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The Crystal Structure of Capaurine Hydrobromide

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(*Received* 22 *July* 1968)

The structure of tetrahydroprotoberberine alkaloid capaurine, C$_{21}$H$_{25}$O$_5$N, has been determined by X-ray analysis of crystals of the hydrobromide which are orthorhombic with four molecules in a unit cell of dimensions, $a = 24.79$, $b = 8.08$ and $c = 10.32$ Å, space group $P2_12_12_1$. The structure was solved by the heavy atom method. The structural parameters were refined by the least-squares method, by use of 1539 independent reflexions. The final R index was 0.101. It has been found that the chemical formula given by Manske (1947) is essentially correct but the quinolizidine ring system in this molecule takes a rather unusual *cis* conformation. The absolute configuration, determined by the anomalous dispersion method, is compatible with that assigned chemically. The organic ions are arranged by N$^+$–H$\cdots$Br$^-$ (3.12 Å) and O–H$\cdots$Br$^-$ (3.39 Å) hydrogen bonds along the b axis.

Introduction

Capaurine, C$_{21}$H$_{25}$O$_5$N, and capaurimine, C$_{20}$H$_{23}$O$_5$N, tetrahydroprotoberberine alkaloids isolated from a number of *Corydalis* species, were given the formulae (I) and (II), respectively, through chemical degradation by Manske & Holmes (1945) and Manske (1947). One

I: R=CH$_3$
II: R=H

of the present authors synthesized the compound (I) (Kametani, Fukumoto, Yagi, Iida & Kikuchi, 1968), but there were some significant differences between the synthetic and natural substances both in nuclear magnetic resonance and infrared spectra. An X-ray analysis of capaurine hydrobromide has been undertaken in order to determine its three-dimensional molecular

structure and absolute configuration. A preliminary report including results of n.m.r., mass spectroscopy and the present X-ray work has already been published elsewhere (Kametani, Ihara, Fukumoto, Yagi, Shimanouchi & Sasada, 1968).

Experimental

Corpaverine was divided into its components, capaurine and sendaverine, by recrystallization and thin-layer chromatography in the form of hydrochloride (Kametani, Ohkubo, Noguchi & Manske, 1965; Kametani, Ohkubo & Noguchi, 1966). Capaurine hydrochloride was converted into the hydrobromide by treatment with potassium bromide in ethanol solution. Crystals of capaurine hydrobromide were grown from methanol solution as pale yellow plates.

The crystallographic and physical data obtained are: Capaurine hydrobromide, C$_{21}$H$_{26}$O$_5$NBr; m.p. 198–199°C, [α_D]-423° ($c = 0.40$ in methanol). Orthorhombic, $a = 24.79 \pm 0.03$ Å, $b = 8.08 \pm 0.01$ Å, $c = 10.32 \pm 0.03$ Å. Space group, $P2_12_12_1$. Four molecules per unit cell. Volume of the unit cell, 2067 Å^3. Density (by flotation), 1.458 g.cm^{-3}; density (calculated), 1.453 g.cm^{-3}. Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu = 32.62$ cm^{-1}. Total number of electrons per unit cell, $F(000) = 936$.

Equi-inclination Weissenberg photographs were taken at room temperature for the 0–6 layers about the b axis and the 0–8 layers about the c axis, with use of Cu $K\alpha$ radiation. The cross-sections of the crystals used, perpendicular to the rotation axes, were 0.004×0.018 cm for the b axis and 0.004×0.020 cm for the c axis.

Intensities were estimated by visual comparison with a standard scale prepared with the same crystal. The multiple-film technique was used to correlate strong and weak reflexions whose relative intensities ranged from 1 to 2150. Reflexions from 1539 planes were observed out of 2700 possible hkl's in the Cu $K\alpha$ sphere. The corrections for Lorentz and polarization factors were made in the usual way, but no absorption correction was applied.

Structure determination

The structure was solved by the heavy atom method. The positional parameters for the bromine atom were derived from three Harker sections, $P(\frac{1}{2}, v, w)$, $P(u, \frac{1}{2}, w)$ and $P(u, v, \frac{1}{2})$. In the first three-dimensional Fourier synthesis based on the bromine atom only, all the atoms in the molecule were recognized as resolved peaks and it was found that the main skeleton of the molecule is cis-dibenzo[a,g]quinolizidine. However, the peaks

for two of four methoxy carbons were low and a few additional peaks of considerable height were found in the map. The structure factors which were calculated, including 26 atoms with an isotropic temperature factor $B = 3.0$ Å², resulted in the R index of 0.21. Successive Fourier syntheses gave the positions for all atoms without any ambiguity. Further refinement of the parameters was made by the block-diagonal matrix least-squares method, by use of 1539 observed reflexions. The anisotropic temperature factors, in the form of

$$\exp\left\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\right\},$$

were applied for the bromine atom, while the thermal motions of the light atoms were assumed to be isotropic. After four cycles of least-squares refinement, the R index was reduced to 0.101 for the observed reflexions. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and temperature factors are given in Table 1 and their standard deviations in Table 2. Observed and calculated structure factors are listed in Table 3. The final three-dimensional electron density distribution, calculated with phases based on these parameters, is shown in Fig. 1.

The computation was done on a HITAC 5020 computer in the University of Tokyo with programs written by T. Ashida.

Table 1. *Final atomic coordinates and temperature factors*

The anisotropic temperature factors are expressed in the form

$$\exp\left\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\right\}.$$

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0.3320	0.8938	0.6980	0.00101	0.01162	0.00858	0.00014	−0.00086	−0.00015

	x/a	y/b	z/c	B (Å²)
N(7)	0.2497	0.7524	0.4979	2.76
O(1)	0.2980	0.2546	0.5518	2.60
O(2)	0.3963	0.1527	0.4602	3.22
O(3)	0.4553	0.3481	0.2962	3.04
O(4)	0.0998	0.9735	0.5769	2.77
O(5)	0.0076	0.8650	0.4614	3.56
C(1)	0.3259	0.3531	0.4714	2.89
C(2)	0.3762	0.3054	0.4196	2.58
C(3)	0.4058	0.4115	0.3358	2.39
C(4)	0.3855	0.5651	0.3009	3.83
C(5)	0.3155	0.7926	0.3278	3.89
C(6)	0.2577	0.8298	0.3725	3.40
C(8)	0.1977	0.8137	0.5634	3.03
C(9)	0.1017	0.8303	0.5049	2.87
C(10)	0.0543	0.7670	0.4460	2.03
C(11)	0.0549	0.6228	0.3723	2.94
C(12)	0.1052	0.5286	0.3609	2.58
C(13)	0.2041	0.4909	0.4070	3.91
C(14)	0.2500	0.5588	0.4935	1.81
C(15)	0.3049	0.5103	0.4351	2.08
C(16)	0.3346	0.6185	0.3532	3.19
C(17)	0.1494	0.7336	0.4986	2.43
C(18)	0.1507	0.5860	0.4265	2.49
C(19)	0.4359	0.1702	0.5667	3.55
C(20)	0.4888	0.4576	0.2232	2.81
C(21)	0.0862	1.1281	0.5064	3.04
C(22)	−0.0429	0.8070	0.4028	3.58

Absolute configuration

Even if the errors due to the neglect of the correction for absorption were taken into account, significantly different intensities were found for thirteen sets of Bijvoet pairs in photographs around the c axis. For such pairs, $|F(hkl)|$ and $|F(h\bar{k}l)|$ were calculated using $\Delta f'$ and $\Delta f''$ for the bromine atom on the basis of the

Table 2. *Estimated standard deviations*

[$\sigma(x)$, $\sigma(y)$ and $\sigma(z)$, in Å, $\sigma(B)$ in Å^2]

