

AN X-RAY STUDY
OF
THE STRUCTURE OF SOME
TERPENOID DERIVATIVES

by

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A B S T R A C T

The unit cells and space groups of derivatives of four natural products and three chlorinated insecticides were determined.

The structures of two of these,

1). Bromoisotenulin (BIT) ($C_{17} H_{21} O_5 Br$)

and 2). Caryophyllene chlorohydrin (CC) ($C_{14} H_{23} O_2 Cl$)

have been studied in detail, using the heavy-atom technique.

Bromoisotenulin is monoclinic ($P2_1$) ($a = 8.75\text{\AA}$, $b = 23.15\text{\AA}$, $c = 10.28\text{\AA}$, $\beta = 121^\circ$) and there are two molecules in the asymmetric unit. It was none-the-less fairly easily solved, but has been a rather large structure to refine. The work has revised our knowledge of this and a number of related sesquiterpenes, and has supplied both the stereochemistry and the absolute configuration. The two independent molecules are in very good agreement.

Caryophyllene chlorohydrin is trigonal ($P3_1$) ($a = 13.12\text{\AA}$, $b = 7.11\text{\AA}$) with one molecule in the asymmetric unit. This was considerably more difficult to solve, and its refinement has posed special problems on the computer, where, through lack of suitable programs, it has often had to be treated as triclinic. The final structure is a little more accurate than that of BIT. Its structure was unexpected and has opened up new lines of chemical study. It is in remarkably good agreement with a 2-D study of the caryophyllene halides carried out by Robertson and Todd (1955).

The molecular and crystal structures of both substances are discussed.

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CHAPTER 1.

THE TERPENES.

Terpenes are hydrocarbons occurring widely in the oils, resins and tissues of plants and trees, and are believed to have been made up of isoprene (C_5H_8) units, ⁽¹⁾(Wallach), Fig. (1).

The C_{10} , C_{15} , C_{20} and C_{30} compounds are known as mono, sesqui, di and triterpenes respectively. Polyterpenes of very high molecular weight, e.g. rubber latex are also found in nature.

In addition to the hydrocarbons there are also many naturally occurring derivatives with similar skeletal structures. Most contain oxygen functions. Thus terpene alcohols, ketones, aldehydes, acids and lactones all occur frequently in the oils and resins of plants and trees.

The term terpene was originally reserved for those C_{10} hydrocarbons based on isoprene, but by common usage, the term now includes all the higher isoprenoids. The term "terpenoid" is used both as a noun and as an adjective to describe all the terpenes and all their immediate derivatives, natural or synthetic.

The so called "Isoprene Rule" regards all the terpenes as having been formed by,

1. the formation of a chain of isoprene units either "head-to-tail" (regularly) Fig. (2), or "head-to-head", or "tail-to-tail" (irregularly) Fig (3), and
2. the cross-linking of this chain to form the numerous and varied terpene skeletons.

Thus, in the monoterpene menthene, Fig. (4), the isoprene units are linked "head-to-tail" by the bond A B,; the other bond, C D is a cross-link. Lavandulol is derived from two irregularly linked isoprene units, Fig. (5).

Most of the sesquiterpenoids seem to have been formed from a chain of three isoprenoid residues joined "head-to-tail". The typical example of the acyclic sesquiterpene is farnesol, Fig. (6), in which three isoprene units are linked "head-to-tail". The "farnesol rule" proposed that the sesquiterpene structures should be derivable from farnesol by some cross-linking as in the four examples, α - santalene, cedrene, caryophyllene and guaialol, Fig. (7). In all these examples the bonds - - show the primary links between

