X-ray Studies of C25 Terpenoids. III. The Crystal Structure of Ceroplastol I p-Bromobenzoate

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(Received 30 August 1968)

The structure of ceroplastol I, $C_{25}H_{40}O$, a C_{25} terpenoid isolated from an insect wax, has been determined by X-ray analysis of its heavy atom derivative, ceroplastol I *p*-bromobenzoate. Crystals of the *p*-bromobenzoate are orthorhombic, space group $P2_12_12_1$ with four molecules contained in the unit cell of dimensions, a = 18.67, b = 21.74, c = 7.02 Å. The crystal structure was solved by means of threedimensional Fourier syntheses using the heavy atom technique. The atomic parameters were refined by block-matrix least-squares calculations with anisotropic temperature factors. The final *R* index was 0.12 for 2590 observed reflexions. The absolute configuration was determined by the use of the anomalous dispersion effect of Cu K α radiation by bromine atoms.

The molecule was found to consist of a five-, eight-, five-membered tricyclic ring system very similar to those found in other C_{25} terpenoids. However, the juncture between the rings A and B and that between B and C in the present structure are both found to be *trans* in contrast to the *cis*, *trans* disposition in ophiobolins A, B and C.

Introduction

Ceroplastol was isolated by Rios & Colunga (1965) from the wax secreted by the parasitic insect Ceroplastes albolineatus. The host plant is a shrub, Senecio praecox which grows on volcanic layers in the south of Mexico City. The wax is produced by the female of this insect to prevent desiccation. Saponification of the wax gave a mixture of n-alkanoic acids, n-alkanols and smaller amounts of the alcohols, ceroplastol I $(C_{25}H_{40}O)$ and II $(C_{25}H_{40}O)$, together with ceroplasteric acid: The latter was first isolated by us (litaka, Watanabe, Harrison & Harrison, 1968). The acid is converted into ceroplastol I by lithium aluminum hydride reduction. Little was known of the chemistry of ceroplastol I, but on the basis of some chemical reactions coupled with the data derived from the nuclear magnetic resonance and infrared spectra, Rios & Colunga (1965) suggested a tricyclic structure with three double bonds, one being a terminal methylene group and the second in the side chain containing the alcohol group, $-CH_2-CH=C(Me)CH_2OH_1$

Of the C_{25} terpenoids the ophiobolins were the only, known examples (Fig. 1). The structure of ophiobolin *A* was first elucidated by X-ray diffraction by Nozoe, Morisaki, Tsuda, Iitaka, Takahashi, Tamura, Ishibashi & Shirasaka (1965); Morisaki, Nozoe & Iitaka (1968). Subsequently, an X-ray study on cephalonic acid (Ophiobolin *D*; Itai, Nozoe, Okuda & Iitaka, 1969) was carried out. These comprized a series of papers under the title of *X-ray studies of* C_{25} terpenoids, I and II. The present structure determination was undertaken in the expectation that ceroplastol would be an additional example of the rare C_{25} terpenoids. A preliminary report of the present work has already been published (Iitaka, Watanabe, Harrison & Harrison, 1968).

Experimental

Crystals of ceroplastol I *p*-bromobenzoate were grown from acetone solution as orthorhombic colourless prisms elongated along the *c* axis. The unit-cell dimensions and space group were determined from precession photographs taken with Cu $K\alpha$ radiation.

Crystal data

Ceroplastol I *p*-bromobenzoate, $C_{32}H_{43}O_2Br$, m.p. 101-102°C, mol. wt. 539.6 Orthorhombic, $a=18.67\pm0.03$, $b=21.74\pm0.03$, $c=7.02\pm0.02$ Å; U=2926 Å³; $D_x=1.225$ g.cm⁻³; F(000)=1144, Z=4, $\mu(Cu K\alpha)=23.5$ cm⁻¹. Absent spectra, (h00)when h is odd, (0k0) when k is odd, (00l) when l is odd; Space group $P2_12_12_1$.

Three-dimensional diffraction data were recorded on multiple film equi-inclination Weissenberg photographs with Cu K α radiation. Layer lines of zero to five around c and zero to three around the *a* axis were collected. Measurement of the intensities was made by visual

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comparison with standard intensity scales prepared for each axis. After correcting for Lorentz and polarization factors, the structure factors were put on a common scale by correlating the various layers. The total number of independent observed structure factors was 2590.

Determination and refinement of the structure

Sharpened Patterson maps on Harker sections at $u=\frac{1}{2}, v=\frac{1}{2}$ and $w=\frac{1}{2}$, respectively, were calculated and the coordinates of the bromine atom (x=0.1485,y=0.1015, z=0.009) were determined by referring to the coordinate system given in International Tables for X-ray Crystallography (1952). The structure factors were then calculated to obtain the angles determined by the bromine atoms. The R value at this stage was 0.56. A three-dimensional Fourier synthesis calculated with these phase angles revealed many peaks. Because the bromine atoms are located close to rather special positions, there appeared pseudo mirror-image peaks related to the real ones by the planes of symmetry at $z=0,\frac{1}{2}$. The benzene ring attached to the bromine atom was easily recognized on this map but again it lies on the pseudo mirror plane. Several repeated cycles of structure factors and Fourier or difference Fourier calculations in which the chemical structure of the molecule was considered, yielded all of the thirty five atomic positions in the electron density map. No effort was made to distinguish between carbon and oxygen atoms until all the atoms were successfully located. Finally these were identified by considering the observed heights of the peaks on the electron density map and the calculated C-O and C=O bond lengths. The R value at this stage was 0.33. The molecular structure derived in this way could well account for the observed nuclear magnetic resonance spectrum of this compound.

Six cycles and then three cycles of least-squares refinement with the block-matrix approximation (program by Okaya & Ashida, 1957) gave the R value of 0.12 for 2590 observed structure factors. In the latter calculations, anisotropic thermal vibrations for all atoms were allowed for, and the following weight system was adopted,

$\sqrt{w} = 15.0/F_o$	when $F_o > 15.0$,
$\sqrt{w} = 1.0$	when $15 \cdot 0 \ge F_o > 2 \cdot 0$,
$\sqrt{w=0}$	when $2 \cdot 0 \ge F_0$.

Atomic scattering factors were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and carbon, and for bromine those cited as SX-71 in *International Tables for X-ray Crystallography* (1962).

The final atomic parameters are given in Table 1 together with their standard deviations. The observed and calculated structure factors are listed in Table 2. A composite electron density map obtained from the final Fourier synthesis is shown in Fig2 together with the perspective drawing of the molecule.

Absolute configuration

The absolute configuration has been determined by the anomalous dispersion method (Bijvoet, Peerdeman





& van Bommel, 1951). The values of the real and imaginary dispersion correction terms for Cu K α radiation by bromine atoms ($\Delta f' = -0.9$, $\Delta f'' = 1.5$) were those given by Dauben & Templeton (1955). Intensities of the Friedel pairs of reflexions were calculated assuming that the atomic parameters given in Table 1 are referred to a right-handed set of axes. A comparison of the observed and calculated intensities are listed in Table 3 which definitely indicates that the assumed absolute configuration is the correct one. All figures shown in this paper are drawn with correct absolute configuration.

Discussion of the structure

The present determination of the crystal structure of ceroplastol I *p*-bromobenzoate reveals the structure of

ceroplastol I as in Fig. 1(e) and ceroplasteric acid as in Fig. 1(f). These structures are in good agreement with the results from nuclear magnetic resonance and mass spectra as well as the chemical examinations based on the dehydrogenation and ozonolysis reactions (Harrison & Harrison, 1969).

The main skeleton of ceroplastol I consists of an unique five- eight- and five-membered tricyclic ring system indicating that it is a close relative of the ophiobolins. Ophiobolin A is the first example of a C₂₅ terpenoid. Of the several ophiobolins known to date (Fig.1) (ophiobolin A from the Cochliobolus miyabeanus and Helminthosporium species (Nozoe, Morisaki, Tsuda, Iitaka, Takahashi, Tamura, Ishibashi & Shirasaka, 1965); ophiobolin B (zizanin B; Nozoe, Hirai & Tsuda, 1966) and ophiobolin C (zizanin A; Nozoe, Hirai &



Fig.2. (a) Composite electron density map superimposed on (001). Contours are drawn with intervals of 1 e.Å⁻³ starting from 2 e.Å⁻³. Those for the bromine atom are omitted. (b) The molecular structure in correct absolute configuration. Black bonds indicate double bonds.



Fig. 3. Bond lengths and their standard deviations. The e.s.d.'s are given in parentheses denoting the least significant digits in the bond lengths.

Table 1. The final atomic parameters and their standard deviations

x, y and z are the fractional coordinates. The temperature factors are expressed in the form of

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

The e.s d.'s given in parentheses are in the units of the least significant digits given for the corresponding parameters. To represent the correct absolute configuration, the parameters should be referred to a right handed set of axes.

	x	у	z	β11	B22	B23	B12	<i>B</i> 13	Baa
Br	0.3517	-0.1020	0.5150	0.0051	0.0026	0.0274	0.0009	0.0008	0,0000
	(1)	(1)	(2)	(1)	(0)	(4)	0 0005	(1)	(1)
O(1)	0.2623	0.2031	0.5352	0.0028	0.0022	0.0414	-0.0002	0.0003	0.0002
	(4)	(3)	(17)	(2)	(2)	(33)	(2)	(8)	(7)
O(2)	0.1537	0.1604	0.5236	0.0023	0.0024	0.0410	-0.0001	-0.0020	0.0003
· · /	(4)	(4)	(17)	(2)	(2)	(34)	(1)	(8)	(7)
C (1)	-0·3820́	0·103̀4́	1.2947	0.0036	0.0021	0.0065	-0.0007	0.0002	-0.0027
	(6)	(5)	(15)	(3)	(2)	(24)	(2)	(7)	(6)
C(2)	-0.4471	0.0633	1.2296	0.0024	0·0020	0.0212	-0.0007	0.0009	-0.0008
	(5)	(5)	(20)	(3)	(2)	(33)	(2)	(8)	(7)
C(3)	-0.4535	-0.0010	1.3195	0.0031	0.0019	0.0316	-0·0007	0.0014	-0.0012
	(6)	(5)	(24)	(3)	(2)	(43)	(2)	(11)	(8)
C(4)	-0.4889	-0.0396	1.1650	0.0047	0.0029	0.0167	-0.0012	0.0001	-0.0010
	(8)	(6)	(21)	(5)	(3)	(33)	(3)	(11)	(8)
C(5)	-0.5163	0.0033	0.9969	0.0034	0.0021	0.0401	-0.0014	0.0030	-0·0034
~ ~	(6)	(5)	(28)	(4)	(2)	(54)	(2)	(13)	(10)
C(6)	-0.4564	0.0547	1.0253	0.0024	0.0020	0.0500	-0.0003	0.0011	0.0003
~	(5)	(4)	(20)	(3)	(2)	(32)	(2)	(8)	(7)
C (7)	-0.4700	0.1110	0.9033	0.0030	0.0027	0.0176	0.0000	-0.0011	0.0016
C(A)	(6)	(5)	(21)	(3)	(3)	(34)	(2)	(9)	(8)
C(8)	-0.4167	0.1423	0.8279	0.0019	0.0027	0.0309	-0.0000	-0.0001	0.0009
C (0)	(5)	(5)	(22)	(3)	(3)	(41)	(2)	(8)	(9)
C(9)	-0.3382	0.1248	0.8376	0.0030	0.0023	0.0194	-0.0001	0.0004	-0.0011
0(10)	(6)	(5)	(20)	(3)	(2)	(32)	(2)	(8)	(7)
C(10)	-0.3001	0.1412	1.0190	0.0023	0.0019	0.0201	0.0001	-0.0001	0.0012
C(11)	(5)	(4)	(20)	(2)	(2)	(32)	(2)	(8)	(7)
$\mathcal{C}(\Pi)$	-0.30/8	0.0992	1.2053	0.0026	0.0011	0.0097	0.0002	0.0002	0.0009
C(12)	(5)	0.1204	(14)	(2)	(2)	(22)	(2)	(6)	(5)
C(12)	-0.2319	0.1294	1.3330	0.0030	0.0024	0.0039	-0.0006	0.0012	-0.0011
C(12)	0.1870	0.1462	1.2001	(3)	(2)	(23)	(2)	(7)	(6)
U(13)	-0.10/0	0.1402	(21)	0.0073	0.0032	0.0191	-0.0004	-0.0008	-0.0021
C(14)	-0.2161	0.1458	0.0022	(3)	0.0020	(33)	(3)	(9)	(8)
C(14)	(5)	(4)	(10)	(2)	0.0020	0.0130	-0.0004	-0.0000	-0.0004
	(3)	(4)	(17)	(4)	(4)	(30)	(2)	(ð)	(7)

