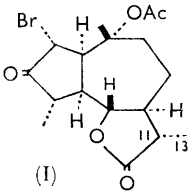
1129. *Sesquiterpenoids. Part III.*[1] *The Stereochemistry of Santonin: X-Ray Analysis of 2-Bromo-α-santonin* [2]

By J. D. M. Asher and G. A. Sim

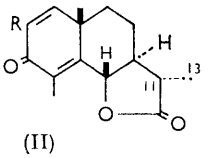
X-Ray analysis of 2-bromo-α-santonin has defined the stereochemistry of α-santonin as (II; R = H). Crystals of the bromo-derivative are orthorhombic, space group $P2_12_12_1$, and have four molecules of $C_{15}H_{17}BrO_3$ in the unit cell of dimensions $a = 7{\cdot}34$, $b = 23{\cdot}34$, $c = 8{\cdot}28$ Å. The crystal structure was solved by the heavy-atom method, and the atomic co-ordinates were refined by Fourier and least-squares calculations. The final value of the discrepancy R over 1277 independent reflexions was 15·2%.

The sesquiterpenoid lactone α-santonin has been the subject of chemical investigation for more than a century.[3] The constitution was established by classical degradative methods [4] and confirmed later by synthesis.[5] Most of the stereochemistry was unambiguously established, but the configuration at position 11 led to controversy,[6] though opinion generally favoured the β-methyl orientation.[7]

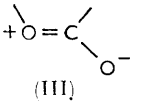
In Part II [1] we defined the stereochemistry of 2-bromodihydroisophoto-α-santonic lactone acetate as that shown in (I) with the configuration of the 13-methyl group opposite to that previously accepted.[7] Barton and his co-workers [8] demonstrated that epimerisation at C(11) does not occur in the sequence of reactions involved in the conversion of



(I)



(II)



(III)

α-santonin into bromodihydroisophoto-α-santonic lactone acetate, and it thus appeared that the stereochemistry of α-santonin must be as in (II; R = H). In order to obtain incontrovertible proof of the revised configuration, we undertook an *X*-ray crystal-structure analysis of 2-bromo-α-santonin, and our results established the constitution and relative stereochemistry shown in (II; R = Br). It follows that the stereochemistry of α-santonin is indeed that in (II; R = H), the absolute configuration shown being firmly established chemically.[7] During our study, Nakazaki and Arakawa obtained further support for the α-methyl configuration at position 11 by the degradation of α-santonin to (+)-benzoylalanine.[9]

The crystal structure of 2-bromo-α-santonin was elucidated by the usual phase-determining heavy-atom method.[10] The proximity of the *x*- and *z*-co-ordinates of the

[1] Part II, J. D. M. Asher and G. A. Sim, *J.*, 1965, 1584.
[2] Preliminary communication, *Proc. Chem. Soc.*, 1962, 335.
[3] For earlier literature see J. L. Simonsen and D. H. R. Barton, "The Terpenes," Cambridge University Press, 1952, vol. III.
[4] G. R. Clemo, R. D. Haworth, and E. Walton, *J.*, 1929, 2368; 1930, 1110; G. R. Clemo and R. D. Haworth, *J.*, 1930, 2579.
[5] Y. Abe, T. Harukawa, H. Ishikawa, T. Miki, M. Sumi, and T. Toga, *Proc. Japan Acad.*, 1954, **30**, 116, 119; *J. Amer. Chem. Soc.*, 1953, **75**, 2567; 1956, **78**, 1416.
[6] E. J. Corey, *J. Amer. Chem. Soc.*, 1955, **77**, 1044; W. Cocker and T. B. H. McMurry, *J.*, 1955, 4430; T. Miki, *J. Pharm. Soc. Japan*, 1955, **75**, 416.
[7] W. Cocker and T. B. H. McMurry, *Tetrahedron*, 1960, **8**, 181.
[8] D. H. R. Barton, T. Miki, J. T. Pinhey, and R. J. Wells, *Proc. Chem. Soc.*, 1962, 112; D. H. R. Barton, J. E. D. Levisalles, and J. T. Pinhey, *J.*, 1962, 3472.
[9] M. Nakazaki and H. Arakawa, *Proc. Chem. Soc.*, 1962, 151.
[10] (*a*) J. M. Robertson and I. Woodward, *J.*, 1937, 219; 1940, 36; (*b*) G. A. Sim, in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," ed. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon, Oxford, 1961, p. 227.

bromine atom to the special value 1/4 introduced spurious planes of symmetry in the first three-dimensional electron-density distribution, and, as in our analysis of 2-bromodihydroisophoto-α-santonic lactone acetate,[1] made the unambiguous choice of atomic sites difficult. The recognition that the cyclohexadienone ring system lay approximately in the *bc*-plane allowed us to disentangle a major fraction of the molecule from spurious images, and permitted the normal process of Fourier refinement to proceed. Final refinement of the positional and thermal atomic parameters by the method of least squares reduced the average discrepancy between measured and calculated structure amplitudes (R) to 15·2% over 1277 observed reflexions.

The final electron-density distribution over one molecule is shown in Figure 1 as superimposed contour sections drawn parallel to (100). The atomic arrangement corresponding to this electron-density distribution is explained in Figure 2. The final atomic co-ordinates are listed in Table 1, and the interatomic distances and valency angles in Table 2. The

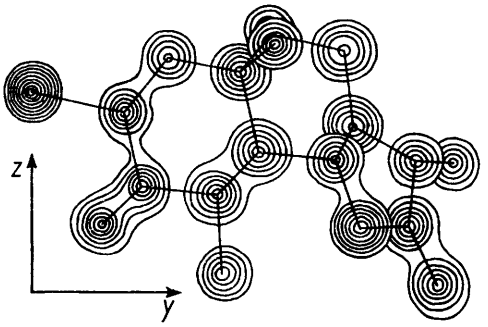


FIGURE 1. The final three-dimensional electron-density distribution for 2-bromo-α-santonin, shown by means of superimposed contour sections drawn parallel to (100). Contours around the bromine atom are at intervals of 4e Å^{-3} and around the other atoms are at intervals of 1e Å^{-3}

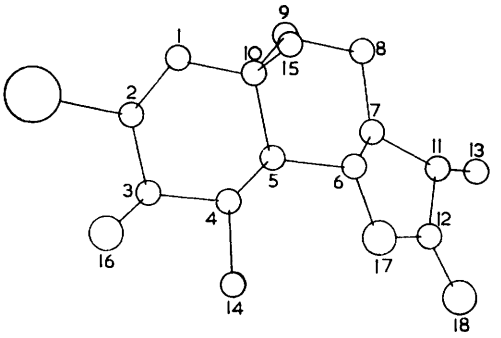


FIGURE 2. Atomic arrangement corresponding to Figure 1

TABLE 1

Atomic co-ordinates (origin of co-ordinates as in " International Tables " *)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
C(1)	0·2283	0·2590	0·1818	C(8)	0·4485	0·4067	0·1568	C(14)	0·2214	0·3045	0·6881
C(2)	0·2292	0·2188	0·2920	C(9)	0·4087	0·3444	0·1238	C(15)	0·0552	0·3468	0·1346
C(3)	0·2309	0·2332	0·4720	C(10)	0·2322	0·3191	0·2096	O(16)	0·2234	0·1986	0·5682
C(4)	0·2326	0·2944	0·5043	C(11)	0·4672	0·4730	0·4175	O(17)	0·2712	0·4196	0·5775
C(5)	0·2391	0·3349	0·3926	C(12)	0·3948	0·4633	0·5779	O(18)	0·4189	0·4876	0·7097
C(6)	0·2668	0·3980	0·4132	C(13)	0·6763	0·4966	0·4267	Br	0·2255	0·1381	0·2453
C(7)	0·4452	0·4146	0·3400								

* " International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, 1952, vol. I.

standard deviations of the final atomic co-ordinates were estimated in the usual manner from the least-squares residuals (see Experimental section) and are given in Table 3; from the results the average e.s.d. of a carbon–carbon or carbon–oxygen bond length is about 0·04 Å, and the average e.s.d. of a valency angle about 3°.