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Br	0·0020	0·0022	0·0022	0·00003	0·00029	0·00019	0·00022	0·00017	0·00058

|	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
N(7)	0·0164	0·0184	0·0177	0·32
O(1)	0·0124	0·0138	0·0130	0·26
O(2)	0·0132	0·0139	0·0138	0·29
O(3)	0·0121	0·0127	0·0149	0·26
O(4)	0·0129	0·0135	0·0134	0·27
O(5)	0·0133	0·0151	0·0138	0·29
C(1)	0·0206	0·0196	0·0193	0·40
C(2)	0·0191	0·0208	0·0202	0·39
C(3)	0·0169	0·0204	0·0175	0·36
C(4)	0·0204	0·0217	0·0249	0·45
C(5)	0·0207	0·0226	0·0233	0·50
C(6)	0·0212	0·0224	0·0222	0·46
C(8)	0·0201	0·0220	0·0214	0·42
C(9)	0·0201	0·0207	0·0208	0·41
C(10)	0·0176	0·0192	0·0191	0·36
C(11)	0·0182	0·0228	0·0199	0·39
C(12)	0·0190	0·0201	0·0198	0·39
C(13)	0·0222	0·0248	0·0238	0·49
C(14)	0·0174	0·0171	0·0179	0·35
C(15)	0·0179	0·0195	0·0187	0·35
C(16)	0·0210	0·0222	0·0185	0·38
C(17)	0·0182	0·0211	0·0210	0·39
C(18)	0·0170	0·0216	0·0189	0·38
C(19)	0·0213	0·0232	0·0232	0·48
C(20)	0·0189	0·0199	0·0207	0·41
C(21)	0·0190	0·0224	0·0203	0·41
C(22)	0·0220	0·0234	0·0237	0·46
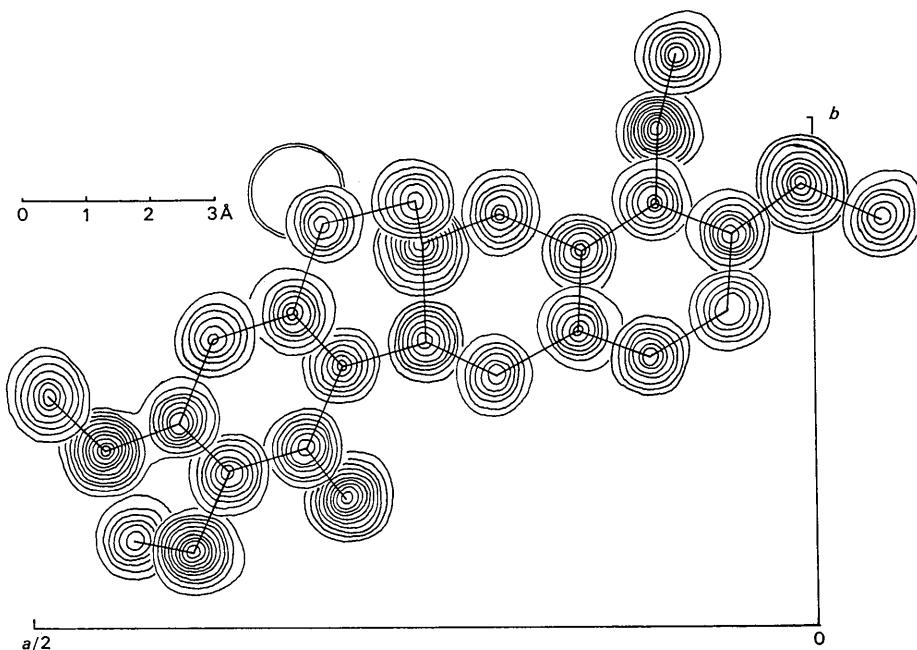
Fig. 1. Composite electron density diagram of sections parallel to (001). The contours are at intervals of 1·0 e.Å^{-3} starting with 1·0 e.Å^{-3}. The contours of the bromine atom are omitted.

