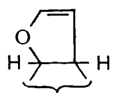
802. *The Structure of Clerodin: X-Ray Analysis of Clerodin Bromo-lactone.*

By I. C. Paul, G. A. Sim, T. A. Hamor, and J. Monteath Robertson.

The molecular structure of clerodin, $C_{24}H_{34}O_7$, the bitter principle of *Clerodendron infortunatum*, has been determined by an *X*-ray study of the heavy-atom derivative, clerodin bromo-lactone, $C_{24}H_{33}BrO_8$, which crystallizes in the orthorhombic system, space group $P2_12_12_1$ (D_2^4), with four molecules in the unit cell. After a number of three-dimensional Fourier syntheses and extensive least-squares refinement our final results define the constitution and stereochemistry of the bromo-lactone as (IV) and hence of clerodin as (V). The absolute stereochemistry shown in (IV), and hence in (V), was established by Bijvoet's anomalous-dispersion method. The chemical behaviour of clerodin is in accord with structure (V).

Clerodin, the bitter principle of *Clerodendron infortunatum*, contains a cyclic vinyl ether (I); this readily adds hypobromous acid to form clerodin bromohydrin which on oxidation yields the bromo-γ-lactone (II).[1] At the suggestion of Professor D. H. R. Barton, F.R.S., we examined these bromo-derivatives with a view to elucidating the structure of clerodin by *X*-ray analysis. Both derivatives crystallize in the orthorhombic system, space group $P2_12_12_1$ (D_2^4); we chose the bromo-lactone for detailed study because the crystals are better formed and the *X*-ray data more extensive than in the case of the bromohydrin.

(I)



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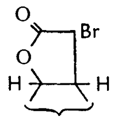

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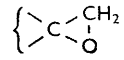

When we began our *X*-ray work the information available to us about clerodin was very limited. We knew that the earlier chemical investigations[2] had been inconclusive, that analytical results for various derivatives were consistent with a molecular formula $C_{21}H_{30}O_6$ for clerodin, and that in addition to the vinyl ether grouping (I) the molecule contains two acetate groups and an epoxide (III).

At an early stage of the structure analysis the C_{21} formula was recognized as inadequate and a consideration of the crystal density of the bromo-lactone and of the C : H : O ratios for clerodin led us to propose $C_{24}H_{34}O_7$ for clerodin and $C_{24}H_{33}O_8Br$ for clerodin bromo-lactone. Further evidence for the C_{24} formula was provided by the preliminary crystallographic study of clerodin bromohydrin; the unit-cell dimensions and crystal density of this derivative are consistent with $C_{24}H_{35}BrO_8$, but not $C_{21}H_{31}BrO_7$, as molecular formula.

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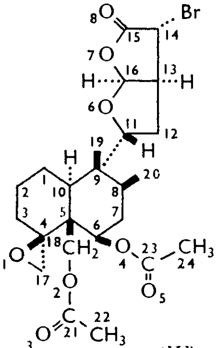
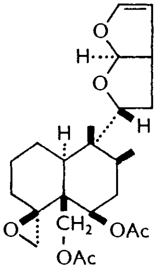
[1] Barton, Cheung, Cross, Jackman, and Martin-Smith, *Proc. Chem. Soc.*, 1961, 76; *J.*, 1961, 5061.

[2] Banerjee, *Science and Culture*, 1936, **2**, 163; *J. Indian Chem. Soc.*, 1937, **14**, 51; *Trans. Bose Res. Inst.*, 1935—36, **11**, 71; 1936—37, **12**, 75; Chaudhury and Dutta, *J. Indian Chem. Soc.*, 1951, **28**, 295; 1954, **31**, 8.

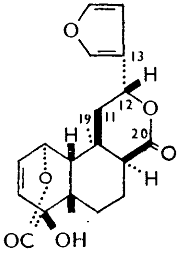
The crystal structure of the bromo-lactone was elucidated by application of the usual phase-determining heavy-atom method.[3] Extensive three-dimensional refinement by Fourier and least-squares methods was carried out and at the end the value of R, the average discrepancy between measured and calculated structure amplitudes, is 16·0% over 1514 reflexions (see Table 4). From our final results the bromo-lactone has to be assigned formula (IV); it follows that clerodin is represented by formula (V). The absolute configuration shown was decided by Bijvoet's method,[4] the anomalous dispersion of the bromine atom giving rise to small intensity differences between equivalent reflexions. Optical rotatory-dispersion measurements[1] support this stereochemical assignment. The basic carbon skeleton is identical with that of columbin (VI); if the stereochemistry[5] in (VI) is correct, however, the biogenesis of columbin must differ fundamentally from that of clerodin. The chemical implications of (V) as the structure of clerodin have been discussed by Barton *et al.*[1]



(IV)



(V)



(VI)

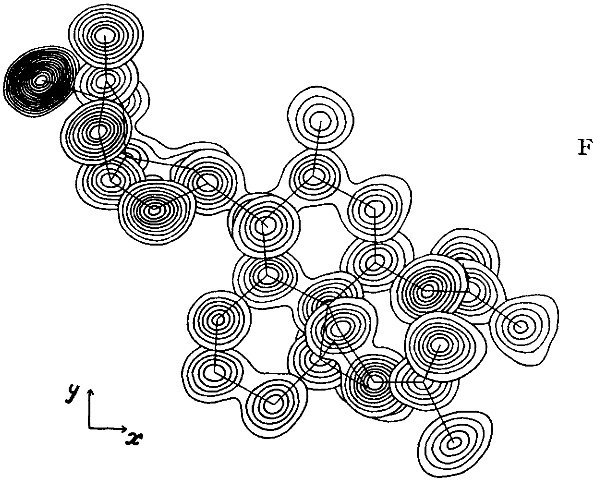


FIG. 1. The final three-dimensional electron-density distribution for clerodin bromo-lactone shown by means of superimposed contour sections drawn parallel to (001). Contour interval 1 eÅ^{-3} except around the bromine atom where it is 3 eÅ^{-3}.

The distinction between carbon and oxygen atoms in the structure was based mainly on a consideration of the peak heights of the atoms and of the interatomic distances within the molecule. In the case of the epoxide group further evidence was provided by three-dimensional difference Fourier syntheses (Fig. 5) and by the temperature factors resulting

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[3] Robertson and Woodward, *J.*, 1937, 219; 1940, 36; Sim, in "Computing Methods and the Phase Problem in X-ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 227.

[4] Bijvoet, Peerdeman, and van Bommel, *Nature*, 1951, **168**, 271.

[5] Overton, Weir, and Wylie, *Proc. Chem. Soc.*, 1961, 211.

from least-squares refinement in which C(17) and O(1) were weighted, respectively, as (i) carbon and oxygen, (ii) carbon, and (iii) oxygen and carbon (see Table 5).

The final three-dimensional electron-density distribution is shown in Fig. 1 as superimposed contour sections drawn parallel to (001) and covering the region of one molecule.

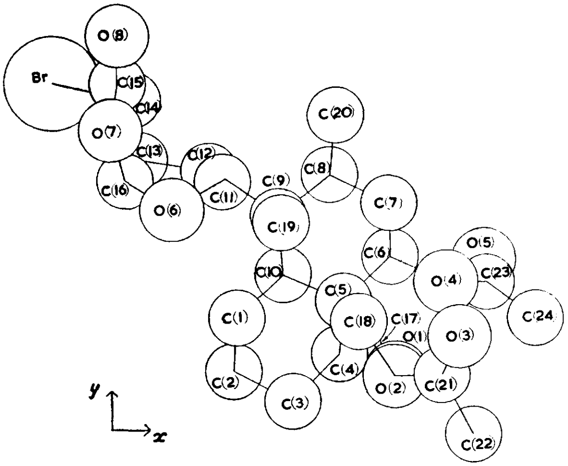
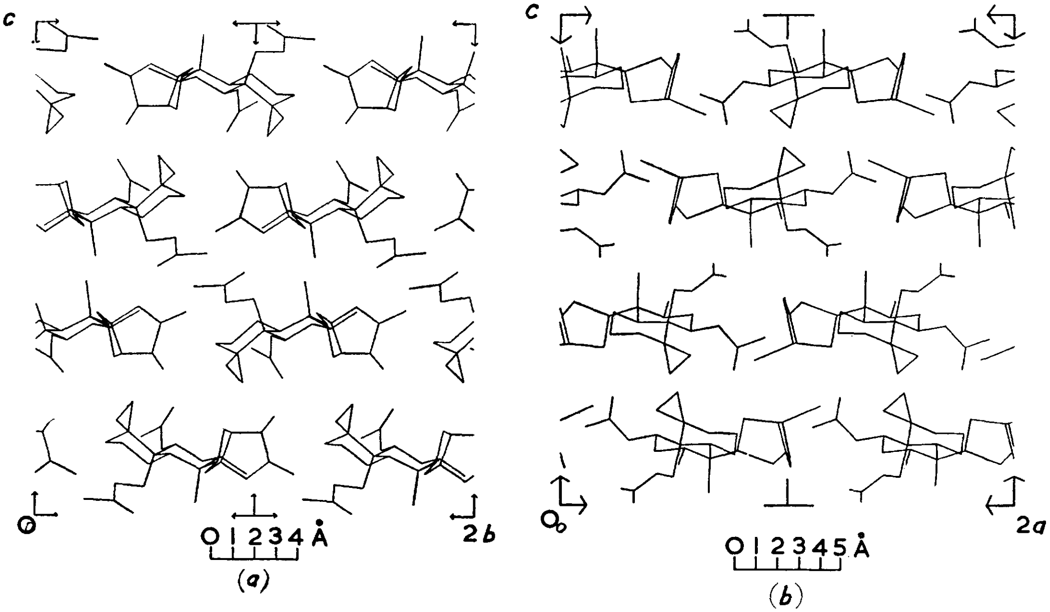


FIG. 2. The arrangement of atoms corresponding to Fig. 1.