The average sp^3-carbon–sp^3-carbon single bond length of 1·55 Å is in excellent agreement with the value of 1·545 Å in diamond. The average carbon–carbon double bond length, 1·32 Å, is identical with that reported for *p*-benzoquinone.[11]

[11] J. Trotter, *Acta Cryst.*, 1960, **13**, 86.

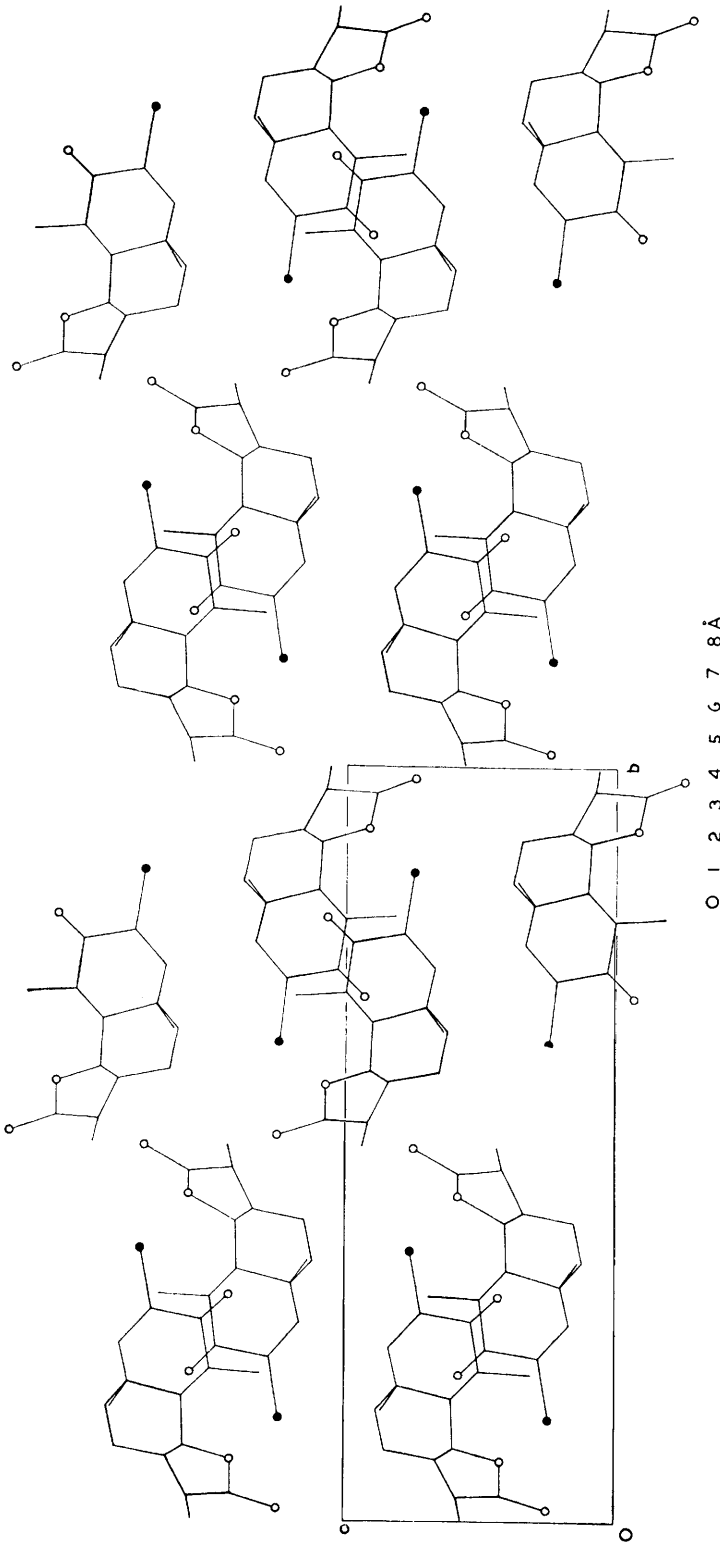


FIGURE 3. The arrangement of molecules in the crystal as seen in projection along the *a*-axis

TABLE 2

Interatomic distances (Å) and angles

Intramolecular bonded distances

C(1)–C(2)	1·31	C(4)–C(5)	1·32	C(6)–O(17)	1·45	C(10)–C(15) ...	1·58
C(1)–C(10)	1·42	C(4)–C(14)	1·54	C(7)–C(8)	1·53	C(11)–C(12) ...	1·45
C(2)–Br	1·92	C(5)–C(6)	1·50	C(7)–C(11)	1·51	C(11)–C(13) ...	1·63
C(2)–C(3)	1·53	C(5)–C(10)	1·56	C(8)–C(9)	1·51	C(12)–O(17) ...	1·34
C(3)–C(4)	1·45	C(6)–C(7)	1·49	C(9)–C(10)	1·59	C(12)–O(18) ...	1·24
C(3)–O(16)	1·14						

Intramolecular non-bonded distances

C(1) · · · C(4)	2·80	C(4) · · · C(15)	3·54	C(6) · · · C(15)	3·03	C(8) · · · O(17)	3·72
C(2) · · · C(5)	2·84	C(4) · · · O(17)	3·00	C(6) · · · O(18)	3·41	C(9) · · · C(11)	3·89
C(2) · · · C(9)	3·50	C(5) · · · C(8)	3·00	C(7) · · · C(10)	2·93	C(10) · · · C(14)	3·98
C(2) · · · C(14)	3·84	C(5) · · · C(11)	3·64	C(7) · · · C(15)	3·69	C(10) · · · O(17)	3·86
C(2) · · · C(15)	3·50	C(5) · · · C(12)	3·56	C(7) · · · O(18)	3·51	C(13) · · · O(17)	3·66
C(3) · · · C(6)	3·89	C(6) · · · C(9)	2·90	C(8) · · · C(12)	3·75	C(13) · · · O(18)	3·02
C(3) · · · C(10)	2·95	C(6) · · · C(13)	3·79	C(8) · · · C(13)	3·49	C(14) · · · O(17)	2·87
C(4) · · · C(7)	3·49	C(6) · · · C(14)	3·17	C(8) · · · C(15)	3·21	O(16) · · · Br	3·02

Intermolecular distances (<4 Å)