Table 3. *Observed and calculated structure factors*

```
L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FC  FC

H,K= 0  0      3   0   1      6  57  49      H,K= 11  1      2  40  42      0  39  25      5  36  37     11  17  20      8   0   3
2 111 117      4  48  50      7   0   5      0  65  57      3   0  14      1  62  60      6  14  15     H,K=  5  3      9   0  12
4  59  58      5  19  19      8  24  24      1  44  36      4   0   7      2  52  45      7  20  17      0   0  12     10  17  24
6  40  33      6  55  66      9  18  20      2  89  80      5  15  15      3  14  13      8  20   9      1  58  56     H,K= 15  3
8  55  68      H,K= 13  0     10  25  17      3  76  72      6  19  20      4  70  70      H,K= 20  2      2  75  76      1  20  13
10  27  31     1  53  48      H,K=  1  1      4  23  19      7  17  17      5  12   9      0   0   9      3  50  51      2  26  27
H,K= 1  0      2  28  28      1  38  45      5  38  38      H,K= 24  1      6  25  25      1  29  30      4   5   5      3  14  12
2  52  47      3   0   4      2  86 101      6  23  18      0   0   2      7   0   5      2  35  37      5  24  26      4  52  56
3  51  37      4  60  59      3  65  66      7  35  32      1  12  10      8  16  13      3  39  37      6  45  48      5  19  14
4  52  47      5  25  28      4  34  29      8  27  27      2  12  13      H,K=  9  2      4  42  43      7  28  26      6  34  32
5   0   4      6  37  40      5  24  18      H,K= 12  1      3  16  19      0 142 138      5  15  15      8  26  21      7  25  25
6  65  63      7  33  33      6  42  38      0   0   3      4  28  31      1  38  31      6  27  30      9   0  18      H,K= 16  3
7   0   3      8  43  49      7  26  19      1  57  48      5  58  48      2  58  48      H,K= 21  2     10  23  15      0  40  36
8  29  33      9  26  28      8  30  28      2  40  34      6  21  23      3  44  38      0  33  36     11  19  23      1  36  31
H,K= 2  0      H,K= 14  0     9  28  28      3  39  39      H,K= 25  1      4  60  60      1  12  14      H,K=  6  3      2  50  54
1  30  29      0 112 108     10  24  19      4  52  50      1  17  24      5   0   4      2  23  20      0  12  10      3  26  25
2  21  15      1  14  13      H,K=  2  1      5  52  52      2  12  18      6  28  30      3  12  13      1  54  51      4  26  24
3 118 138      2  36  32      0  69  73      6  30  29      3  16  17      7   0  14      4  22  19      2  56  51      5  10   7
4  10   1      3  68  72      1  86  92      7  20  20      4  16  12      8  34  38      5  12  11      3  66  63      6  19  10
5  76  80      4   0  13      2 135 167     H,K= 13  1      H,K= 26  1      9   0  13      H,K= 22  2      4  25  26      7  20  18
6  32  29      5  25  29      3  97 107      0   0  13      0   0   3     10  29  30      0   0   5      5  63  64      8  22  24
7  48  58      6  31  34      4  19  19      1  47  46      1  26  28      H,K= 10  2      1  29  27      6  28  22      9  17  13
H,K= 3  0      H,K= 15  0     5  54  56      2  26  22      2  16  14      0  61  51      2  30  33      7  38  39      H,K= 17  3
1  74  81      1  42  43      6  54  54      3  30  25      H,K=  0  2      1  38  33      3  19  21      8  16  16      0  18  13
2  32  33      2  24  22      7  43  39      4  10  10      0  37  29      2  46  42      4  36  38      9   0   2      1  37  32
3 133 141      3  68  67      8  21  13      5  26  27      1  69  80      3  29  25      5   0   4     10  20  15      2  21  13
4  31  29      4   0   7      9  25  30      6  25  22      2  93 100      4  69  67      6  21  13      H,K=  7  3      3  26  24
5  19  15      5  18  19      H,K=  3  1      7  38  43      3  42  39      5  21  19      7  19  17      0   9   9      4  29  31
6  26  27      H,K= 16  0     0  13   9      8  27  29      4  42  33      6  31  30      H,K= 23  2      1  71  75      5   0   9
7  13  14      0   0   7      1  46  42      H,K= 14  1      5  11  13      7  20  19      0  32  40      2  37  31      6  21  16
8   0  15      1  52  44      2 109 111      0  69  66      6  22  13      8  26  25      1   0   7      3  57  52      7  21  22
9  48  47      2  36  30      3  55  54      1  54  53      7  31  26      H,K= 11  2      2   0  16      4  12  11      H,K= 18  3
H,K= 4  0      3  51  54      4  65  69      2  45  38      H,K=  8  2      0  12  17      3  24  25      5  24  22      0   0   7
0  76  94      4   0   4      5  52  56      3  42  41      8  14  14      1  24  12      4  22  24      6  35  34      1  25  22
1  82  88      5  56  67      6  35  29      4  40  39      10   0   7      2  66  58      5   0  15      7  36  32      2  26  23
2  31  32      6  19  15      7  34  32      5  26  24      H,K=  1  2      3  65  63      6  15  11      8  34  39      3  48  49
3  51  56      7  29  32      8  23  21      6  31  31      0  61  55      4  13  12      7  18  18      9  24  26      4  24  24
4  19  13      8   0   8      9   0   4      7  25  16      1  31  28      5  53  54      H,K= 24  2      H,K=  8  3      5  42  43
5  67  76      9  26  17     10   0   4      8  25  24      2  92 103      6  24  22      0   0   1      0  56  55      6   0   6
6  19  16      H,K= 17  0     H,K=  4  1      H,K= 15  1      3  77  83      7  32  29      1  25  27      1  29  30      7  13  11
7  18  15      1  28  29      0 102 107      0   0  11      4  44  44      8  19  13      2   0   6      2  68  64      H,K= 19  3
8  31  31      2  17  22      1  93  89      1  10  10      5  60  66      H,K= 12  2      3  24  20      3  33  31      0  15  14
H,K= 5  0      3  23  19      2 136 143      2  47  41      6  23  24      0  45  39      4  14  10      4  14   9      1  27  31
1  65  65      4  23  23      3  52  56      3  31  30      7  43  41      1  79  78      H,K= 25  2      5  25  27      2  36  33
2  32  37      5   0   0      4  35  34      4  22  22      8   0  10      2  23  21      0   0  12      6  36  37      3  25  25
3  30  23      6  26  20      5  26  28      5  42  43      9   0   3      3  49  45      1  26  17      7  37  33      4  17  11
4  95 104      H,K= 18  0     6  39  37      6  41  46     10  24  21      4  11   9      2   0  11      8  20  20      5   0   6
5  45  40      0  65  68      7  30  24      7  25  22      H,K=  2  2      5  15  14      3  20  24      9   0   6      6   0   6
6  45  49      1  27  24      8  27  29      8  17  10      0   8   5      6  22  18      4   0   7     10  22  18      7  12  11
7  35  35      2  60  65      H,K=  5  1      H,K= 16  1      1  86  90      7  20  18      5  21  24      H,K=  9  3      8   0  12
8  20  14      3   0   4      0  74  65      0  52  45      2   8   6      8  24  21      H,K= 26  2      0  53  44      9  13  16
9  30  25      4   0   1      1  53  47      1  49  44      3   0   3      9  31  39      0   0   5      1  37  27      H,K= 20  3
H,K= 6  0      5   0   7      2  95  88      2  38  37      4  75  83      H,K= 13  2      1  22  19      2  50  43      0  36  38
0  65  64      6   0  11      3  64  65      3  38  38      5  56  56      0  45  40      2  12  15      3  36  31      1  24  19
1  45  34      7   0   1      4  52  50      4  23  23      6  56  55      1  39  32      3  20  14      4  67  71      2  41  39
2 129 150      8  23  29      5  44  44      5   0   6      7  34  32      2  31  29      4  18  18      5  23  22      3  24  23
3   0   3      H,K= 19  0     6  27  28      6   0   8      8  22  15      3  54  54      H,K= 27  2      6  43  44      4  15  12
