.1	22.0	543
8	18.8	19.6	157
9	18.5	15.6	871
10 2 1	36.2	36.4	512
11	50.8	51.5	957
12	8.9*	5.3	500
13	10.0*	20.9	78
0 3 1	39.5	19.0	750
1	108.5	100.7	521
2	68.5	58.7	725
3	87.2	84.0	552
4	17.4	19.5	59
5	106.5	88.1	526
6	33.0	39.7	288
7	48.1	52.3	472
8	18.4	33.6	601
9	49.1	73.4	446
10	12.9*	10.0	750
0 4 1	5.4*	4.1	0
1	8.6	16.4	671
2	29.5	33.0	874
3	10.7	14.2	750
4	32.8	29.6	876
5	23.6	24.1	431
6	20.1	13.9	131
7	27.0	26.9	405
8	35.4	36.9	132
9	24.2	27.0	585
10	13.5	14.6	225
11	18.2	21.7	628
12	16.5	16.8	198
13	13.0*	22.9	417
0 5 1	52.0	49.0	750
1	91.3	57.5	942
2	34.5	33.5	815
3	40.8	40.1	15
4	44.9	40.5	742
5	108.1	67.5	5
6	49.9	44.1	765
7	57.3	46.3	930
8	44.5	36.8	713
9	26.7	28.6	990
10	9.7*	20.4	811
11	10.7*	19.0	54
12	32.6	30.2	750
13	53.6	42.7	964
0 6 1	9.4*	12.6	500
1	20.7	22.9	325
2	13.5	14.8	728
3	9.8*	14.9	256
4	10.1*	16.1	776
5	10.5*	4.2	250
6	15.7	19.9	699
7	11.8*	8.5	851
8	12.5*	11.5	862
9	13.5*	10.5	55
10	14.5*	16.4	667
11	15.7*	16.7	224
0 7 1	58.1	56.2	250
1	12.5*	11.7	668
2	55.4	48.7	285
3	13.0*	7.7	133
4	26.1	27.0	210
5	13.9*	8.4	563
6	29.0	34.1	250
7	15.2*	6.0	600
8	27.9	21.2	214
9	17.1*	15.4	315
10	25.9	28.7	195
11	19.6*	3.1	187
0 0 2	120.0	142.0	0
1	104.3	115.7	0
2	78.9	88.7	0
3	30.8	34.9	500
4	146.0	140.6	0
5	4.5*	9.6	500
6	142.1	123.2	0
7	5.1*	4.7	0
8	63.2	60.5	0
9	30.5	29.6	0
10	13.8	14.5	0
11	20.0	16.4	500
12	45.2	45.6	0
13	15.3	11.9	0
14	32.5	34.3	0
15	28.5	27.9	0
16	21.7	22.6	0
17	9.4*	1.7	0
18	35.9	31.7	0
19	14.2	11.6	0
0 1 2	198.1	168.0	250
1	30.0	30.9	550
2	71.1	70.3	898
3	68.2	58.7	589
4	34.2	36.8	14
5	27.6	25.6	637
6	59.0	51.0	153
7	34.0	33.5	469
8	33.9	27.2	939
9	52.3	49.7	554
10	43.9	35.6	85
11	22.3	20.7	665
12	28.0	24.3	90
13	26.6	24.4	610
14	23.3	24.1	52
15 1 2	23.8	25.9	568
16	36.0	34.2	127
17	11.9	13.8	656
18	20.4	22.5	938
0 2 2	92.4	92.5	500
1	89.8	72.1	309
2	59.4	47.9	388
3	121.5	89.3	258
4	107.8	71.0	496
5	53.8	54.5	158
6	87.5	77.8	453
7	34.9	42.7	281
8	24.2	32.6	458
0 3 2	4.1*	1.6	250
1	4.2*	3.9	81
2	97.5	76.3	698
3	17.2	17.8	300
4	54.8	37.9	757
5	25.8	18.3	71
6	17.4	14.4	770
7	24.3	25.1	146
8	42.6	40.4	801
9	52.0	35.7	316
10	34.8	21.6	835
11	27.7	23.2	190
12	51.3	30.7	687
1 0 3	77.5	91.1	250
2	1.1*	14.6	250
3	112.0	102.2	250
4	25.9	27.8	750
5	38.9	37.2	250
6	2.0*	3.1	250
7	30.8	33.3	250
8	7.7	5.8	750
9	42.4	39.6	250
10	2.8*	2.5	750
11	36.8	33.8	250
12	21.8	23.0	750
13	38.5	36.2	250
14	32.6	29.1	750
15	26.6	25.6	250
16	11.4	10.6	750
0 1 3	74.6	65.5	250
1	95.1	94.5	824
2	45.1	44.3	184
3	16.5	15.7	107
4	54.0	51.0	395
5	59.8	54.3	160
6	51.4	46.3	216
7	46.9	38.6	138
8	56.4	54.3	174
9	11.8	17.2	106
10	41.1	36.1	174
11	32.5	28.3	162
12	38.4	38.3	147
13	9.7	8.6	210
14	18.2	21.8	182
15	20.1	25.2	73
16	18.8	16.5	331
17	21.0	23.6	141
18	10.7	11.0	272
0 2 3	25.3	25.5	500
1	65.3	55.9	791
2	43.0	51.1	419
3	39.3	38.7	750
4	48.5	47.6	555
5	30.3	28.2	823
6	47.1	47.0	512
7	29.2	31.9	882
8	49.3	45.1	471
9	31.2	33.0	832
10	56.1	47.4	463
11	37.1	29.7	785
12	7.4	10.8	172
13	13.4	16.7	862
14	3.8*	7.6	791
15	15.4	18.7	905
16	15.4	17.4	398
17	21.1	25.6	915
18	12.1	15.0	413
0 3 3	5.2	7.1	250
1	49.7	47.2	441
2	16.3	17.6	500
3	84.3	73.2	486
4	26.1	27.6	815
5	44.5	44.3	465
6	37.0	29.2	580
7	37.0	41.0	449
8	15.8	17.2	389
9	33.0	38.3	561
10	17.5	16.8	605
11	36.6	30.0	616
12	16.5	18.6	530
13	38.0	37.6	461
14	28.5	25.9	519
15	27.2	23.3	384
16	13.8	13.0	836
17	15.5	13.5	685
18	11.6	13.0	589
19	10.6	14.2	500
20	10.2	13.1	544
0 4 3	57.0	57.8	0