C(7) · · · $O(16)_I$	3·42	C(2) · · · $C(14)_I$	3·66	C(14) · · · $C(2)_I$	3·77	O(18) · · · $C(15)_{II}$	3·92
O(18) · · · $C(6)_{II}$	3·44	C(13) · · · Br_{IV}	3·67	C(3) · · · $C(3)_I$	3·78	C(3) · · · $C(14)_I$	3·94
O(18) · · · $C(11)_{II}$	3·44	O(18) · · · $C(7)_{\Pi}$	3·68	O(16) · · · $C(4)_I$	3·79	C(3) · · · $O(16)_I$	3·96
C(13) · · · $O(18)_{III}$	3·49	O(18) · · · $C(8)_{II}$	3·68	O(17) · · · Br_I	3·85	$C(14)_I$ · · · $C(9)_{VI}$	3·97
C(9) · · · $O(16)_I$	3·58	C(12) · · · Br_I	3·69	Br · · · $C(9)_V$	3·86	C(14) · · · Br_I	3·97
O(16) · · · $C(15)_I$	3·62	O(18) · · · Br_I	3·72	O(16) · · · $C(5)_I$	3·88	C(15) · · · Br_V	3·98
C(5) · · · $O(16)_I$	3·65	C(4) · · · $C(3)_I$	3·72	C(8) · · · $O(16)_I$	3·91	O(18) · · · $C(12)_{II}$	3·99
C(4) · · · $O(16)_I$	3·66	C(3) · · · $C(4)_I$	3·74	Br · · · $C(14)_I$	3·92		

The subscripts refer to the following positions:

I $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ III $1\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$ V $-\frac{1}{2}+x, \frac{1}{2}-y, -z$
II $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$ IV $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ VI $x, y, 1+z$

Valency angles

C(2)C(1)C(10)	126°	C(5)C(4)C(14)	126°	C(8)C(7)C(11)	122°	C(9)C(10)C(15)	110°
C(1)C(2)Br	124	C(4)C(5)C(6)	129	C(7)C(8)C(9)	107	C(7)C(11)C(12)	102
C(3)C(2)Br	114	C(4)C(5)C(10)	121	C(8)C(9)C(10)	116	C(7)C(11)C(13)	115
C(1)C(2)C(3)	122	C(6)C(5)C(10)	110	C(1)C(10)C(5)	113	C(12)C(11)C(13)	111
C(2)C(3)C(4)	113	C(5)C(6)C(7)	109	C(1)C(10)C(9)	108	C(11)C(12)O(17)	105
C(2)C(3)O(16)	122	C(5)C(6)O(17)	117	C(1)C(10)C(15)	109	C(11)C(12)O(18)	133
C(4)C(3)O(16)	125	C(7)C(6)O(17)	104	C(5)C(10)C(9)	109	O(17)C(12)O(18)	116
C(3)C(4)C(5)	125	C(6)C(7)C(8)	113	C(5)C(10)C(15)	108	C(6)O(17)C(12)	108
C(3)C(4)C(14)	109	C(6)C(7)C(11)	99				

TABLE 3

Standard deviations of the final atomic co-ordinates (Å)

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0·034	0·030	0·031	C(8)	0·038	0·032	0·034	C(14)	0·038	0·030	0·029
C(2)	0·029	0·021	0·028	C(9)	0·033	0·029	0·039	C(15)	0·033	0·029	0·036
C(3)	0·031	0·025	0·033	C(10)	0·029	0·025	0·030	O(16)	0·028	0·019	0·023
C(4)	0·030	0·025	0·030	C(11)	0·035	0·030	0·043	O(17)	0·024	0·020	0·021
C(5)	0·031	0·028	0·030	C(12)	0·032	0·026	0·038	O(18)	0·023	0·022	0·026
C(6)	0·032	0·024	0·032	C(13)	0·043	0·041	0·049	Br	0·003	0·003	0·002
C(7)	0·037	0·029	0·035								

None of the atoms of the cyclohexadienone ring is displaced significantly from the mean plane through these atoms, and it can be concluded that the cyclohexadienone system is planar. In agreement with this, the average valency angle in the ring is 120°. In the cyclohexane ring, on the other hand, the average valency angle is 111°, and the ring adopts the expected chair conformation. In the five-membered lactone ring the average valency angle is 105°, in excellent agreement with the average values for five-membered rings in other molecules, *e.g.*, hydroxy-L-proline (106°),[12] isoclovene hydrochloride (105°),[13]

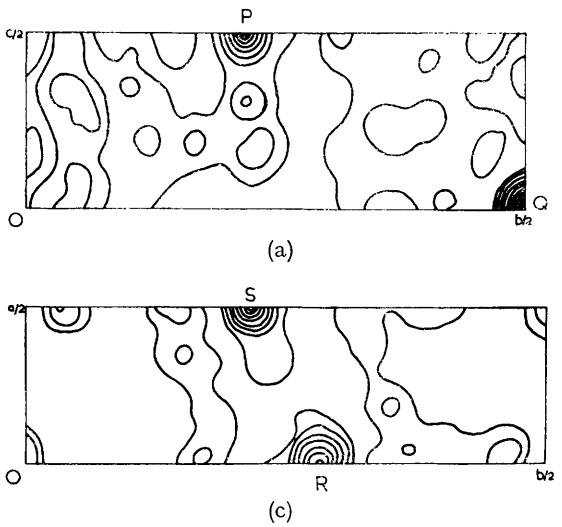
[12] J. Donohue and K. N. Trueblood, *Acta Cryst.*, 1952, **5**, 419.
[13] J. S. Clunie and J. M. Robertson, *J.*, 1961, 4382.

2-bromodihydroisophoto-α-santonic lactone acetate (105°),[1] and the ring adopts the envelope conformation with C(7) displaced by 0·61 Å from the plane through C(6), C(11), C(12), O(17), and O(18). The contribution of (III) to the molecular structure of lactones accounts for the planarity of these atoms and for the bond C(12)–O(17) adjacent to the carbon–oxygen double bond having a length of 1·34 Å, distinctly shorter than the length, 1·45 Å, of the bond C(6)–O(17).

Figure 3 shows the arrangement of the molecules in the crystal as viewed in projection along the *a*-axis. The intermolecular contacts (see Table 2) are all greater than 3·4 Å and correspond to normal van der Waals interactions; the shortest separations involve oxygen atoms.

Experimental

Crystal Data.—2-Bromo-α-santonin, $C_{15}H_{17}BrO_3$; $M = 325{\cdot}2$. Orthorhombic, $a = 7{\cdot}34$, $b = 23{\cdot}34$, $c = 8{\cdot}28$ Å, $U = 1418$ Å^3, $Z = 4$, $D_c = 1{\cdot}522$, $D_m = 1{\cdot}525$ g. cm.$^{-3}$ (flotation in aqueous KI), $F(000) = 664$, space group $P2_12_12_1$ (D_2^4). Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}542$ Å) $\mu = 43{\cdot}7$ cm.$^{-1}$.



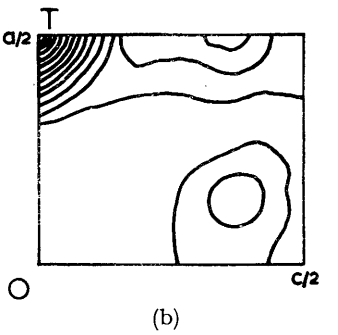


FIGURE 4. Sections through the three-dimensional Patterson synthesis, (a) at $U = \frac{1}{2}$ (b) at $V = \frac{1}{2}$, and (c) at $W = \frac{1}{2}$

Crystallographic Measurements.—Rotation, oscillation, and Weissenberg photographs were taken with copper K_α ($\lambda = 1{\cdot}542$ Å) radiation; precession photographs were taken with molybdenum K_α ($\lambda = 0{\cdot}7107$ Å) radiation. The unit-cell dimensions were obtained from precession photographs. The space group was determined uniquely from the systematic halvings in the *X*-ray spectra. The *hk*0—*hk*6 reflexions were recorded photographically by means of an equi-inclination Weissenberg camera, and the 0*kl* spectra were obtained with a precession camera. The intensities were estimated visually and corrected by the usual factors (Lorentz, polarization, and rotation [14]). The various layers were placed on the same relative scale by comparison of common reflexions on different photographs; the absolute scale was obtained at a later stage by correlation with the calculated structure amplitudes, $|F_c|$. In all, 1277 independent structure amplitudes, $|F_o|$, were evaluated.