4  28  22      1  32  29      7  36  35      7  24  25      9  27  26      4  12  12      2  20  22      7  15  10      5  24  27
5  16  13      2  22  26      8  26  24      8  18  18      H,K=  3  2      5  43  40      3  19   8      8  36  36      6  19  16
6   7   3      3  18  16      9   0  18      H,K= 17  1      0 112 124      6  26  19      H,K= 28  2      9   0   7      7  13   8
7   0   3      4  54  61     10  30  29      0  43  40      1  81  70      7  24  24      2  18  13     10  16   5      8  19  11
8  53  58      5   0   3      H,K=  6  1      1  45  43      2  32  30      8  19  19      H,K=  0  3      H,K= 10  5      9   0   6
H,K= 7  0      6  29  31      0  18  14      2  21  23      3   0   3      H,K= 14  2      1  38  39      0  69  66      0  30  27
1  24  29      7   0   8      1  45  38      3  29  29      4  61  64      0   0  11      2  14   9      1  37  31      1   0   8
2  74  62      8  19  19      2  37  30      4  25  25      5  21  18      1  39  37      3  86  86      2  70  64      2  27  20
3  39  39      H,K= 20  0     3  69  63      5  23  23      6  31  35      2  48  50      4  57  66      3  54  49      3  19  13
4  68  72      0  50  42      4  48  52      6  27  28      7   0   1      3  20  18      5  26  34      4  18  19      4  20  23
5   0   2      1   0   5      5  52  58      7  24  23      8  39  42      4  42  40      6  31  30      5  17  13      5  21  24
6  42  44      2  60  67      6  40  39      8  19  19      9   0   9      5  24  19      7  51  56      6  24  26      6  21  25
7  32  32      3  16  16      7  37  38      H,K= 18  1     10  29  26      6  38  37      8  16  15      7  13  10      7  13   8
8  21  18      4   0   0      8  22  23      0  26  28      H,K=  4  2      7  24  20      H,K=  1  3      8  23  19      H,K= 22  3
H,K= 8  0      5  35  34      H,K=  7  1      1  25  21      0  48  44      8  12  14      0  99  91      9   0   4      0  40  46
0  84  68      6  15   5      0  25  21      2  36  34      1  98  97      H,K= 15  2      1  70  76     10  21  17      1  27  28
1  47  32      H,K= 21  0     1  60  54      3  42  40      2  90  87      0  76  72      2  37  36      H,K= 11  3      2  29  34
2  55  55      1  48  54      2  99  99      4  49  55      3  23  15      1  16  19      3  42  37      0   0   5      3  18  17
3  79  83      2   0  13      3  67  67      5  30  32      4  41  31      2  51  51      4  37  35      1  50  45      4   0   1
4  28  24      3  27  27      4  36  30      6  22  20      5  15  16      3  15   9      5  16  12      2  50  42      5  17  14
5  52  52      4   0   0      5  40  39      7  18  16      6  29  29      4  20  17      6  26  25      3  52  48      H,K= 23  3
6  16  13      5   0   1      6  47  52      H,K= 19  1      7  27  28      5  19  14      7  41  40      4  27  24      0   0   6
7  27  23      6  23  23      7  27  25      0  52  47      8  35  31      6  24  17      8  16  14      5   0   7      1  24  21
8  38  48      7  23  23      8  20  22      1  22  24      9  21  15      7  22  21      9  27  26      6  35  32      2  21  12
9  17  20      8  28  23      9  28  23      2  30  31      H,K=  5  2      8  31  33      H,K=  2  3      7  39  39      3  15  15
H,K= 9  0      H,K= 22  0    10  24  21      3  20  19      0  62  59      H,K= 16  2      0  84  82      8  16  11      4  24  26
1 120 122      0  31  26      H,K=  8  1      4  18  14      1  51  48      0  30  28      1  57  54      9  23  24      5   0   6
2  30  22      1  45  39      0  72  63      5   0   7      2  61  51      1  32  28      2  39  37     10  19  12      6  16  16
3   0   9      2   0   5      1 102  96      6  16  13      3  30  30      2  24  22      3  28  29      H,K= 12  3      H,K= 24  3
4  35  32      3  25  29      2  71  61      H,K= 20  1      4  37  36      3  13  11      4  46  44      0  14  11      0   0  10
5  31  22      4   0   4      3  66  68      0   0   3      5  54  53      4  46  44      5  28  24      1  17  11      1  21  13
6  29  24      5  26  32      4  17  16      1  43  42      6   0   9      5  22  18      6  30  27      2  22  16      2  23  16
7  27  22      6   0   8      5  21  17      2  35  37      7  26  23      6  33  35      7  28  25      3  60  55      3  18  22
8   0   5      7  20  22      6  39  38      3  40  41      8  21  22      7  22  19      8  30  26      4  21  20      4   0  13
9  42  48      H,K= 23  0     7  37  35      4  25  25      9  21  20      H,K= 17  2      9  19  19      5  41  43      5  23  29
H,K= 10  0     1  20  21      8  23  27      5  19  16     10  20  20      0  31  30     10  32  25      6  21  18      6  14  14
0   0   3      2  26  25      9  22  19      6  25  22      H,K=  6  2      1  15  11      H,K=  3  3      H,K= 13  3      H,K= 25  3
1  42  34      3  16  14      H,K=  9  1      7  19  22      0  27  20      2  34  35      0  31  27      0   0   4      0   0   4
2  54  62      4  21  23      0  47  39      8  19  12      1 102 102      3  38  32      1  25  20      0  60  50      1  28  33
3  69  67      5  15   4      1  48  42      H,K= 21  1      2  40  30      4  21  14      2  68  66      1  63  63      H,K= 26  3
4   0   2      6  18  25      2  53  46      0   0  17      3  53  49      5  47  52      3  34  28      2  34  28      0  25  29
5  64  68      H,K= 24  0     3  43  41      1  27  25      4  28  20      6  19  21      4  60  62      3  41  38      1   0   8
6  29  27      0  38  43      4  56  58      2   0  15      5  44  40      7  17  20      5  47  47      4  23  20      2   0   9
7  26  26      1   0   9      5  15  14      3  28  27      6   7   8      H,K= 18  2      6  63  66      5  18  10      3  15  14
H,K= 11  0     2  25  30      6  42  38      4  23  22      7  27  21      0  18  18      7  31  31      6  26  29      4   0   6
1  14  18      H,K= 25  0     7  37  39      5  29  30      8   0   9      1  60  61      8  14  19      7  15  15      H,K= 27  3
2  36  35      4  27  31      8  20  24      6  15  16      9  34  44      2  25  20      9  24  27      8  21  11      3  13  12
3  71  72      5   0   2      H,K= 10  1      7  19  23      H,K=  7  2      3  28  29      H,K=  4  3      9  24  27      H,K=  0  4
4  69  67      6  18  23      0  74  69      H,K= 22  1      2  38  29      4  12  14      0 115 121      H,K= 14  3      1  75  77
5  19  14      H,K= 26  0     1 101  91      0  54  56      3  12  10      5  25  25      1  17  16     10  16  15      2  68  74
6  44  43      0  29  35      2  59  43      1  34  39      4  23  18      6  18  15      2  55  57      H,K=  4  4      3  22  16
7   0   8      1  24  20      3  22  17      2  16  14      4  14   9      7  14  20      3  58  57      0  19  20      4  19  16
8  19  19      H,K= 27  0     4  44  39      3   0   9      H,K= 19  2      0  23  20      5  17  16      4  23  20      5   0   0
9  24  19      1  89 105      5  15  14      4  18  16      5 103  105      1  26  22      6  21  15      5  15  15      6  41  39
H,K= 12  0     2 164 183      6  36  37      5  21  14      6  22  21      R,K= 19  2      7  30  28      H,K= 14  3      7  16  11
0 100 103      3  67  58      7  26  24      H,K= 23  1      7   0   9      1  26  22      8  27  25      6  33  33      8  21  20
1  12  16      4  50  51      8  20  20      0   0  14      8  29  30      2   0   6      9   0   2      7  17  15      9  23  24
2  43  36      5  57  52      9  17  17      1  21  19      H,K=  8  2      4   0   9     10  20  17
```