(*a*)

(*b*)

FIG. 3. Line drawings of the molecular frameworks of two unit cells as seen in projection along (*a*) the *a*-axis, and (*b*) the *b*-axis.

The corresponding atomic arrangement is illustrated in Fig. 2. The stereochemistry of the molecule is also evident in Fig. 3 which shows, by means of line drawings of the molecular frameworks, the packing of the molecules in the crystal as viewed in projections along the *a*- and *b*-axes. Both cyclohexane rings of the *trans*-decalin have the chair conformation. The 19-methyl group is axial and the 20-methyl group equatorial. The 6-acetoxy-substituent is equatorial.

TABLE 1.

Atomic co-ordinates.

(Origin of co-ordinates as in " International Tables."*)

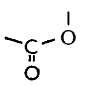
Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
C(1)	−0·2340	−0·4830	0·1046	C(12)	−0·1913	−0·1412	0·1772	C(23)	−0·7862	−0·4308	0·1781
C(2)	−0·2205	−0·6047	0·1485	C(13)	−0·0416	−0·1062	0·1705	C(24)	−0·8913	−0·5203	0·1596
C(3)	−0·3459	−0·6827	0·1480	C(14)	−0·0299	0·0315	0·1697	O(1)	−0·5769	−0·6297	0·1945
C(4)	−0·4551	−0·5788	0·1694	C(15)	−0·0010	0·0694	0·1088	O(2)	−0·5740	−0·6361	0·0648
C(5)	−0·4712	−0·4565	0·1243	C(16)	−0·0059	−0·1542	0·1104	O(3)	−0·7226	−0·5540	0·0057
C(6)	−0·5782	−0·3592	0·1446	C(17)	−0·4860	−0·5576	0·2316	O(4)	−0·6974	−0·4258	0·1338
C(7)	−0·5830	−0·2370	0·1098	C(18)	−0·5011	−0·5049	0·0585	O(5)	−0·7683	−0·3728	0·2214
C(8)	−0·4554	−0·1638	0·1182	C(19)	−0·3415	−0·2705	0·0251	O(6)	−0·1050	−0·2260	0·0856
C(9)	−0·3393	−0·2520	0·0952	C(20)	−0·4761	−0·0267	0·0831	O(7)	0·0193	−0·0360	0·0761
C(10)	−0·3424	−0·3863	0·1262	C(21)	−0·6762	−0·6400	0·0304	O(8)	−0·0093	0·1830	0·0854
C(11)	−0·2184	−0·1656	0·1121	C(22)	−0·7371	−0·7815	0·0345	Br	0·1442	0·0828	0·2036

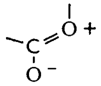
* " International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, 1952, Vol. I.

The interatomic distances and valency angles calculated from the final atomic co-ordinates (see Table 1) are listed in Table 2. The standard deviations of the final atomic co-ordinates were estimated in the usual manner from the least-squares residuals (see Experimental section) and are shown in Table 3; from the results the average e.s.d. of a carbon–carbon bond is about 0·04 Å and of a carbon–oxygen bond about 0·03 Å.

The average carbon–carbon single bond length is 1·56 Å, not significantly different from the value of 1·545 Å in diamond. The carbon–oxygen single bonds fall into two categories; those immediately adjacent to a carbon–oxygen double bond as in (VII) have a mean length of 1·34 Å, whereas those not adjacent to a carbon–oxygen double bond have a mean length of 1·47 Å. This difference is highly significant and indicates that in lactone and ester groupings, just as in carboxylic acids, the structure (VIII) plays an important role. The angles around carbon atoms C(15), C(21), and C(23), moreover, conform to the pattern observed in carboxylic acids[6] where the angle CC(OH) is approximately tetrahedral and the angles CCO and OC(OH) exceed 120°. Similar conclusions were reached in our recent analyses of bromogeigerin acetate[7] and epilimonol iodoacetate. In the epoxide ring the average carbon–oxygen bond length is 1·49 Å, while the values quoted for ethylene oxide[9] and cyclopentene oxide[10] are 1·44 and 1·47 Å, respectively. The carbon–bromine bond length of 2·06 Å is somewhat greater than the average value of 1·94 Å reported[11] for various alkyl bromides. In bromogeigerin acetate[7] and isoclovene hydrochloride[12] similar increases in carbon–halogen bond lengths were ascribed, at least in part, to steric effects; for clerodin bromo-lactone such an explanation appears unlikely and since the adjoining C(14)–C(13) bond length is rather short (1·40 Å) it is possible that the refinement procedure has misplaced C(14) by about 0·1 Å. The average interbond angle in the decalin system, 110°, approximates closely to tetrahedral; the average interbond angle in the two five-membered rings, 106°, on the other hand, is distinctly smaller

(VII)





(VIII)

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[6] Cochran, *Acta Cryst.*, 1953, **6**, 260; Ahmed and Cruickshank, *Acta Cryst.*, 1953, **6**, 385; Broadley, Cruickshank, Morrison, Robertson, and Shearer, *Proc. Roy. Soc.*, 1959, *A*, **251**, 441; Ferguson and Sim, *Acta Cryst.*, 1961, **14**, 1262.

[7] Hamilton, McPhail, and Sim, *J.*, 1962, 708.

[8] Arnott, Davie, Robertson, Sim, and Watson, *J.*, 1961, 4183.

[9] Cunningham, Boyd, Myers, Gwinn, and Le Van, *J. Chem. Phys.*, 1951, **19**, 676.

[10] Erlandsson, *Arkiv. Fys.*, 1955, **9**, 341.

[11] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.

[12] Clunie and Robertson, *J.*, 1961, 4382.

TABLE 2.

Interatomic distances (Å) and angles.

Intramolecular bonded distances

C(1)–C(2)	1·59	C(10)–C(1)	1·58	O(4)–C(23)	1·38	C(15)–O(7)	1·32
C(2)–C(3)	1·54	C(4)–C(17)	1·47	C(23)–C(24)	1·49	C(16)–O(7)	1·45
C(3)–C(4)	1·63	C(4)–O(1)	1·50	C(23)–O(5)	1·17	C(16)–O(6)	1·40
C(4)–C(5)	1·62	C(17)–O(1)	1·47	C(8)–C(20)	1·62	C(16)–C(13)	1·50
C(5)–C(6)	1·57	C(5)–C(18)	1·61	C(9)–C(19)	1·61	C(11)–O(6)	1·47
C(6)–C(7)	1·47	C(18)–O(2)	1·54	C(9)–C(11)	1·59	C(14)–Br	2·06
C(7)–C(8)	1·55	O(2)–C(21)	1·33	C(11)–C(12)	1·53	C(15)–O(8)	1·27
C(8)–C(9)	1·61	C(21)–C(22)	1·57	C(12)–C(13)	1·63		
C(9)–C(10)	1·53	C(21)–O(3)	1·15	C(13)–C(14)	1·40		
C(10)–C(5)	1·53	C(6)–O(4)	1·45	C(14)–C(15)	1·48		

Intramolecular non-bonded distances

C(1) ··· C(4)	2·94	C(7) ··· O(5)	3·49	C(12) ··· C(20)	3·87	C(23) ··· O(1)	3·01
C(1) ··· C(11)	3·22	C(8) ··· C(12)	3·10	C(12) ··· O(7)	3·37	C(24) ··· O(3)	3·95
C(1) ··· C(12)	3·86	C(8) ··· O(6)	3·82	C(14) ··· O(6)	3·33	O(1) ··· O(2)	2·96
C(1) ··· O(6)	2·96	C(10) ··· C(12)	3·17	C(15) ··· O(6)	3·23	O(1) ··· O(4)	2·79
C(2) ··· C(5)	3·09	C(10) ··· O(6)	3·13	C(18) ··· C(19)	3·01	O(1) ··· O(5)	3·35
C(3) ··· C(10)	3·04	C(11) ··· C(14)	3·11	C(18) ··· O(1)	3·45	O(2) ··· O(4)	2·95
C(4) ··· O(2)	2·76	C(11) ··· C(15)	3·31	C(18) ··· O(3)	2·68	O(3) ··· O(4)	3·21
C(5) ··· C(8)	2·97	C(11) ··· C(20)	3·13	C(18) ··· O(4)	2·81	O(8) ··· Br	3·31
C(6) ··· C(9)	2·97	C(11) ··· O(7)	2·95	C(19) ··· C(20)	3·14		
C(7) ··· C(10)	2·98	C(12) ··· C(15)	3·32	C(19) ··· O(6)	2·87		

Intermolecular distances (<4 Å)

O(7) ··· C(18)$_{\mathrm{I}}$	3·11	C(15) ··· O(3)$_{\mathrm{I}}$	3·52	O(6) ··· O(3)$_{\mathrm{I}}$	3·73	C(15) ··· C(18)$_{\mathrm{I}}$	3·87
O(8) ··· C(22)$_{\mathrm{II}}$	3·12	O(8) ··· O(2)$_{\mathrm{I}}$	3·53	C(15) ··· C(21)$_{\mathrm{I}}$	3·75	C(20) ··· C(22)$_{\mathrm{III}}$	3·87
O(8) ··· C(21)$_{\mathrm{I}}$	3·21	C(15) ··· C(22)$_{\mathrm{II}}$	3·58	O(5) ··· C(3)$_{\mathrm{IV}}$	3·75	Br ··· C(12)$_{\mathrm{VI}}$	3·93
O(7) ··· O(3)$_{\mathrm{I}}$	3·29	C(2) ··· C(24)$_{\mathrm{V}}$	3·59	O(8) ··· C(18)$_{\mathrm{I}}$	3·75	C(12) ··· C(23)$_{\mathrm{IV}}$	3·94
O(8) ··· O(3)$_{\mathrm{I}}$	3·33	C(12) ··· O(5)$_{\mathrm{IV}}$	3·59	O(6) ··· C(19)$_{\mathrm{I}}$	3·76	C(16) ··· C(23)$_{\mathrm{V}}$	3·95
O(7) ··· C(19)$_{\mathrm{I}}$	3·36	C(19) ··· O(3)$_{\mathrm{I}}$	3·59	O(7) ··· C(22)$_{\mathrm{II}}$	3·76	Br ··· C(2)$_{\mathrm{VI}}$	3·95
O(8) ··· C(2)$_{\mathrm{III}}$	3·41	C(16) ··· C(19)$_{\mathrm{I}}$	3·63	O(8) ··· C(22)$_{\mathrm{I}}$	3·78	C(13) ··· O(5)$_{\mathrm{IV}}$	3·96
C(14) ··· O(5)$_{\mathrm{IV}}$	3·41	C(8) ··· C(17)$_{\mathrm{IV}}$	3·64	O(7) ··· O(2)$_{\mathrm{I}}$	3·79		
C(20) ··· O(3)$_{\mathrm{I}}$	3·45	O(7) ··· C(21)$_{\mathrm{I}}$	3·65	C(12) ··· O(1)$_{\mathrm{IV}}$	3·82		
C(11) ··· O(3)$_{\mathrm{I}}$	3·49	O(8) ··· C(24)$_{\mathrm{II}}$	3·67	C(1) ··· C(24)$_{\mathrm{V}}$	3·85		