Structure Analysis.—The position of the bromine atom was determined from two-dimensional Patterson syntheses and sections through the three-dimensional Patterson synthesis $P(UVW)$ at $U = \frac{1}{2}$, $V = \frac{1}{2}$, and $W = \frac{1}{2}$. These sections are shown in Figure 4. The co-ordinates initially derived for the bromine atom were $x = 0{\cdot}233$, $y = 0{\cdot}139$, $z = 0{\cdot}230$.

Structure factors based on the bromine atom alone were calculated and the value of R found

[14] G. Tunell, *Amer. Min.*, 1939, **24**, 448.

TABLE 4

Measured and calculated values of the structure factors

h	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α	*h*	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α
0	1	3	33	47	270			2	51	50	180
		4	22	20	90			3	5	13	180
		5	6	8	90			4	34	38	0
		6	6	1	270			5	14	11	180
0	2	3	123	122	0			6	16	15	180
		4	37	33	180	0	15	1	12	10	270
		5	69	72	180			2	6	8	90
		6	11	11	180			3	4	1	90
0	3	2	25	22	90			5	7	8	270
		3	15	14	90	0	16	0	18	15	180
		4	24	19	270			1	68	62	180
		5	25	26	90			2	12	17	180
		6	2	4	270			3	49	50	0
0	4	0	54	69	180			4	20	23	0
		1	26	20	0			5	27	25	180
		2	84	102	0	0	17	1	10	5	270
		3	64	67	180			3	4	0	90
		4	18	22	180			4	13	8	90
		5	3	2	180			6	11	10	270
		6	35	33	0	0	18	0	52	61	180
0	5	1	59	74	270			1	6	11	180
		2	3	3	270			2	36	34	0
		3	5	10	90			3	12	7	180
		4	49	53	90			4	30	24	180
		5	2	1	270			5	5	1	0
		6	16	15	270			6	17	15	0
0	6	0	24	78	0	0	19	2	4	1	90
		1	37	53	0			3	11	9	90
		2	51	56	180			4	8	9	90
		3	53	64	180			5	9	8	270
		4	27	28	0			6	7	6	90
		5	37	46	0	0	20	0	18	11	0
		6	25	25	180			1	33	29	0
0	7	1	19	25	270			2	9	1	0
		2	13	14	90			3	13	14	180
		3	5	6	90			5	28	24	0
		4	11	1	270	0	21	1	6	5	90
		5	3	0	90			2	4	3	270
		6	15	18	90			3	9	5	270
0	8	0	50	59	0			5	5	6	270
		1	42	48	180			6	5	6	90
		2	67	76	180	0	22	0	25	26	0
		3	51	56	0			1	11	2	180
		4	40	46	0			2	35	34	180
		5	19	22	180			3	26	15	0
		6	18	22	180			4	26	20	0
0	9	1	31	37	90			5	3	0	0
		2	13	9	90			6	8	11	180
		3	13	17	270	0	23	1	6	8	90
		4	22	23	90			6	5	3	270
		6	11	8	270	0	24	0	11	7	180
0	10	0	11	14	180			1	28	27	180
		1	79	93	180			2	18	11	0
		2	51	56	0			3	24	17	0
		3	51	58	0			4	15	10	180
		4	28	27	180			5	9	10	180
		5	21	22	180			6	7	5	0
		6	20	25	0	0	25	2	5	5	270
0	11	1	45	46	270			3	7	6	90
		2	13	14	90			4	9	3	270
		3	19	16	90			5	3	1	270
		4	20	22	90			6	3	1	90
		5	8	9	270	0	26	0	11	10	180
		6	6	5	270			1	21	13	0
0	12	0	16	9	180			2	21	19	0
		1	70	63	0			3	15	9	180
		2	13	20	0			4	12	15	180
		3	29	30	180			5	3	4	0
		4	39	46	180	0	27	2	4	5	270
		5	41	42	0			4	4	4	270
		6	15	16	0	0	28	0	13	8	0
0	13	1	6	6	270			1	6	7	0
		2	20	19	270			2	15	10	180
		3	4	1	270			3	13	10	180
		4	17	15	270			4	6	8	0
		5	18	14	90	0	29	1	6	4	90
0	14	0	60	62	0	0	30	0	10	9	0
		1	34	42	0			1	9	11	180

TABLE 4 (*Continued*)

h	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α	*h*	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α
1	0	1	7	10	90			1	40	34	85
		2	61	68	180			2	91	80	90
		3	33	35	270			3	5	3	15
		4	9	10	0			4	45	50	257
		5	18	20	90			5	6	4	171
		6	17	18	180			6	21	24	68
1	1	0	10	14	270	1	12	0	14	15	90
		1	109	155	251			1	14	17	217
		2	46	63	266			2	11	7	117
		3	31	77	84			3	6	3	327
		4	48	59	85			4	15	14	311
		5	23	27	285			5	5	3	90
		6	13	16	264			6	7	4	155
1	2	0	52	74	90	1	13	0	17	18	90
		1	28	37	185			1	40	48	88
		2	14	17	271			2	25	18	276
		3	15	11	268			3	55	61	277
		4	25	21	190			4	29	27	99
		5	12	9	38			5	31	32	102
		6	5	3	302			6	5	2	301
1	3	0	40	55	270	1	14	0	20	23	90
		1	42	54	226			1	15	12	104
		2	68	80	86			2	10	11	199
		3	28	35	78			3	11	9	267
		4	62	65	271			4	16	16	196
		5	12	14	275			5	14	16	5
		6	34	35	90			6	5	5	72
1	4	0	55	61	90	1	15	0	72	67	90
		1	42	50	162			1	25	24	282
		2	22	19	185			2	43	43	265
		3	5	6	327			3	25	20	80
		4	16	18	239			4	13	14	100
		5	22	20	318			5	7	5	256
		6	5	8	46			6	29	30	275
1	5	0	5	11	270	1	16	0	21	18	90
		1	94	114	102			1	11	11	133
		2	69	74	87			2	17	17	247
		3	40	46	279			3	4	4	2
		4	32	39	266			4	5	8	39
		5	41	45	91			5	20	21	125
		6	11	7	295			6	7	7	166
1	6	0	18	18	90	1	17	0	22	15	270
		1	39	41	76			1	19	21	289
		2	24	27	130			2	51	39	99
		3	20	21	246			3	45	38	89
		4	15	14	318			4	22	17	335
		5	9	11	281						
		6	14	14	201			6	12	15	249
1	7	0	87	100	90	1	18	1	13	12	85
		1	36	43	98			2	12	10	3
		2	59	70	268			3	18	18	354
		3	10	7	302			4	6	6	61
		4	42	55	90			5	8	5	98
		5	13	15	99			6	9	10	309
		6	21	25	275	1	19	0	7	8	2
1	8	0	7	11	90			1	24	24	270
		1	23	25	90			2	25	20	71
		2	15	13	11			3	11	13	83
		3	18	21	298			4	31	24	269
		4	23	32	40			5	18	16	254
		5	9	11	177			6	12	8	100
		6	17	17	295	1	20	0	8	9	78
1	9	0	46	41	90			1	13	11	270
		1	86	99	267			2	10	9	172
		2	8	1	291			3	4	6	172
		3	35	41	88			4	8	6	11
		4	9	2	197			5	4	2	216
		5	40	44	267			6	4	2	149
		6	6	9	290	1	21	0	42	25	90
1	10	0	26	24	90			1	20	22	86
		1	29	28	308			2	16	10	272
		2	7	8	210			3	20	24	270
		3	10	5	260			4	24	20	104
		4	14	17	139			5	12	11	95
		5	4	5	158	1	22	6	17	13	268
		6	11	11	258			1	10	9	20
								2	6	4	269
								3	6	6	2
1	11	0	105	113	270			4	5	5	61