Table 3 (cont.)

```
 L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC      L  FO  FC

H,K= 1  4       7  19  19      5  35  36      6  28  25      1  55  56      5  23  30      1  30  31     H,K= 19  6       6  19  24
 0  49  45      8   0   7      6  20  17      7  34  35      2  48  45     H,K= 22  5       2  21  21      4  18  15     H,K= 10  7
 1  41  38      9  19  11      7  26  26      8  20  21      3  48  45      1  26  26      3  25  21      5  18  20      0  32  35
 2  18  21     H,K= 9   4     H,K= 17  4     H,K= 2   5      4   0  11      2   0   1      4  24  31     H,K= 20  6       1  35  35
 3  23  24      0  27  28      0   0   2      0  13   9      5  25  19      3  20  16      5  18  18      1  21  19      2  22  21
 4  58  56      1  60  58      1  36  38      1  63  71      6  17  13     H,K= 23  5       6  19  13      2  16  20      3   0   9
 5  23  15      2  27  21      2   0   9      2  19  14      7  24  20      2  22  14      7  19  12      3  17  15      4   0   9
 6  32  29      3  30  26      3  22  15      3  46  44     H,K= 11  5     H,K= 24  5     H,K= 9   6       4  17  13      5  19  17
 7  18  14      4  17  14      4  30  31      4  39  37      1   0   4      4  13  21      0  54  56     H,K= 21  6       6  17  11
 8  23  22      5  19  17      5   0   9      5  22  19      2  46  42     H,K= 0   6       1  40  41      4  11  10     H,K= 11  7
 9  23  18      6  17  16      6  19  17      6  23  20      3  22  17      0  25  18      2  21  21     H,K= 22  6       1  27  33
H,K= 2   4      7  18  16      7  16  13      7  32  37      4  33  30      1  37  45      3  27  27      4  14  19      2   0  15
 0  34  22      8  21  25     H,K= 18  4     H,K= 3   5      5  28  23      2  31  32      4  21  17     H,K= 0   7       3  12   9
 1  51  47      9  19  21      0  66  64      0  18  12      6  29  29      3  25  23      5  14  11      2  10   8       4  18  17
 2  64  49     H,K= 10  4      1  29  27      1  32  29      7  13  18      4  17  18      6  12   8       3  24  27      5   0  11
 3  58  62      0  49  43      2  27  25      2   0   4      8  21  17      5   0  12      7  18  16      4   0   0       6  16  18
 4  41  34      1  41  39      3   0   6      3  29  29     H,K= 12  5      6  23  26     H,K= 10  6       5  28  33     H,K= 12  7
 5  49  50      2  50  48      4  11  13      4   9   9      1  31  26     H,K= 1   6       0  40  38      6   0   2       3  19  20
 6  31  26      3  37  36      5   0   2      5  38  42      2  51  48      0  34  26      1  25  24      7  19  18      4   0   3
 7  27  24      4  40  38      6  15  15      6  21  15      3  38  36      1  22  20      2  33  31     H,K= 1   7       5  20  25
 8  20  20      5  41  39      7   0  11      7  42  47      4  37  43      2  28  28      3  36  32      1  30  32     H,K= 13  7
H,K= 3   4      6  27  26     H,K= 19  4     H,K= 4   5      5   0   3      3  23  21      4  44  43      2  22  22      1  32  36
 0   0   8      7  29  25      0  27  26      1  64  66      6  31  32      4  17  16      5  16  19      3  30  34      2   0  16
 1  62  64      8  25  24      1   0  10      2  20  19      7  13  13      5  39  42      6  22  21      4   0  13      3  12  11
 2  40  34     H,K= 11  4      2  24  22      3  30  28     H,K= 13  5      6  23  20      7  17  10      5  21  20     H,K= 14  7
 3  54  56      0  41  29      3   0   9      4  35  31      0  30  31      7  15  15     H,K= 11  6       6  19  21      6  19  24
 4  13   8      1  44  39      4  30  30      5  25  22      1  18  13     H,K= 2   6       0  17   9     H,K= 2   7     H,K= 15  7
 5  14  12      2  27  29      5   0  15      6  26  26      2  39  38      0  37  35      1  17  16      0  49  47      4  20  25
 6  15  11      3  37  32      6  23  24      7  24  23      3  27  27      1  23  20      2   0   3      1   9   4     H,K= 16  7
 7  23  18      4  31  28     H,K= 20  4     H,K= 5   5      4  15  16      2  32  36      3   0   5      2  24  24      0  27  34
 8  14  17      5  26  26      0  34  39      0  55  58      5  24  19      3  41  40      4  39  42      3  16  19     H,K= 17  7
 9  37  44      6  49  52      1  21  18      1  19  15     H,K= 14  5      4  30  30      5  23  22      4   0   9      3  14  17
H,K= 4   4      7  26  23      2   0   4      2  37  35      0  27  24      5  27  27      6   0   6      5  24  23     H,K= 18  7
 0  62  50      8   0   6      3  20  21      3  29  27      1  48  49      6  22  21      7  17  15     H,K= 3   7       3  17  19
 1  34  30      9  24  22      4  21  20      4   0  13      2  33  29      7  18  13     H,K= 12  6       1   9   9     H,K= 0   8
 2  38  33     H,K= 12  4      5  22  20      5  30  30      3  17  16     H,K= 3   6       0  42  40      2  19  24      1  25  26
 3  45  43      0  86  84      6  13  12      6  19  19      4  28  27      0  35  38      1  41  41      3   0   7      2   0   1
 4  30  30      1  15  14      7  17  14      7  17  13      5   0   8      1  35  39      2  27  27      4  31  34     H,K= 1   8
 5  45  49      2  20  17     H,K= 21  4      8  21  18      6  22  18      2  30  33      3  29  32      5   0   6      0  24  21
 6  27  24      3  24  21      0   0   8     H,K= 6   5      7  20  18      3  23  21      4  14   8      6  24  25      1   0  15
 7   0   7      4   0   8      1  29  32      0   0   5     H,K= 15  5      4  25  26      5  13   8     H,K= 4   7       2   0   9
 8  19  14      5   0   7      2  26  19      1  40  34      0   0   2      5  21  19     H,K= 13  6       1   9   9      3  19  22
 9  26  32      6  14  13      3  22  24      2  41  41      1  23  18      6   0   2      0   0   0      2  41  40      4  18  17
H,K= 5   4      7  20  13      4   0   3      3  17  14      2  22   7      7  22  19      1  19  16      3  20  21     H,K= 2   8
 0   0  10      8  28  31      5   0   6      4  48  52      3  26  26     H,K= 4   6       2  23  16      4   0   2      4  15  18
 1  46  40     H,K= 13  4      6   0   9      5  16  15      4   0   6      0  14  13      3  22  23      5   0  11     H,K= 3   8
 2  49  45      0  26  22      7  14  15      6  36  35      5  29  36      1  21  19      4  15  13      6  13  12      0  36  43
 3  39  34      1  29  29     H,K= 22  4      7   0   7      6  19  18      2  43  44      5  20  26      7  15  17     H,K= 4   8
 4  61  61      2  23  26      0   0   5      8  22  19      7  22  25      3  24  24      6  19  18     H,K= 5   7       4  20  23
 5  42  44      3  26  24      1   0   9     H,K= 7   5     H,K= 16  5      4  47  48      7  16  13      1  34  37     H,K= 5   8
 6  37  34      4  52  56      2  26  23      0  63  64      0   0   8      5  22  18     H,K= 14  6       2   0  13      3  22  28
 7  24  24      5  15  13      3  24  24      1  22  15      1  44  45      6  21  20      0   0   1      3  22  23      4  12   8
 8  27  25      6  18  20      4   0   9      2  39  36      2  25  19      7  23  30      1  16  16      4  19  20     H,K= 6   8
H,K= 6   4      7  28  30     H,K= 23  4      3  23  19     H,K= 5   6       2  28  28      5   0   7      0  29  26
 0  77  74      8  24  23      0  26  21      4  22  18      0   0   8      3  21  22      6  18  14     H,K= 7   8
 1  41  33     H,K= 14  4      1  41  41      5  14  12      1  25  29      4  19  18     H,K= 6   7       3  18  17
 2  47  50      0  37  34      2  19  21      6   0  14      2  21  20      5   0  17      1  27  26      4  17  20
 3  29  21      1  43  41      3  16  16      7  18  13      3  22  20      6  18  16      2   0  15     H,K= 8   8
 4  14  13      2  29  30      4   0  17     H,K= 17  5      4  10  10     H,K= 15  6       3  33  34      0  25  25
 5  13   9      3  44  43      5   0  10      0  29  22      5  24  25      0  32  33      4   0  11      1   0  12
 6  16   3      4  30  31      6  12  14      1  26  17      6  21  21      1  23  22      5  27  32      2   0  12
 7  26  26      5  28  24     H,K= 24  4      2  30  30      7  15  17      2  24  20     H,K= 7   7       3  17  20
 8  29  29      6  18  10      0  21  32      3  23  18     H,K= 6   6       3   0  14      0  43  37      4  19  22
H,K= 7   4      7  19  12      1   0  15      4   0  13      0  40  39      4  14  14      1  22  24      5   0  12
 1  46  41     H,K= 15  4      2  23  26      5  21  21      1  43  50      5  18   7      2   0   7      6  15  17
 2  41  42      0  29  23     H,K= 26  4      6  17  14      2  27  27     H,K= 16  6       3  20  21     H,K= 10  8
 3  20  18      1  32  36      3  20  24      5   0  12      3  31  31      0   0  11      4  18  20      2  24  19
 4  31  31      2  23  17     H,K= 0   5     H,K= 18  5      4  10   9      1   0   4      5   0   7     H,K= 11  8
 5  28  26      3  31  25      1  45  36      2  29  32      5  16  14      2  21  22      6  19  17      0  24  23
 6  41  38      4   0   5      2  48  45      3  12  14      6   0   0      3  16  20      7  15  13     H,K= 13  8
 7  18  22      5   0  12      3  27  28     H,K= 9   5     H,K= 7   6       7  15  10     H,K= 8   7       3  16  24
 8  20  19      6  18  18      4  74  84      1   0   2      5   0  18      4  21  23      2  45  48     H,K= 14  8
 9  23  23      7   0  15      5  22  21      2  26  25      0  17   9     H,K= 17  6       3  29  31      3  17  23
H,K= 8   4      8   0   4      6  40  31      3  41  35      1  24  22      2  19  14      4   0  11     H,K= 15  8
 0  42  35      9  22  28     H,K= 1   5      4  30  32      2  99  31      3  24  26      5   0  16      3  13  16
 1  32  28     H,K= 16  4      0  41  41      5   0  12      3  13  13      4  21  22      6  17  15
 2  60  55      0  32  30      1  30  27      6  19  15     H,K= 8   6       5  25  26     H,K= 9   7
 3  38  33      1  44  43      2  43  44      7  21  18      4  20  16      6  27  30      2  25  25
 4  33  31      2  22  17      3  17  17      8  14   4     H,K= 9   6       7  24  28      3   0  11
 5  58  65      3  23  24      4  20  18     H,K= 10  5      3  24  28      3  11   6      4  20  22
 6  29  29      4  30  27      5  26  23      0   0  11     H,K= 8   6                      5   0   9
```