The subscripts refer to the following positions:

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

Valency angles

C(1)C(2)C(3)	109°	C(5)C(4)O(1)	115°	C(7)C(6)O(4)	106°	C(11)C(12)C(13)	97°
C(2)C(3)C(4)	106	C(17)C(4)O(1)	59	C(6)O(4)C(23)	119	C(12)C(13)C(16)	106
C(3)C(4)C(5)	112	C(4)C(17)O(1)	61	O(4)C(23)O(5)	120	C(12)C(13)C(14)	108
C(4)C(5)C(10)	104	C(4)O(1)C(17)	59	O(4)C(23)C(24)	109	C(16)C(13)C(14)	107
C(5)C(10)C(1)	111	C(10)C(5)C(18)	110	O(5)C(23)C(24)	132	C(13)C(14)C(15)	107
C(10)C(1)C(2)	110	C(4)C(5)C(18)	112	C(7)C(8)C(20)	103	C(13)C(14)Br	109
C(10)C(5)C(6)	110	C(4)C(5)C(6)	112	C(9)C(8)C(20)	115	C(15)C(14)Br	96
C(5)C(6)C(7)	113	C(6)C(5)C(18)	109	C(8)C(9)C(19)	103	C(14)C(15)O(7)	111
C(6)C(7)C(8)	108	C(5)C(18)O(2)	106	C(8)C(9)C(11)	112	C(14)C(15)O(8)	128
C(7)C(8)C(9)	111	C(18)O(2)C(21)	112	C(10)C(9)C(19)	111	O(7)C(15)O(8)	120
C(8)C(9)C(10)	109	O(2)C(21)C(22)	109	C(10)C(9)C(11)	113	C(15)O(7)C(16)	109
C(9)C(10)C(5)	115	O(2)C(21)O(3)	128	C(11)C(9)C(19)	108	O(7)C(16)C(13)	106
C(3)C(4)C(17)	123	O(3)C(21)C(22)	123	C(9)C(11)C(12)	118	O(7)C(16)O(5)	110
C(3)C(4)O(1)	120	C(5)C(6)O(4)	106	C(9)C(11)O(6)	109	O(7)C(16)C(13)	111
C(5)C(4)C(17)	119	C(1)C(10)C(9)	113	O(6)C(11)C(12)	108	C(11)O(7)C(16)	103

than tetrahedral but is in good agreement with the average values for the angles of the five-membered rings in other molecules.[13]

The close intermolecular contacts (Table 2) correspond to normal van der Waals interactions; the shortest separations, 3·11—3·53 Å, involve oxygen atoms.

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[13] Hamilton, Hamor, Robertson, and Sim, *J.*, 1962, in the press.

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)	0·031	0·032	0·027	C(12)	0·027	0·030	0·026	C(23)	0·029	0·030	0·026
C(2)	0·031	0·028	0·027	C(13)	0·028	0·033	0·028	C(24)	0·029	0·031	0·029
C(3)	0·027	0·030	0·026	C(14)	0·029	0·030	0·030	O(1)	0·021	0·021	0·018
C(4)	0·030	0·033	0·029	C(15)	0·030	0·032	0·026	O(2)	0·019	0·021	0·017
C(5)	0·026	0·025	0·024	C(16)	0·028	0·029	0·024	O(3)	0·021	0·021	0·019
C(6)	0·028	0·029	0·027	C(17)	0·029	0·033	0·025	O(4)	0·018	0·021	0·017
C(7)	0·031	0·032	0·027	C(18)	0·027	0·027	0·025	O(5)	0·020	0·024	0·019
C(8)	0·032	0·030	0·029	C(19)	0·033	0·029	0·025	O(6)	0·019	0·019	0·018
C(9)	0·029	0·028	0·024	C(20)	0·030	0·033	0·031	O(7)	0·017	0·017	0·018
C(10)	0·027	0·024	0·025	C(21)	0·032	0·032	0·029	O(8)	0·018	0·018	0·019
C(11)	0·027	0·030	0·025	C(22)	0·031	0·030	0·026	Br	0·004	0·005	0·004

EXPERIMENTAL

Crystal Data.—Clerodin bromo-lactone, $C_{24}H_{33}O_8Br$; $M = 528{\cdot}9$; m. p. 168—169°. Orthorhombic, $a = 10{\cdot}55$, $b = 10{\cdot}12$, $c = 22{\cdot}82$ Å (each $\pm 0{\cdot}3\%$), $U = 2436$ Å^3, $D_m = 1{\cdot}432$ (by flotation), $Z = 4$, $D_c = 1{\cdot}442$, $F(000) = 1104$, space group $P2_12_12_1$ (D_2^4). Absorption coefficient for X-rays ($\lambda = 1{\cdot}542$ Å), $\mu = 28{\cdot}4$ cm.$^{-1}$.

Experimental Measurements.—Rotation, oscillation, Weissenberg, and precession photographs were taken with copper K_α ($\lambda = 1{\cdot}542$ Å) and molybdenum K_α ($\lambda = 0{\cdot}7107$ Å) radiation. Cell dimensions were obtained from rotation and precession photographs. The space group was determined uniquely from the systematic halvings in the reflexions. For the intensity measurements small crystals were employed, completely bathed in a uniform X-ray beam. No corrections for absorption were applied. The multiple-film technique with visual intensity estimation was applied to equatorial and equi-inclination upper-layer Weissenberg photographs taken from crystals rotated about the a- and b-crystal axes. The intensities were corrected for Lorentz polarization, and the rotation factors appropriate to upper layers [14] and values of $|F_o|$ were then evaluated by the mosaic crystal formula. The various layers were put on the same relative scale by comparison of common reflexions on different photographs. The absolute scale was obtained at a later stage by correlation of the measured structure amplitudes with the calculated values, $|F_c|$. In all 1514 independent structure amplitudes were measured (Table 4). The crystal density was determined by flotation in aqueous zinc chloride and in aqueous potassium iodide.

Structure Analysis.—In view of the lengths of the unit-cell edges it was evident that there would be considerable overlap of atoms in projection along the crystallographic axes. In consequence three-dimensional methods were used throughout for the elucidation of the structure and for the refinement of the atomic parameters.

The position of the bromine atom was determined from sections through the three-dimensional sharpened Patterson function at $x = \frac{1}{2}$, $y = \frac{1}{2}$, and $z = \frac{1}{2}$, respectively. These sections are shown in Fig. 4.

Structure factors based on the bromine atom alone were calculated; the value of R was 51%. With the measured $|F|$ values and phase constants appropriate to the bromine atom alone we then evaluated a three-dimensional electron-density distribution. This was drawn out and compared with a minimum function prepared from the three-dimensional Patterson synthesis by the superposition method,[15] the bromine sites in the unit cell being used as origins for the transposed Patterson sections. The most significant structural features were a five-membered ring [C(11), C(12), C(13), C(16), O(6)] near to the bromine atom, a three-membered ring [C(4), C(17), O(1)] which was presumed to be the epoxide group present in clerodin, and a group of five atoms [C(6), O(4), C(23), O(5), C(24)] in the general shape of an acetate group attached to a carbon atom. Fifteen well-defined peaks were selected as atoms and were included in the next structure-factor calculations as carbon atoms. The discrepancy factor R was reduced to 43%.

In the electron-density distribution derived from the improved phase constants three of

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

[15] Buerger, *Acta Cryst.*, 1951, **4**, 531; Robertson and Beevers, *ibid.*, 1951, **4**, 270.

TABLE 4.