TABLE 4 (*Continued*)

h	*k*	*l*	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α	*h*	*k*	*l*	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α
1	28	1	7	5	66	2	7	0	13	11	0
1	29	0	11	10	90			1	3	8	237
		1	6	3	237			2	41	42	270
		2	16	14	275			3	10	12	322
2	0	0	132	210	180			4	15	17	72
		1	11	5	90			5	11	15	169
		2	45	53	0			6	12	12	234
		3	14	15	270	2	8	0	30	29	180
		4	60	75	180			1	23	25	355
		5	4	1	90			2	47	54	348
		6	37	41	0			3	28	26	197
2	1	0	33	32	180			4	32	34	174
		1	73	82	93			5	20	22	20
		2	23	26	329			6	13	17	344
		3	20	26	35	2	9	0	13	12	180
		4	20	24	174			1	44	40	275
		5	13	13	295			2	24	24	18
		6	9	8	37			3	5	4	124
2	2	0	120	131	0			4	10	10	223
		1	110	118	15			5	3	2	280
		2	33	30	204	2	10	0	29	17	0
		3	59	69	184			1	37	47	346
		4	23	25	342			2	61	63	181
		5	26	26	358			3	30	39	181
		6	5	6	357			4	31	32	9
2	3	0	53	53	0			5	27	28	359
		1	48	55	352			6	8	9	196
		2	25	28	62	2	11	0	10	9	0
		3	20	23	222			1	21	20	7
		4	28	30	125			2	15	10	210
		5	22	23	305			3	16	18	185
		6	17	14	290			4	11	11	293
2	4	0	55	58	0			5	21	24	46
		1	17	11	190			6	4	4	165
		2	60	71	185	2	12	0	34	39	0
		3	46	49	350			1	67	63	182
		4	38	45	4			2	33	38	182
		5	8	8	182			3	30	30	350
		6	43	47	184			4	22	26	0
2	5	0	57	52	0			5	36	36	168
		1	33	39	347			6	5	3	343
		2	22	23	180	2	13	0	38	37	0
		3	21	20	94			1	9	9	219
		4	22	29	292			2	19	17	180
		5	14	17	83			3	5	1	16
		6	14	15	147			4	19	18	63
2	6	0	18	19	180			5	15	13	255
		1	62	75	189			6	4	7	135
		2	48	50	355	2	14	0	51	49	180
		3	43	54	356			1	13	16	212
		4	27	25	210			2	32	30	359
		5	28	31	160			3	26	31	351
		6	8	5	20			4	34	35	175
		5	12	9	145			5	8	10	150
1	23	0	9	14	90			6	20	18	359
		1	35	26	269	2	15	1	9	13	130
		2	13	18	275			2	5	2	39
		3	19	15	80			3	10	14	345
		4	7	9	107			4	8	6	187
		5	22	17	269			5	7	8	183
1	24	1	5	4	250			6	9	9	301
		2	10	9	259	2	16	0	24	27	180
		3	6	4	90			1	55	55	354
		4	9	9	167			2	8	13	353
		5	3	3	19			3	29	28	187
		6	3	3	64			5	20	17	13
1	25	0	35	25	270			6	6	5	266
		1	6	7	250	2	17	0	14	11	180
		2	28	21	86			1	15	16	337
		4	11	12	265			2	4	5	40
1	26	2	9	6	191			3	15	16	125
		3	3	5	72			4	7	5	251
		4	4	4	236			6	7	6	46
		5	2	2	210	2	18	0	40	32	0
1	27	0	6	0	270			4	26	26	7
		1	28	21	96			5	8	10	10
		2	4	1	318			6	14	12	181
		3	18	15	271	2	19	0	8	4	0

TABLE 4 (*Continued*)

h	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α
		1	3	7	335
		2	27	21	248
		3	4	5	214
		4	13	10	338
2	20	0	12	5	180
		1	37	32	190
		3	20	18	355
		4	5	4	94
		5	19	15	176
		6	4	2	10
2	21	1	11	12	129
		2	10	10	208
		3	7	8	343
		4	5	6	342
		5	7	5	199
2	22	0	24	25	180
		1	6	3	110
		2	28	25	2
		3	15	7	198
		4	21	19	164
		6	12	13	359
2	23	0	17	10	180
		2	8	6	48
		3	4	6	19
		4	5	4	183
		5	3	4	278
		6	4	5	9
2	24	0	13	7	0
		1	20	19	3
		2	17	10	176
		3	21	17	184
		4	10	7	31
		5	6	10	353
		6	2	2	157
2	25	1	10	7	5
		2	5	3	167
		5	4	5	355
2	26	0	15	14	0
		1	17	10	171
		2	17	15	185
		3	11	7	359
		4	7	8	353
		5	2	6	198
2	27	0	8	6	0
		1	5	4	84
		2	8	7	180
		3	5	4	8
		4	2	1	7
2	28	0	11	10	180
		1	7	7	150
		2	16	12	356
		3	7	9	1
2	29	0	3	0	0
		1	3	2	249
		2	1	3	304
3	0	1	48	50	270
		2	14	13	180
		3	24	26	90
		4	5	6	180
		5	16	16	270
		6	15	17	0
3	1	0	80	80	270
		1	59	61	80
		2	51	57	89
		3	54	59	274
		4	21	23	248
		5	35	33	101
		6	8	9	59
3	2	0	35	38	270
		1	37	31	5
		2	21	21	108
		3	19	20	232
		4	24	22	310
		5	16	12	155
		6	23	21	113
3	3	0	27	30	90
		1	12	12	49
		3	42	46	254
		3	22	27	261
		4	26	27	102
		5	26	25	86
		6	18	17	273
3	4	0	13	13	90
		1	31	31	100
		2	19	19	318
		3	22	25	290
		4	7	8	17
		5	11	14	87
		6	15	15	182
3	5	0	8	1	90
		1	41	46	243
		2	36	40	260
		3	41	43	89
		4	19	17	101
		5	31	31	275
		6	15	14	120
3	6	0	32	30	90
		1	34	33	175
		2	29	34	232
		3	25	26	51
		4	16	16	93
		5	11	13	296
		6	14	14	331
3	7	0	92	83	270
		1	10	15	218
		2	49	52	98
		3	10	7	9
		4	34	36	264
		5	8	9	286
		6	19	21	77
3	8	0	18	16	270
		1	17	20	258
		2	34	30	124
		3	24	28	126
		4	11	9	237
		5	9	10	299
		6	12	8	211
3	9	0	17	17	270
		1	76	77	81
		2	18	18	117
		3	29	35	262
		4	10	13	242
		5	30	30	94
3	10	0	19	20	270
		1	37	35	158
		2	22	26	55
		3	11	9	290
		4	18	19	316
		5	17	19	69
		6	8	7	152
3	11	0	67	71	90
		1	6	6	29
		2	36	37	281
		3	8	4	113
		4	33	32	84
		5	7	5	224
		6	27	28	266
3	12	0	44	35	90
		1	7	8	135
		2	22	22	257
		3	6	10	309
		4	15	13	95
		5	8	8	63
		6	8	8	317
3	13	0	26	25	270
		1	32	34	276
		2	29	23	98
		3	33	34	83
		4	15	11	246
		5	14	14	278
		6	8	8	261
3	14	0	7	7	90
		1	15	14	286
		2	7	8	298
		3	22	21	104
		4	17	14	3