Table 3. *(Continued)*

h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α_c	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α_c	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α_c	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α_c
1 4 3	5.2	3.7	0	13 1 4	27.3	25.4	579	18 0 5	16.7	10.9	750	5 0 7	17.4	18.5	250
2	53.7	48.2	72	14	30.7	26.7	141	0 1 5	45.9	44.2	250	6	9.4*	1.8	750
3	29.6	28.4	665	15	16.0	16.9	444	1	17.8	16.0	26	7	21.9	21.5	250
4	39.5	36.3	980	0 2 4	58.5	63.9	500	2	16.3	17.1	963	8	9.7*	9.3	250
5	34.1	25.9	677	1	18.0	19.8	284	3	33.3	30.7	174	9	21.7	18.6	250
6	22.6	22.4	977	2	18.3	19.3	500	4	16.3	14.2	164	10	10.0*	2.1	250
7	3.1*	5.0	946	3	20.2	22.8	118	5	19.0	19.9	261	11	23.3	23.0	250
8	32.3	25.9	27	4	23.8	29.1	408	6	17.7	17.7	285	12	9.9*	0.6	750
9	28.2	27.1	451	5	52.6	39.2	301	7	14.5	17.3	287	13	23.6	25.0	250
10	29.9	25.7	131	6	26.3	28.4	417	8	18.9	21.8	109	14	9.6*	0.8	750
11	19.5	17.2	461	7	35.7	39.6	303	9	12.7	16.9	250	15	14.7	10.0	250
12	35.3	33.1	70	8	22.8	22.6	293	10	7.8	9.5	926	0 1 7	8.2	11.9	250
13	4.0*	11.7	609	9	19.9	20.5	217	11	11.0	15.5	154	1	13.5	15.7	388
14	19.6	27.7	42	10	38.2	34.3	514	12	4.9*	11.5	188	2	4.9*	8.4	729
15	26.2	22.6	529	11	6.3*	7.2	190	13	8.6	15.2	135	3	4.9*	10.2	163
16	10.8	13.8	131	12	12.0	9.7	455	14	16.7	20.8	79	4	5.0*	8.2	823
0 5 3	25.8	24.9	750	13	13.5	11.3	412	15	16.8	17.2	223	5	5.0*	12.6	280
1	43.3	41.4	943	14	8.9*	17.5	277	16	5.4*	5.1	83	6	5.1*	8.4	812
2	25.6	21.1	844	15	10.0*	13.0	459	17	16.0	19.1	294	7	10.8	10.3	155
3	34.4	26.3	965	16	34.5	32.3	352	18	5.2*	6.6	250	8	12.3	7.7	893
4	31.5	30.4	727	0 3 4	74.0	79.0	750	0 4 5	39.7	38.5	0	9	5.3*	14.7	296
5	29.1	28.4	918	1	13.5	12.9	952	1	15.4	15.2	788	10	5.4*	13.3	945
6	37.1	35.7	852	2	37.1	39.1	757	2	33.1	27.0	51	11	5.4*	14.9	423
7	38.3	36.6	933	3	9.7	6.3	866	3	15.3	19.4	784	12	5.3*	5.2	936
8	8.8	10.0	702	4	49.2	42.5	839	4	46.1	47.2	986	13	5.3*	10.2	182
9	37.5	30.8	964	5	22.8	18.9	142	5	3.0*	3.5	846	0 4 7	37.2	32.0	0
10	32.6	27.9	695	6	61.8	64.7	711	6	48.3	40.0	9	1	17.3	18.7	665
11	20.4	20.3	0	7	10.1	11.5	213	7	10.0	10.3	455	2	23.2	22.8	71
12	8.3	15.8	630	8	29.7	28.6	715	8	20.3	22.2	97	3	3.7*	5.5	450
13	17.9	18.4	830	9	15.4	11.9	415	9	9.8	9.9	437	4	16.7	16.0	43
14	14.1	14.2	987	10	32.0	33.2	717	10	27.0	26.8	0	5	3.7*	6.2	104
15	9.9	13.6	909	11	21.4	12.1	250	11	8.1	8.8	441	6	23.6	21.1	957
0 6 3	9.5	7.9	500	12	24.6	27.7	718	12	16.3	20.8	969	7	5.3	5.6	616
1	25.4	25.9	206	13	18.3	22.2	96	13	14.1	16.1	692	8	17.6	19.5	0
2	3.5*	6.4	544	14	28.7	25.0	812	14	13.3	13.8	42	9	3.7*	6.6	950
3	22.7	22.7	323	15	10.9*	12.3	162	15	5.2	3.9	446	10	15.1	16.2	0
4	3.6*	5.1	413	16	32.0	26.6	750	16	15.9	14.6	66	11	6.3	4.4	250
5	30.0	25.5	223	0 4 4	9.2	12.7	500	17	3.5*	5.8	311	12	11.9	11.2	977
6	18.0	19.0	626	1	42.4	37.2	794	18	13.6	12.2	0	13	3.4*	3.3	500
7	32.3	29.6	197	2	10.6	14.0	19	19	6.2	6.8	655	14	11.7	10.2	973
8	22.2	18.8	770	3	30.0	26.4	727	20	4.9	8.0	26	15	4.4	6.2	854
9	13.3	19.1	319	4	8.3	12.3	527	21	4.4	4.2	441	16	5.0	8.4	977
10	14.4	9.5	651	5	26.5	20.3	720	0 0 6	23.8	24.2	500	17	3.8	4.5	544
11	8.6	8.9	127	6	9.3	13.4	620	1	16.9	17.8	500	18	4.7	5.3	950
12	11.5	18.2	649	7	5.9*	8.0	849	2	7.9*	4.6	0	0 0 8	19.4	13.8	500
13	12.4	15.7	104	8	16.8	16.1	856	3	8.0*	4.1	500	1	21.8	21.8	500
14	14.1	19.3	609	9	32.6	22.0	727	4	8.1*	8.6	0	2	9.9*	13.4	500
0 7 3	33.4	31.7	250	10	7.6*	9.4	677	5	8.2*	1.8	0	3	10.0*	5.6	500