	x	У	Z	β_{11}	β22	β_{33}	β_{12}	β_{13}	β_{23}
C(15)	-0.1902	0.2014	0.8717	0.0027	0.0016	0.0126	0.0000	0.0005	0.0002
	(5)	(4)	(17)	(3)	(2)	(28)	(2)	(7)	(6)
C(16)	-0.1092	0.1973	0.8569	0.0022	0.0023	0·0387	-0.0004	0.0010	0.0015
	(5)	(5)	(26)	(3)	(3)	(50)	(2)	(10)	(9)
C(17)	-0.0815	0.2356	0.6820	0.0031	0.0026	0.0252	-0.0001	0.0008	-0.0005
	(6)	(6)	(23)	(3)	(3)	(39)	(2)	(10)	(9)
C(18)	0.0010	0.2348	0.6747	0.0032	0.0018	0.0225	0.0000	0.0007	0.0004
	(6)	(5)	(21)	(4)	(2)	(36)	(2)	(10)	(7)
C(19)	0.0410	0.2137	0.5443	0.0027	0.0020	0.0160	-0.0005	-0.0008	-0.0013
-	(5)	(5)	(17)	(3)	(2)	(29)	(2)	(7)	(6)
C(20)	-0.4387	-0.0177	1.4977	0.0038	0.0031	0.0286	0.0008	-0.0009	0.0005
0(01)	(7)	(6)	(25)	(4)	(3)	(42)	(3)	(13)	(11)
C(21)	-0.5477	0.1375	0.8997	0.0022	0.0039	0.0750	0.0012	-0.0010	-0.0004
C(22)	(7)	(/)	(42)	(3)	(4)	(98)	(3)	(15)	(18)
C(22)	-0.2852	0.0313	1.1620	0.0031	0.0019	0.0147	0.0001	0.0007	-0.0023
C(22)	(6)	0.2640	(17)	0.0028	(2)	(30)	(2)	(8)	(6)
C(23)	-0.2104	0.2049	(26)	(4)	0.0021	(52)	-0.0001	0.0024	-0.0003
C(24)	0.0152	0.1853	0.3/35	0.0031	0.0033	0.0415	0.0004	0.0003	0.0008
C(24)	(7)	(7)	(30)	(4)	(4)	(58)	-0.0004	-0.0003	-0.0008
C(25)	0.1232	0.2205	0.5481	0.0026	0.0022	0.0542	- 0.0000	0.0021	0.0008
0(23)	(6)	(5)	(33)	(3)	(2)	(75)	(2)	(14)	(12)
C(26)	0.2251	0.1581	0.5152	0.0020	0.0024	0.0408	0.0001	0.0002	
0(20)	(5)	(5)	(27)	(3)	(2)	(49)	(2)	(11)	(11)
C(27)	0.2544	0.0944	0.5187	0.0030	0.0022	0.0131	-0.0001	0.0004	0.0013
-()	(5)	(4)	(17)	(3)	(2)	(28)	(2)	(8)	(7)
C(28)	0.3278	0.0861	0.5165	0·0027	0.0028	0.0263	-0.0002	-0.0015	0.0018
```	(6)	(5)	(22)	(3)	(2)	(38)	(2)	(10)	(9)
C(29)	0.3588	0.0274	0.5074	0.0034	0.0029	0·0216	0.0000	0.0001	0.0032
	(6)	(6)	(21)	(3)	(3)	(36)	(2)	(11)	(9)
C(30)	0.3126	-0.0222	0.2030	0.0032	0.0028	0.0123	0.0003	-0.0010	0.0022
	(6)	(5)	(20)	(3)	(3)	(30)	(2)	(9)	(8)
C(31)	0.2386	-0.0122	0.5190	0.0037	0.0020	0.0290	-0.0004	0.0011	0.0009
	(6)	(5)	(25)	(4)	(2)	(43)	(2)	(12)	(9)
C(32)	0.2085	0.0428	0.5206	0.0030	0.0022	0.0286	-0.0005	0.0002	0.0003
	(6)	(5)	(24)	(3)	(2)	(41)	(2)	(10)	(9)

Table 1 (cont.)

Mean standard deviations of bond lengths: (Br-C)=0.011 Å, (C-O)=0.013 Å, (C-C)=0.017 Å Mean standard deviation of tetrahedral bond angles:  $(C-C-C)=0.9^{\circ}$ .



Fig.4. Bond angles and their standard deviations. The e.s.d.'s are given in parentheses denoting the least significant digits in the bond angles.

# X-RAY STUDIES OF $C_{25}$ TERPENOIDS. III

# Table 2. Observed and calculated structure factors

H K L FCORSH FCCALH				
8 4 C 69.95 54.69 6 0 C 82	.90 82.19 11 20 n 6.nc 3.73	18 10 0 10.08 11.38 4 2 1	45.77 43.84 11	0 <u>1 1 29.63 23.11</u>
8 6 0 13.77 13.27 6 1 C 6C	.40 50.27 11 21 0 8.95 5.09	18 11 0 10.36 11.00 4 3 1	58.44 59.21 1	0 2 1 12.88 15.32
0 10 0 42,30 80.29 6 3 6 6	<u>.32 42,80</u> 11 22 0 6,02 5.90 .21 2.43 11 23 0 16,25 15,42	18 12 0 6,65 2,71 4 4 18 13 0 2,25 2,36 4 5	45.21 41.83 1	0 3 1 64.22 62.34 0 4 1 10.94 10.32
0 12 0 14.23 18.12 6 4 0 72	.52 49.60 12 0 0 11,95 8.0?	18 14 0 5,98 4.71 4 6 1	17.00 24.23 1	6 1 28.61 24.65
8 14 0 26,82 25.11 6 5 0 43	.94 42.21 12 1 0 23.80 21.78	18 15 0 1.97 2.22 4 7	55.37 <u>66.15</u> 1	
6 16 0 54,97 52,93 6 5 C 49 0 18 0 10,20 9,20 6 7 0 89 0 44 6 44 7 0 8 7 0 89	1.94 85.24 12 2 0 12.07 13.93 1.94 85.24 12 3 0 32.93 37.17 10 31.81 13 4 0 19 33 31.24	18 10 0 5.64 7.65 4 8 1 18 17 0 3.11 7.23 4 9 1 10 1 0 7.63 4 69 4 10	80.97 75.75 1	0 8 1 23.01 21.97 0 9 1 18.05 13.83
6 22 0 2,74 4.43 4 9 0 37	26 21.39 12 5 0 16,99 15,89	10 2 0 10.61 9.02 4 11	48.75 48.84 1	0 10 1 12.63 11.23
6 24 0 21,33 20,76 6 10 0 49	46 43,45 12 6 C 2.50 3.62	19 3 0 2.04 4.05 4 12	8.72 8.10 1	0 11 1 22.18 22.01
1 2 0 28,65 28,99 6 11 0 12	2.07 14.66 12 7 0 17.21 17.37	19 4 0 2.62 1.81 4 13	<u>32,18 29.13</u> 1	0 12 1 13.79 12.75
1 3 0 47,99 35,86 6 12 0 16	5.95 13.40 12 8 0 17.55 15.92	19 5 0 10.99 10.26 4 14	19.14 20.56 1	8 13 1 27.65 30.15
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1,74 32,35 17 9 0 27,40 24,39 <u>3.30 46,26</u> 12 10 0 14,22 10,66 <u>50 18,95</u> 12 11 0 8 44 7 72	19 5 0 5.20 4.14 4 15 19 7 5 5.02 3.10 4 16	19.33 18.2A 1	0 14 1 13.77 13.77 0 15 1 27.63 26.58 0 17 1 23.46 22.27
1 7 0 82.52 74.92 6 16 0 17	7.43 18.64 12 12 0 11.76 9.61	10 10 0 2.31 2.11 4 18	13.31 12.69 1	0 18 1 9.25 8.45
1 8 0 62.51 56.58 6 17 0 12	2.93 14.07 12 13 0 8.45 7.87	19 11 0 6.28 5.60 4 19		0 21 1 9.93 8.85
1 9 0 54.42 51.82 6 18 C 18	8,57 18,32 12 14 0 14,34 12,75	19 12 0 9.89 13.79 4 20	7.73 3.00 1	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
1 10 0 16.23 17.46 6 19 0 13	1,93 6,22 12 15 0 7,93 8,95	19 13 0 7.41 11.78 4 21	1 10.74 11.17 1	
1 11 0 44.58 67.13 6 20 0 14 1 12 0 32.52 36.26 6 21 0 8	121         13.06         12         16         0         9.61         6.94           3.61         9.16         12         17         0         23.04         23.01	19 14 0 1.83 2.53 4 23 19 15 0 13.09 12.26 4 24	1 6.03 6.08 1 1 7.91 6.58 1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
1 13 0 5,37 0.82 6 22 0 2 1 14 0 36,39 36,70 6 23 0 13	2.61 0.50 12.18 0 2.62 2.47 3.4 ⁹ 13.9 ² 12.19 0 8.65 10.15 4.54 6.27 13.20 0 4.71 2.81	19 17 0 0.87 7.43 5 0 20 0 0 18.62 19.94 5 1 20 1 0 2.49 1.83 5 2	1 10.72 10.10 1 <u>47.71 58.19</u> 1 <u>98.65 105.48</u> 1	$1 \ 3 \ 1 \ 1 \ 7.88 \ 9.05$ 1 5 1 34.16 34.39
<u>1 16 0 23.32 20.66</u> 7 1 0 22	2.12 22.63 12 21 0 8.14 9.55	20 2 0 7,00 9,10 5 3	45.05 37.03 1	1 6 1 34.79 30.14
<u>1 17 0 2.65 5.21</u> 7 2 0 123	3.73 196.62 12 22 0 1.96 3.61	20 3 0 2,45 5,17 5 4		1 7 1 21.78 19.16
1 18 0 22.37 18.66 7 3 0 29	9.20 24.39 13 1 <u>3 2.50</u> 3.2 ³	20 4 0 7.68 10.56 5 5	1 14.04 10.13 1	1 8 1 24.82 22.45
1 19 0 28.97 77.12 7 4 0 20	0.65 19.07 13 2 0 41.79 42.73	20 5 0 4.78 0.91 5 6	1 26.80 25.94 1	1 9 1 34.09 29.28
1 20 0 2.81 1.69 7 5 0 13	3.15 13.77 13 3 0 27.88 26.04	20 7 0 4,50 5,68 5 7	1 89.40 97.61	<u>1 10 1 29,10 23,43</u>
1 21 0 2.80 0.08 7 6 0 20	0.50 27.29 13 4 0 41.55 34.44	20 8 0 4,44 1,30 5 8		<u>1 11 1 28,25 26,75</u>
1 22 0 5,47 7,54 7 7 0 20 1 23 0 2,63 4,49 7 8 0 66	0.75 10.80 13 5 6 75.82 24.17 6.73 $64.24$ 13 6 0 56.22 50.62 4 20 8.48 13 7 0 8.38 6.03	20 9 C • 79 2.07 5 9 20 10 0 5.01 4.27 5 10 20 11 0 1.04 5.7C 5 11	1 4.74 2.21 4 1 10.36 13.4\ 1 1 7.36 8.02 1	1 13 1 13.82 13.60
2 0 0 113,11 109,23 7 11 0	4,38 4,23 13 8 0 15.66 11.97	21 4 0 2,17 3.04 5 12	1 58.92 62.82 1	1 15 1 16.46 13.21
	5,68 5,74 13 9 0 9,44 9,12	21 9 0 6.33 0.59 5 13	1 19.85 19.20 1	1 16 1 15.91 13.74
2 1 0 92.74 108.83 7 12 0 31	1,09 26.37 13 10 0 8.72 9.97	21 11 0 1,56 3,44 5 15	1 10.74 13.66 1	1.17.1.10.06.9.65
2 2 0 16.25 11.70 7 13 0 5	9.28 8.12 13 11 0 16.25 16.23	22 0 0 2,74 2,93 5 16	1 27.19 28.95 1	1.18 1.12.28 10.05
2 3 0 163,05 195,80 7 <u>14 0 24</u> 2 4 0 118,32 120,20 7 15 0 14	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22 4 0 0.91 0.74 7 17 22 8 0 8.60 1.54 5 18 0 1 1 32.80 38.77 8 20	1 37.62 40.57 1	1 21 1 15.36 14.95
2 6 0 3.40 4.36 7 17 0 6	6.82 2.72 13 15 0 14.64 15.95	0 2 1 14.55 15.03 5 21	1 8,42 10,33	2 0 1 23.69 26.04
2 7 0 106.02 101.76 7 18 0 21	1.03 19.15 13 16 0 33.18 34.56	0 3 1 146.72 159.82 5 22	1 21,42 21,71	
2 8 0 26.42 20.58 7 19 C 2	2.80 6.43 13 17 0 7.43 0.21	0 4 1 72,02 72,05 5 24	1 7.04 5.03 1	12 2 1 13.35 13.19