TABLE 4 (*Continued*)

h	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α
		5	18	20	206
		6	4	3	274
3	15	0	30	27	270
		1	10	5	79
		2	41	37	100
		3	27	27	277
		4	15	17	273
		5	15	15	120
		6	15	20	89
3	16	0	22	16	270
		1	9	7	33
		2	24	24	42
		3	7	6	59
		4	10	10	259
		5	9	9	2
		6	10	9	87
3	17	0	39	31	90
		1	20	23	76
		2	31	25	277
		3	34	32	264
		4	6	4	146
		5	7	8	57
		6	10	9	283
3	18	0	8	4	90
		1	25	21	129
		2	22	19	187
		3	10	8	319
		5	13	9	129
		6	4	4	221
3	19	0	21	20	90
		1	9	5	281
		2	4	6	255
		3	16	12	96
		4	17	17	80
		5	14	12	261
		6	9	9	252
3	20	0	11	9	90
		1	13	12	21
		2	7	8	232
		3	12	7	67
		4	10	10	109
		5	3	4	154
		6	9	10	309
3	21	0	31	18	270
		1	17	17	285
		2	14	10	58
		3	7	10	81
		4	14	11	286
		5	8	10	247
		6	7	7	77
3	22	0	12	5	270
		1	15	14	278
		2	4	2	46
		3	13	10	129
		4	5	4	196
		5	4	4	272
		6	4	2	108
3	23	0	10	9	270
		1	26	20	82
		2	14	15	75
		3	18	13	263
		5	13	10	93
		6	2	1	21
3	24	0	7	7	270
		1	5	3	70
		2	7	7	90
		3	9	7	317
		4	5	6	296
		5	6	5	130
3	25	0	17	12	90
		1	5	7	76
		2	18	16	275
		3	4	5	288
		4	12	13	80
3	26	0	7	5	90
		1	7	6	82
		2	8	7	259
		3	6	5	288
		4	3	5	117
3	27	1	24	17	273
		3	8	8	83
3	28	1	6	5	61
4	0	0	97	116	0
		1	25	21	90
		2	33	35	180
		3	7	4	90
		4	27	33	0
		6	15	16	180
4	1	0	50	60	0
		1	45	38	296
		2	30	31	155
		3	31	35	200
		4	23	21	117
		5	15	14	27
		6	66	5	208
4	2	0	51	51	180
		1	39	37	181
		2	14	12	32
		3	44	45	349
		4	16	16	161
		5	22	23	180
		6	4	3	178
4	3	1	25	24	174
		2	25	24	183
		3	19	18	23
		4	14	12	293
		5	19	17	156
		6	12	8	90
4	4	0	45	45	180
		1	33	29	54
		2	43	42	4
		3	16	14	188
		4	20	18	191
		5	6	5	18
		6	23	24	8
4	5	0	16	13	180
		1	7	5	343
		2	28	25	5
		3	7	7	257
		4	23	24	146
		5	16	17	221
		6	17	15	355
4	6	0	8	3	0
		1	48	44	24
		2	28	24	183
		3	24	24	189
		4	19	17	43
		5	22	23	340
		6	10	9	221
4	7	0	10	10	0
		1	43	40	1
		2	20	20	61
		3	24	22	169
		4	5	6	254
		5	9	9	5
		6	12	11	141
4	8	0	21	17	0
		1	13	11	172
		2	27	28	170
		3	27	23	7
		4	19	19	347
		5	5	6	209
		6	10	11	175
4	9	0	36	30	0
		1	19	17	72
		2	22	21	206
		3	4	6	212
		4	19	19	0
		5	5	5	31
		6	21	20	177
4	10	0	16	8	180
		1	27	28	171
		2	35	31	348
		3	30	29	354
		4	19	18	186
		5	15	15	140

TABLE 4 (*Continued*)

h	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α
		6	7	8	349
4	11	0	6	12	0
		1	36	34	188
		2	11	7	350
		3	12	12	1
		5	17	15	216
4	12	0	17	16	180
		1	46	40	350
		2	14	18	347
		3	11	12	190
		4	19	21	160
		5	23	22	2
		6	4	2	333
4	13	0	11	10	180
		1	7	5	337
		2	12	14	332
		3	16	11	182
		4	25	21	222
		5	18	14	65
		6	10	10	342
4	14	0	24	24	0
		1	15	17	6
		2	20	19	177
		3	14	14	197
		4	23	21	2
		5	5	3	49
		6	10	9	197
4	15	0	24	17	0
		1	23	22	334
		2	18	14	214
		3	18	19	172
		4	10	10	315
		5	4	2	12
		6	5	4	112
4	16	1	33	30	183
		2	10	13	128
		3	17	16	359
		4	6	7	22
		5	13	12	181
4	17	0	21	16	0
		1	10	8	170
		2	13	14	204
		3	17	14	335
		4	8	9	351
		5	10	8	158
		6	5	6	232
4	18	0	34	25	180
		1	8	2	268
		2	20	18	357
		3	9	6	193
		4	15	13	163
		6	8	7	337
4	19	0	21	12	180
		2	12	9	38
		3	6	8	20
		4	7	5	167
		5	5	7	183
4	20	1	12	14	358
		3	15	13	171
		4	5	3	89
		5	10	10	1
4	21	0	7	8	180
		1	16	11	333
		2	5	7	357
		3	9	5	191
		5	8	7	14
		6	2	3	44
4	22	0	16	13	0
		1	4	3	279
		2	20	18	189
		3	4	1	338
		4	11	12	1
4	23	0	15	8	0
		2	15	13	188
		4	8	8	350
		5	2	4	37
4	24	0	11	7	180
		1	13	12	173
		2	5	3	336
		3	8	9	348
		4	4	2	165
4	25	1	13	10	178
		3	6	6	6
4	26	1	8	6	19
		2	10	8	8
		3	4	6	196
4	27	0	2	5	180
		1	5	3	341
5	0	1	35	30	90
		3	28	26	270
		4	13	13	0
		5	12	12	90
		6	5	4	180
5	1	0	16	16	270
		1	46	44	263
		2	20	20	246
		3	19	16	101
		4	25	23	73
		5	13	9	321
		6	7	7	255
5	2	0	21	27	90
		1	27	22	247
		2	23	22	289
		3	6	5	147
		4	20	17	91
		5	8	8	307
		6	16	14	270
5	3	0	16	17	270
		1	18	19	278
		2	21	21	93
		3	8	7	130
		4	24	25	267
		6	13	13	96
5	4	1	36	35	256
		2	12	11	68
		3	13	15	71
		4	11	8	280
		5	17	15	273
		6	4	4	70
5	5	0	6	10	270
		1	30	29	83
		2	12	13	84
		3	17	17	270
		4	13	14	250
		5	13	12	97
		6	4	4	42
5	6	0	28	28	270
		1	6	6	93
		2	24	23	94
		3	16	13	259
		4	23	18	295
		5	5	3	69
		6	8	8	121
5	7	0	29	21	90
		1	12	10	62
		2	25	24	246
		3	8	8	240
		4	24	19	98
		5	4	4	55
		6	4	7	233
5	8	1	16	16	85
		2	18	16	280
		3	15	16	278
		4	18	15	63
		5	8	9	110
		6	6	5	14
5	9	0	5	6	90
		1	28	25	256
		2	8	10	211
		3	4	9	98
		5	18	17	281
5	10	0	22	18	90
		1	33	26	279
		2	13	15	277
		3	12	12	93
		4	11	11	103