1	4.0*	6.7	750	11	30.4	28.4	589	6	19.5	17.0	0	4	10.0*	7.0	500
2	32.7	25.8	281	12	31.5	29.2	760	7	8.6*	6.3	0	5	10.0*	7.3	0
3	19.5	14.1	306	13	26.9	26.7	650	8	8.8*	0.6	0	6	10.0*	6.8	500
4	32.3	26.5	129	14	9.3*	6.6	948	9	9.1*	7.3	0	7	10.0*	2.1	0
5	9.2	8.9	500	15	12.0*	9.2	638	10	9.3*	15.2	0	8	9.9*	11.9	500
6	25.4	25.9	189	0 5 4	21.6	22.3	250	11	16.6	15.4	0	9	9.8*	3.4	0
7	4.2*	5.1	750	1	21.2	24.0	39	12	9.8*	13.2	500	10	9.7*	7.6	500
8	24.7	23.8	250	2	35.2	33.3	309	13	10.0*	15.6	0	11	16.4	16.1	0
9	4.4*	4.1	289	3	36.2	33.8	925	14	10.0*	3.7	500	1 1 8	19.1	14.7	604
10	4.4*	7.8	250	4	29.6	28.2	203	15	14.0	15.1	0	2	11.2	11.6	429
11	14.1	12.8	334	5	11.1	14.7	903	16	9.7*	11.1	0	3	19.4	17.4	547
12	18.3	16.6	112	6	45.4	34.2	361	17	9.4*	7.2	0	4	5.4*	3.6	338
0 8 3	4.3*	12.7	500	7	31.0	25.7	15	0 1 6	4.2*	6.0	750	5	14.5	17.8	465
1	13.9	15.8	750	8	28.7	29.5	257	1	27.5	26.9	450	6	5.4*	14.2	262
2	16.1	14.3	513	9	38.0	33.1	0	2	28.5	33.4	229	7	15.8	17.8	425
3	4.4*	2.9	555	10	26.1	26.7	206	3	32.0	31.3	491	8	5.3*	0.9	739
4	16.0	15.0	383	11	9.9*	10.7	0	4	11.4	19.3	271	9	12.7	15.0	500
5	12.3	11.9	820	12	28.2	21.6	378	5	46.5	38.1	528	10	5.2*	12.5	296
6	10.8	7.2	415	13	11.7*	5.7	972	6	4.6*	9.1	250	0 4 8	7.5	9.4	0
7	23.0	22.9	806	0 6 4	12.7	12.6	0	7	30.6	32.2	507	1	3.7*	4.3	250
0 9 3	4.3*	5.3	750	1	15.6	16.0	261	8	13.8	21.5	230	2	3.7*	5.6	0
1	4.3*	7.9	473	2	12.9	15.1	926	9	31.2	33.5	448	3	8.3	12.8	219
2	8.7	12.3	822	3	7.8*	9.0	883	10	14.5	14.6	250	4	5.2	4.4	885
3	8.6	6.7	568	4	21.1	22.1	156	11	17.4	20.6	531	5	5.6*	4.1	250
4	11.5	15.5	681	5	14.1	13.9	139	12	11.0	10.9	136	6	6.3	3.7	750
5	11.5	10.6	430	6	22.9	25.8	902	13	14.1	20.7	530	7	7.2	3.9	329
1 0 4	60.1	62.8	0	7	9.2*	12.8	183	14	9.1	8.1	142	8	5.0	6.6	703
2	109.3	110.3	0	8	16.5	15.3	941	15	11.1	11.1	517	9	4.9	9.2	381
3	2.0*	4.8	0	9	17.6	15.9	987	16	8.8	5.3	163	10	10.3	11.2	846
4	38.9	33.3	0	10	11.1*	14.6	250	0 4 6	17.9	23.5	0	11	4.6	6.9	380
5	56.1	39.6	500	0 7 4	9.7*	6.7	750	1	3.3*	5.2	0	12	5.4	2.8	938
6	5.3	1.9	0	1	16.5	16.9	500	2	15.6	11.1	750	13	7.2	6.4	433
7	6.0	8.6	500	2	9.8*	3.4	596	3	4.8	7.8	0	14	9.7	9.2	693
8	46.4	43.2	0	3	28.7	36.2	523	4	15.9	11.1	500	15	6.1	4.5	403
9	51.5	44.0	0	4	17.4	13.9	58	5	17.9	15.7	717	0 4 9	7.6	4.6	0
10	36.8	33.0	0	5	31.7	30.3	558	6	18.2	21.3	868	1	3.3*	1.2	750
11	13.8	10.8	0	6	11.0*	2.3	500	7	5.0	5.8	330	2	10.3	9.9	18
12	20.2	21.5	0	1 0 5	54.5	53.2	250	8	8.8	5.3	860	3	3.3*	1.8	500
13	19.2	20.1	0	2	6.7*	0.4	750	9	7.2	8.7	456	4	10.3	9.7	46
14	24.5	23.0	0	3	102.7	86.8	250	10	8.4	5.1	621	5	3.2*	4.0	903
15	19.2	17.2	0	4	7.0*	6.6	750	11	12.7	14.8	535	6	10.0	8.5	936
0 1 4	4.4	9.2	750	5	83.4	69.7	250	12	13.3	17.1	706	7	3.1*	2.8	122
1	55.5	56.0	385	6	7.4*	0.5	250	13	11.7	10.1	576	8	10.1	7.9	957
2	57.8	44.5	296	7	40.2	35.3	250	14	12.0	9.3	840	9	2.8*	2.9	347
3	57.2	46.2	472	8	7.9*	8.3	750	15	9.1	8.0	352	10	5.5	5.3	40
4	70.1	52.9	237	9	30.4	30.2	250	16	12.3	11.5	868	11	2.5*	2.4	875
5	29.6	31.5	506	10	12.0	12.8	750	17	9.8	8.6	576	12	7.4	4.7	938
6	27.2	23.2	0	11	35.4	34.9	250	18	12.7	13.8	716	0 4 10	2.6*	1.2	0
7	60.9	45.1	543	12	9.1*	1.0	250	19	3.8	6.0	550	1	6.5	8.5	226
8	19.6	21.0	73	13	9.4*	5.7	250	20	2.3	3.6	750	2	2.6*	3.7	957
9	73.2	57.3	513	14	9.7*	3.6	250	1 0 7	68.8	54.4	250	3	2.6*	4.3	205
10	15.7	16.1	102	15	33.8	32.1	250	2	12.8	17.0	750	4	5.7	2.8	926
11	31.0	32.7	602	16	10.0*	2.5	750	3	44.6	41.0	250	5	4.9	6.8	348
12	32.8	31.4	180	17	22.2	24.7	250	4	9.2*	3.6	750	6	5.8	3.4	750