2 9 0 25.82 25.90 7 20 C 2	2.76 2.19 13 18 0 9.40 6.60	0 5 1 33,54 35,55 5 25	1 4.00 4.58 1	12 3 1 19.43 13.93
2 10 0 18,74 15.57 7 21 0 2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 6 1 37.71 36.99 6 0	1 A9.71 90.57 1	12 4 1 25.90 21.07
2 11 0 35.43 35.65 7 22 0 17		0 7 1 94.70 93.96 6 1	1 A2.14 A1.30 1	12 5 1 9.75 9.15
2 13 0 39,94 41,13 8 0 0 11	1.99 14.53 14 0 0 22.53 20.62	0 9 1 38.73 29.05 6 3	1 44.60 41.33	2 <u>8 1 8.87 8.24</u>
2 14 0 16,94 16.60 8 1 0 108	8.51 192.19 14 1 0 10.48 9.37	7 10 1 79.64 31.26 6 4		2 9 1 7.37 3.47
2 15 0 24.07 13.65 8 2 0 29	9.56 28.05 14 2 0 8.32 8.23	0 11 1 68,15 64,52 6 5	1 39.28 32.38	12 10 1 54.03 52.06
2 16 0 53.52 43.77 8 3 0 12	2.63 13.83 14 3 0 6.48 9.02	9 12 1 97,16 21,70 6 6	1 10,31 7.08	12 11 1 22.81 20.82
2 17 0 45.83 A2.26 6 9 0 9 2 18 0 20.84 24.72 8 6 0 38	0.40 2.32 14 4 0 8.42 5.81 8.03 30,49 14 5 0 51.66 50,37 7.00 74.01 14 4 0 8.53 8.04	0 13 1 43.32 43.13 8 7 0 14 1 12.19 0.55 6 0	1 41.45 38.53	
2 20 0 15.61 9.27 6 8 0 0	6.00 5.36 14 7 0 7.74 5.37	0 16 1 5.04 4.46 6 10	1 34.78 35.38	12 15 1 6.68 8.25
2 21 0 14.53 17.52 8 9 0 57	7.03 50.90 14 8 0 15.63 15.24	0 18 1 6.57 3.09 6 11		12 16 1 7,60 8.43
2 22 0 13.47 8.24 8 10 0 55	5.04 50.20 14 9 0 8,81 11.46	0 21 1 26,16 28,72 6 12	1 20,84 18,50	12 17 1 12.85 9.61
2 23 0 15.69 15.27 9 11 0 32	2.27 31.55 14 10 0 16.82 15.65	0 23 1 24,40 27,42 6 13	1 16.62 14.05	12 18 1 5.06 4.93
2 24 0 0,94 4.01 A 12 0 5 2 25 0 2,25 3.44 8 13 0 23	9.86 9.62 14 11 0 7,99 2187. 3,97 22.34 14 12 0 15,69 12.95 3 80 25 92 14 13 6 7 86 4 03	0 24 1 6,71 6,10 <u>6,14</u> 0 25 1 6,14 7,75 6 15	1 21.57 19.97	17 10 1 11.26 13.31 17 20 1 17.15 16.00
3 2 0 107.79 117.73 8 15 h 17	7.98 17.33 14 14 0 21.66 22.35	1 1 1 12,90 12,43 4 17	1 25.40 23.90	13 0 1 17.84 17.93
3 3 9 68.63 67.92 8 16 0 15	9.57 16.62 14 15 0 8.52 7.65	1 2 1 74,59 73,35 6 18		13 1 1 27.37 25.83
3 4 0 10.46 12.35 8 17 0 25	5,67 22,03 14 16 0 16.90 18.16	1 3 <u>3 80,26</u> 76,39 6 19	1 6.71 7.71	13 2 1 21,39 17.30
3 5 0 66.14 64.93 8 18 0 2	2,81 7,03 14 17 0 2,50 0,90	1 4 1 123,44 133,23 <u>6 20</u>	1 13.25 15.06	13 3 1 15.43 14.63
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6,82 7,45 14 18 0 2,37 1,01 2,72 2,32 14 19 0 2,20 0,51 4 47 3,03 14 21 0 1,72 4,85	1 5 1 76.23 58.39 6 21 1 6 1 88.82 91.16 6 22	1 14.87 15.96 1 7,95 9,29	$13 \ 4 \ 1 \ 12.3/ \ 12.72$ $13 \ 5 \ 1 \ 42.09 \ 42.72$ $13 \ 6 \ 1 \ 22.51 \ 21.83$
3 9 0 16,25 8,37 8 22 0 3	2,48 4,81 19 1 0 34,89 31,95	1 8 1 84,11 78,13 7 0	1 35.63 29.70	13 7 1 31.16 28.74
3 10 0 19,89 20,29 8 23 0 7	7,96 8,70 19 2 0 13,92 12,50	1 9 1 47,95 43,27 7 1		13 8 1 50,95 49,49
3 11 0 7.07 5.47 9 1 0 01	1.60 85.00 15 3 0 9.49 6.66	1 10 1 10.33 17.49 7 2	1 23.22 17.35	13 9 1 32.84 29.79
3 12 0 31.53 27.03 9 2 0 1	1.94 0.81 15 4 0 15.08 12.82	1 11 1 76.04 69.23 7 5		13 10 1 35.95 33.44
<u>3 13 0 10.40 7.25</u> 9 3 0 90	6.80 43.83 15 5 0 16.60 15.93	1 12 1 60.55 60.15 7 4	1 21.99 <u>16.66</u>	
3 14 0 9.23 6.52 <u>9 4 0</u>	2.00 2.93 15 6 0 11.61 13.61	1 13 1 28.31 26.00 7 5	1 92.41 97.36	
3 16 0 26.05 22.35 9 7 0 5 3 17 0 19.40 18.76 9 8 0 24	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.15 <u>.</u> 1.28,43.25,13 1.16 1.40,65 38.99 7 8	1 30.17 24.04	13 14 1 5.44 5.78 13 15 1 8.48 9.42
3 18 0 36.91 35.66 9 9 0 54	4.43 50.07 15 10 0 9.73 6.96	1 17 1 22.41 21.33 7 9	1 39.20 36.18	13 16 1 6,41 5.05
3 19 0 2.80 3.27 9 10 0 24	4.16 21.74 15 11 0 28.23 27.83	1 18 1 18.35 18.52 7 10	1 20.58 17.25	13 17 1 6.19 2.92
<b>3 20 0 28.06 27.35 <u>9 11 0 3</u> <b>3 21 0 2.79 2.86 9 12 0 4</b> <b>9 20 24.5</b> 22.47 0 13 0 4</b>	5.32 30.6A 19 12 0 8.75 7.88 5.97 46.35 15 13 0 9.44 8.69	1 19 1 10.72 5.47 7 11 1 20 3 9.50 9.87 7 12	1 30.98 28.66 1 16.11 18.41	13 18 1 8.35 8.07 13 19 1 13.59 13.71 13 20 1 9.81 9.44
3 23 0 10,69 A,79 9 14 0 10	2.05 25.72 15 16 0 7.81 3.08	1 22 1 17.71 17.47 7 14	1 10.82 8.42	14 0 1 21.66 23.49
3 24 0 5,95 1,47 9 15 0 25		1 23 1 13.10 10.88 7 15	1 43.76 46.59	14 1 1 31.75 26.62
<u>3 25 0 8,82 10,23</u> 9 16 0 10	0.46 6.11 15 17 0 13,63 13.69	1 24 1 7.87 5.61 7 16	1 8.50 6.12	14 2 1 9.73 10.00
4 0 0 50,86 51,64 9 17 0 33	1.06 30.21 15 18 0 5,34 3.67	1 25 1 5.30 7.64 7 17	1 7.71 8.01	14 3 1 25,60 20,14
4 2 0 15.36 7.24 9 19 0 1 4 3 0 A1.58 81.43 9 20 0 1	5,56 17.35 15 21 0 1.47 8.62.	2 1 1 51.66 55.71 7 19 2 2 1 107.30 118.57 7 21	1 13.36 11.14	14 5 1 17.16 14.20 14 6 1 32.70 29.14
4 4 0 111.34 111.51 9 21 0 14	4.40 16.12 16 1 0 18.09 21.04	2 3 1 59.65 52.35 7 23	1 7.90 8.58	14 7 1 46,63 43.85
4 5 0 19.62 20.94 9 22 0 4	6.75 7.93 16 2 0 2.80 1.51	2 4 1 08.11 107.13 7 25	1 10.59 11.41	14 8 1 7.68 8.56
4 6 0 47.13 81.90 9 23 0 8	<u>8.75 9.70 16 3 0 20.95 19.01</u>	2 5 1 24.15 15.56 5 0	1 47.10 95.16	14 9 1 22.87 23.09
4 7 0 17,00 30.96 9 25 0 1	5.61 11.65 <u>16 4 0 20.98 21.95</u>	2 6 1 110.89 114.77 8 1	1 43.83 51.21	14 10 1 27.69 25.26
4 7 0 13,45 11.43 10 0 7	5.28 72.20 <u>16 4 5 0 15 18 18 18</u>	2 7 1 50.01 54.00 8 2	1 48.63 47.50	14 11 1 14.52 10.52
4 9 0 93,14 45,19 10 1 0 20	6.44 20.17 16 6 0 6.89 0.13	2 8 1 42,94 41,46 8 3	1 19.88 16.49	14 12 1 25.64 24.17
4 10 0 59,31 56,30 10 2 0 51	1.95 44.30 16 7 0 10.52 9.59	2 9 1 33,81 32,58 8 4	1 64.77 39.11	14 13 1 10.83 9.57
<u>4 11 0 40.04 41.64</u> 10 3 0 1	7.87 5.89 16 8 0 7.93 8.12	2 10 1 84,56 83.73 8 5	1 7.73 7.66	14 14 1 10.65 9.26
4 12 0 17.41 19.33 10 4 0 66	8.39 60.63 16 9 0 16.28 13.60	2 11 1 40,85 34,54 8 6		14 15 1 10.39 10.75
4 14 0 41,63 41.40 10 6 0 30 4 15 0 7,95 6.51 10 7 0 10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 <u>13</u> <u>1</u> <u>72.76</u> <u>19.16</u> <u>8</u> <u>8</u> 2 <u>14</u> <u>1</u> <u>65.70</u> <u>62.73</u> <u>8</u> <u>9</u>	1 22.92 23.21	14 18 1 7.14 5.58 14 19 1 9.82 10.86
4 16 0 37.32 33.37 10 8 0 21	1.00 16.90 16 13 0 11.67 14.30	2 15 1 10.96 8.97 8 10	1 32.17 32.47	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
4 17 0 23.54 20.42 10 9 0 26	2.48 22.15 16 14 0 10,10 11.22	2 16 1 24.38 22.5° 9 11	1 14.22 12.03	
4 18 0 14.11 14.03 <u>10 10 0 44</u> 4 19 0 2.80 1.55 10 11 0 1 4 20 0 13 10 0 155	<u>9.54 48.17</u> 16 15 0 4.84 7.35 2.57 5.66 16 16 0 6.48 2.40	2 20 1 21.34 19.67 8 12 2 21 1 13.36 8.31 8 13	1 14.30 10.74	15 2 1 13.17 12.93 15 3 1 18.20 18.85
4 21 0 2.77 3.06 10 13 0 10	0.11 10.32 16 18 0 9.57 8.67	2 $23$ 1 10.29 9.40 8 15	1 - 11,33 - 9,90	15 5 1 8.59 7.01
4 22 0 2.69 4.45 10 14 0 1	4.57 12.74 16 19 0 13.87 15.35	2 $24$ 1 15.61 15.24 8 16		15 6 1 11.57 9.81
<u>4 23 0 6,27 5,21</u> 10 15 0	2,80 3,12 17 1 0 2,81 3,57	2 25 1 9.92 9.33 8 17	1 10.97 12.20	15 7 1 18.57 17.14
4 24 0 11,21 12,04 <u>10 16 0</u>	7,95 9,42 17 2 0 21,03 21,03	3 0 1 5.06 6.05 8 18	1 18.17 13.49	15 8 1 60,48 53.64
4 29 0 2.17 2.59 10 17 0 14 5 1 0 133.35 139.82 10 18 0 21 5 2 0 21.85 14.09 10 10 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 7,65 5.00 1 17,45 15.19	15 9 1 8.67 5.92 15 11 1 6.65 8.51 15 12 1 18.19 16.68
<b>5</b> 3 0 48.73 40.98 10 20 0 0	6.35 7.47 17 6 0 10.44 9.67	3 4 1 20.34 20.88 8 24	1 15.48 12.72	15 14 1 6.28 5.59
<b>5</b> 4 0 19.31 20.53 10 21 0	4.89 7.52 17 7 0 6.79 6.75	3 5 1 81.76 81.74 9 0		15 16 1 11.58 11.97
5 0 101,56 102,17 <u>10 22 0</u>	7,86 6.91 17 8 0 23.96 22.65	3 6 1 68.46 58.92 9 1	1 41.01 51.32	15 17 1 7.05 2.55