TABLE 4 (*Continued*)

h	k	l	$\|F_o\|$	$\|F_c\|$	α
		5	12	9	262
		6	4	5	261
5	11	0	46	44	270
		1	10	8	113
		2	26	24	108
		3	4	1	243
		4	18	17	236
		5	7	6	317
		6	8	8	104
5	12	0	27	23	270
		1	6	9	199
		2	22	20	94
		3	18	18	90
		4	23	19	282
		5	4	4	300
		6	6	6	109
5	13	1	14	15	124
		2	7	3	230
		3	25	23	267
		4	15	12	83
		5	14	12	86
5	14	1	20	19	95
		2	9	11	114
		3	9	9	285
		4	8	8	194
		5	14	13	56
5	15	0	23	22	90
		1	13	10	283
		2	17	19	273
		3	6	5	140
		5	8	7	19
		6	9	10	271
5	16	0	23	17	90
		1	8	6	177
		2	16	14	249
		4	7	7	80
		5	8	8	154
		6	10	11	251
5	17	1	6	6	247
		2	15	13	88
		3	18	16	92
		4	9	9	310
		5	8	9	226
		6	8	8	122
5	18	1	16	11	288
		2	14	9	51
		3	15	12	68
		4	5	1	294
		5	7	6	305
		6	2	2	352
5	19	0	11	11	270
		1	15	10	83
		2	7	6	25
		3	11	6	285
		4	5	7	276
		6	3	4	59
5	20	0	11	11	270
		1	5	4	203
		2	10	10	114
		3	5	4	209
		4	10	9	291
5	21	0	10	8	90
		1	11	10	93
		2	3	3	192
		3	10	10	253
		4	6	7	83
		5	3	5	73
5	22	0	7	4	90
		1	11	11	68
		2	3	1	58
		3	8	9	274
		4	3	2	70
5	23	1	11	8	288
		2	5	7	272
		3	7	6	86
		4	1	4	44
5	24	1	6	4	268
		2	7	7	288
		3	5	3	94
5	25	0	8	8	270
		1	5	4	285
		2	22	8	79
6	0	0	57	59	180
		2	16	15	0
		3	11	10	270
		4	10	9	180
		6	4	6	0
6	1	0	38	34	180
		1	21	21	147
		2	17	18	22
		3	14	13	37
		4	16	16	180
		5	6	5	181
		6	6	6	26
6	2	0	12	14	0
		1	14	13	45
		2	6	4	54
		3	19	20	166
		5	12	13	0
6	3	0	11	11	0
		1	19	15	358
		2	13	12	19
		3	25	23	191
		4	11	11	140
		5	11	11	331
		6	8	6	355
6	4	0	13	16	0
		1	12	9	280
		2	10	11	184
		3	11	9	5
		4	6	5	88
		6	11	11	190
6	5	0	24	25	0
		1	12	12	34
		2	20	21	157
		3	7	6	177
		4	8	9	337
		6	11	11	152
6	6	0	9	9	180
		1	8	8	197
		2	14	14	20
		3	18	17	354
		4	7	5	246
		5	7	7	141
		6	6	6	55
6	7	0	11	8	180
		1	14	14	185
		3	17	14	356
		4	7	7	9
		5	15	14	182
		6	4	4	265
6	8	0	8	8	180
		1	6	6	23
		2	14	14	13
		3	9	8	195
		4	11	11	151
		5	5	6	7
		6	5	6	314
6	9	0	26	26	180
		1	10	9	220
		2	18	17	7
		3	4	2	146
		4	7	7	196
		6	7	8	14
6	10	0	8	7	0
		1	20	20	353
		2	9	9	142
		3	8	8	151
		4	8	8	79
		5	8	9	316
		6	4	5	170
6	11	0	8	4	0
		1	19	19	15
		2	6	6	214
		3	13	12	190
		5	20	17	12

TABLE 4 (*Continued*)

h	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α
6	12	0	5	3	0
		1	13	12	142
		2	4	4	174
		3	7	8	341
		4	11	12	359
		5	10	8	171
		6	33	3	139
6	13	0	24	22	0
		1	6	2	159
		2	13	13	166
		3	12	10	357
		4	9	8	18
		5	7	6	241
		6	4	5	176
6	14	0	11	9	180
		1	9	8	176
		2	11	10	18
		3	4	2	325
		4	8	8	179
		5	4	3	323
6	15	0	7	3	180
		1	11	10	172
		2	7	6	9
		3	15	16	356
		4	6	6	180
		5	5	6	125
		6	3	3	327
6	16	0	5	4	0
		1	19	14	351
		2	6	8	327
		3	6	8	173
		4	7	6	25
		5	1	3	272
6	17	0	5	6	180
		1	17	12	349
		2	7	9	349
		3	10	8	177
		4	6	8	202
		5	3	3	2
6	18	0	7	9	0
		1	4	4	322
		2	8	7	195
		3	5	3	60
		4	7	7	337
6	19	0	9	7	0
		1	5	7	0
		2	7	5	194
		4	6	6	333
6	20	1	8	6	197
		2	3	3	226
		4	5	3	329
6	21	1	10	9	188
		2	3	6	177
		3	5	5	10
6	22	0	5	5	180
		2	6	7	0
6	23	0	5	7	180
		1	3	5	199
7	0	1	22	23	270
		3	15	14	90
		5	13	14	270
7	1	1	11	12	72
		2	8	9	81
		4	7	7	222
		6	3	2	296
7	2	1	8	7	42
		2	13	14	74
		3	4	3	274
		4	9	9	289
		6	8	8	93
7	3	2	6	8	270
		4	5	7	91
		5	5	4	62
7	4	1	9	10	84
		2	8	7	314
		3	12	12	266
		4	5	5	75
		5	7	8	84
7	5	0	13	14	90
		1	12	11	266
		2	11	12	269
		3	7	8	66
		4	8	9	90
		6	3	5	310
7	7	0	8	5	270
		1	4	5	213
		2	4	5	94
		3	4	3	314
		4	7	7	260
		5	5	5	281
		6	3	4	56
7	8	1	15	14	271
		2	10	10	104
		3	10	11	107
		4	12	10	260
		5	5	5	280
		6	3	2	159
7	9	0	9	5	270
		1	10	7	57
		2	6	3	100
		3	7	7	256
7	10	0	12	13	270
		1	17	13	99
		2	10	11	99
		3	7	5	270
		4	9	9	257
		5	5	5	75
		6	3	5	92
7	11	0	12	12	90
		2	5	6	286
		3	5	5	258
		4	8	8	50
		6	1	4	262
7	12	0	16	12	90
		2	10	10	252
		3	8	8	283
		4	12	12	113
7	13	1	9	7	301
		3	8	7	89
		4	4	3	241
		5	3	4	304
7	14	0	4	4	270
		1	14	11	264
		2	3	5	245
		3	9	8	110
		5	4	6	250
7	15	0	6	6	270
		1	3	3	194
		2	6	7	108
7	16	0	13	12	270
		2	14	12	87
		4	4	6	228
7	17	1	4	3	65
		2	6	6	279
		3	7	6	273
7	18	1	7	8	130
		2	9	6	209
		3	5	5	258
7	19	0	7	8	90
		1	4	3	167
		2	3	3	159
		3	5	8	90
7	20	0	17	17	0
		1	8	8	300
		2	8	8	172
		3	8	8	189
		4	10	11	0
		5	2	2	28
8	2	0	7	8	180
		1	9	9	240
		6	3	2	232
7	5	0	9	8	90
		1	11	13	253
		2	8	6	247
		5	5	6	308
		6	5	5	154
7	6	0	13	14	90
		1	12	11	266
		2	11	12	269
		3	7	8	66
		4	8	9	90
		6	3	5	310
7	7	0	8	5	270
		1	4	5	213
		2	4	5	94
		3	4	3	314
		4	7	7	260
		5	5	5	281
		6	3	4	56
7	8	1	15	14	271
		2	10	10	104
		3	10	11	107
		4	12	10	260
		5	5	5	280
		6	3	2	159
7	9	0	9	5	270
		1	10	7	57
		2	6	3	100
		3	7	7	256
7	10	0	12	13	270
		1	17	13	99
		2	10	11	99
		3	7	5	270
		4	9	9	257
		5	5	5	75
		6	3	5	92
7	11	0	12	12	90
		2	5	6	286
		3	5	5	258
		4	8	8	50
		6	1	4	262
7	12	0	16	12	90
		2	10	10	252
		3	8	8	283
		4	12	12	113
7	13	1	9	7	301
		3	8	7	89
		4	4	3	241
		5	3	4	304
7	14	0	4	4	270
		1	14	11	264
		2	3	5	245
		3	9	8	110
		5	4	6	250
7	15	0	6	6	270
		1	3	3	194
		2	6	7	108
7	16	0	13	12	270
		2	14	12	87
		4	4	6	228
7	17	1	4	3	65
		2	6	6	279
		3	7	6	273
7	18	1	7	8	130
		2	9	6	209
		3	5	5	258
7	19	0	7	8	90
		1	4	3	167
		2	3	3	159
		3	5	8	90
7	20	0	17	17	0
		1	8	8	300
		2	8	8	172
		3	8	8	189
		4	10	11	0
		5	2	2	28
8	2	0	7	8	180
		1	9	9	240