Measured and calculated values of the structure factors.

h	*k*	*l*	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°
0	0	2	39	60	180
		4	183	185	180
		6	27	11	0
		8	47	51	180
		10	113	113	0
		12	37	37	180
		14	14	19	0
		18	12	7	180
		20	9	5	0
		22	25	26	180
		24	10	9	0
0	1	1	36	37	270
		2	26	18	270
		3	43	40	90
		4	7	15	270
		5	152	151	90
		6	72	70	90
		7	55	61	270
		8	114	122	270
		9	54	53	270
		10	43	49	270
		11	12	8	270
		12	77	66	90
		13	10	5	90
		14	12	20	270
		15	42	39	90
		16	27	25	90
		17	36	34	270
		18	38	33	270
		19	22	14	90
		20	18	13	90
		23	11	11	270
		24	11	16	270
		26	8	10	90
		28	4	3	270
0	2	0	107	120	0
		1	23	40	180
		2	89	98	180
		3	76	93	0
		5	5	3	180
		6	44	52	0
		7	23	18	0
		8	39	38	180
		9	15	23	0
		10	6	9	0
		11	75	76	180
		12	8	7	180
		13	57	63	0
		14	40	35	0
		15	28	27	180
		16	33	28	0
		17	20	9	180
		18	16	14	0
		19	32	29	0
		22	13	7	180
		24	11	9	0
		25	12	17	180
0	3	1	53	61	90
		2	39	36	270
		3	26	29	270
		4	41	30	270
		5	89	106	90
		6	54	58	90
		7	80	85	270
		8	26	25	90
		9	45	47	90
		10	7	12	270
		11	44	40	90
		12	37	40	270
		13	20	18	270
		15	19	24	90
		16	42	39	90
		17	41	37	270
		18	10	7	270
		19	36	34	90
		20	17	12	270
		23	20	20	270
		25	9	12	90
		27	6	10	270
0	4	0	62	65	180
		1	94	99	180
		2	90	105	0
		3	5	12	0
		4	7	10	180
		5	72	64	0
		6	58	60	180
		7	19	12	0
		8	16	20	0
		9	17	25	0
		10	5	11	180
		11	75	82	180
		12	49	51	0
		13	37	41	0
		14	27	18	180
		15	32	29	0
		16	10	19	180
		17	8	4	180
		19	11	4	0
		21	16	19	180
		22	7	8	0
		23	8	14	0
		24	6	1	0
0	5	1	35	27	270
		2	40	32	90
		3	49	43	270
		4	51	53	90
		5	77	79	90
		6	46	48	270
		7	25	22	90
		9	30	33	90
		12	19	18	270
		13	12	12	270
		14	21	22	90
		17	24	15	90
		18	15	21	90
		19	23	26	90
		20	17	19	270
		22	9	15	270
0	6	0	46	46	180
		1	16	12	180
0	6	2	49	50	0
		3	12	10	180
		4	31	28	180
		5	17	12	0
		6	27	29	180
		7	29	31	180
		8	16	13	0
		9	8	0	360
		10	30	36	180
		11	14	20	180
		12	21	22	0
		13	11	12	180
		14	8	12	180
		15	21	23	0
		16	13	7	0
		18	15	15	0
		20	8	8	180
		23	6	3	0
		24	8	8	180
0	7	2	28	26	270
		3	14	11	90
		4	13	3	270
		5	6	3	270
		6	41	44	270
		7	14	16	90
		8	20	27	90
		9	15	8	270
		13	17	21	90
		14	12	16	90
		15	21	21	270
		16	21	22	270
		18	15	22	90
		19	7	3	270
		21	7	7	90
		22	6	6	270
		23	9	6	90
		24	7	7	90
0	8	0	7	3	180
		1	21	25	0
		2	15	13	0
		3	9	1	0
		5	17	19	0
		6	13	6	180
		7	11	11	0
		8	8	8	180
		10	12	10	180
		11	23	24	0
		13	7	8	180
		15	7	1	180
		17	7	8	0
		21	8	7	0
0	9	1	22	23	270
		2	10	12	270
		3	25	21	90
		4	11	8	270
		5	14	8	90
		6	10	5	90
		9	20	21	270
		11	9	9	270
		12	7	1	90
		14	8	6	90
		15	7	1	270
		17	10	12	90
		19	7	8	270
		20	8	8	270
		21	2	1	270
0	10	1	10	14	0
		2	12	8	180
		3	11	4	0
		5	15	10	0
		8	8	8	180
		9	24	25	180
		11	6	3	180
		14	10	6	0
		15	7	7	0
		17	7	7	0
		18	3	3	180
0	11	7	6	7	90
		10	10	9	90
		13	6	3	270
		14	7	5	270
0	12	5	4	4	180
		8	7	1	180
		10	5	6	0
		11	3	3	180
1	0	2	24	2	180
		3	64	58	270
		4	95	112	0
		5	22	11	270
		6	172	182	180
		7	13	17	90
		8	25	24	0
		9	112	115	270
		10	35	38	180
		11	19	14	90
		12	15	5	0
		13	24	24	90
		14	46	49	0
		15	28	29	90
		16	45	48	180
		17	19	17	270
		18	17	16	0
		19	11	14	270
		21	6	9	90
		23	13	18	270
		24	7	8	0
		25	10	10	90
		29	5	7	90
1	1	0	16	15	270
		1	142	174	341
		2	58	67	243
		3	134	134	203
		4	6	5	282
		5	75	79	305
		6	57	53	319
		7	77	77	208
		8	32	42	312
		9	39	46	82
		10	60	60	140
		11	64	61	271
1	1	12	59	55	253
		13	23	22	229
		14	21	19	47
		15	28	32	13
		16	16	20	220
		17	7	9	282
		18	24	23	308
		19	9	9	55
		20	22	25	96
		21	14	9	208
		22	22	21	275
		23	12	16	113
		24	7	7	73
		25	6	4	327
		27	6	8	177
		28	6	5	297
		29	5	9	40
1	2	0	83	113	90
		1	59	53	133
		2	71	82	218
		3	191	170	352
		4	74	76	52
		5	73	76	212
		6	34	35	215
		7	65	55	46
		8	67	72	285
		9	18	16	205
		10	55	55	86
		11	34	31	57
		12	31	28	248
		13	11	12	3
		14	19	17	87
		15	17	14	169
		16	27	30	176
		17	23	25	341
		18	12	8	309
		19	12	12	198
		20	14	14	99
		21	10	15	91
		22	15	15	266
		23	7	9	273
		28	5	5	311
1	3	0	37	43	90
		1	47	54	218
		2	32	28	221
		3	71	65	65
		4	51	45	347
		5	6	8	319
		6	55	46	284
		7	26	27	291
		8	29	30	326
		9	60	60	80
		10	41	43	137
		11	61	58	245
		12	20	11	266
		13	34	33	103
		14	39	34	338
		15	15	9	76
		16	32	31	179
		17	24	24	337
		18	26	22	17
		19	7	6	72
		20	6	5	222
		21	22	29	255
		23	15	15	75
		25	5	5	301
		26	8	10	181
1	4	0	37	35	90
		1	18	10	335
		2	44	59	295
		3	61	61	16
		4	51	43	91
		5	60	57	192
		6	58	57	18
		7	51	47	14
		8	58	52	201
		9	12	8	89
		10	35	34	79
		11	39	34	284
		12	13	15	297
		13	29	21	354
		14	9	6	239
		15	21	25	165
		16	24	23	331
		17	24	24	28
		18	15	14	158
		20	13	13	106
		21	8	9	281
		22	7	8	299
		23	7	4	357
		27	7	10	22
1	5	0	9	10	270
		1	17	16	251
		2	56	50	134
		3	57	57	17
		4	23	23	11
		5	59	55	205
		6	11	9	186
		8	25	19	85
		9	25	21	142
		10	35	28	240
		11	26	19	281
		12	32	30	151
		13	23	24	15
		14	27	27	320
		15	26	33	249
		16	8	5	343
		18	11	10	36
		19	26	18	123
		20	12	16	224
		21	10	11	294
		22	8	12	104
		24	7	10	289
		25	4	6	207
1	6	1	24	19	262
		2	28	34	332
		3	18	16	103
		4	39	42	196