5 0 0 4.62 4.92 10 23 0	2.05 0.45 <u>17 9 0 7.68 0.74</u>	3 7 1 45.04 50.41 9 2	1 51.43 45.34	15 18 1 10.15 8.51
5 8 0 78,94 69,57 11 2 0 2 5 9 0 19,92 23.04 11 3 0 4	1,07 72,10 17 10 0 15,50 11,65 7,25 19,85 17 11 0 12,80 12,15 4,62 44,54 17 12 0 12,45 11,47	3 9 1 96.44 00.34 9 4 3 10 1 46.04 40.34 9 5	1 46.54 43.06 1 7.13 5.55	16 2 1 18.54 14.07
<u>5 10 0 2.02 4.77 11 4 0 1</u>	1.16 5.30 17 13 0 6.00 2.26	3 11 1 A4.96 A0.94 9 6	1 18.29 57.01	16 3 1 16.44 12.87
5 11 0 21.49 25.13 <u>11 5 0 5</u>	5.74 54.54 17 14 0 2.34 1.04	3 12 1 18,19 14.43 9 8	1 27.94 29.47	16 4 1 15.51 13.49
<b>5</b> 12 0 11.83 13.11 11 6 0 5	9.07 60.24 <u>17 15 0 7.01 6.75</u>	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	1 39.97 38.9)	16 6 1 20.53 16.87
5 13 0 6.63 7.75 11 7 0	6.84 4.29 <u>17 16 0 8.76</u> 9.54		1 8.91 8.26	16 7 1 32.64 30.95
		3 16 1 10,22 6.51 9 12 3 17 1 12,88 0.45 0.45	1 31.61 28.84 1 31.16 48.34	16 9 1 7.67 5.94 16 10 1 6.57 5.78
<b>5</b> 17 0 12.20 9.72 11 11 0 3	5,24 33,47 19 1 0 15,17 13,86	3 18 1 33,68 34,53 9 14	1 10.05 13.19	16 11 1 13.46 12.4?
<b>5</b> 18 0 10.42 7.92 11 12 0 1	2,72 11,51 18 2 0 2,77 0,45	3 19 1 27.61 26.37 9 15	1 29.42 31.17	16 15 1 13.07 12.22
<b>9</b> 19 0 24,51 21,73 11 13 0 2	1,01 22,84 18 3 0 19,49 21.63	<u>3 20 1 14.87 12.72 9 16</u>	1 10.24 9.93	16 16 1 12.71 13.55
5 20 0 2,60 2,29 11 14 0 2	4,03 21.41 18 4 0 14,00 10.17	3 21 1 14.39 15.97 <u>9 17</u>	1 13.44 12.91	16 17 1 8.10 6.71
7 21 0 0.74 7.58 11 15 0 .2 9 22 0 2,66 0.76 11 16 0 9 23 0 10,07 10.11 11 17 0 2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 23 1 10.77 11.12 9 20 3 25 1 12.06 10.86 9 22	1 8.91 8.30	17 2 1 6.71 4.45 17 3 1 5.47 1.98
<u>9 24 0 0,10 7.23 11 16 0 20</u>	2.35         26.45         18         8         0         7,44         3.88           2.19         21.57         19         9         6.33         4.24	4 0 1 A3.80 A7.85 9 23	1 8.31 4.77	17 4 1 8.63 6.54
9 25 0 7.90 12.53 11 19 0 20		4 1 1 A1.98 64.97 10 0	1 38.50 35.40	17 5 1 15.86 18.97

Table 2 (cont.)

17 6 1 10.83 A.47 17 7 1 14.72 11.21	3 12 2 48.77 54.50 3 13 2 17.88 14.76	9 1 2 A2,55 67,24 9 2 2 19,64 23,75	15 6 2 11.57 12.27 15 7 2 4.72 5.91	2 12 3 9.77 4.88 2 13 3 14.45 10.69	8 1 <u>3 25.00 26.79</u> 8 2 <u>3 36.03 33.20</u>
17 8 1 13.04 12.16 17 9 1 13.38 11.10	3 14 2 23.96 21.04	9 3 7 24.41 24.04	15 8 2 13,75 15.54	2 14 3 34.17 32.67	8 3 3 32.64 53.77 8 4 3 25.99 22.32
17 10 1 7.29 5.27	3 16 7 48.67 48.64	9 5 2 28.80 53.42	19 10 , 7 14,73 14.54	2 16 3 15.13 14.90	A 5 3 15,5A 18.3A
17 12 1 6.90 4.81	3 19 2 11.90 10.92	9 8 2 36.25 15.67	15 12 2 15,32 15,39	2 18 3 11.01 0.83	8 7 3 28,99 27,47
$-\frac{17}{17}\frac{14}{15}\frac{1}{1}\frac{7.74}{8.94}\frac{9.31}{9.36}$	3 20 2 13.66 10.6 ⁿ 3 21 2 9.28 5.82	9 9 2 46.68 42.51 9 10 2 17.56 17.78	15 13 2 7.63 7.10 19 15 2 14.71 19.12	2 19 3 11.81 10.36 2 20 3 20.81 22.75	8 8 3 20,73 21.74 8 9 3 12.62 13.04
17 16 1 5.53 3.12 18 0 1 7.59 6.35	3 22 2 17.63 19.33	9 11 2 29.68 33.74	15 16 2 3.87 3.45	2 21 3 9,73 A.30 2 22 3 6.73 P.44	8 10 3 15.32 15.27 8 12 3 7.49 9.58
	3 24 2 5.48 3.18	9 13 2 4.58 4.36	19 19 2 6.59 6.82	2 23 3 7,64 6.02	8 13 3 7.62 7.71
18 3 1 11.33 10.68	4 0 2 24.02 22.05	9 16 2 11.57 13.33	14 1 2 13.36 11.89	2 26 3 5.20 5.84	8 15 3 13.45 14.29
15 4 1 7.51 7.37 18 7 1 9.64 8.46	4 1 2	9 17 2 11.50 13.34 9 18 2 8.63 8.84	16 3 2 7.44 21.61 16 4 2 23.83 26.82	3 0 3 35,64 3,50 3 1 3 68,84 59,05	8 16 3 15,88 18,40 8 17 3 8,38 9,31
18 6 1 11.69 9.77 18 9 1 6.08 7.43	4 3 2 64.37 67.02	9 19 2 14.82 16.14 9 20 2 9.56 11.25	$\frac{16}{14}$ $\frac{5}{5}$ $\frac{2}{7}$ $\frac{4.71}{9.36}$ $\frac{5.79}{10.71}$	3 2 3 56.90 58.66	8 19 3 5,57 8,93 8 20 3 9,44 11,44
18 10 1 9.66 9.53	4 5 2 49.22 51.27	9 22 2 7.40 9.34	16 7 2 15.85 16.73	3 4 3 24.81 20.15	8 21 3 6.96 8.51
18 12 1 4.49 5.02	4 7 2 22.29 20.38	10 0 2 76.21 85.91	16 9 2 9,17 10.78	3 6 3 69.12 60.28	8 24 3 10,82 11.75
18 13 1 8,53 9.96 18 15 1 5.24 6.96	4 8 2 7.59 8.87 4 9 2 20.86 19.17	$\frac{10}{10}$ , $\frac{1}{2}$ , $\frac{2}{2}$ , $\frac{10}{5}$ , $\frac{97}{35}$ , $\frac{9}{4}$ , $\frac{27}{35}$ .	16 10 2 4.53 2.48 16 11 2 4.42 4.07	3 7 3 7.65 6.12 3 8 3 17.49 17.20	0 0 3 11.18 15.38 9 1 3 32.55 34.14
19 0 1 9.61 9.50 19 1 1 5.12 3.96	4 10 2 26.43 28.54	10 3 2 22.78 22.87	16 12 7 5.27 7.10	3 9 3 73,21 72,06	9 2 3 5.64 9.91 9 3 3 16.62 20.00
19 2 1 8.85 9.31	4 12 2 18.44 23.23	10 5 2 10.80 9.04	14 14 2 8.89 8.85	3 11 3 47.83 46.71	9 4 3 19.84 21.83
10 6 1 B.51 10.06	4 14 2 32.00 39.44	10 6 2 33.54 34.99	16 19 2 8.59 10.35 16 19 2 4.79 5.38	3 13 3 22.52 20.3	0 6 3 23.47 27.64
19 7 1 4.82 5.75 19 8 1 6.65 7.81	4 16 2 22,34 22.83	10 8 2 10.31 12.17	17 0 2 4,68 3.27	3 14 3 17.92 19.87 3 15 3 22.87 22.61	9 7 3 16,83 18,47 9 8 3 27,93 30,81
19 9 1 8.55 8.93 19 10 1 6.23 2.85	4 18 2 13.34 12.77	18 10 2 44.94 48.01	17 3 ? 9.31 A.35	3 16 3 14.00 13.19	9 9 3 29.29 37.27
19 11 1 5.06 6.50	4 21 2 11.07 14.44	10 12 2 17.78 15.34	17 6 2 5.61 9.65	3 18 3 16.35 14.24	0 11 3 18.05 17.72
20 0 1 16.17 17.35	4 23 2 4,97 5.60	10 14 2 28.06 36.99	17 9 2 5,37 7.44	3 20 3 9.73 9.13	9 13 3 14.64 16.51
20 1 1 0.73 10.14	4 24 2 5.25 9.44	10 16 2 30,65 32.46 10 17 2 10.86 15.41	17 10 2 5.25 4.47	3 24 3 4.99 4.28	9 15 3 9,81 9.31
$-\frac{20}{20}$ $\frac{6}{7}$ $\frac{1}{1}$ $\frac{5,49}{7,57}$ $\frac{2,22}{8,94}$	5 0 2 18.70 19.19 5 1 2 85.32 75.80	10 18 2 4.51 8.94	17 13 7 4,70 0.89 17 14 2 4,44 4,28	3 25 3 12.16 11.19 3 26 3 4.36 5.80	9 16 3 13.31 15.28 9 17 3 5.83 5.18
20 8 1 5,18 1,77	5 2 2 23.91 21.21	10 20 3 14,81 16.00	17 15 2 3.37 2.12	4 0 3 56.21 51.94	9 18 3 5,65 1.84
28 11 1 5.77 4.14	4 2 21.54 17.33	10 22 2 6.50 7.99	18 0 2 7.84 4.22	4 2 3 18.22 21.71	9 21 3 3.82 3.05
21 2 1 6.00 4.86	5 6 2 18.32 17.41	11 0 2 13.79 14.85	18 1 2 11.94 13.85 18 2 2 13.15 15.51	4 4 3 71.64 19.23	0 23 3 5.12 4.75
21 6 1 4.81 5.73 21 7 1 6.57 9.16	5 7 2 7.55 6.30 5 8 2 32.39 31.70	11 1 2 32.53 34.25 11 2 2 38.57 45.65	18 6 2 9.24 8.15 18 7 2 5.26 6.07	4 5 3 9.00 8.16 4 6 3 29.74 27.68	10 0 3 4,18 0.57 10 1 3 6.62 A.08
21 9 1 6.85 11.10	5 9 2 32.80 33.96	11 3 2 40.14 47.24	18 9 2 9.61 10.36	4 7 3 58.51 65.97	10 2 3 12.64 13.38
22 2 1 3.61 2.77	5 11 2 32,16 34.AP	11 5 2 46.77 46.05	18 11 2 10.45 11.04	4 9 3 52.07 56.59	10 4 3 16.39 16.08
$-\frac{22}{22}$ $\frac{3}{6}$ $\frac{5}{1}$ $\frac{5}{600}$ $\frac{7}{6042}$	5 12 2 31.03 0.17 5 13 2 .27.80	11 8 2 92.32 27.80 11 7 2 8.59 9.10	18 13 2 5.94 7.27 18 14 2 6.35 4.82	4 11 3 26.31 29.50	10 6 3 15.06 15.86
0 0 2 218.61 236.94 0 2 2 78.40 66.48	\$ 14 2 12.30 16.1ª 5 15 2 50.58 52.44	$\begin{array}{c}11 \\ 11 \\ 9 \\ 2 \\ \end{array} \begin{array}{c}23,57 \\ 27,31 \\ \end{array} \begin{array}{c}23,78 \\ 26,28 \\ \end{array}$	18 15 2 2.88 3.67 19 0 2 4.27 5.09	4 12 3 10.67 17.57 4 13 3 33.80 34.77	10 7 3 23,48 23.11 10 8 3 12,61 10,48
0 3 2 72.82 59.83	5 16 2 10.80 7.49		10 1 2 7.07 0.10	4 <u>15 3 9.56 6.51</u> 4 <u>16 3 9.74 12.92</u>	10 9 3 23.43 20.50 10 10 3 13.04 10.61
0 5 2 24.40 13.30	5 18 2 6.68 3.62	11 12 2 4.67 4.31	19 5 2 5.04 5.54	4 17 3 32.20 35.46	10 11 3 22.41 24.47
0 6 2 8,46 7.74 0 7 2 <u>54</u> 55 55,77	$\frac{9}{5} \frac{10}{20} - \frac{2}{7} - \frac{10.11}{6.54} - \frac{18.41}{5.15}$	11 13 2 4.71 4.81 11 14 2 16.71 16.55	19 9 2 8.30 9.19	4 19 3 9.66 12.75	10 13 3 13.89 16.37