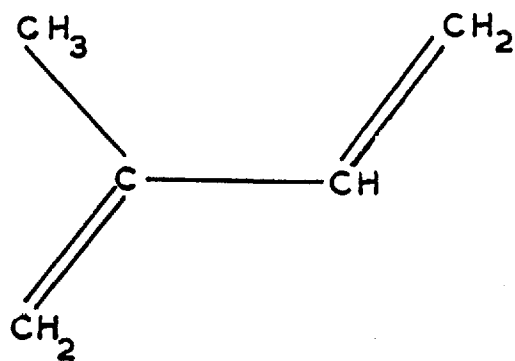


FIG. 1

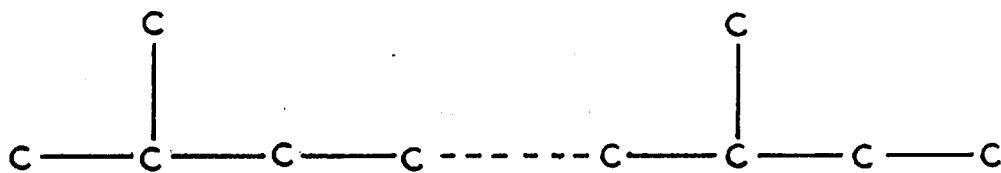


FIG. 2

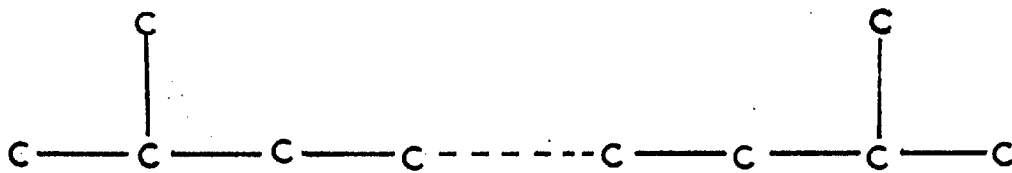


FIG. 3

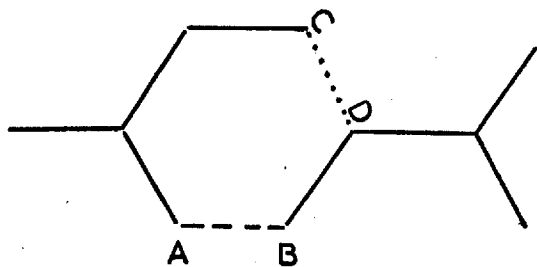


FIG. 4

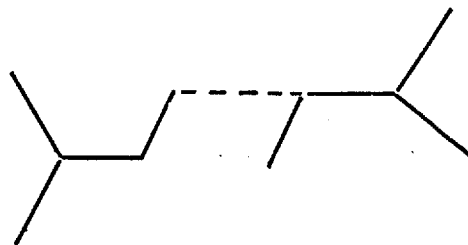
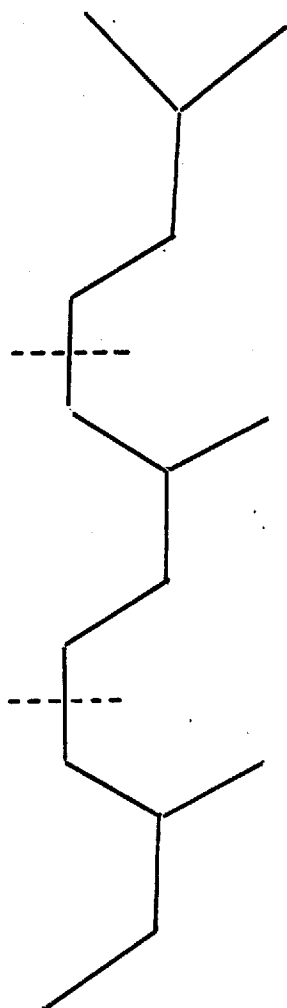


FIG. 5



OR

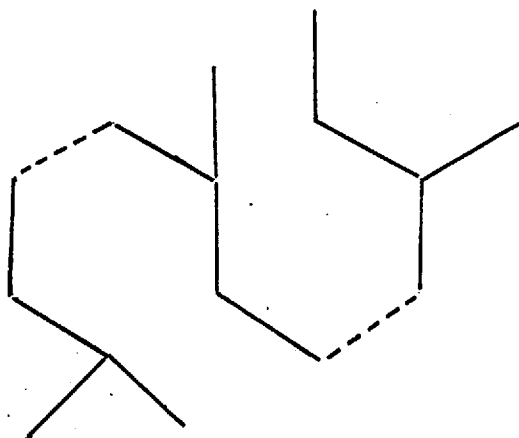


FIG. 6

the isoprene units, and are, therefore, necessary terpene links.

The cross-links are shown as Of the sesquiterpenes, only carotol, Fig. (8), does not follow the "farnesol rule"; its three isoprene units are irregularly constructed.

The one exception to the isoprene rule among the sesquiterpenes is eremophilone, Fig. (9), but this has probably arisen in the plant by a re-arrangement from the true polyisoprenoid, Fig. (10), either at or after the time of cyclisation, (Penfold and Simonsen⁽²⁾).