		5	14	16	318
		6	28	21	36
1	6	7	22	23	303
		8	25	30	143
		9	18	19	57
		10	14	13	335
		12	21	18	37
		13	24	29	63
		14	28	27	201
		15	7	6	185
		16	6	10	311
		17	9	10	308
		18	13	11	116
		21	11	11	273
		22	8	5	75
		24	7	4	207
		23	5	4	117
1	7	0	28	37	270
		1	6	9	118
		2	20	22	106
		3	18	18	352
		4	20	21	268
		5	8	11	138
		6	11	12	318
		7	13	14	52
		8	25	25	107
		9	24	27	213
		10	15	17	330
		11	12	8	139
		12	22	23	95
		14	7	6	183
		15	9	4	35
		16	10	11	56
		17	8	14	32
		18	6	8	138
		19	9	9	256
		22	12	15	55
		24	5	4	179
		23	6	5	218
1	8	1	21	20	325
		2	24	22	45
		3	25	21	237
		4	8	9	171
		5	22	22	320
		7	12	11	175
		8	7	6	168
		9	13	17	94
		10	14	11	264
		11	6	7	286
		12	15	17	55
		14	7	6	219
		17	9	12	192
		18	5	2	245
		19	5	5	69
		20	6	6	248
		21	6	7	291
		22	6	5	100
1	9	0	12	16	90
		2	10	12	53
		3	18	20	280
		4	11	9	320
		5	9	10	46
		6	18	20	29
		7	9	4	155
		8	18	22	147
		9	12	13	235
		12	9	5	300
		13	12	14	254
		14	9	10	216
		15	7	4	33
		16	11	11	14
1	10	0	12	20	270
		1	13	13	40
		3	13	15	188
		4	11	7	79
		6	6	6	150
		8	10	6	11
		11	8	6	106
		12	7	3	221
		13	10	9	182
2	0	1	14	11	270
		2	8	21	0
		3	88	88	270
		4	94	104	180
		5	90	100	90
		6	111	112	180
		7	52	52	270
		8	56	55	180
		9	55	50	90
		10	21	16	180
		11	19	16	270
		12	46	46	0
		13	25	27	270
		15	21	27	90
		16	9	16	0
		17	32	37	270
		18	16	16	0
		19	24	22	90
		20	16	15	180
		21	10	12	270
		22	8	10	180
		25	13	14	90
		27	13	14	270
2	1	0	43	42	180
		1	54	66	186
		3	42	45	320
		4	68	57	49
		5	64	57	178
		6	82	65	258
		7	57	55	246
		8	28	21	323
		9	61	61	1
		10	20	21	187
		11	69	69	168
		12	16	16	72
		13	63	60	12
		14	45	44	118
		15	26	22	193
		16	11	8	351
		17	23	25	159
		19	27	29	347
		20	16	16	176
2	1	21	19	24	178
		22	11	11	294
		23	8	11	25
		24	7	9	149
		25	8	9	263
2	2	0	44	41	0
		1	81	86	21
		2	77	80	282
		3	74	72	242
		4	61	67	87
		5	30	30	33
		6	113	124	262
		7	66	64	282
		8	66	69	116
		9	35	33	165
		10	48	44	184
		11	20	19	51
		12	48	42	284
		13	24	22	202
		14	42	45	102
		15	21	19	127
		16	27	32	253
		17	15	13	291
		18	11	11	66
		19	9	14	40
		20	18	19	220
		22	9	2	155
		25	9	11	93
		26	5	8	261
2	3	0	55	56	180
		1	7	7	313
		2	77	83	0
		3	49	45	249
		4	55	41	171
		5	10	2	176
		6	40	40	174
		7	32	29	351
		8	39	38	18
		9	6	6	325
		10	52	50	223
		11	25	24	248
		12	51	46	21
		13	14	16	226
		14	12	15	167
		15	22	24	253
		16	20	13	7
		17	26	21	81
		18	11	13	15
		20	16	19	190
		21	8	7	335
		22	12	14	8
		25	8	9	238
		26	9	10	336
2	4	0	27	27	0
		1	60	59	23
		2	7	23	225
		3	28	19	103
		4	64	67	92
		5	12	8	313
		6	37	44	257
		7	24	27	75
		8	25	27	103
		9	59	57	225
		10	24	26	232
		11	22	22	181
		12	15	8	291
		13	13	14	88
		14	30	35	62
		15	26	21	310
		16	29	25	277
		17	14	9	28
		18	19	20	93
		19	11	12	232
		20	10	10	227
		25	8	8	284
2	5	0	41	45	180
		1	64	67	340
		2	19	25	25
		3	30	26	240
		4	18	10	131
		5	22	14	299
		6	21	16	22
		8	36	38	306
		9	29	27	191
		10	31	29	230
		11	26	31	333
		12	31	31	32
		13	30	25	202
		14	10	14	145
		15	38	35	305
		16	17	14	111
		17	10	11	56
		18	7	4	352
		19	17	21	171
		21	15	16	5
		23	7	9	206
		25	6	6	266
2	6	0	43	40	0
		1	19	16	282
		2	24	25	61
		3	15	25	70
		4	12	15	252
		5	49	52	285
		6	14	12	97
		7	43	41	76
		8	17	13	137
		9	9	12	273
		12	9	7	233
		13	24	23	87
		14	16	18	332
		15	12	14	302
		16	13	11	351
		17	10	15	80
		18	20	12	165
		19	10	12	214
		22	6	1	296
2	7	0	8	8	0
		1	13	14	340
		2	19	12	212
		3	31	34	193
2	7	4	13	13	316
		5	15	9	184
		6	15	12	95
		7	13	6	43
		8	18	19	218
		9	18	16	226
		10	24	23	42
		11	16	18	18
		12	8	8	107
		13	16	20	173
		15	15	16	275
2	8	0	9	1	180
		2	18	24	92
		3	16	18	62
		4	16	15	300
		5	13	18	300
		6	15	19	33
		7	20	24	144
		8	15	19	234
		9	13	12	150
		13	9	6	156
		14	11	7	335
		16	18	16	50
		18	7	8	274
		20	9	9	8
		21	5	8	8
2	9	0	27	26	0
		1	10	11	289
		3	13	10	345
		4	15	16	294
		5	16	16	86
		7	9	6	200
		8	10	12	194
		9	7	5	303
		10	10	14	28
		12	7	12	190
2	10	2	8	7	285
		3	18	18	340
		4	12	15	313
		5	14	16	30
		6	8	11	62
		7	11	11	183
		8	7	9	212
		9	8	7	180
2	11	9	8	9	52
		11	8	6	177
		12	6	6	190
3	0	2	38	26	180
		3	142	142	90
		4	42	30	0
		5	12	11	270
		6	12	13	180
		7	58	47	270
		8	37	32	0
		9	85	82	90
		10	8	14	0
		11	45	33	270
		12	9	2	0
		13	58	56	90
		14	48	39	0
		15	17	12	90
		16	29	22	180
		18	21	24	0
		20	19	17	180
		21	23	20	270
		22	13	22	180
		24	10	13	0
3	1	0	11	20	90
		1	78	59	284
		2	48	28	284
		3	37	26	66
		4	93	73	125
		5	82	81	193
		6	32	34	15
		7	17	13	313
		8	34	27	126
		9	75	71	138
		10	39	38	63
		11	9	6	350
		12	26	24	285
		13	51	46	35
		14	31	26	143
		15	46	50	194
		16	18	16	22
		17	49	45	342
		18	11	9	165
		19	8	4	182
		21	10	4	195
		24	11	11	107
		25	12	11	206
		26	6	5	319
		28	5	9	174
3	2	0	9	22	270
		1	100	75	284
		2	47	47	105
		3	16	14	150
		4	87	75	250
		5	38	34	231
		6	32	36	236
		7	34	27	229
		8	40	50	67
		9	25	29	131
		10	45	45	272
		11	30	28	251
		12	41	36	89
		13	10	10	109
		14	22	23	247
		15	8	13	255
		16	16	15	152
		17	16	15	14
		18	21	24	28
		19	18	22	128
		20	18	23	279
		21	10	11	280
		22	12	17	81
		23	7	4	159
3	3	0	27	25	90
		1	67	80	297
		2	63	66	29
		3	32	34	133