Table 4. The determination of the absolute configuration

Indices	Observed I(hkl) I(hkl)	Calculated |F(hkl)| |F(hkl)|
1 1 1	<	42 < 46
11 1 1	>	38 > 34
25 1 1	<	23 < 24
25 3 1	>	33 > 31
5 7 1	<	35 < 37
10 7 1	<	34 < 35
2 2 2	<	3 < 7
3 2 2	>	30 > 26
7 2 2	>	19 > 16
9 2 2	>	48 > 44
12 5 2	<	46 < 48
1 1 4	>	30 > 27
2 5 5	>	20 > 19

model in the right-handed coordinate system. As shown in Table 4, the inequality relationships for observed intensities in all pairs are in good agreement with those calculated for the corresponding pairs, suggesting that the model used in these calculations has a correct absolute configuration.

The absolute structure thus determined is shown in Fig. 2. The asymmetric centre at C(14) has the S-configuration.

Results and discussion

Conformation

As mentioned in the preceding section, it has been established that capaurine hydrobromide is cis-1-hydroxy-2,3,9,10-tetramethoxy-5,6,13,13a-tetrahydro-8H-

dibenzo[a,g]quinolizine hydrobromide. This structure corresponds to (I) given by Manske & Holmes (1945), except in the steric conformation.

In the quinolizidine ring system, the *BC* ring junction is *cis*-fused and both the component rings are in the half chair conformation as seen from Figs. 3 and 4. Natural tetrahydroprotoberberines containing the *cis*-quinolizidine skeleton have rarely been found.

Uskoković, Bruderer, von Planta, Williams & Brossi (1964) have confirmed the existence of one *trans* and two *cis* forms of quinolizidine skeleton in large molecules, using Bohlmann band and n.m.r. spectra. The

one *trans* (III) and two possible *cis* forms (IV) and (V) are shown in Fig. 5. The present molecule in the crystal takes the conformation (IV). The observed O(1)··· C(13) distance is 3·36 Å. If the capaurine molecule took the form (V), the corresponding distance should be about 2·8 Å. Such a short contact might give rise to a strong repulsion between these atoms. Thus it seems that the *cis* conformation of (IV) is more favourable in this case.

The n.m.r. spectrum of capaurine showed a quartet centered at 5·97τ assigned to the proton at C(14). According to Uskoković *et al.* (1964), this characteristic indicates that the present molecule is of the form (IV) in solution as it is in the crystalline state.

Natural capaurine was studied by means of variable-temperature n.m.r. spectroscopy from −50 to 150°C, but no change was observed (Kametani, 1968). Therefore, it is improbable that conformational change involving nitrogen inversion, or between two possible *cis* forms, occurs easily.

Corrodi & Hardegger (1956) have determined the absolute configurations of many derivatives of tetrahydroisoquinoline; capaurine was assigned the *S*-configuration on the basis of a comparison of optical rotation with (−)-norcoralidine (VI)
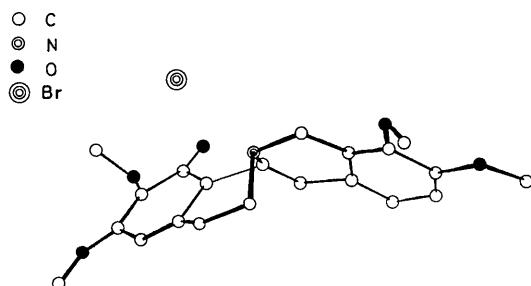
Fig. 2. The projection of capaurine hydrobromide along the *b* axis.
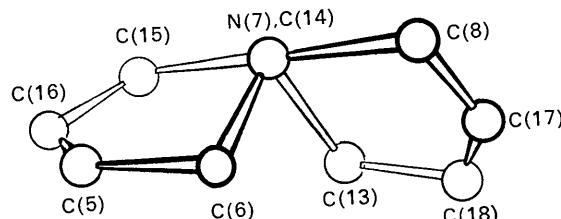
Fig. 3. Rings *B* and *C*, viewed along the line N(7)–C(14).

VI
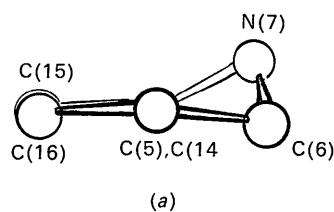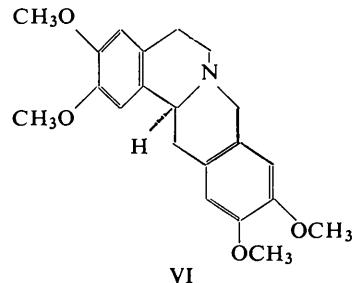
(a)
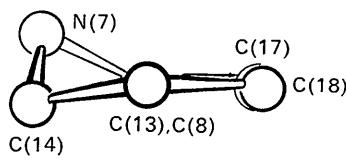
(b)

Fig. 4. (a) Ring *B*, viewed along the line C(5)···C(14). (b) Ring *C*, viewed along the line C(13)···C(8).

III

IV

V
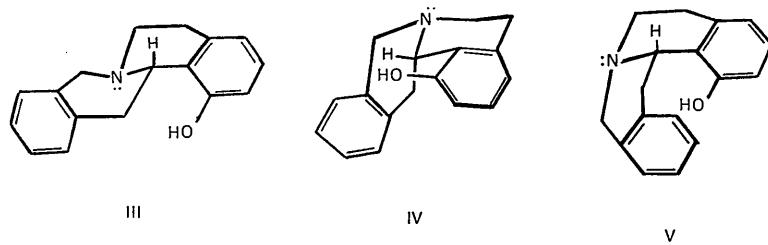
Fig. 5. Three possible conformations of dibenzo[a,g]quinolizidine. III, *trans*-fused. IV and V, *cis*-fused.

which belongs to the *trans* conformer. It seems that the allocation of absolute configuration to tetrahydro-protoberberine alkaloids is hardly influenced by the *cis* or *trans* conformation.

Molecular dimensions

Intramolecular bond lengths and angles are shown in Figs. 6 and 7, respectively, and listed in Table 5 with their estimated standard deviations. Because of the small size of the crystals used, only 57% of the reflexions in the Cu sphere had measurable intensities. Therefore the standard deviations for the atomic coordinates were rather large. In view of the large standard deviations, the variation among the bond lengths

of a certain type may not be significant. The average is 1·416 Å for the aromatic C–C bonds in two benzene rings, 1·532 Å for the C–C single bonds in the quinolizidine moiety, 1·382 Å for the C(aromatic)–O single bonds and 1·465 Å for the O–CH₃ bonds. These mean values are very close to those given by Sutton (1965).