The di - and triterpenes are higher members of the terpene family and the bicyclofarnesol skeleton, Fig. (11), is common to most of them. A typical example of a diterpene is phytol, Fig. (12), and although there are exceptions to this regular arrangement, e.g. abietic acid, Fig. (13), rings A and B are always in the bicyclofarnesol pattern.

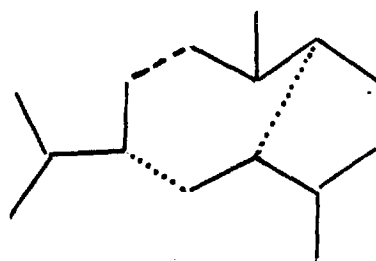
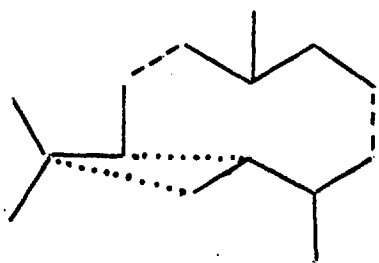
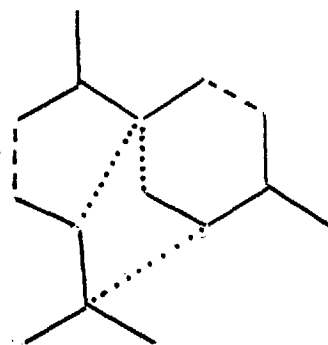
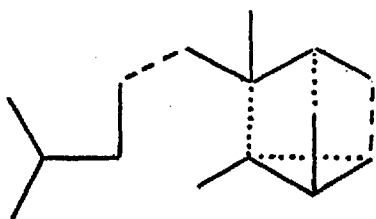


FIG. 7

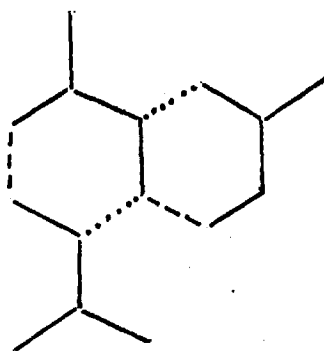


FIG. 8

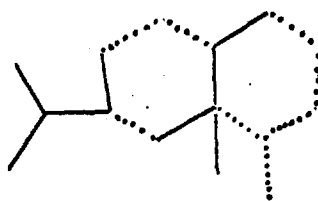


FIG. 9

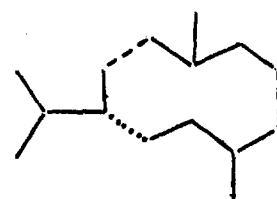


FIG. 10

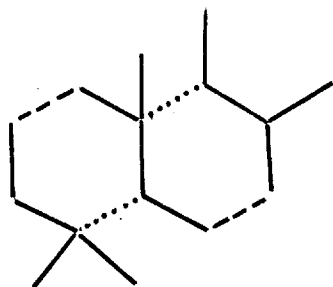


FIG. 11

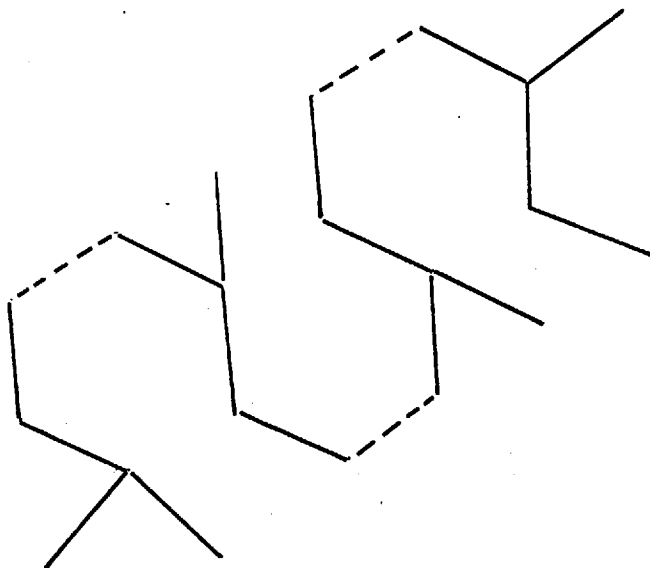


FIG. 12

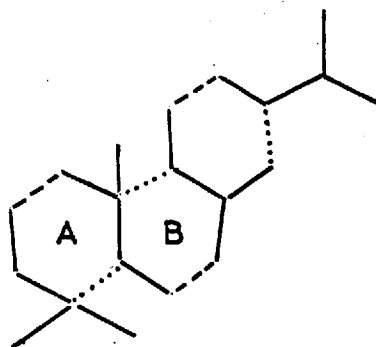


FIG. 13

Previous X-ray work done on Terpenes.