* Unobserved reflection

Least-squares refinement using the program of BUSING, MARTIN and LEVY (1962) into which was incorporated the weighting scheme of HUGHES (1941) and the facility to refine isotropic and anisotropic thermal parameters simultaneously gave the results in column 3.

Inspection of the structure-factor listings revealed definite trends in the values of ($|F_o| - |F_c|$) for certain sets of reflections corresponding to the different crystals used and to their state of decomposition

Table 4. *Atomic positional and temperature parameters*

The numbers in brackets are the standard deviations $\times 10^4$ for the x, y and z parameters of the C, N and O atoms and for the U_{ij} parameters of Br, $\times 10^5$ for the x, y and z parameters of Br and $\times 10^2$ for the B parameters

	x	y	z	B
C (1)	0.3396(16)	−0.1260(38)	0.4146(45)	3.78(77) Å^2
C (2)	0.3590(19)	−0.1545(50)	0.2514(56)	5.62(99)
C (3)	0.3742(14)	−0.0231(35)	0.1781(39)	2.35(67)
C (4)	0.4168(15)	0.0775(39)	0.2708(42)	3.34(78)
C (5)	0.3837(16)	0.1043(45)	0.4278(41)	3.36(83)
C (6)	0.3509(16)	−0.0188(41)	0.4873(48)	3.64(85)
C (7)	0.3457(19)	0.0007(52)	0.6624(57)	5.11(100)
C (8)	0.3969(17)	0.1126(49)	0.6923(42)	3.91(87)
C(10)	0.4840(17)	0.2277(38)	0.5318(44)	4.43(79)
C(11)	0.4571(18)	0.3686(44)	0.5523(52)	5.60(102)
C(12)	0.4297(19)	0.4087(44)	0.3927(51)	5.04(88)
C(13)	0.3615(18)	0.3610(45)	0.3888(57)	5.40(105)
C(14)	0.3391(14)	0.2295(32)	0.4186(37)	2.27(64)
C(15)	0.2756(18)	0.2043(44)	0.4279(44)	5.09(98)
C(16)	0.2314(18)	0.3008(45)	0.3998(52)	5.53(100)
C(17)	0.2577(24)	0.4525(55)	0.3963(65)	7.30(136)
C(18)	0.3125(16)	0.4740(42)	0.3516(43)	3.51(81)
C(19)	0.3196(17)	0.1634(51)	0.0512(53)	5.86(97)
C(20)	0.1477(21)	0.4331(52)	0.3814(62)	6.87(121)
O(21)	0.4099(14)	−0.2464(37)	0.2543(37)	7.23(77)
O(22)	0.3131 (9)	0.0447(26)	0.1455(27)	3.53(52)
O(23)	0.1665(14)	0.2996(34)	0.4102(38)	7.01(76)
O(24)	0.1994(18)	0.5257(44)	0.3585(44)	9.69(96)
N (9)	0.4318(14)	0.1179(34)	0.5482(37)	4.31(71)
Br	0.50730(18)	−0.17709(55)	0.53972(55)	
	β_{11}	0.00277	U_{11}	0.0631(27) Å^2
	β_{22}	0.01524	U_{22}	0.0717(30)
	β_{33}	0.01722	U_{33}	0.0694(35)
	β_{12}	0.00213	U_{12}	0.0221(25)
	β_{13}	−0.00031	U_{13}	−0.0030(24)
	β_{23}	0.00156	U_{23}	0.0068(28)