Table 5. *Bond lengths and angles with their e.s.d.'s*

	Distance (Å)	e.s.d.
C(1)—C(2)	1·410	0·029
C(2)—C(3)	1·423	0·029
C(3)—C(4)	1·386	0·032
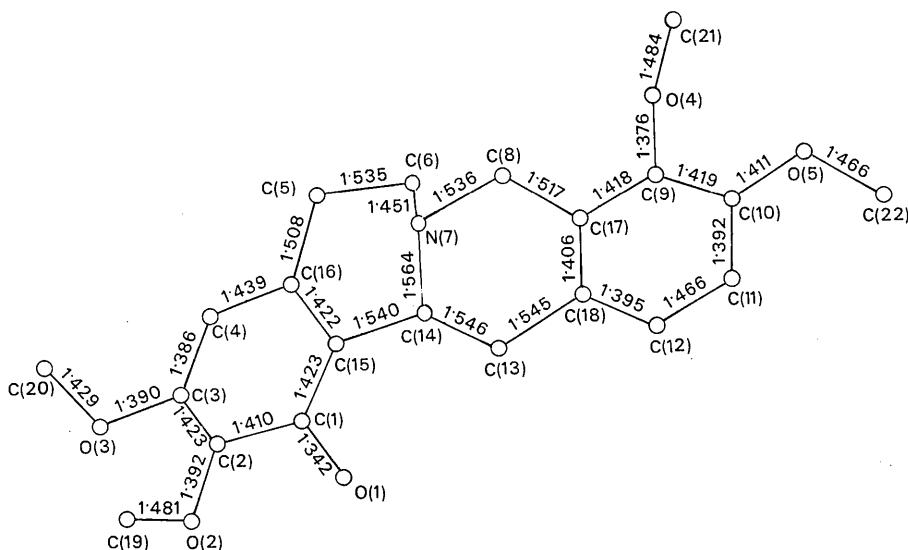
Fig. 6. Bond lengths (Å).
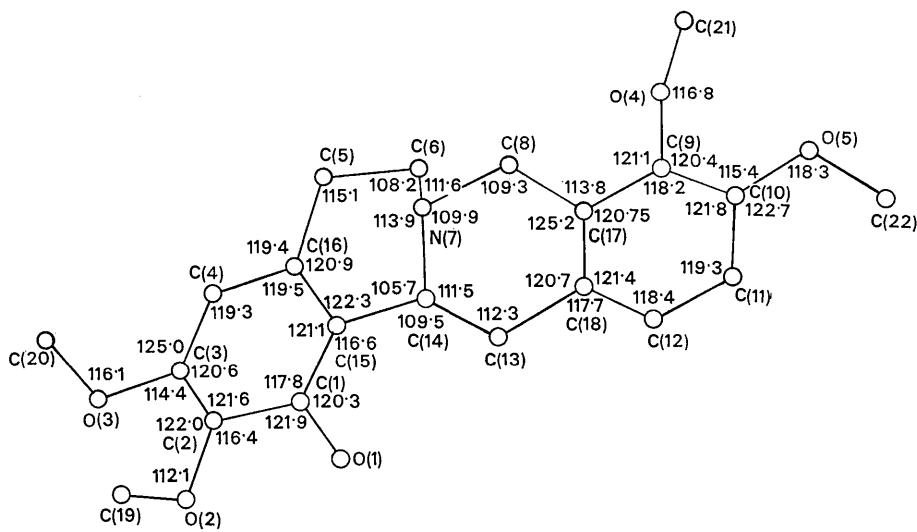
Fig. 7. Bond angles (degrees).

Table 5 (cont.)

	Angle (deg.)	e.s.d.
C(4)—C(16)	1·439	0·033
C(15)-C(16)	1·422	0·029
C(1)—C(15)	1·423	0·028
C(9)—C(10)	1·419	0·028
C(10)-C(11)	1·392	0·030
C(11)-C(12)	1·466	0·030
C(12)-C(18)	1·395	0·029
C(17)-C(18)	1·406	0·030
C(9)—C(17)	1·418	0·030
C(5)—C(16)	1·508	0·032
C(5)—C(6)	1·535	0·032
C(8)—C(17)	1·517	0·031
C(14)-C(15)	1·540	0·026
C(13)-C(18)	1·545	0·033
C(13)-C(14)	1·546	0·031
O(1)—C(1)	1·342	0·025
O(2)—C(2)	1·395	0·025
O(3)—C(3)	1·390	0·025
O(4)—C(9)	1·376	0·025
O(5)—C(10)	1·411	0·024
O(2)—C(19)	1·481	0·027
O(3)—C(20)	1·429	0·025
O(4)—C(21)	1·484	0·026
O(5)—C(22)	1·466	0·028
N(7) -C(6)	1·451	0·029
N(7) -C(8)	1·536	0·029
N(7) -C(14)	1·564	0·026
O(1)—C(1)—C(2)	121·9	1·8
O(1)—C(1)—C(15)	120·3	1·8
C(2)—C(1)—C(15)	117·8	1·8
O(2)—C(2)—C(1)	116·4	1·8
O(2)—C(2)—C(3)	122·0	1·8
C(1)—C(2)—C(3)	121·6	1·9
O(3)—C(3)—C(2)	114·4	1·8
O(3)—C(3)—C(4)	125·0	1·9
C(2)—C(3)—C(4)	120·6	2·0
C(3)—C(4)—C(16)	119·3	2·1
C(6)—C(5)—C(16)	115·1	1·9
C(5)—C(6)—N(7)	108·2	1·8
C(6)—N(7) -C(8)	111·6	1·7
C(6)—N(7) -C(14)	113·9	1·6
C(8)—N(7) -C(14)	109·9	1·5
N(7) -C(8)—C(17)	109·3	1·7
O(4)—C(9)—C(17)	121·1	1·8
O(4)—C(9)—C(10)	120·4	1·8
C(10)-C(9)—C(17)	118·2	1·8
O(5)—C(10)-C(9)	115·4	1·7
O(5)—C(10)-C(11)	122·7	1·8
C(9)—C(10)-C(11)	121·8	1·9
C(10)-C(11)-C(12)	119·3	1·9
C(11)-C(12)-C(18)	118·4	1·9
C(14)-C(13)-C(18)	112·3	1·9
C(13)-C(14)-C(15)	109·5	1·6
N(7) -C(14)-C(13)	111·5	1·6
N(7) -C(14)-C(15)	105·7	1·4
C(1)—C(15)-C(14)	121·1	1·8
C(1)—C(15)-C(16)	116·6	1·7
C(14)-C(15)-C(16)	122·3	1·7
C(4)—C(16)-C(5)	119·4	2·0
C(4)—C(16)-C(15)	119·5	2·0
C(5)—C(16)-C(15)	120·9	1·9
C(8)—C(17)-C(9)	113·8	1·8
C(8)—C(17)-C(18)	125·2	1·9
C(9)—C(17)-C(18)	120·8	1·9
C(12)-C(18)-C(13)	117·7	1·9
C(12)-C(18)-C(17)	121·4	2·0
C(13)-C(18)-C(17)	120·7	1·9
C(2)—O(2)—C(19)	112·1	1·5
C(3)—O(3)—C(20)	116·1	1·6
C(9)—O(4)—C(21)	116·8	1·5
C(10)-O(5)—C(22)	118·3	1·6

The C–N bond lengths are 1·451, 1·536 and 1·564 Å. The last value seems to be somewhat larger than the standard C–N length 1·47 Å, but no chemical significance can be given to this observation, as yet.

The three bonds at N(7) are arranged nearly tetrahedrally around the nitrogen atom; the angles range from 109·9 to 113·9° and their mean is 111·5°. The angles C–O–C are in the range from 112·1 to 118·3°, the mean being 115·8°.

Planarity of the rings

The equations for the best planes of the six carbon atoms in the benzene rings *A* and *D* are

$$-0·459x - 0·406y - 0·790z + 8·706 = 0$$

and

$$-0·249x + 0·508y - 0·824z + 0·280 = 0,$$

respectively. Displacements of the atoms from these planes are shown in Table 6. Each benzene ring is planar within the range of experimental error. The oxygen atoms attached to the ring lie almost on the plane, but C(5) and C(13) involved in the quinolizidine skeleton deviate significantly out of the plane. It seems that these shifts are provoked by the fusion of the *B* and *C* rings.

Table 6. *Deviations from mean planes of A and D*

	A		D
C(1)	−0·005 (Å)	C(9)	0·025 (Å)
C(2)	0·001	C(10)	−0·029
C(3)	−0·003	C(11)	0·011
C(4)	0·009	C(12)	0·032
C(15)	0·012	C(17)	−0·024
C(16)	−0·014	C(18)	−0·009
O(1)*	−0·019	O(4)*	−0·011
O(2)*	−0·058	O(5)*	−0·044
O(3)*	−0·034	C(8)*	0·052
C(14)*	0·002	C(13)*	0·096
C(5)*	−0·160		

* Not included in the calculation of the mean plane.

The dihedral angle between the planes of the *A* and *D* rings is 70·7°.

Crystal structure

The packing diagrams of the crystal viewed along the *b* and *c* axes are shown in Figs. 8 and 9, respectively, and intermolecular distances below 4·0 Å are listed in Table 7.

The bromine ion is located nearly at the apex of the triad of C(6), C(8) and C(14), above N(7) at a distance of 3·12 Å, as shown in Fig. 10. This situation favours the formation of N⁺–H···Br⁻ hydrogen bond, similar to that in himbacine hydrobromide (Fridrichsons & Mathieson, 1962). The O(1) in the molecule translated by *b* has a short approach distance of 3·39 Å to the bromide ion; the angle C(1)–O(1)···Br⁻ is 131·1°.