0 8 2 34.05 29.93 0 9 2 10.34 4.87	5 21 2 7.07 7.96 5 22 2 5.21 5.91	11 15 2 4.71 5.32 11 16 2 6.56 8.67	20 1 2 5.85 9.43	4 20 3 5.75 5.0V 4 21 3 12.2P 14.49	10 14 3 4.91 4.48 10 15 3 8.43 9.77
0 10 2 63.28 63.92	5 23 2 9.71 10.62	11 17 2 4,53 4,85	28 1 2 3.89 4.37	4 22 3 5.15 5.97 4 23 3 6.11 4.94	10 16 3 5.86 6.61 10 17 3 11.39 13.66
£ 12 2 13.11 10.50	\$ 25 2 <u>10,99</u> <u>11,34</u>	11 19 7 6.59 5.50	21 5 2 5.26 6.03	4 24 3 9.11 9.23	10 18 3 6.31 7.88
0 14 2 24.39 22.03	4 1 2 44,53 45.28	11 22 2 3.21 4.00	20 7 2 3.52 3.26	5 0 3 16.52 11.05	10 21 3 10.45 11.19
0 15 2 43,43 44.85 0 16 2 49,37 97.64	6 2 7 29.36 33.87 6 3 2 28.30 24.39	11 23 2 6.40 7.29	20 8 2 3,39 5.30 20 9 2 3.96 3.61	5 2 3 84.87 85.08	10 22 3 4.46 6.65
- <u>61727,966,59</u> 018213,6612,02	6 4 2 55.30 54.74 6 5 2 21.22 20.90	12 1 2 14.87 14.31 12 2 2 23.71 25.04	<b>20</b> 11 2 4.89 5.39 <b>21</b> 1 2 4.85 3.39	5 3 3 7.02 11.57 5 4 3 24.56 24.59	11 0 3 11.22 11.48 11 1 3 12.85 12.80
0 19 2 4,72 2,55	6 6 2 28.11 31.72	12 3 2 26,57 28,55	<b>B1</b> 3 2 3.35 2.17	5 5 3 13.65 10.98 5 6 3 35.65 39.23	11 2 3 17.71 17.64
# 21 2 4,60 4.77	4 8 2 26.30 34.15	12 5 2 16.83 16.81	21 5 2 5.56 8.91	7 3 31.23 27.92	11 4 3 24.24 25.R1
1 0 2 73.71 59.04	6 9 2 32.97 34.95 6 10 2 26.86 24.98	12 6 2 12.45 15.76 12 7 2 38.66 42.76	21 8 2 9.31 10.50 21 9 2 4.50 6.08	5 9 3 15.59 17.89	1 6 5 - 30.05 - 31.85
1 1 2 180,51 206,38 1 2 2 74,35 80,79	6 11 2	12 8 2 11.09 11.58 12 9 2 30.45 32.28	21 10 2 4.66 7.41 22 3 2 6.10 8.69	5 10 3 25.91 26.29 5 11 3 19.87 21.09	11 8 3 9,49 8.55 11 9 3 9,61 8.96
1 3 2 58,51 51.00	6 13 2 30,61 35,48	12 10 2 37.03 37.25	22 5 2 7,58 9.81	5 12 3 29,14 28,64 5 13 3 21,28 23,41	11 10 3 14.15 14.A1 14 11 3 11.09 14.29
1 5 2 43.37 47.60	6 15 2 11.60 11.54	12 12 2 17.01 17.14	0 3 3 52,18 50.32	5 14 3 4.71 6.0A	11 13 3 13.87 15.05
1 7 2 53.16 55.17	6 16 2 8.70 13.35 6 17 2 8.81 8.10	12 13 2 25,44 28.42	0 4 3 26,54 19,14 0 5 3 27,55 23,78	5 16 3 16.22 17.11	11 14 3 4.8e 7.81 11 15 3 4.79 1.87
1 8 2 47.83 40.27 1 9 2 77.77 84.21	6 18 2 13.77 15.19 6 19 2 4.68 2.41	<u>12 15 2 8.03 10.69</u> 12 16 2 8.48 10.05	0 6 3 7.92 12.32 0 7 3 66.93 72.81	5 18 3 (8,27 22.42 5 19 3 10.17 13.67	11 16 3 13.50 14.10 11 17 3 9.53 12.46
1 10 2 33.30 36.52 1 11 2 40.81 43.24	6 20 2 8.55 8.88 6 21 2 8.80 11.03		0 8 3 10.27 4.75	<u>5 20 3 5.67 3.03</u> 5 21 3 5.39 7.08	11 18 3 7.99 9.74 11 19 3 4.01 5.43
1 12 2 36.97 35.8A	6 23 2 7.70 11.28	12 19 2 6.83 6.03	0 10 3 10.12 6.82	5 22 3 11,26 12,63 5 23 3 5,31 5,03	11 20 3 6.37 6.34
14 2 21.62 19.86	7 0 2 35.98 29.51	12 21 2 5.71 8.66	0 12 3 11.00 1.85	5 24 3 6.63 6.28	11 22 3 6.27 5.56
1 16 2 10.66 9.36	7 1 2 30.45 31.58	12 22 2 7.03 10.32	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<u>6 0 3 62.49 62.55</u>	12 1 3 4.80 7.01
1 17 2 20.08 18.8A 1 18 2 22.49 21.88	7 3 2 24.36 22.06 7 4 2 20.18 19.28	13 0 2 6,22 7,13 13 1 2 12,47 11,77	0 15 3 16,91 20.85 0 16 3 8,33 11.41	6 1 3 77.80 27.61 6 2 3 33.50 35.54	<u>37.3316.08 14.64</u> 17.4312.81 16.50
1 19 2 25.36 23.14	7 5 2 32.97 31.80	13 2 2 32.64 35.62	0 17 3 9.14 10.28	6 3 3 31,13 26,27 6 4 3 15,97 18,01	12 5 3 26.89 29.08
1 21 2 7.28 7.34	7 7 2 19.59 16.55	13 4 2 16.14 13.95	19- <u>3</u> _8-45_5.71_	6 5 3 17.22 17.88	17 7 3 4.81 5.14
1 23 2 9.46 10.97	7 9 7 8.10 8.08	13 6 2 45.24 43.67	0 21 3 10.80 10.20	6 7 3 27.04 27.75	12 9 3 14.19 15.69
<u>1 67 6 248 21/</u>	7 11 2 21.33 20.25	15 / 2 20.32 21.54 15 8 2 13.14 14.69	0 23 3 25,71 25.60	6 9 3 28.07 30.81	12 11 3 18,71 20.34
2 2 2 20.33 14.84	7 12 2 27.21 29.18	13 10 2 10.00 2.91 13 11 2 4.72 5.10	1 0 3 24.21 26.39	6 10 3 27.63 25.22 6 11 3 27.63 25.22	12 12 3 6.02 1.82
2 3 2 39,42 34,09 2 4 2 23,24 17,39	7 14 2 13.53 15.71 7 15 2 4.61 4.35	13 12 2 11.55 11.52 13 15 2 12.77 16.57	1 2 3 34.38 30.96 - 1 3 3 25.68 25.36	6 13 3 18.09 19.10	12 14 3 16.53 16.94 12 15 3 11.40 13.50
2 5 2 22,57 20.77	7 16 2 20.70 23.13 7 17 2 8.18 11 53	13 16 2 8.17 8.03	1 4 3 50.84 47.92	6 14 3 27.25 30.96 6 15 3 11.91 13.30	12 16 3 4.49 7.04
2 7 2 53.31 .52.64	7 18 2 18.23 17.20	. 13 18 2 10.83 11.79	1 6 3 34.78 37.24	6 16 3 23,80 26,42	12 18 3 12.76 11.54
2 9 2 23.53 22.32	7 20 2 7.80 4.85	13 19 2 4,50 5.80 <u>-</u> 13 20 2 4,73 4,46	$\frac{1}{1} \frac{7}{8} \frac{3}{3} \frac{31.04}{47.85} \frac{30.14}{47.07}$	. 6.19 3 10.04 10.35	12 20 3 9.54 11.56
2 10 2 10.72 10.24 2 11 2 31.75 31.00	7 22 2 13,08 14,51 7 23 2 4.54 0.62	13 22 2 8.20 9.57 14 0 2 25.22 27.83	1 9 3 28.00 28.52 1 10 3 22.28 21.6A	6 20 3 9.65 8.47 6 21 3 8.61 9.34	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
2 12 2 26.28 20.83	7 24 2 4.68 7.44	14 1 2 17.70 16.27	1 11 3 14,68 11.33	6 23 3 6.26 7.93 6 24 3 7.05 7.39	13 2 3 13.08 17.17
2 14 2 13.66 9.80	1 2 51.72 53.09	14 3 2 16.89 18.27	1 13 3 25,47 24.38	6 25 3 5.38 4.54	13 4 3 18,64 14.52
2 16 2 18.06 16.40	5 3 2 42.98 46.62	14 4 2 28,85 31.60	1 14 3 15,36 16,41	7 1 3 45.68 45.73	13 5 3 13.26 13.38
2 18 2 13.92 13.23	8 2 20.08 18.19 8 5 2 25.55 24.93	14 6 2 10,96 7.19 14 7 2 15,22 17,85	1 16 3 18.45 15.35 1 17 3 7.33 5.84	7 2 3 34.89 37.34 7 3 3 13.86 15.02	13 7 3 16.94 16.92 13 8 3 27.98 29.40
2 19 7 7.47 9.31 2 28 7 13.72 11.24	6 6 2 18.29 17.87 8 7 2 43.11 47.41	14 8 2 17.00 15.50	1 19 3 11,83 11,53	7 4 3 12.40 11.58 7 5 3 39.44 43.40	13 9 3 26.46 29.07 13 10 3 9 81 11 81
2 21 2 16.35 14.43	8 8 2 10.55 15.49	14 10 2 10.56 11.72	1 21 3 7.27 9.24	7 6 3 30,15 31,04	13 11 3 8.45 6.01
2 23 2 10.09 9.63	8 10 2 30.74 31.94	14 12 2 4,65 8.55	1 22 3 14.08 13.05 1 23 3 12.50 12.78	7 8 3 26.47 26.94	13 13 3 10.59 13.26
2 24 2 7.56 7.91 2 25 2 10.57 4.14	0 11 2 27,64 10,15 8 12 2 26.02 26.39	14 13 2 14.93 16.27	1 24 3 9.70 8.14 1 25 3 7.0P 7.44	7 9 3 28,47 29.92 7 10 3 15.79 17.35	13 14 3 7.30 7.74 13 15 3 4.46 4.95
2 26 2 9.11 2.32 3 0 2 4.21 4.86	8 13 2 21.05 22.05 8 14 2 12.57 15.00	14 15 2 13.60 14.20 14 16 2 7.76 8.60	1 26 3	7 11 3 15.63 16.31 7 12 3 21.51 23.32	13 16 3 8,53 8,20
3 1 2 15.02 19.80	8 16 2 12.03 13.26	14 17 2 13.03 13.04	2 1 3 30.49 26.35	7 13 3 22.02 23.35	13 18 3 3.75 6.65
3 3 2 47.68 46.64	8 <u>18 ? 8.74</u> 8.43	14 19 2 4.10 7.28	2 3 19.83 37.89 2 3 3 13.57 9.84	7 15 3 19.86 23.4	13 19 3 4,16 6,97 13 20 3 5,59 4,00
3 4 7 50,32 47,89 3 5 7 54,54 55.02	8 19 2 5.59 4.62 8 20 2 12.06 12.93	$\frac{14}{14} \frac{20}{21} \frac{2}{2} \frac{10.92}{8.23} \frac{10.79}{9.03}$	2 4 3 83.11 51.54 2 5 3 50.32 46.64	7 16 1 9.83 11.30 7 17 3 4.88 3.82	13 21 3 8.05 10.29 14 0 3 10.33 12.04
3 6 2 52.6A 54.6D 3 7 2 10.87 10.12	8 21 2 15.62 18.55 8 22 2 4.74 A.04	15 0 2 6.62 4.33	2 6 3 42.79 49.29 2 7 3 41 47 47.27	7 18 3 5.88 1.57 7 19 3 9.70 9.95	14 1 3 25,33 27,70
3 8 2 36.44 40.77 3 9 2 18.21 10 E	# 23 2 B.66 9.37	15 2 2 4.69 5.71	2 8 3 10.27 5.30	7 20 3 4.44 8.25	14 6 3 24.57 24.09
3 10 2 24.88 23.55	6 25 2 4.77 6.04	15 4 2 25.35 28.86	2 10 3 74.94 74.02	7 72 3 6.09 6.45	14 8 3 19.61 21.11
• ** c :0+01 :****	- U F 36.74 14.11	47 7 2 17.04 14.01	e 11 0 13.51 11.14		1- ¥ 3 22.47 74.1"

# X-RAY STUDIES OF C25 TERPENOIDS. III

Table 2 (cont.)

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.73 10.71 11.38 9.91	7 13 4 8,40 7 14 4 9,11 7 15 4 11	8,47 5,91 9,04	4 13 4 7.74 4 14 4 4.82	8.60 3 5.01 3	14 5 <u>12.5</u> 3 15 5 <u>17.5</u> 2	10.09 1 15.86 1	0 15 5	12.78 12.99