in the x-ray beam. Independent scale and atomic thermal parameters were obtained for these reflections and then the F_0 values modified to place them on the same temperature scale as the rest of the data. R-factor values after further refinement are given in the last column of Table 1 and in Table 2 and a listing of observed and calculated structure factors and phase angles expressed in millicycles given in Table 3.

The final atomic positional and temperature parameters and their standard deviations arising from the least-squares calculations are listed in Table 4.

In Table 4 the temperature parameters of Br^- are given in terms of the usual β_{ij} parameters in the expression $\exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$, and in terms of the vibration elements of the type $U_{12} = \beta_{12}/2\pi^2a^*b^*$ along with standard deviations for the latter.

The atomic scattering curves of Berghuis, Haanappel, Potters, Loopstra, MacGillavry and Veenendaal (1955) were used for C and O. Values for N^+ were obtained by extrapolation using data by Freeman (1959). The International tables for x-ray crystallography, Volume 3, were used for the bromide ion and corrections made for anomalous scattering, using data of Dauben and Templeton (1955).

Absolute configuration

The absolute configuration was determined by the method of Bijvoet, Peerdeman and van Bommel (1951). The differences between the intensities of $h1l$ and $\bar{h}1l$ reflections on Weissenberg patterns taken with Co$K\alpha$ radiation were examined and the results listed in Table 5. The comparisons of $I(h1l)$ and $I(\bar{h}1l)$ were carried out by three observers independently, and where there was not unanimity, a question mark (?) has been entered in the Table. Only those reflections for which the ratio, expressed as a percentage, of the difference between $F^2(h1l)$ and $F^2(\bar{h}1l)$ and their mean value exceeded 10% and for which $(\sin\theta)/\lambda \leqslant 0.45$ were considered. The value of $f''_{\mathrm{Br}} = 2.0$ at $(\sin\theta)/\lambda = 0$ was obtained by extrapolation of graphical data given by Ramaseshan (1964).

It will be seen that out of twenty-two observations, sixteen are consistent and one inconsistent with the F^2 values calculated from the parameters given in Table 4, and the remaining five are doubtful because of lack of unanimity among the observers. Therefore the parameters in Table 4 and the perspective drawing in Fig. 1 represent the absolute configuration with respect to a right-handed set of axes.

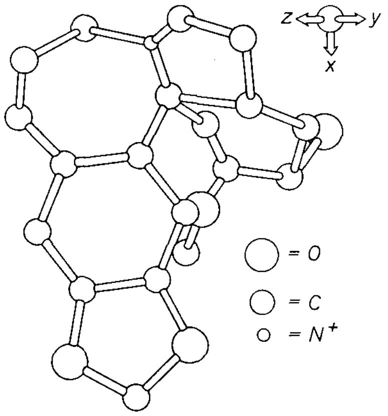


Fig. 1. Perspective view of the molecule indicating the absolute configuration

Table 5. *Reflections used to determine the absolute configuration*

$h\,1\,l$	Calculated		$\frac{\lvert F^2(h1l) - F^2(\bar{h}1l)\rvert \cdot 100}{\frac{1}{2}[F^2(h1l) + F^2(\bar{h}1l)]}$	Observed
	$F^2(h1l)$	$F^2(\bar{h}1l)$		
3 1 1	3433	2760	21.7	$I(h1l) > I(\bar{h}1l)$
5 1 1	1046	928	11.9	?
11 1 1	619	495	22.3	>
15 1 1	129	107	18.6	?
1 1 2	1012	915	10.1	>
4 1 2	1249	1450	14.9	<
5 1 2	748	578	25.6	>
7 1 2	1047	1233	16.3	<
8 1 2	642	824	24.8	<
11 1 2	477	388	20.6	?
2 1 3	1845	2109	13.4	<
3 1 3	277	211	22.5	<
4 1 3	2946	2249	26.8	>
15 1 3	605	678	11.4	<
1 1 4	2812	3452	20.4	<
6 1 4	460	633	31.7	<
8 1 4	426	488	13.6	<
10 1 4	245	279	13.0	<
11 1 4	1148	1000	13.8	?
2 1 5	250	347	32.4	<
7 1 5	329	279	16.4	?
9 1 6	1067	1182	10.2	<

Discussion of the structure

The crystal structure confirmed the deductions made from chemical and spectroscopic, especially nuclear magnetic resonance, data run in parallel with the x-ray work, namely that schelhammerine and related bases are the first members of the "homoerythrina" group of alkaloids in which the additional methylene group is incorporated in ring *C*. In line with the mechanisms advanced for the biosyntheses of a number of recently characterized homoaporphine (Battersby *et al.*, 1967) and homomorphine (Fridrichsons *et al.*, 1968; Hart *et al.*, 1968) alkaloids, it is considered likely that the *Schelhammera* bases are derived by oxidative intramolecular coupling of 1-phenyl-ethyl-1,2,3,4-tetrahydroisoquinoline precursors (Johns *et al* ., 1968) resulting in 7-membered rings in each case.