This distance is close to the O–H · · · Br⁻ hydrogen bond distances, 3·26 and 3·40 Å in codeine hydrobromide (Donohue, Sharma & Marsh, 1964) and 3·35 and 3·28 Å in hetisine hydrobromide (Przyblyska, 1963).

The organic ions are arranged in columns through N⁺–H · · · Br⁻ · · · H–O hydrogen bonds along the b axis.

All the other intermolecular distances are longer than 3·4 Å. The packing along the a axis is mainly due
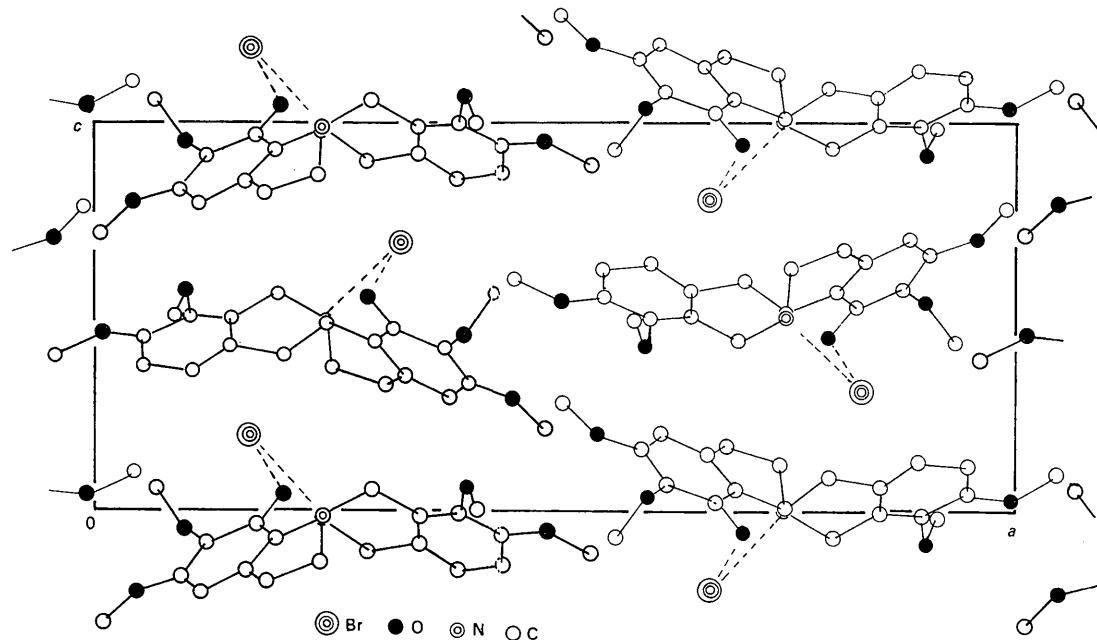
Fig. 8. The crystal structure projected along the b axis. The dotted line indicates a hydrogen bond.
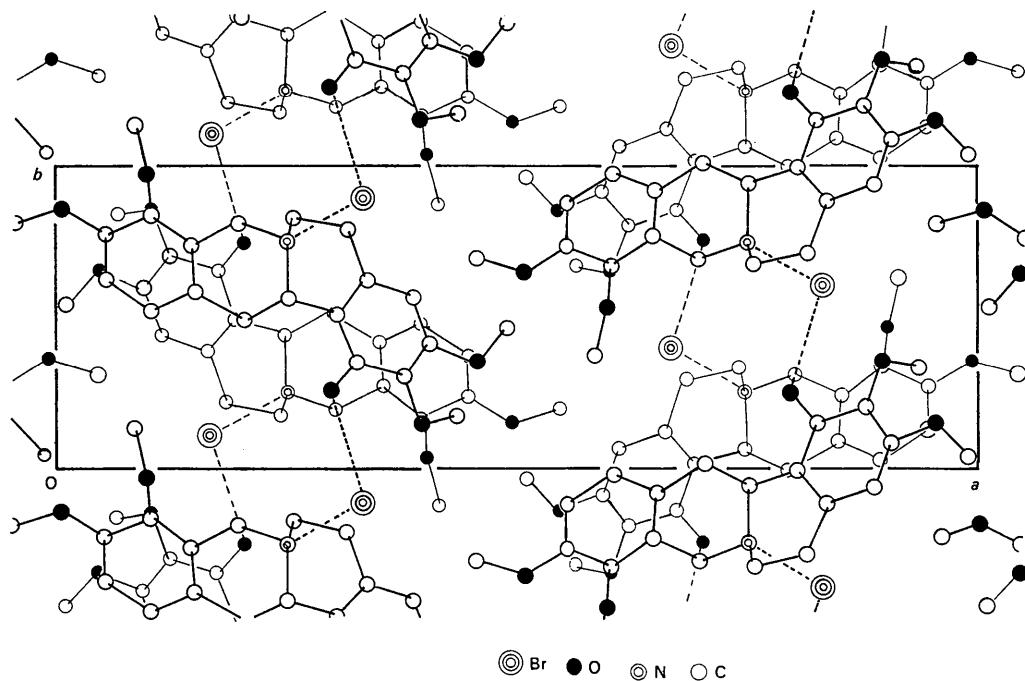
Fig. 9. The crystal structure projected along the c axis. The dotted line indicates a hydrogen bond.

Table 7. *Shorter intermolecular distances*

Atom (molecule 1)	Atom	in molecule	Distance
Br	N(7)	1	3·12 Å
Br	C(5)	1	3·93
Br	C(8)	1	3·67
Br	C(14)	1	3·99
Br	C(6)	1	3·87
Br	O(2)	2	3·60
Br	O(1)	2	3·39
Br	C(19)	2	3·67
C(21)	C(12)	2	3·60
C(5)	O(5)	2	3·79
Br	C(13)	3	3·89
O(5)	O(3)	3	3·97
O(5)	C(20)	3	3·76
O(4)	O(3)	3	3·71
O(1)	C(6)	3	3·65
C(11)	C(20)	3	3·84
C(10)	O(3)	3	3·74
C(10)	C(20)	3	3·55
C(19)	C(11)	3	3·58
C(19)	C(10)	3	3·96
C(9)	O(3)	3	3·62
C(9)	C(20)	3	3·94
C(9)	C(3)	3	3·94
C(17)	C(3)	3	3·92
Br	C(21)	4	3·78
Br	C(6)	4	3·63
O(4)	C(5)	4	3·83
Br	N(7)	4	4·61*
C(21)	C(4)	4	3·99
C(19)	C(22)	5	3·90
C(19)	C(11)	5	3·83
Br	C(22)	6	3·65

Table 7 (*cont.*)

Atom (molecule 1)	Atom	in molecule	Distance
O(3)	O(5)	6	3·65
O(3)	C(21)	6	3·84
C(20)	O(5)	6	3·59
C(20)	O(4)	6	3·48
C(20)	C(21)	6	3·75
C(3)	O(5)	6	3·74
C(3)	C(22)	6	3·75
C(4)	O(5)	6	3·94
C(4)	C(22)	6	3·68
C(16)	C(22)	6	3·99
C(22)	C(11)	7	3·83
C(22)	C(12)	7	3·61
C(20)	O(3)	8	3·45
C(20)	O(4)	8	3·77
C(20)	C(19)	8	3·92

* Listed for investigating ionic interaction.

Molecule	General coordinates
1	$x, \quad y, \quad z$
2	$x, 1+y, \quad z$
3	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$
4	$\frac{1}{2}-x, 2-y, \frac{1}{2}+z$
5	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
6	$\frac{1}{2}+x, 1\frac{1}{2}-y, 1-z$
7	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$
8	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$

to van der Waals forces. Four methoxy carbon atoms are oriented so that the most favourable van der Waals packing is achieved. Ionic interaction may also play a role in the packing along the c axis ($Br^-\cdots N(7^4)$ = 4·61 Å).

Fig. 10. The environment of the nitrogen atom.

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