TABLE 4. (*Continued.*)

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°
3	3	4	73	76	181
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		7	23	31	317
		8	30	40	192
		9	27	21	158
		10	15	9	276
		11	27	35	247
		12	17	20	169
		13	30	34	100
		14	40	35	161
		15	11	6	144
		16	40	39	24
		17	13	14	359
		18	13	19	218
		19	12	6	159
		21	12	9	229
		22	8	3	66
		24	7	9	175
		25	6	1	148
		26	9	12	13
3	4	0	67	59	270
		1	20	28	115
		2	28	26	19
		3	41	42	241
		4	29	30	265
		5	33	36	179
		6	45	40	11
		7	38	35	49
		8	44	49	89
		9	40	36	238
		10	52	58	256
		11	8	19	119
		12	11	16	88
		13	9	8	12
		14	14	21	228
		15	12	10	94
		16	34	29	351
		18	20	16	105
		19	17	17	202
		22	10	12	69
		24	9	14	254
3	5	0	49	44	270
		1	27	25	12
		2	42	34	26
		3	9	18	192
		4	17	18	214
		5	24	29	53
		6	46	43	5
		7	25	38	170
		8	14	18	154
		9	14	13	328
		10	19	20	288
		11	9	6	115
		13	11	18	180
		14	8	2	290
		15	26	29	345
		16	18	21	29
		17	8	10	182
		18	10	9	169
		19	10	9	61
		20	8	5	185
		24	7	9	245
3	6	1	26	34	104
		2	23	17	156
		3	33	40	255
		5	17	6	67
		6	9	15	322
		7	28	29	57
		8	17	17	183
		9	20	32	253
		10	19	14	357
		11	10	16	114
		12	11	8	94
		13	15	17	226
		14	13	16	225
		15	14	16	116
		16	18	19	304
		18	10	9	185
		19	10	13	268
3	7	0	25	30	270
		1	25	29	69
		2	34	38	164
		3	9	11	197
		4	11	14	38
		5	14	20	18
		6	9	14	301
		7	20	21	162
		9	11	16	300
		10	9	8	221
		12	12	13	174
		15	22	25	22
		16	8	11	240
		17	8	15	171
3	8	2	27	30	234
		3	12	23	238
		4	11	11	55
		5	10	11	358
		7	19	20	166
		8	20	21	254
		10	8	10	56
		11	15	21	56
3	9	0	14	15	270
		1	8	8	126
		2	11	9	251
		4	22	27	10
		5	8	11	333
		6	8	14	189
		12	9	9	247
3	10	2	8	10	263
		4	9	9	52
		5	9	12	331
		6	8	11	107
		8	7	8	289
3	11	3	7	9	15
4	0	1	4	10	270
		2	83	73	0
		3	49	54	90
		4	51	42	180
		5	52	48	270
4	0	6	51	47	180
		7	73	75	90
		8	39	49	0
		9	22	10	90
		10	23	29	180
		11	27	21	270
		12	41	47	0
		13	16	13	90
		14	29	33	180
		15	19	21	270
		16	16	15	0
		17	17	23	90
		18	32	39	0
		20	18	27	180
		21	8	6	270
		22	8	17	0
		23	8	11	90
		25	7	3	90
4	1	0	22	4	180
		1	46	39	38
		2	46	33	172
		3	98	67	112
		4	95	79	99
		5	64	62	243
		6	75	76	267
		7	28	29	53
		8	40	46	125
		9	25	21	318
		10	45	45	284
		11	23	26	38
		12	9	17	171
		13	23	22	87
		14	27	31	73
		15	17	27	283
		16	34	33	326
		18	9	13	92
		19	17	17	243
		20	10	7	315
		21	9	12	48
		23	8	10	125
4	2	0	117	72	0
		1	103	75	50
		2	69	65	40
		3	34	35	159
		4	66	52	226
		5	66	61	259
		6	36	32	157
		7	22	22	52
		8	11	14	353
		9	24	28	146
		10	12	16	113
		11	41	39	6
		12	48	45	29
		13	31	35	135
		14	7	8	125
		15	9	9	282
		16	8	7	0
		19	11	8	231
		20	16	9	163
		21	17	20	15
		23	9	11	175
4	3	0	41	50	0
		1	116	85	315
		2	42	38	266
		3	34	46	88
		4	35	29	245
		5	37	39	227
		6	48	41	151
		7	88	83	83
		8	20	26	187
		9	30	22	292
		10	46	48	331
		11	23	20	318
		12	27	30	206
		13	28	29	127
		14	16	15	71
		15	16	20	236
		16	14	12	55
		17	33	36	81
		18	19	21	194
		19	8	9	340
		20	10	9	336
		21	9	12	49
		22	10	11	223
		24	6	2	93
4	4	0	31	26	0
		1	42	47	4
		2	13	18	97
		3	19	24	223
		4	36	35	305
		5	45	45	10
		6	54	49	87
		7	25	30	320
		8	27	32	196
		9	47	44	184
		10	29	28	286
		11	7	5	295
		12	28	23	176
		13	17	20	169
		14	18	15	7
		15	38	42	35
		16	19	19	35
		17	10	10	12
		18	10	14	219
		19	17	18	179
		21	7	3	47
		22	8	10	137
		24	6	7	322
4	5	0	5	9	180
		1	23	22	127
		2	40	40	121
		3	13	15	92
		4	50	48	275
		5	12	7	356
		6	36	39	79
		7	16	19	134
		8	13	12	287
		9	11	19	116
		11	9	5	133
		12	30	26	183
4	5	13	9	5	296
		14	18	19	358
		15	21	24	256
		16	17	23	106
		17	8	13	94
		18	19	20	226
		19	8	6	30
		23	6	7	306
4	6	0	30	45	0
		1	29	24	132
		3	16	23	209
		5	29	31	5
		6	52	47	136
		7	13	21	283
		8	29	26	205
		9	16	17	102
		10	38	46	331
		11	18	19	121
		12	18	19	169
		13	22	24	252
		15	10	11	326
		20	12	10	35
		22	10	12	164
4	7	0	32	32	0
		1	32	39	201
		2	17	25	89
		4	29	41	226
		5	31	37	74
		7	18	19	273
		8	9	17	303
		9	16	17	0
		13	15	16	7
		15	9	8	77
		16	8	12	121
		20	6	6	166
4	8	0	10	16	180
		1	18	19	222
		2	9	13	147
		3	21	25	354
		4	9	14	30
		5	21	20	54
		7	19	18	205
		8	9	8	168
		13	9	10	345
		14	8	10	62
		16	7	4	205
		19	5	5	42
4	9	2	9	14	277
		3	8	10	314
		5	16	22	104
		8	14	15	126
		11	7	9	208
		12	8	9	7
		13	7	8	320
		15	6	8	116
		16	6	6	341
		17	6	8	226
		18	8	7	33
4	10	0	7	7	180
		2	8	8	329
		6	7	5	260
		8	8	12	106
		10	8	9	164
		12	6	9	302
5	0	1	43	31	90
		2	37	36	0
		3	17	20	90
		4	79	79	180
		5	38	30	270
		6	11	19	0
		8	26	34	180
		9	49	44	270
		10	7	1	0
		11	8	4	270
		12	28	29	0
		13	27	21	90
		14	23	25	180
		15	29	24	270
		18	18	17	180
		20	16	18	0
		21	9	9	90
		24	8	12	180
		25	8	15	270
		26	6	15	0
5	1	0	92	93	270
		1	72	66	40
		2	48	56	95
		3	17	21	269
		4	49	47	216
		5	37	25	155
		6	36	27	296
		7	40	29	5
		8	43	39	72
		9	16	21	274
		10	60	56	300
		11	26	25	94
		12	29	33	73
		14	16	26	258
		15	16	20	102
		16	14	22	201
		17	16	23	359
		18	9	6	122
		19	11	13	244
		20	19	20	315
		21	10	3	167
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		1	18	18	286
		2	67	65	14
		3	12	15	186
		4	36	38	139
		5	41	45	11
		6	21	25	347
		7	53	58	170
		8	15	10	132
		9	27	24	292
		10	11	10	350
		11	23	24	353
		12	29	30	62
		13	28	21	127
		14	12	4	275
5	2	15	35	43	6
		17	18	24	179
		18	10	17	177
		19	12	17	327
		22	9	10	85
		23	8	9	197
5	3	0	67	58	90
		1	74	69	75
		2	11	10	269
		3	52	54	256
		4	53	42	265
		5	40	31	353
		6	49	49	338
		7	47	38	111
		8	35	27	139
		9	18	25	227
		10	14	17	172
		11	18	27	133
		12	9	12	286
		13	33	37	296
		14	30	25	4
		15	31	26	25
		16	11	8	77
		17	8	6	138
		18	9	5	126
		19	8	13	287
		23	7	12	255
5	4	0	19	7	90
		1	24	35	314
		2	7	10	219
		3	33	26	245
		4	14	19	101
		6	29	28	134
		7	25	26	194
		9	36	40	8
		10	17	13	107
		11	26	22	86
		12	32	27	169
		13	33	30	192
		14	28	29	260
		15	21	24	357
		16	9	8	132
		17	15	14	187
		18	18	24	57
		19	7	9	342
		23	6	7	249
		24	7	10	313
5	5	0	46	48	90
		1	47	38	70
		2	36	35	238
		3	15	16	193
		4	18	13	62
		5	14	15	9
		6	10	19	354
		7	18	22	149
		8	13	19	271
		9	34	31	255
		10	29	34	120
		11	11	5	116
		12	31	28	245
		13	11	6	342
		14	8	9	44
		15	9	10	352
		16	10	6	84
		18	9	9	333
		21	8	14	119
5	6	0	33	38	90
		1	28	25	56
		2	13	16	250
		3	21	22	161
		4	40	45	355
		5	9	8	194
		6	32	35	176
		7	18	22	311
		8	17	19	284
		9	18	17	329
		10	28	19	62
		11	11	9	114
		12	14	20	48
		14	10	15	3
		15	9	9	86
		16	14	19	178
		18	8	9	10
5	7	1	20	23	262
		2	11	14	295
		3	16	14	312
		4	30	21	55
		5	13	13	80
		6	14	14	133
		7	16	16	115
		8	9	15	319
		9	15	17	204
		10	16	21	93
		11	17	22	285
		12	10	10	229
		14	7	7	42
		15	11	10	173
		18	7	7	311
5	8	0	9	10	90
		1	8	7	6
		2	16	19	202
		4	15	11	36
		6	14	15	123
		7	15	16	1
		8	14	12	17
		9	16	18	136
		10	10	11	212
		11	8	0	90
		12	8	7	258
		13	8	9	342
		14	8	11	42
5	9	1	16	19	221
		2	14	10	21
		3	10	11	39
		9	15	18	136
6	0	1	40	44	270
		2	13	7	180
		3	51	44	90
		4	14	9	180
		5	47	53	270
6	0	7	23	16	270
		8	15	16	180
		9	8	8	270
		10	25	21	0
		11	10	6	90
		12	16	19	180
		13	16	17	90
		15	16	14	270
		17	12	17	90
		18	15	15	180
		19	14	23	270
6	1	0	40	45	0
		1	27	39	357
		2	56	55	97
		3	69	67	202
		4	38	35	293
		5	11	3	221
		6	40	33	103
		7	28	33	336
		8	38	40	244
		9	32	34	154
		10	31	33	306
		11	18	23	355
		12	19	21	123
		14	21	20	351
		16	17	18	115
		17	18	15	223
		18	10	16	238
		19	10	8	41
6	2	0	41	41	0
		1	35	28	185
		2	23	22	135
		3	24	17	121
		4	6	6	285
		5	25	24	286
		6	26	24	146
		7	8	9	220
		8	53	41	233
		9	33	37	346
		16	24	26	56
		17	17	21	158
		18	10	12	259
		19	9	15	302
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		1	13	15	209
		2	23	21	177
		3	8	8	231
		4	29	29	3
		5	49	49	100
		6	12	11	313
		7	23	25	271
		8	19	21	158
		9	17	26	41
		10	37	36	18
		11	16	10	214
		12	23	25	144
		13	21	23	245
		14	17	20	27
		15	10	12	236
		17	11	16	289
		18	10	9	261
		20	9	10	9
6	4	0	20	11	0
		1	45	38	139
		2	26	20	98
		3	32	33	310
		4	25	23	297
		5	28	32	4
		6	18	20	118
		7	31	27	221
		8	31	25	220
		9	10	10	166
		10	17	14	172
		11	32	27	174
		12	11	13	310
		13	15	19	347
		14	20	20	338
		15	17	18	79
		17	10	10	274
		18	8	8	273
		19	7	11	345
		20	7	6	82
		21	8	12	169
6	5	0	16	15	0
		11	16	15	136
		12	14	11	354
		13	13	20	268
		15	12	11	134
		17	12	11	70
		19	8	11	94
		21	7	6	190
		22	7	9	276
6	6	1	20	9	163
		2	20	27	29
		3	18	12	306
		4	15	12	96
		5	18	18	65
		6	8	9	119
		7	8	8	272
		9	20	19	98
		10	19	23	216
		11	21	17	216
		12	19	19	346
		13	8	8	226
		14	13	13	97
		15	13	21	109
		16	7	5	250
		17	10	14	294
		18	7	6	351
		20	7	7	216
6	7	1	18	17	150
		2	17	17	26
		4	20	16	146
		6	19	14	295
		7	10	10	166
		8	10	9	45
		10	11	11	174
		12	14	15	342
		14	11	12	108
6	8	0	19	26	180
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		2	18	19	324
		3	19	16	46
		4	10	12	70
		5	8	2	183
		6	10	10	306
		9	9	10	119
		10	9	15	228
		14	10	11	144
6	9	1	9	10	246
7	0	1	35	36	90
		2	49	39	0
		3	6	4	270
		4	46	34	180
		5	22	10	90
		6	7	3	180
		7	7	14	90
		8	6	12	0
		9	33	39	270
		10	17	5	0
		11	19	28	90
		13	21	25	270
		14	18	14	0
		16	21	21	180
		17	12	17	90
		18	9	6	0
		19	10	13	270
		20	9	9	0
		21	12	19	90
		22	8	9	180
7	1	0	8	9	90
		1	20	23	352
		2	32	29	198
		3	45	39	175
		4	12	12	57
		5	15	18	25
		6	55	46	182
		7	54	45	182
		8	31	27	2
		9	27	23	328
		10	12	9	354
		11	11	14	237
		12	18	22	173
		13	18	15	194
		14	8	14	56
		15	13	12	61
		16	11	11	142
		17	9	11	176
		18	10	4	292
7	2	0	23	31	90
		1	20	13	85
		2	22	32	256
		3	24	25	321
		4	13	13	218
		5	8	8	219
		6	16	10	100
		7	20	18	134
		8	9	9	330
		9	21	15	340
		11	20	22	132
		12	17	20	232
		14	16	15	49
		15	14	15	99
		16	13	17	244
		17	10	15	162
		18	11	16	295
		19	9	6	272
		20	11	14	81
7	3	0	26	18	90
		1	11	3	347
		2	29	27	183
		3	9	6	175
		4	38	45	3
		5	8	2	235
		6	33	36	169
		7	19	17	200
		8	25	27	354
		9	17	16	177
		12	20	22	198
		14	19	27	347
		15	11	6	36
		17	9	13	341
7	4	0	15	15	90
		1	23	24	234
		2	33	36	248
		3	13	7	266
		4	17	16	40
		5	10	18	230
		6	8	7	230
		7	12	11	305
		8	35	26	342
		9	15	20	83
		10	15	19	69
		12	22	29	273
		13	9	9	102
		14	9	10	55
		17	10	9	321
7	5	0	18	7	90
		1	15	16	37
		2	16	7	210
		3	18	24	25
		4	18	14	352
		5	18	25	181
		7	9	13	28
		9	21	23	146
		10	15	11	202
		11	18	16	271
		12	12	13	174
		13	15	15	37
		14	10	10	114
7	6	1	18	19	271
		3	18	15	59
		4	8	8	167
		5	11	12	170
		6	19	17	240
		9	13	17	136
		11	22	22	300
		13	13	15	81
7	7	0	14	15	270
		3	12	19	18