The relative stereochemistry of the hydroxyl and methoxyl substituents at C(2) and C(3)* respectively is shown to be *trans* diaxial whereas in erythratine, the normal *Erythrina* base corresponding to schelhammerine, configuration of these groups is *trans* diequatorial (Barton *et al.*, 1966; Barton, 1967). The absolute configuration at C(5)* is the same as that found in both the non-aromatic alkaloids [e.g. dihydro-β-erythroidine (Hanson, 1963)] and in the aromatic series [e.g. erythraline (Nowacki and Bonsma, 1958, and Boekelheide and Chang, 1964)].

The bond lengths and angles are listed in Tables 6 and 7 respectively but because of their large average standard deviations (0.05 Å and 3.3° respectively), it would be inappropriate to analyse them in any detail. Suffice it to say that the averaged values are consistent with the characteristic values of bond lengths and angles found in 5-, 6- and 7-membered rings (Sutton, 1965; Asher and Sim, 1965).

The three projections of the structure (Fig. 2 *a*, *b* and *c*) show that the aromatic and methylene-dioxy rings along with C(5) and C(12) lie roughly in the x,y plane and the equation of the least-squares plane (Schomaker, Waser, Marsh and Bergman, 1959; Norment, 1963) through these eleven atoms is given by $0.300x + 1.546y + 8.803z - 4.091 = 0$, the average deviation of atoms from this plane being 0.055 Å. It is obvious from both Table 6 and Fig. 2*b* and 2*c* that C(17) is greatly displaced from the site corresponding to accepted stereochemistry but neither difference maps nor least-squares refine-

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* The half-chair conformation of ring *A* and the relative configuration at this centre was deduced independently from the 100 Mc/sec nuclear magnetic resonance spectra using the double irradiation technique.

Table 6. *Interatomic distances*

C_{te}—C_{te}* (characteristic value = 1.537 ± 0.005 Å)**	
C (2)—C (3)	1.46 Å
C (3)—C (4)	1.56
C (4)—C (5)	1.59
C (7)—C (8)	1.55
C(10)—C(11)	1.48
C(11)—C(12)	1.58
Average	1.54

C_{te}—C_{tr}* (characteristic value = 1.501 ± 0.004 Å)	
C(2)—C(1)	1.53
C(5)—C(6)	1.47
C(7)—C(6)	1.58
Average	1.53

C_{te}—C_{arom}* (characteristic value = 1.505 ± 0.005 Å)	
C (5)—C(14)	1.54
C(12)—C(13)	1.52
Average	1.53

C_{tr}—C_{tr} (characteristic value = 1.335 ± 0.010 Å)	
C(1)—C(6)	1.24

C_{arom}—C_{arom} (characteristic value = 1.394 ± 0.005 Å)	
C(13)—C(14)	1.38
C(14)—C(15)	1.37
C(15)—C(16)	1.34
C(16)—C(17)	1.57
C(17)—C(18)	1.25
C(18)—C(13)	1.54
Average	1.41

C_{te}—O (characteristic value = 1.426 ± 0.005 Å)	
C (2)—O(21)	1.40 Å
C (3)—O(22)	1.48
C(19)—O(22)	1.43
C(20)—O(23)	1.37
C(20)—O(24)	1.43
Average	1.42

C_{arom}—O (characteristic value = 1.36 ± 0.01 Å)	
C(16)—O(23)	1.38
C(17)—O(24)	1.46
Average	1.42

C_{te}—N^+ (characteristic value = 1.52 ± 0.03 Å)	
C (5)—N(9)	1.49
C (8)—N(9)	1.48
C(10)—N(9)	1.54
Average	1.50

* te = tetrahedral and tr = trigonal corresponding to sp^3 and sp^2 hybridization respectively, and arom = aromatic.

** The characteristic values quoted are those given by HAMILTON *et al.* (1962) for C_{te}—N^+ and by SUTTON (1965) for the other cases.

Table 7. *Bond angles*

X—C_{te}—Y	
C (1)—C (2)—C (3)	109.1°
C (1)—C (2)—O(21)	107.6
C (2)—C (3)—C (4)	115.4
C (2)—C (3)—O(22)	106.0
C (3)—C (2)—O(21)	112.7
C (3)—C (4)—C (5)	108.2
C (4)—C (3)—O(22)	109.7
C (4)—C (5)—C (6)	113.3
C (4)—C (5)—N (9)	110.3
C (4)—C (5)—C(14)	110.7
C (6)—C (5)—N (9)	97.7
C (6)—C (5)—C(14)	111.1
C(14)—C (5)—N (9)	113.1
C (6)—C (7)—C (8)	101.7
C (7)—C (8)—N (9)	102.9
N (9)—C(10)—C(11)	109.9
C(10)—C(11)—C(12)	104.7
C(11)—C(12)—C(13)	107.3
O(23)—C(20)—O(24)	112.8
Average value within	
(*a*) 5-membered ring	104
(*b*) 6-membered ring	112
(*c*) 7-membered ring	109