The last few years have seen a marked increase in the x-ray activity among terpenoids, and the following list demonstrates how many strategic structures have now been established. The two reported in this thesis bring the total known to have been solved to 31 so far. Many were studied to establish their constitution at a time when there was very little reliable chemistry available, and almost all the studies gave badly needed stereochemical data. The value of x-ray work in this and other areas of natural-product chemistry is now well recognised; it has occasionally corrected previous deductions, and often cut decisively through a tangle of conflicting indications.

1. Monoterpenoids.

(3)

Geranylamine hydrochloride, (Jeffrey), by heavy - atom technique.

(4)

α - α -chlorocamphor, (Wiebenga and Krom), by the method of isomorphous replacement.

(5)

Menthyl trimethylammonium iodide, (Gabe and Grant), by heavy--atom technique.

(+) - 10 - Bromo - 2 - chloro - 2 nitrosocamphane, (Ferguson
(6)
et al) by heavy - atom technique.

(-) - 2 - Bromo - 2 - nitrosocamphane, (Bruckner et al),
(7)
by heavy - atom technique.

Iridomyrmecin and isoiridomyrmecin, (McConnell et al) by
(8)
optical - transform techniques.

2. Sesquiterpenoids.

Longifolene hydrochloride, (Moffet and Rogers) by the method
(9)
of isomorphous replacement.

Caryophyllene alcohol. (Robertson and Todd), by the method
(10)
of isomorphous replacement as chloride and bromide.

Hydroxydihydroeremophilone, (Grant et al) by statistical
(11)
methods applied to the (100) and (010) projections.

Isoclovene, (Clunie and Robertson), by heavy - atom technique.
(12)

Cedryl chromate, (Amirthalingam), by the heavy - atom and
(13)
anomalous dispersion methods.

α - Santonin, (Asher and Sim), by heavy - atom technique.
(14)

Isophotosantonin lactone (Asher and Sim), by heavy - atom
(15)

technique.

(16)
Shellolic Acid, (Gabe), by heavy - atom technique.

(17)
2 - bromo - desmotropo-santonin (Robertson), the work is still
in progress.

(18)
Geigerin, (Hamilton et al) by heavy - atom technique.

Patchouli chromate (Dunitz et al, unpublished) by heavy - atom
technique.

Bromohelenalin (Herz et al, unpublished) by heavy - atom
technique.

3. Diterpenoids.

(19)
Clerodin, (Paul et al) by heavy - atom technique.

(20)
Cafestol, (Scott et al), by heavy - atom technique.

(21)
Gibberellic acid, (McCapra et al), by heavy - atom technique.

(22)
Rosololactone, (Sim and Sutherland) by heavy - atom technique.

(23)
Cascarillin, (Robertson), by heavy - atom technique, but the work
is not yet complete.

4. Triterpenoids.

(24)
Lanosteryl iodoacetate, (Fridrichson and Mathieson) by heavy -
atom technique.

(25)
Methyl oleanolate iodoacetate, (Rahim and Carlisle), by heavy -
atom technique.

(26)
Limonin, (Arnott et al), by heavy - atom technique.

(27)
Cedrelone, (Grant et al), by heavy - atom technique.

(28)
Gedunin, (Sutherland et al), by heavy - atom technique.

CHAPTER 2.

The Collection and Processing of X-ray Diffraction Data.

1. The apparatus used.

All the photographs were taken with a Unicam Weissenberg goniometer using filtered Cu K α radiation generated from a Philips sealed-off tube fed from a Solus-Schall unit at 35 kV and 30 mA.

2. Unit cells and space groups.

The unit cells and space groups of seven substances which were determined as exercises are given below. Two of the substances were made the subject of full-scale structure analysis. In each case the space groups were determined uniquely by their Laue symmetries and systematic absences.