TABLE 4. (*Continued.*)

h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°
7	7	5	10	17	187			5	23	17	270			21	4	5	90			13	14	11	90			7	8	23	270	11	0	8	12	12	180
		6	11	13	2			6	38	36	180			22	5	6	180			16	10	14	180			8	7	0	180			13	8	11	90
		7	10	15	4			7	13	11	2700			23	6	11	270			17	14	10	270			9	7	4	270			14	6	6	180
		8	10	10	131			9	42	35	90	9	0	1	42	36	90			18	9	12	0			10	8	11	180			15	4	5	270
		10	11	11	272			10	12	20	0			2	39	33	0			19	9	4	90			11	13	11	270	12	0	0	11	10	0
		11	9	13	259			12	9	4	180			3	43	42	90			20	5	3	180			12	15	16	0			3	6	12	90
		13	11	14	55			13	13	12	270			5	13	14	270			21	5	1	90			13	8	4	90			5	6	14	270
7	8	0	13	14	270			14	9	14	0			6	31	40	180	10	0	0	9	5	180			18	5	5	0			6	7	14	180
		1	10	11	231			15	24	26	90			7	26	23	270			2	17	17	0	11	0	2	7	6	0			10	5	1	180
		2	8	9	45			16	13	15	180			8	15	20	0			3	8	14	270			3	6	11	90			12	5	4	180
8	0	1	73	70	90			17	15	14	270			9	10	2	90			4	13	11	180			4	7	5	180	13	0	1	4	3	270
		3	33	30	270			18	11	7	0			10	7	4	0			6	9	14	180			6	12	13	0			7	4	13	270

the atoms which had been included in the phasing calculations showed up very poorly and were rejected as spurious. On the other hand, the epoxide group, the five-membered ring, and the acetate group seen in the first Fourier synthesis were now clearly established. A six-membered ring, in the chair conformation, involving C(4) of the epoxide group and an additional acetate group could also be discerned.

The closest approach between the bromine atom and the five-membered ring was 3·02 Å and involved C(13). This distance is too great to represent a covalent bond but is distinctly shorter than the sum of the van der Waals radii of carbon and bromine atoms (3·95 Å). Evidently there had to be an atom between C(13) and Br, covalently bonded to both. Moreover, in the electron-density distribution there was a prominent peak at about 1·4 Å from C(16) and the size of the peak suggested that it was an oxygen atom. It seemed likely that this was the oxygen atom in the bromo-lactone ring which, therefore, had to contain C(13), C(16), and O(7). Accordingly we looked for three further atoms lying approximately in the plane of C(13), C(16), and O(7); two of these had to be carbon atoms (one covalently bonded to the bromine atom) and the third the ketonic oxygen atom. Small peaks were found in the desired positions.

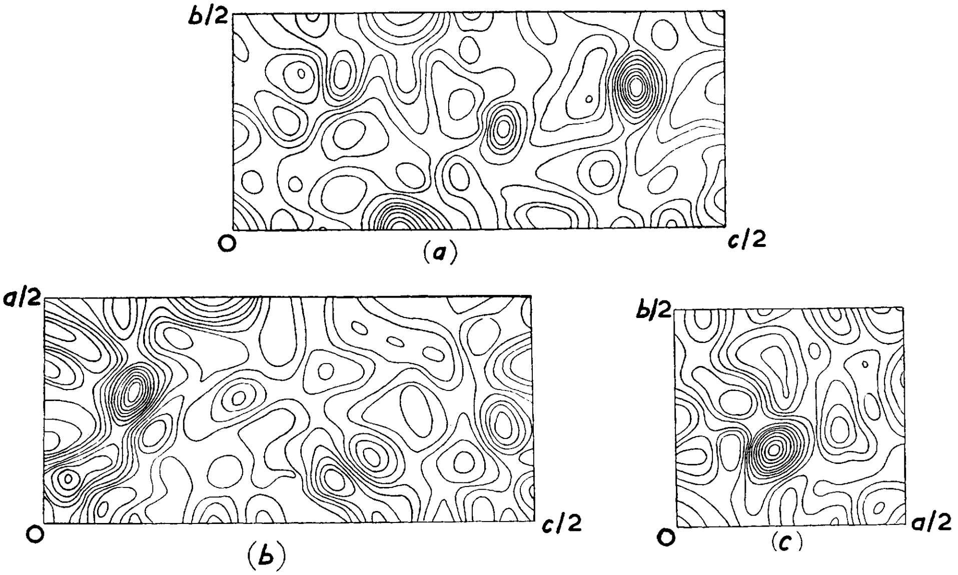
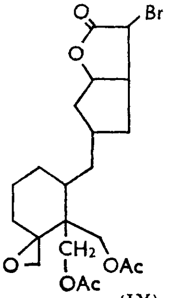


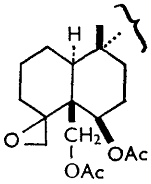
FIG. 4. Sections through the three-dimensional Patterson function (*a*) at $x = \frac{1}{2}$, (*b*) at $y = \frac{1}{2}$, and (*c*) at $z = \frac{1}{2}$. Contour scale arbitrary.

At this stage we still thought that the formula of the bromo-lactone was $C_{21}H_{29}BrO_7$ and we were able, therefore, to postulate structure (IX). On biogenetic grounds, however, such a structure seemed rather improbable. Furthermore this structure ignored three possibly significant peaks in stereochemically acceptable sites. If these peaks were included clerodin contained a decalin fragment (X) and the C_{21} formula could not be correct.

Up to this point we had not yet determined the density of the bromo-lactone crystals. When this essential measurement was made the result ($D_m = 1{\cdot}432$) clearly invalidated the C_{21} formula which required $D_c = 1{\cdot}290$. Consideration of this crystal-density measurement and of the C : H : O ratios for clerodin suggested that we should revise the formula of clerodin to $C_{24}H_{34}O_7$ and that of the bromo-lactone to $C_{24}H_{33}BrO_8$; with this revision the calculated value for the density of the bromo-lactone is $D_c = 1{\cdot}442$. Confirmation of the C_{24} formula was obtained from the results of the preliminary crystallographic study of clerodin bromohydrin. This also crystallizes in the orthorhombic system, space group $P2_12_12_1$, and the approximate cell dimensions are $a = 11{\cdot}44$, $b = 9{\cdot}73$, $c = 22{\cdot}50$ Å. With four molecules of $C_{24}H_{35}BrO_8$ in the unit cell $D_c = 1{\cdot}41$, while the experimental result is $D_m = 1{\cdot}43$ ($C_{21}H_{31}BrO_7$ would require $D_c = 1{\cdot}26$).



(IX)



(X)

Two further three-dimensional Fourier syntheses served to locate unambiguously all the atoms (other than hydrogen) in the molecule. In the phasing calculations the atoms, other than bromine, were treated as carbon atoms. Before the constitution and relative stereochemistry could be finally defined, however, a careful distinction had to be made between oxygen and carbon atoms. The peak heights of the atoms and the interatomic distances were therefore examined. The results clearly indicated (IV) as the structure of the bromo-lactone except for the stereochemistry of the epoxide group which remained in doubt, the two bonds from C(4) to C(17) and O(1) being approximately equal in length, though the peak height of C(17), 6·6 $eÅ^{-3}$, was rather less than that of O(1), 7·1 $eÅ^{-3}$.

Five further cycles of refinement by Fourier methods were carried out. Three-dimensional F_o and F_c syntheses were computed and atomic co-ordinates obtained by numerical interpolation in the results; errors due to termination of series were corrected and individual isotropic temperature factors allocated. In these calculations each atom was assigned its correct chemical type except for O(1) which was still treated as a carbon atom. The average discrepancy between measured and calculated structure amplitudes fell to 21%.

The situation with regard to the epoxide group was still confused. The peak heights, O(1) 6·52 $eÅ^{-3}$, C(17) 5·35 $eÅ^{-3}$, clearly favoured the stereochemical assignment shown in (IV), whereas the bond lengths, C(4)–C(17) = 1·48 Å, C(4)–O(1) = 1·52 Å, suggested that the epoxide configuration should be inverted. Further refinement was clearly necessary.