X—C_{tr}—Y	
C(1)—C(6)—C(5)	124.9
C(1)—C(6)—C(7)	127.0
C(2)—C(1)—C(6)	126.2
C(5)—C(6)—C(7)	107.1
Average value within	
6-membered ring	125

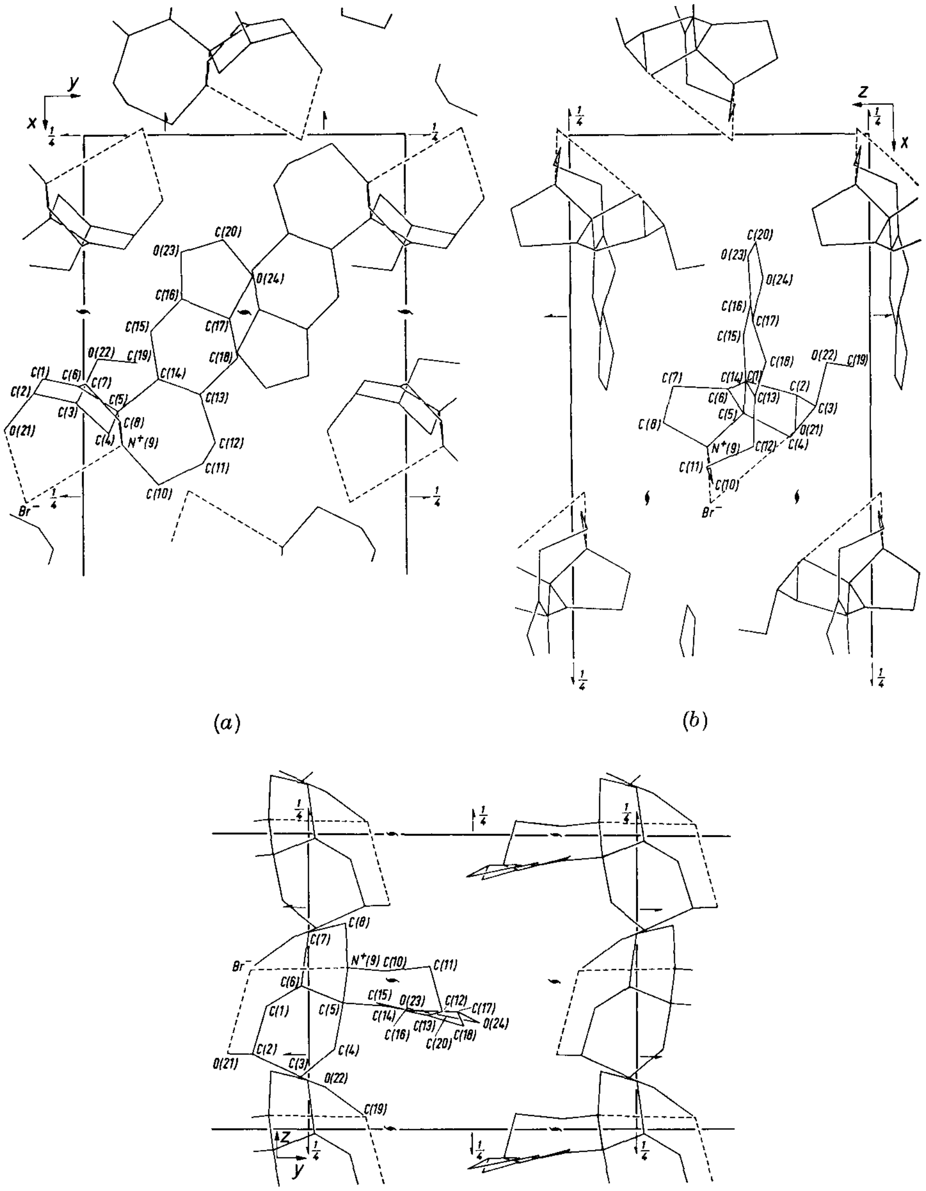
X—C_{arom}—Y	
C (5)—C(14)—C(13)	121.3°
C (5)—C(14)—C(15)	117.6
C(12)—C(13)—C(14)	127.0
C(12)—C(13)—C(18)	115.7
C(13)—C(14)—C(15)	120.9
C(13)—C(18)—C(17)	116.3
C(14)—C(13)—C(18)	117.2
C(14)—C(15)—C(16)	123.5
C(15)—C(16)—C(17)	113.6
C(15)—C(16)—O(23)	132.7
C(16)—C(17)—C(18)	119.6
C(17)—C(16)—O(23)	111.4
C(18)—C(17)—O(24)	129.4
Average value within	
(*a*) 5-membered ring	105
(*b*) 6-membered ring	119
(*c*) 7-membered ring	124

X—O—Y	
C (3)—O(22)—C(19)	112.7
C(16)—O(23)—C(20)	105.7
C(17)—O(24)—C(20)	108.4
Average value within	
5-membered ring	107

X—N^+—Y	
C(5)—N(9)—C (8)	106.3
C(5)—N(9)—C(10)	119.0
C(8)—N(9)—C(10)	117.7
Average value within	
(*a*) 5-membered ring	106
(*b*) 7-membered ring	119

ment indicated any shift from the present position and the correlation-matrix elements did not indicate any unduly large interaction of the parameters of C(17) with those of any other atom.