14 13 3 <u>8,53</u> 7,74 1 20 14 14 3 10,79 14,28 1 21 14 15 3 5,16 5,27 1 23	10.80 <u>8.99</u> 11.13 4.54 5.40 3.93	7 16 4 12,20 7 16 4 0,41 7 20 4 7,45	14.71 8_601 9.57	4 18 4 4,65 5 0 4 13,99	4,91 3 7,54 3 2,80 3 13,41 3	18 5 17.43 19 5 8.21 20 5 8.48	13.25 13.80 9.36 7.27	10 17 5 10 18 5 11 0 5 11 <u>1 5</u>	6.77 8.19 5.67 2.15 6.77 4.69 13.97 13.65
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5,12 4,44 56,4 <u>P</u> 51,40 51,78 48,48	7 21 4 5,15 7 22 4 9,39 7 23 4 4,23 8 1 4 29,85	7.14 12.01 <u>6.26</u> 27.45	5 1 4 17.28 5 2 4 4,78 5 3 4 8,93 5 4 9,45	18,95 4 5,82 4 8,35 4 9,64 4	0 5 28,94 1 5 26,92 2 5 38,26 3 5 24,70	30.27 20.90 35.17 22.19	1 2 5	8.07 11.98 8.31 10.91 11.27 11.62
14 20 3 3,02 3,13 2 3 4 15 0 3 6,02 2,66 2 4 4 15 1 3 8,52 8,04 2 5 4	43,76 42.16 46,40 36,78 13,12 12,91	8 2 4 16,12 8 3 4 28,99 8 4 4 11,89	17.57 35.04 9.60	5 5 4 15.63 5 6 4 7,39 5 7 4 6.52	17.49 <u>4</u> 9.14 <u>4</u> 3.56 <u>4</u>	4 5 9,70 5 5 9.65 6 5 21.98	7.66 10.72 21.44	1 6 5 1 7 5 1 9 5	8,33 9.84 7,59 3.83 22.97 20.11
15 2 3 17.02 17.22 2 6 4 15 3 3 10.99 10.95 2 7 4 15 5 3 10.40 10.20 2 6 4 15 6 3 15.83 17.22 2 9 4	24,24 22,48 31,38 34,65 18,98 18,05 30,88 31,00	8 5 4 15.72 8 6 4 12.73 8 7 4 25.40 8 8 4 12.87	16.08 <u>11.85</u> 21.28 13.31	5 8 4 4,54 5 9 4 6,29 5 11 4 4,18 5 12 4 4,02		7 5 35.48 8 5 23.51 9 5 25.83 10 5 44.59	28.49 1 24.18 1 25.87 1	1 10 5	10,45 9,96 9,74 11.35 6,54 5,58
19, 7, 3, 9,09, 8,66, 2,10,4 19, 8, 3, 25,06, 26,26, 2,11, 19, 12, 3, 14,82, 15,57, 2, 12, 4	13,53 10,54 26,70 24,71 10,90 7,97	8 9 4 13.53 8 10 4 25.45 8 11 4 10.17	19.87 24.26 13.82	15 13 4 4,67 15 14 4 10,72 15 15 4 10,15	4.64 4 11.63 4 12.18 4	11 5 16.97 12 5 18.50 13 5 5.89	15.51 14,97 8,35	1 16 5	5,77 6,47 5,83 4,52 9,63 11,20
15 13 3 4,31 5,90 2 13 4 15 14 3 4,13 1,14 2 14 4 15 15 3 7,30 8.22 2 15 4	16.44 16.53 10.18 16.54 12.65 10.02 18.07 20.02	8 12 4 13,71 8 13 4 9,74 8 14 4 4,86	16.19 12.51 4.77	15 16 4 4,16 15 17 4 5,57 16 0 4 4,63	4,72 4 5.81 4 5.88 4	14 5 15.93 15 5 9.51 16 5 8.71	17.27 1 10.15 1 8.38 1	2 1 5 2 5 2 5 2 5 5	9.63 11.35 5.89 3.94 4.81 7.17
15 17 3 4,07 3,81 2 17 4 15 17 3 4,07 3,81 2 17 4 15 18 3 2,94 3,26 2 18 4 16 1 3 4,86 5,22 2 19 4	28.23 27.23 11.88 9.02 8.83 9.30	8 16 4 8,81 8 17 4 16.47 8 18 4 4,37	7.4A 7.6.61 7.4.10	L6 3 4 10.77 L6 4 4 8.53 L6 5 4 4.51	11.96 4 7.95 4 3.14 5	18 5 8.03 20 5 5.24 0 5 6.49	6.89 1 1.76 ⁷ 1 2.49 1	2 5 5	<u>12.70</u> <u>13.70</u> 6.77 6.06 <u>16.86</u> <u>16.51</u> 12.97 <u>13.82</u>
16 2 3 4.86 7.75 9 20 4 16 3 3 4.85 4.25 2 21 16 4 3 9.66 10.16 9 22 4	10,74 8,33 17.91 17.51 8,77 5.78	8 20 4 6.61 8 21 4 11.14 8 22 4 5.5	8.07 9.87 7 0.86	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	2.40 5 11.64 5 5.88 5	1 5 15.53 2 5 36.41 3 5 15.82	16.43 1 34.27 1 12.64 1	2 8 5	6,62 7.91 4.62 3.07 14,68 14,52
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.70         0.10           7.70         9.06           22.74         17.91           19.40         12.33	9 1 4 36.7 9 2 4 20.8 9 3 4 17.6	38.90 7 19.80 5 17.59	L6 12 4 5.15 L6 13 4 7.23 L6 14 4 4.43 L6 15 4 4.39	0.71 5 8.10 5 3.02 5 3.03 5	4 5 20.16 5 5 14.51 6 5 11.95 7 5 12.30	16.01 1 10.21 1 10.41 1	2 11 5 2 13 5 2 14 5 2 15 5	11.26 11.26 8.19 8.94 11.32 11.13 7.26 4.90
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 54.51 51.59 4 31.70 27.94 4 25.93 30.76	• 4 4 11.6 • 5 4 31.0 • 6 4 14.6	3 19.27 5 35.66 15.65	17 0 4 6.20 17 1 4 6.19 17 2 4 15.09	6,64 5 6,61 5 16,71 5	8 5 25,66 9 5 19.69 12 5 17.30	25.64 1 21.46 1 20.63 1	3 5 5 3 6 5 3 7 5	15.58 15.92 16.14 16.33 16.28 12.87
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4 27.24 24.80 4 10.50 7.59 4 7.71 4.02	9 8 4 18.4 9 9 4 27.0 9 10 4 19.5	17.23 1 17.83 5 30.41	L7 3 4 8.65 L7 4 4 8.00 L7 6 4 5.07 L7 7 4 5.71	11.02 5 8.69 5 4.19 5	13 5 5 90 14 5 5,86 15 5 6.67	7.36 1 5.75 1 6.80 1	3 9 5 3 10 5	- 17,55 - 16,99 6,28 - 8,55 7,49 - 12,52
17 0 3 4,72 3,25 3 9 17 1 3 10,02 10,25 3 10 17 3 3 7,42 8,52 3 11	4 17.30 16.20 4 11.67 6.91 4 11.97 5.96	• 11 4 14.5 • 12 4 23.6 • 15 4 15.7	4 15.68 1 23.30 2 16.49	17 8 4 7.85 17 9 4 3.78 17 10 4 6.26	11.48 5 5.45 5 4.84 5	17 5 8.29 18 5 13.31 19 5 7.35	10.20 13.71 1 5.82 1	3 12 5 3 13 5 3 14 5	4.91 4.80 13.46 11.43 6.17 6.85
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 18.57 15.63 4 19.43 19.50 4 12.24 9.90 4 0.09 4.54	9 16 4 7.2 9 17 4 6.2 9 19 4 7.3 9 20 4 5.0	9 9.64 7 6.73 5 9.86	17 11 4 6.83 17 12 4 7.79 17 13 4 7.37	7.04 5 8.29 6 6.46 <u>6</u>	20 5 5.07 0 5 17.62 1 5 24.99	3.98 1 17.40 1 20.67 1	4 1 5	0.29 9.28 4,63 6.73 15.29 15.27
17 6 3 6.23 8.23 3 16 17 9 3 10.05 11.69 3 17 17 10 3 10.17 10.89 3 18	4 26.31 23.98 4 17.25 12.74 4 11.08 9.84	• 21 4 6.7 • 22 4 5.9 10 0 4 47.0	7 8.09 5 4.12 2 45.76	18 3 4 7.92 18 5 4 3.83 18 6 4 3.74	8.28 6 1.23 6 3.20 6	2 5 24.44 4 5 9.35 5 5 11.30	24.52 1 9.60 1 9.07 1	4 6 5	<u>9,07</u> 8,98 11,41 10.26 15,24 16,42 13,62 13,53
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 9,82 6,95 4 13,01 8,81 4 9,34 5,99	10 1 4 25,5 10 2 4 7,7 10 3 4 6,4	4 26.82 9 8.84 0 7.98	18 7 4 4,44 18 9 4 4.06 18 10 4 4,40	<u>3,89</u> 6 6.76 <u>6</u> 5.75 6	6 5 8.74 7 5 31.15 8 5 20.18	11.12 1 32.60 1 18.49 1	4 9 5 4 10 5 4 11 5	15,41 13,26 7,03 5,56 10,29 8,83
17 15 3 5,24 6,11 3 23 17 16 3 4,16 4,86 3 24 18 2 3 8,92 10,89 4 0	4 5,29 3.98 4 5,27 3.00 4 30,59 33.48	10 5 4 5,6 10 5 4 21,6 10 5 4 5,7	6 7.60 6 22.11 9 4.35	19 1 4 5.66 19 4 4 3.44 19 6 4 6.47	5.02 6 5.34 6 3.08 6 6.91 6	10 5 18.34 11 5 15.88 12 5 9.63	13,68 1 14,83 1 9,98 1	5 2 5	9,73 10,46
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 29.85 29.62 4 20.46 13.87 4 21.47 18.60	18 8 4 15.8 10 9 4 16.3 18 10 4 29.1	5 15.31 6 17.82 5 29.47	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.60 <u>6</u> 6.51 6 8.10 6	13 5 8.08 14 5 4.75 15 5 10,43	<u>12.58</u> 1 3.71 1 10.94 1	565 575 585	6,67 5,44 <u>4,13 5,22</u> 16,30 16,19
18 9 3 6.20 1.73 4 5 18 10 3 7.03 6.84 4 6 19 13 3 5.78 1.96 4 7	4 31,53 34.60 4 37,62 40,52 4 18,64 17,02	10 11 4 4.8 10 13 4 4.8 10 14 4 16.4	6 7.27 2 2.40 4 16.93	$   \begin{array}{ccccccccccccccccccccccccccccccccccc$	7,53 6	16 5 6,40 17 5 10.17 18 5 7,09 19 5 6,58	4,59 1 12,74 1 5,79 1 3,26 1	5 9 5 5 10 5 5 11 5.	11,62 11.49 5,86 3.67 6,57 5,30
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 18.59 19.31 4 8.84 7.56 4 24.67 24.34	10 15 4 9.8 10 16 4 10.9 10 17 4 4.2	2 11.12 5 14.26 6 5.03	20 6 4 4,72 20 7 4 3,99 20 8 4 3.10	6.57 6 4.00 7 2,74 7	20 5 5,42 0 5 15,75 1 5 29,98	3.90 1 18.45 1 29.68 1	6 0 5 6 6 5 6 7 5	6,58 9,33 7,26 10,62 8,42 9,98
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 24.73 27.05 4 25.45 25.56 4 31.56 32.69 4 19.75 23.57	10 10 4 10.2 10 19 4 8.2 10 20 4 8.8 10 21 4 6.1	2 9,00 8 6,02 2 8,96 0 5,80	21 2 4 3.74 21 3 4 2.27 0 2 5 14.41 0 3 5 44.99	<u>3,58</u> 7 20,23 7 45,76 7	2 5 12.39 3 5 14.57 4 5 10.68	12.55 1 11.25 1 11.19 1	6 8 5 6 9 5 6 10 5	9.26 9.85 6.49 6.94 6,55 4.73
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 13,77 15,51 4 11,81 12,86 4 7,45 7,34	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 25.82 4 24.72 1 29.42	0 4 5 21.37 0 5 5 16.19 0 6 5 16.22	18,15 7 10,93 7 9,54 7	6 5 17.47 7 5 17.78 8 5 7.38	18.93 1 14.44 5.09	0 0 5 0 0 6 0 1 6	6,40 6,18 73,51 83,44 34,05 35,31