In the electron-density distributions the bromine atom had consistently appeared ellipsoidal rather than spherical. It was considered desirable, therefore, that in the further refinement of the crystal structure allowance should be made for the marked anisotropic thermal vibration of the bromine atom and the possible anisotropic thermal vibration of the carbon and oxygen atoms. Accordingly, Rollett's least-squares programme [16] for DEUCE was used in the final stages of the analysis to refine positional and anisotropic thermal parameters for all atoms other than hydrogen. Four cycles of least-squares calculations were carried out with C(17) weighted as a carbon atom and O(1) weighted as an oxygen atom. The discrepancy factor R fell to 16·0% and as physically acceptable temperature factors were obtained (see Table 6) the detailed refinement was terminated at this stage. However, to provide a firmer basis for the distinction between oxygen and carbon in the epoxide ring some further least-squares calculations were performed in which only the parameters of C(4), C(17), and O(1) were permitted to vary.

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[16] Rollett, in "Computing Methods and the Phase Problem in X-ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 87.

For three cycles of calculations C(17) was treated as a carbon atom and O(1) as an oxygen atom. The value of *R* fell to 15·8%. With the final values of $(F_o - F_c)$ a three-dimensional difference Fourier synthesis was computed; sections through the atoms of the epoxide group are shown in Fig. 5(*a*). No marked excess or deficit of electron density occurs at the sites of C(17) and O(1).

For three cycles of refinement both C(17) and O(1) were treated as carbon atoms. The discrepancy factor was not reduced below 16·6% and the temperature factor of O(1) became very small. With the values of $(F_o - F_c)$ resulting from this refinement a three-dimensional difference Fourier synthesis was computed; sections through the atoms of the epoxide group show that after subtraction of a carbon atom from the site of O(1) an excess of electron density is still associated with that site [see Fig. 5(*c*)].

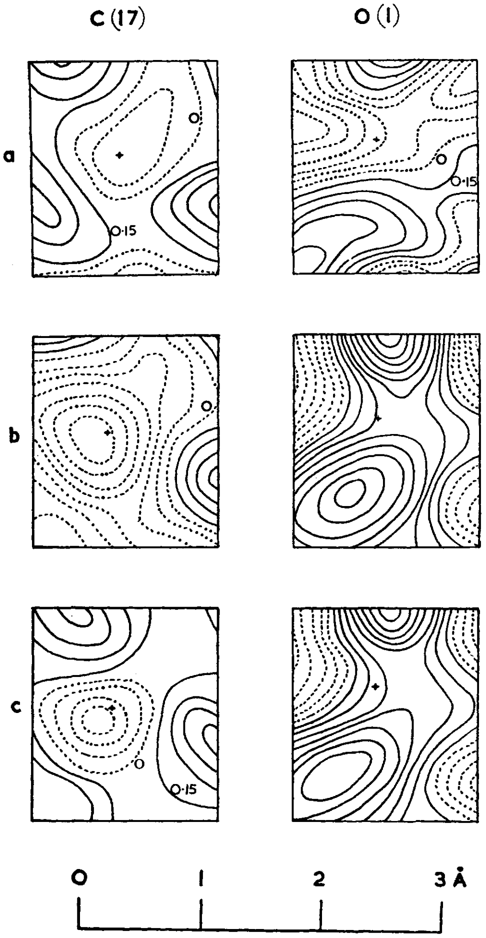

FIG. 5. Sections through three-dimensional difference Fourier syntheses showing the residual electron density still associated with the sites of C(17) and O(1) after subtraction of atoms which had been included in least-squares refinements according to the schemes: (a) C(17) weighted as carbon and O(1) weighted as oxygen; (b) C(17) weighted as oxygen and O(1) weighted as carbon; and (c) C(17) weighted as carbon and O(1) weighted as carbon. Contour interval 0·15 eÅ^{-3}, the first broken contour being the zero level.

Three further cycles of least-squares refinement in which C(17) was treated as an oxygen atom and O(1) as a carbon atom were then carried out. The discrepancy factor did not fall below 17·1%, while the temperature factor of C(17) became large and that of O(1) small. With the values of $(F_o - F_c)$ given by this procedure a further three-dimensional difference Fourier synthesis was computed; sections through the atoms of the epoxide group show that after subtraction of a carbon atom from the site of O(1) an excess of electron density remains associated with that site and that after subtraction of an oxygen atom from the site of C(17) a marked deficit of electron density is associated with that site [see Fig. 5(*b*)].

TABLE 5.

Anisotropic thermal parameters ($b_{ij} \times 10^5$) for atoms C(17) and O(1) of the epoxide ring. These parameters are derived from three least-squares procedures: (*a*) C(17) weighted as carbon and O(1) as oxygen; (*b*) C(17) weighted as carbon and O(1) as carbon; (*c*) C(17) weighted as oxygen and O(1) as carbon.

		b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(17)	(*a*)	1323	2466	330	385	1236	472
	(*b*)	2800	2081	405	1672	1425	1307
	(*c*)	3630	3364	654	1249	1229	1146
O(1)	(*a*)	697	3910	259	1356	214	−401
	(*b*)	−758	2358	18	1122	169	−246
	(*c*)	−928	2401	55	588	−36	−390

The anisotropic temperature-factor parameters corresponding to the various assumptions about the chemical nature of atoms C(17) and O(1) are shown in Table 5; these parameters are values of b_{ij} in the equation:

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

Only the results corresponding to C(17) being a carbon atom and O(1) an oxygen atom are acceptable.

TABLE 6.

Final anisotropic temperature-factor parameters ($b_{ij} \times 10^5$).

	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	521	1277	307	−445	137	−83
C(2)	1257	1269	330	−772	−182	14
C(3)	592	2100	323	−706	−189	45
C(4)	1081	1559	358	−466	−86	−460
C(5)	884	1180	231	−840	38	−225
C(6)	777	1751	312	−1688	−234	−200
C(7)	1118	1988	322	−490	299	55
C(8)	1071	1726	183	−505	−384	81
C(9)	712	1409	239	254	75	−152
C(10)	697	1003	287	−409	122	27
C(11)	588	1888	240	−530	−168	89
C(12)	875	1894	231	198	349	−40
C(13)	956	2101	279	35	−88	−12
C(14)	1014	1680	321	−427	−130	−78
C(15)	1461	1792	287	−2277	−94	122
C(16)	1143	1620	198	−120	−397	−14
C(17)	938	1901	285	386	525	484
C(18)	747	1383	221	−1432	−200	−38
C(19)	1163	1741	227	−634	217	−90
C(20)	909	1918	426	571	303	76
C(21)	1168	1484	342	−169	186	−36
C(22)	1398	1531	301	−2260	−404	83
C(23)	1000	1528	288	241	67	4
C(24)	611	2225	358	555	−304	−3
O(1)	1270	2032	264	673	206	−44
O(2)	1036	1871	260	−633	78	−289
O(3)	1301	2023	327	141	467	290
O(4)	972	1783	288	−610	297	−22
O(5)	1087	2594	398	−488	−401	570
O(6)	1071	1255	304	−381	81	−86
O(7)	674	1060	363	115	47	408
O(8)	1074	985	414	235	256	−434
Br	1928	2525	339	−1770	−44	−318

There is little doubt that the stereochemistry of the epoxide group must be as in (IV); moreover, chemical evidence in favour of this assignment has been obtained by Barton *et al.*[1]

For the structure-factor calculations theoretical atomic scattering factors were employed;

those of Berghuis *et al.*[17] for carbon and oxygen and the Thomas–Fermi values [18] for bromine were chosen. The final calculated structure amplitudes and phase constants, derived from the least-squares refinement in which all the atomic parameters were allowed to vary, are shown with the measured values of the structure amplitudes in Table 4. The final phase constants and the measured structure amplitudes were used to derive a final three-dimensional electron-density distribution which is shown in Fig. 1 by means of superimposed contour sections drawn parallel to (001). All the atoms are well resolved and the oxygen atoms are represented by distinctly higher peaks than the carbon atoms. The atomic co-ordinates, molecular dimensions, and some non-bonded distances are given in Tables 1 and 2. The final anisotropic thermal parameters are in Table 6.

The standard deviations of the final atomic co-ordinates were derived from the least-squares residuals by application of the equation:

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

The results are listed in Table 3.

Determination of the Absolute Configuration.—The absolute configuration of the molecule was determined by Bijvoet's method,[4] the anomalous dispersion of the copper K_α radiation by the bromine atom causing equivalent reflexions to show small differences in intensities. The effect, though small, was visible on the photographic record of the intensities. The proper indexing of the film was accomplished in the manner described by Bijvoet and Peerdeman.[19]

TABLE 7.

Intensity differences which establish the absolute configuration.

	Calculated		Observed				Calculated		Observed		
h k l	$\lvert F(hkl)\rvert^2$	$\lvert F(h\bar{k}l)\rvert^2$	$I(hkl)$		$I(h\bar{k}l)$	*h k l*	$\lvert F(hkl)\rvert^2$	$\lvert F(h\bar{k}l)\rvert^2$	$I(hkl)$		$I(h\bar{k}l)$
1,1,17	57·8	50·6		<		1,2,13	126·3	122·4		<	
1,1,19	107·9	94·3		<		1,2,18	146·0	150·3		<	
1,1,24	39·7	56·6		>		1,2,23	47·7	55·1		>	

For calculating the intensity differences to be expected we used $f' = -0{\cdot}9$ and $f'' = +1{\cdot}5$.[20] The atomic co-ordinates of Table 1 considered in relation to a right-handed set of axes in space group $P2_12_12_1$ gave rise to intensity differences opposite to those observed (see Table 7); as these co-ordinates define the mirror-image of molecule (IV) it follows that the absolute configuration of clerodin bromolactone is as in formula (IV).

Figs. 1 and 2 show the molecule of clerodin bromolactone in the correct absolute configuration.

The extensive calculations were performed on the Glasgow University DEUCE computer, with programmes devised by Dr. J. S. Rollett and Dr. J. G. Sime. We thank the Carnegie Trust for a Scholarship (to I. C. P.) and the University of Glasgow for an I.C.I. Fellowship (to T. A. H.).

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[19] Bijvoet and Peerdeman, *Acta Cryst.*, 1956, **9**, 1012.

[20] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.