TABLE 4 (*Continued*)

h	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α	*h*	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α
8	3	0	7	5	180			5	3	6	274
		1	11	13	179	8	7	1	9	9	358
		2	8	9	207			2	3	5	57
		3	8	6	21			3	6	6	166
		4	4	4	309			5	2	4	29
		5	5	6	147	8	8	2	6	8	107
8	4	3	5	3	132	8	9	2	6	7	196
		5	2	2	47	8	10	2	3	2	337
8	5	2	8	10	351	8	11	1	12	12	179
		3	5	4	293			3	8	9	347
		4	5	7	185	8	12	1	4	5	342
		5	2	4	221	8	13	1	4	4	5
8	6	3	5	5	191			2	5	6	17
		4	5	5	103	8	14	2	2	3	128
						8	15	1	5	7	352

to be 43·6%. The measured $|F|$ values and the calculated phase angles were then used to evaluate a three-dimensional electron-density distribution. The almost special values of the *x*- and *z*-co-ordinates led to spurious planes of symmetry in the Fourier synthesis, but nevertheless we were able to recognise that the cyclohexadienone ring system lay approximately parallel to the *bc*-plane and we were eventually able to assign approximate co-ordinates to all the carbon and oxygen atoms apart from the controversial methyl group.

The inclusion of the fourteen carbon and three oxygen atoms in the calculation of a second set of structure factors caused the value of *R* to fall to 39·1%. The next electron-density distribution gave improved co-ordinates and the value of *R* was 34·5%. In the subsequent Fourier synthesis C(13) was prominent (peak height >3 eÅ^{-3}), and with the inclusion of all the carbon and oxygen atoms in the calculation of a fourth set of structure factors the value of *R* was reduced to 30·4%. Five further rounds of Fourier and structure-factor calculations were carried out; both F_o and F_c syntheses were evaluated, atomic co-ordinates obtained by numerical interpolation in the results, and errors due to termination of series corrected. The value of *R* was 23·3%.

For the final stages of the analysis Rollett's least-squares programme [15] for DEUCE was used to refine positional and anisotropic thermal parameters for all atoms other than hydrogen. After five cycles of calculations the value of *R* was 15·2% and as the parameter shifts were small the refinement was terminated.

The theoretical atomic scattering factors used in all the structure-factor calculations were these of Berghuis *et al.*[16] for carbon and oxygen, and the Thomas–Fermi values [17] for bromine. The final calculated structure amplitudes and phase constants are listed with the measured values of the structure amplitudes in Table 4. The phase constants of Table 4 and the measured structure amplitudes were used to calculate a final three-dimensional electron-density distribution which is shown in Figure 1 by means of superimposed contour sections drawn parallel to (100). All the atoms are well resolved, and the oxygen atoms have distinctly higher peak heights than the carbon atoms.

The final atomic co-ordinates, molecular dimensions, and some non-bonded distances are listed in Tables 1 and 2. The standard deviations of the final atomic co-ordinates were derived from the least-squares residuals by means of the equation:

$$\sigma^2(x_i) = \sum w_j(\Delta F_j)^2/[(n - s)\sum w_j(\partial F_j/\partial x_i)^2].$$

The results are listed in Table 3. The parameters defining the anisotropic thermal vibrations are shown in Table 5; they are values of b_{ij} in the equation:

$$\exp(-B \sin^2\theta/\lambda^2) = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{13}hl)}$$

[15] J. S. Rollett, in ref. 10*b*, p. 87.
[16] J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[17] "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Borntraeger, Berlin, 1935, vol. II, p. 572.

TABLE 5

Anisotropic temperature factors ($b_{ij} \times 10^5$)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}	Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	4001	298	2694	−162	181	157	C(11)	2873	220	3682	−45	69	465
C(2)	2845	164	2323	−368	−238	615	C(12)	2624	155	2960	394	−732	−794
C(3)	1805	240	3239	−75	−169	1165	C(13)	4636	539	4527	−905	−205	452
C(4)	1932	240	2246	−240	−294	418	C(14)	4642	310	1814	−98	179	−613
C(5)	1640	346	1911	105	−128	−1272	C(15)	2963	275	2273	−45	−202	−927
C(6)	2122	224	2306	30	−196	−707	O(16)	5884	270	2951	−605	218	−601
C(7)	3567	201	2356	−123	177	−536	O(17)	3119	358	2173	−32	−478	530
C(8)	4234	358	958	−76	−10	287	O(18)	3476	380	5819	−26	−865	583
C(9)	3197	245	2989	92	−132	912	Br	3629	244	3173	−172	−154	267
C(10)	2375	280	2492	−367	462	−508	($B = 3$ Å^2	2752	264	2099	0	0	0)

We are grateful to Professor D. H. R. Barton, F.R.S., for a supply of 2-bromo-α-santonin, and to Professor J. M. Robertson, F.R.S., for his encouragement. The calculations were performed on the Glasgow University DEUCE computer with programmes devised by Dr. J. S. Rollett and Dr. J. G. Sime. One of us (J. D. M. A.) is indebted to the D.S.I.R. for financial support.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW W.2.

[Present address (G. A. S.): DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS, U.S.A.]

[*Received, April 20th*, 1965.]