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 6,44 4,16 4 8,65 3,95 4 9,89 11,97	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 5,13 8 36,49 8 15,72	0 7 5 16,99 0 8 5 16,31 0 9 5 6,10	<u>15,51</u> 7 15,41 7 <u>6,28</u> 7	9 5 14.20 10 5 5,86 11 5 12.26	19.73 3.77 13.36	026 036 086	19.68 21.00 19.73 17.49 28.11 23.52
20         2         3         8,55         9.38         5         0           20         3         3         7,20         7,59         5         1           20         4         3         3,54         3,85         5         2	4 5.80 7.85 4 56.24 47.89 4 19.45 20.57	11 8 4 16.8 11 9 4 16.1 11 10 4 5.9	0 19.59 5 17.23 6 10.87	0 13 5 13,52 0 15 5 4,80 0 18 5 4,44	17.21 7 13.70 7 5.86 7 2.18 7	12 5 13.AU 13 5 16.54 14 5 5.76 15 5 15.89	17.23 4.93 18.96	1 1 6	18,28 14.08 22,40 18.67 18.32 19.92
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 22,48 15,62 4 25,02 23,77 4 40,07 38,34 4 0,07 38,34	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 9,69 5 12,78 4 7,98	0 20 5 11.70 1 1 5 28,32 1 2 5 12.17	1.65 7 24.42 7 8.64 7	16 5 7.00 18 5 6.24 19 5 8,89	7.53 3.16 9.42	1 4 6 1 5 6 1 6 6	9.20 7.02 15.98 15.64 13.07 9.45
20         10         3         5,17         5,03         5         7           21         3         3,00         2,65         5         6           21         5         3         5,26         6,79         5         9	4 8.46 5.07 4 22.26 22.48 4 12.84 13.19	11 16 4 4.2 11 17 4 6.4 11 18 4 13.0	9 6.56 0 4.59 4 15.01	1 4 5 13,93 1 5 5 31,56 1 6 5 14,00	11.42 7 13.78 8 	20 5 0.00	9.04 23.17 20.50 19.47	1 7 6 1 8 A 1 9 6	13,09 17,01 13,08 10,09 13,04 11,31
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 8,27 9,66 4 15,78 20,68 4 10,97 12,79	11 19 4 4.1 11 20 4 6.7 12 0 4 8.2	9 5.02 3 7.88 7 5.94	1 7 5 21.70 1 8 5 33.06 1 9 5 28.67	15.52 A 32.46 8 25.36 8	3 5 15.50 4 5 25.98 5 5 12.53	14.78 24.40 16.25	<u>i 11 6</u> 1 12 6 1 13 6	25.64 23.63 12.61 10.97 8.71 8.56
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 <u>16.87</u> <u>17.63</u> 4 7.09 9.44 4 8.48 7.21	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 9.46 1 21.65 5 15.90	1 10 5 17.38 1 11 5 23.17 1 12 5 31.86 1 13 5 22.05	15.72 8 21.09 8 28.24 8 19.61 8	6 5 16.39 7 5 8.13 8 5 4.74	16.76 6.81 5.92	1 14 6 1 15 6 1 16 A	11,95 9,19 19,87 18,49 13,35 13,35
0         4         124,32         120,47         5         21           0         1         4         39,98         44,05         5         52           0         2         4         64,35         56,54         5         23	4 6.22 4.78 4 7.56 7.55 4 9.06 9.66	12 6 4 13.3 12 7 4 26.8 12 8 4 12.8	0 14.77 8 29.56 9 <u>11.68</u>	1 14 5 22,56 1 15 5 12,78 1 16 5 16,02	12.42 8 13.27 A 15.57 8	10 5 7.60 12 5 8.94 13 5 4.72	9.44 6.13 6.96	2 0 4 2 1 4 2 2 4	24,46 24.41 22,34 19,51 22,37 14,01
0 4 4 37,93 40,05 6 0 0 5 4 14,35 5,73 6 1 0 6 4 28,39 27,90 6 2	4 30.77 31.58 4 17.47 13.35 4 23.48 20.73	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	e 13.34 6 19.03 4 8.73 3 10.15	1 19 5 7,26 1 19 5 7,26 1 20 5 10,16 2 0 5 42,90	<u>     6.30</u> 4     5.98     8     9.97     8     41.30	14 5 15.66 15 5 9,49 16 5 7,43	14.86 <u>8.47</u> 8.54	2 3 6 2 5 6 2 5 6	26,53 24,54 28,43 29,31 17,45 10,85
6 7 4 9.91 4.17 <u>6 3</u> <u>0 8 4 26.44 23.88</u> 6 4 0 9 4 24.60 26.26 6 5	4 17,20 19,25 4 36,41 38,67 4 21,53 17,19	12 13 4 13,4 12 14 4 7,7 12 15 4 7,9	0 11.41 1 7.90 9 5.74	2 1 5 21,29 2 2 5 20,11 2 3 5 12,44	27.39 A 15.59 A 7.43 9	19 5 6.40 20 5 6.68 0 5 5.60	2.07 6.55 10.51	7 6 8 A 9 A	72.60 19.85 14.28 11.37 17.43 9.76
0 11 4 16.71 18.62 6 7 0 12 4 25.60 24.42 6 8 0 13 4 4.62 6.05 6 9	4 34.02 33.82 4 33.35 34.65 4 15.24 13.43	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 5.89 9 15.04 7 4.78 8 3.78	2 4 5 25,36 2 5 5 39,33 2 6 5 36,78 2 7 5 23,00	26.37 • 38.79 • 33.48 9	1 5 22.19 2 5 25.80 3 5 14.98 4 5 15.70	16.34 29.87 14.38		14.13 3.61 <u>19.76</u> 15.72 13.74 7.87
0         14         4         12,99         16.22         6         10           0         15         4         8,36         8.23         6         11           1         4         33,35         29,83         6         12	4 16.32 18.19 4 19.41 29.06 4 19.25 21.77	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 16.17 4 28.84 8 14.83	2 8 5 18.50 2 9 5 16.34 2 10 5 26.20	16.81 9 13.64 9 24.07 0	5 5 6.64 6 5 27.20 7 5 16.18	10.09 31.80 17.51	14 6	13.01 5.30 12.71 10.89 20.15 18.77
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4 17.86 19.31 4 4.87 6.59 4 12.78 13.85	13 4 4 4,8 13 5 4 14,9 13 6 4 18,5 13 7 4 9,0	7 2.62 0 8.12 3 18.09 8 7.15	2 11 5 17,24 2 12 4 13,12 2 13 5 11,72 2 14 5 18,77	13.24 9 9.85 9 10.28 9	8 5 16.62 9 5 13.18 10 5 8.99	14.83. 13,23 8,49	5 6	15.64 12.11 18.10 12.38 12.82 14.04
8 22 4 3,88 0.13 6 17 9 23 4 6,02 6.79 6 18 0 24 4 12.27 15.00 6 19	4 9,48 8,83 4 8,59 7,15 4 5,38 3,60	13 8 4 5.9 13 10 4 8.2 13 11 4 8.0	2 11.18 0 6.19 6 7.03	2 15 5 14.01 2 16 5 11.61 2 17 5 9.37	7.17 19.33 3.22	12 5 15,66 14 5 6,36 15 5 4,33	15.72 5.17 5.82	8 6 9 A 10	12.81 13.31 12.77 5.56 15.51 11.10
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4 7.15 6.85 4 6.59 4.92 4 5.91 3.56 4 4.13 4.20	13 13 4 6,9 13 14 4 4,2 13 15 4 12,0	8.03 2 2.63 3 12.78	2 18 5 4.40 2 19 5 8.43 2 20 5 15.60	1.83 9 4.24 9 8.14 9	16 5 7.14 17 5 4.72 18 5 9.04	1.01	5 11 A L 0 7 L 1 7	12.51 5.82 9.02 2.65 9.02 8.67
1         4         10,77         8.90         7         0           1         5         4         20,82         17.32         7         1           1         6         4         44,75         44.25         7         2	4 17.75 19.01 4 21.20 20.86 4 34.53 34.10	13 17 4 6,4 13 18 4 9,2 14 0 4 17,8	7 5.33 7 8.74 8 17.19	3 1 5 31.97 3 2 5 24,89 3 3 5 6.94	34.01 10 25.12 10 3.63 10	0 5 19.11 1 5 12.90 3 5 11.40	0.11 <u>19.83</u> 9.06 8.47	1 7 2 7 4 7	13.90 13.38 13.87 19.16 13.74 14.82
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 3,93 1,88 4 32,87 27,47 4 16,86 17,11	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7.36 5.5.43 8.16.99	3 4 5 4,44 3 5 5 26,23 3 6 5 23,01	6.29 10 27.27 10 	4 5 21.00 5 5 18.50 7 5 14.02	23.00 15.60 12.80	57 87 97	13,63 12,96 13.07 11.12 12,77 9,78
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 14,50 13.20 4 13.67 47.54 4 16.61 19.63	14 - 7 = 14.0 14 - 6 - 4 = 8.3 14 - 7 - 4 = 9.5 14 - 8 - 4 = 7.4	7 12.90 3 4.30 5 6.96 7 8.33	3 8 5 25.40 3 9 5 25.10 3 10 5 25.67	14.00 - 18 27.10 10 26.37 10 24.45 10	0 5 11.70 9 5 12.23 10 5 9.53 11 5 12.44	<u>9.43</u> 11.91 9.64 12.85	10 7 11 7 5 0 7 5 1 7	12,42 12,49 14,69 11,87 17,60 19,30 19,67 15,94
<u>1 14 4 21.02 19.12 7 10</u> <u>1 15 4 28.09 26.38 7 11</u> <u>1 16 4 28.23 24.89 7 12</u>	4 4.63 10.33 4 8.83 8.59 4 18.59 20.63	14 9 4 8,0 14 10 4 7.2 14 11 4 6,3	7 5.91 2 6.87 0 4.67	3 11 5 12.54 3 1 <u>2 5 8.89</u> 3 13 5 14.61	11.34 10 9.32 10 11.08 10	12 5 8,65 13 5 8,42 14 5 5,32	6,14 .6.90 .2.55	3 3 7 L 0 R L 1 A	12.36 8.24 18.18 19.71 14.81 14.47

Table 3. Comparison of the calculated and observed intensity ratios of some of the Friedel pairs of reflexions used for the establishment of the absolute configuration