The cyclohexene ring (A) is in the same expected half-chair conformation as was found in erythraline and dihydro-β-erythroidine. The five C atoms forming the ethylenic system form a least-squares plane given by $19.253x - 3.480y + 1.914z - 7.835 = 0$, the maxi-



(a) (b)

(c)

Fig. 2. Projections of the structure of schelhammerine hydrobromide viewed (*a*) along the *c* axis, (*b*) along the *b* axis, (*c*) along the *a* axis but only the molecular ions lying between $x = 0$ and $x = {}^{1}/_{2}$ along with their H-bonded Br ions are shown. H bonds are represented by dashed lines

mum deviation from it being 0.06 Å. The 5-membered ring (*B*) is in the envelope (ideal C_s symmetry) conformation with C(5) at the apex and in accord with this distortion from planarity, the average angle at the sp^3 hybridized atoms C(5), C(7), C(8) and N(9) is 102 ° and that at the sp^2 hybridized C(6) is 107 °. Similar values to the latter have been found in a cyclopentanone ring, 113 ° (McEachan, McPhail and Sim, 1966) and in a pyrrolidone ring, 108 ° (Karle, Karle and Estlin, 1967). The least-squares plane through C(6), C(7), C(8) and N(9) is given by $-12.472x + 7.442y - 2.151z + 5.652 = 0$, the maximum deviation from this plane being 0.07 Å and the distance of the apical atom C(5) from it being 0.72 Å.

Since the 7-membered ring (*C*) contains an aromatic bond between C(13) and C(14), the atoms C(5), N(9), C(11) and C(12) are approximately coplanar as are necessarily C(12), C(13), C(14) and C(5). Atom C(10) determines the conformation of the ring and its position results in the sterically more favourable chair form.

Molecular packing

On seeking criteria upon which to propose a hydrogen bonding scheme, it was noted that values not significantly shorter than the sum of van der Waals radii and ranging between 3.2 and 3.6 Å have been found for both O—H···Br and N—H···Br hydrogen bonds (e.g. Nowacki and Bonsma, 1958; Hamilton *et al.*, 1962; Hanson, 1963; Mazumdar and Srinivasan, 1966, and Tamura *et al.*, 1966). Invariably, however, the valence angles at the O and N atoms are near tetrahedral. On the basis of this background data and of the values of the distances and especially of the angles given in Table 8, it is proposed that both N(9) and O(21) form hydrogen bonds with the bromide ion and that these bonds represent the major factor controlling the packing of the molecules. The non-polar aromatic and methylenedioxy rings are necessarily remotest from the Br ion and are arranged roughly parallel to each other and staggered down the *c* axis. These features are illustrated in Figs. 2*a*, *b* and *c* and in Table 9

Table 8. *Hydrogen-bond distances and angles*

N (9)···Br	3.27 Å	O(21)···Br	3.45 Å
C (5)—N(9)—Br	104.1 °	C (2)—O(21)—Br	111.4 °
C (8)—N(9)—Br	103.6		
C(10)—N(9)—Br	104.1		

Table 9. *Intermolecular distances less than* 4 Å

C(1)···C(18)	(vii)*	3.96 Å	C (8)···C(19)	(vi)	3.64 Å
C(1)···C(19)	(i)	3.61	C (8)···Br	(vii)	3.73
C(1)···O(22)	(i)	3.92	C(10)···C(20)	(ix)	3.88
C(2)···C(16)	(iv)	3.93	C(10)···O(21)	(x)	3.41
C(2)···C(18)	(vii)	3.84	C(10)···O(23)	(ix)	3.92
C(2)···O(23)	(iv)	3.39	C(10)···Br	(viii)	3.94
C(3)···O(23)	(iv)	3.69	C(11)···Br	(viii)	3.74
C(4)···C(12)	(v)	3.92	C(12)···O(21)	(vii)	3.57
C(4)···Br	(v)	3.98	C(12)···O(21)	(x)	3.94
C(6)···C(19)	(i)	3.91	C(15)···O(22)	(i)	3.61
C(6)···O(22)	(i)	3.76	C(18)···O(21)	(vii)	3.52
C(7)···C(16)	(i)	3.93	C(19)···O(24)	(xi)	3.48
C(7)···C(19)	(i)	3.96	C(20)···O(21)	(i)	3.96
C(7)···C(19)	(vi)	3.85	C(20)···Br	(iii)	3.87
C(7)···O(22)	(i)	3.40	O(21)···O(23)	(iv)	3.51
C(7)···O(23)	(i)	3.64	O(22)···O(23)	(iv)	3.95

* The Roman numerals in parenthesis refer to the following symmetry related positions:

(i)	$\frac{1}{2}-x$,	$-y$,	$\frac{1}{2}+z$	(vii)	x,	$1+y$,	z
(ii)	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	(viii)	$1-x$,	$\frac{1}{2}+y$,	$1\frac{1}{2}-z$
(iii)	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1-z$	(ix)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1-z$
(iv)	$\frac{1}{2}-x$,	$-y$,	$-\frac{1}{2}+z$	(x)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
(v)	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	(xi)	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$
(vi)	x,	y,	$1+z$				

are listed the intermolecular contacts less than 4 Å. It may be noted that the minimum C···O, O···O, C···C and C···Br^- distances in the structure are 3.39, 3.51, 3.61 and 3.73 Å respectively for which the corresponding sum of van der Waals radii are 3.2, 3.0, 3.4 and 3.65 Å respectively (BONDI, 1964; PAULING, 1960).

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