h	k	l	$ F_{c}(hkl) ^{2}/ F_{c}(hkl) ^{2}$	Io(hkl)/Io(hkl)
3	4	1	1.24	>1
3	14	1	1.22	>1
3	16	1	0.68	<1
4	18	1	0.75	< 1
5	14	1	2.46	>1
6	4	1	0.73	< 1
6	6	1	0.24	< 1
6	14	1	1.34	>1
7	2	1	0.81	< 1
7	3	1	2.10	>1
7	6	1	0.72	< 1
7	11	1	0.74	<1
8	3	1	1.43	> 1
9	5	1	2.16	>1
9	8	1	0.72	< 1
9	12	1	0.84	< 1
9	13	1	0.77	<1
9	14	1	0.72	< 1
9	16	1	1.59	>1
10	1	1	0.20	< 1

Tsuda, 1966) from the *Helminthosporium* species, and ophiobolin D (cephalonic acid; Itai, Nozoe, Tsuda, Iitaka & Nakayana, 1967) from *cephalosporium caerulens*) all have the same unique tricyclic system composed of fused five- eight- and five-membered rings. It should be noted here that the juncture between the rings A and B and that between B and C in ceroplasteric acid and ceroplastol I are both found to be *trans* in contrast to the *cis, trans* disposition in ophiobolins A, B and C.

Furthermore, the absolute configurations at C(6), C(10) and C(11) are opposite to those found in the ophiobolins A, B and C. In ophiobolin D, the situation is the same as in the other ophiobolins except around C(6), where C(7) is bonded through a double bond.

Bond lengths and angles found in the molecule of ceroplastol I p-bromobenzoate are shown in Figs. 3 and 4. The standard deviations of bond lengths and angles for each type of bond are calculated from those of the positional parameters and are listed in Table 1.

The average values of the bond lengths for the various types of bond are calculated to be 1.547 Å for C-C single bonds, 1.305 Å for C=C double bonds and 1.393 Å for the aromatic C===C bonds in the benzene ring. The mean C-C bond lengths and C-C-C angles averaged within each ring are listed in Table 4. Most of the unusual bond lengths are found at the junctions of two rings. Thus, the lengths 1.46 Å and 1.60 Å are found at the junctions between A and B, B and C, respectively.

The planarity and the conformation of each A, Band C ring will be seen in Table 5. As was found in ophiobolins A and D, the five-membered A and Crings take a puckered form and the eight-membered Bring takes a distorted chair conformation even though the juncture between the rings A and B is *trans* fused in this case. The dihedral angles between the median planes of each ring are 136° for rings A and B, and 171° for B and C. The atoms of the p-bromobenzoate group lie roughly on a plane. The equation of the plane

 Table 4. Mean values and their standard deviations of the C-C single bond lengths

 and C-C-C angles averaged in each ring

	Ring A	Ring B	Ring C
Number of single bonds	5	7	5
Mean bond lengths	1·54 Å	1.54	1.58
E.s.d.	0.02	0.02	0.05
Mean bond angles	104·6°	118.0	103.8
E.s.d.	1.0	0.9	0.8

Ring A	Ring B	Ring C	Benzene ring
$\begin{array}{ccc} C(2) & -0.036 \text{ Å} \\ C(3) & 0.058 \\ C(4) & -0.058 \\ C(5) & 0.036 \\ C(6) & -0.592* \end{array}$	$\begin{array}{rrrr} C(1) & -0.028 \\ C(8) & 0.029 \\ C(9) & -0.037 \\ C(11) & 0.036 \\ C(2) & -1.194* \\ C(6) & -1.683* \\ C(7) & -0.720* \\ C(10) & 0.691* \end{array}$	$\begin{array}{cccc} C(10) & 0.040 \\ C(12) & -0.041 \\ C(13) & 0.064 \\ C(14) & -0.063 \\ C(11) & -0.681* \end{array}$	$\begin{array}{cccc} C(27) & -0.017 \\ C(28) & 0.019 \\ C(29) & 0.005 \\ C(30) & -0.030 \\ C(31) & 0.031 \\ C(32) & 0.007 \\ Br & 0.1217 \\ \end{array}$
Plane involving C(7)=C(8)	Plane involving C(3)=C(20)	Plane involving C(18)=C(19)	Plane involving C(26)=O(1)
$\begin{array}{ccc} C(6) & 0.014 \\ C(7) & -0.067 \\ C(8) & -0.012 \\ C(9) & 0.026 \\ C(21) & 0.038 \end{array}$	$\begin{array}{ccc} C(2) & -0.011 \\ C(3) & 0.036 \\ C(4) & -0.011 \\ C(20) & -0.015 \end{array}$	$\begin{array}{rrrr} C(17) & -0.020 \\ C(18) & 0.008 \\ C(19) & 0.050 \\ C(24) & -0.010 \\ C(25) & -0.028 \end{array}$	$\begin{array}{ccc} O(1) & 0.007 \\ O(2) & 0.012 \\ C(25) & -0.006 \\ C(26) & -0.013 \\ C(19) & -0.042 \end{array}$

Table 5. Best planes and the perpendicular distances of the atoms from the planes

* Not included in the calculation of the plane.



Fig. 5. Internal rotation angles (°). The definition and illustration of the internal rotation angles are given in the preceding paper (Morisaki, Nozoe & Iitaka, 1968).



Fig. 6. Projection of the crystal structure along the *c* axis. Intermolecular short contacts of less than or equal to 3.8 Å are shown in the Figure. I, II, III and IV indicate the molecules at (x, y, z),  $(\frac{1}{2} - x, -y, z - \frac{1}{2})$ ,  $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$  and  $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ , respectively. The translations are denoted in parentheses.



Fig. 7. Projection of the crystal structure along the b axis.

passing through the benzene ring  $[C(27) \sim C(32)]$  is

0.035 X - 0.024 Y + 0.999 Z - 3.257 = 0,

where, X, Y and Z are taken along the crystallographic a, b and c axes, respectively, and are measured in Å units. As shown in Table 5, the bromine atom lies nearly on the plane, whereas the atoms of the carbonyl group, C(26), O(1) and O(2), lie on another plane, the angle between these two planes being 6.4°.

The internal rotation angles calculated for each bond of the molecule are shown in Fig. 5. The definition of the internal rotation angles and the way of representing the values in the Figure are illustrated in Fig. 5(b)of the preceding paper (Morisaki, Nozoe & Iitaka, 1968).

In Figs.6 and 7 are shown the projections of the crystal structure along the *b* and *c* axes, respectively. Intermolecular short distances of less than 3.8 Å are indicated by broken lines. It is seen that the closest approaches of the molecules take place mainly between the bromobenzene moieties which are stacked antiparallel along the twofold screw axis. Other close

contacts involve the carbonyl oxygen atoms but there are no abnormally short distances.

The authors wish to express their thanks to C. Itoh Electronic Computing Service for the use of a CDC 3600 computer. This work was supported by research grants from Hohansha and Yoshitomi Seiyaku Co. Ltd.

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## The Crystal Structure of Capaurine Hydrobromide

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### (Received 22 July 1968)

The structure of tetrahydroprotoberberine alkaloid capaurine,  $C_{21}H_{25}O_5N$ , 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  $P_{21}2_{121}$ . 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⁺ · · ·Br⁻ (3·12 Å) and O-H⁺ · · ·Br⁻ (3·39 Å) hydrogen bonds along the *b* axis.

### Introduction

Capaurine,  $C_{21}H_{25}O_5N$ , and capaurimine,  $C_{20}H_{23}O_5N$ , 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

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 thinlayer 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,  $C_{21}H_{26}O_5NBr$ ; m.p. 198– 199 °C,  $[\alpha_D]$ -423 ° (c=0.40 in methanol). Orthorhombic,  $a=24.79\pm0.03$  Å,  $b=8.08\pm0.01$  Å,  $c=10.32\pm0.03$  Å. Space group,  $P2_12_12_1$ . Four molecules per unit cell. Volume of the unit cell, 2067 Å³. Density (by flotation), 1.458 g.cm⁻³; density (calculated), 1.453 g.cm⁻³. Linear absorption coefficient for Cu Ka radiation,  $\mu=$ 32.62 cm⁻¹. Total number of electrons per unit cell, F(000)=936.