1. Bromoisotenulin (C₁₇ H₂₁ O₅ Br) Mol. wt. = 385.

(abbreviated throughout this thesis to B I T)

Oscillation and Weissenberg photographs showed that B I T crystallizes in the monoclinic system and has cell dimensions.

$$\left. \begin{array}{l} a = 8.75 \\ b = 23.15 \\ c = 10.28 \end{array} \right\} \text{Å}$$

$$\beta = 121^\circ$$

The systematic absences found were 0 k 0 when $k=2n+1$, which, with the optical activity of the molecule, led to the conclusion that the space group is $P2_1$. The observed density is 1.457 gm. cm.⁻³ and calculated density is 1.451 gm. cm.⁻³ There are 4 molecules per unit cell. Hence there are two molecules per asymmetric unit.

2. Caryophyllene Chlorohydrin. ($C_{14}H_{23}O_2Cl$) Mol. wt. = 258.5.

(abbreviated to C C throughout the thesis)

Trigonal; Laue symmetry, $\bar{3}$

$$\left. \begin{array}{l} a = 13.12 \\ c = 7.11 \end{array} \right\} \text{Å}$$

The systematic absences found were 0 0 l when $l \neq 3n$, which, together with the optical activity of the molecule, led to the conclusion that the space groups is $P\bar{3}_1$, or its enantiomorph, $P\bar{3}_2$.

$$d \text{ obs.} = 1.209 \text{ gm. cm.}^{-3}$$

$$d \text{ calc.} = 1.21 \text{ gm. cm.}^{-3}$$

There are three molecules per unit cell with one molecule in the asymmetric unit.

3. Leucodrin ($C_{15}H_{16}O_8$) Mol. wt. = 324.

It crystallizes in the orthorhombic system with cell dimensions.

$$\left. \begin{array}{l} a = 6.0_8 \\ b = 9.0_1 \\ c = 25.9 \end{array} \right\} \text{ \AA}$$

The systematic absences were confined to $h00$, $0k0$ and $00l \neq 2n$, thus the space group is $P2_12_12_1$ and is uniquely determined.

$$d \text{ obs.} = 1.540 \text{ gm. cm.}^{-3}$$

$$d \text{ calc.} = 1.580 \text{ gm. cm.}^{-3}$$

There are 4 molecules per unit cell, i.e. one molecule in the asymmetric unit.

4. Photodrin ($C_{12}H_8Cl_6$) Mol. wt. = 365

(29)
(Compound IV in the paper of Bird, Cookson and Grundwell.)

Monoclinic; Laue symmetry 2/m.

$$\left. \begin{array}{l} a = 13.0_8 \\ b = 13.8_9 \\ c = 15.7_7 \end{array} \right\} \text{Å}$$

$$\beta = 114^\circ$$

The systematic absences were confined to $h \neq 1$, ($h = 2n+1$), and to $0 \neq 0$, ($k = 2n+1$), thus the space group is $P2_1/a$ and is uniquely determined.

$$d \text{ obs. } \approx 1.75 \text{ gm. cm.}^{-3}$$

$$d \text{ calc. } = 1.86 \text{ gm. cm.}^{-3}$$

The cell contains 8 molecules, so the asymmetric unit comprises 2 unrelated molecules.

5. S D 2506 ($C_{12}H_7Cl_5$) Mol. wt. = 328.5

(A model compound produced by Shell Research Laboratories: it is an analogue of Aldrin.)

Orthorhombic; Laue symmetry mmm

$$\left. \begin{array}{l} a = 7.8_3 \\ b = 12.0_6 \\ c = 14.3_0 \end{array} \right\} \text{Å}$$

Space group is $P2_12_12_1$ uniquely determined as in Leucodrin.

$$d \text{ obs.} = 1.62 \text{ gm. cm.}^{-3}$$

$$d \text{ calc.} = 1.63 \text{ gm. cm.}^{-3}$$

There are 4 molecules per unit cell, i.e. one molecule in the asymmetric unit.

6. Cookson's Half - cage compound ($C_{12}H_8Cl_6$) Mol. wt. = 365
(29)
(Compound XIII in the paper of Bird et al)

Monoclinic; Laue symmetry $2/m$

$$\left. \begin{array}{l} a = 15.12 \\ b = 12.74 \\ c = 13.59 \end{array} \right\} \overset{o}{\text{\AA}}$$

$$\beta = 92^\circ$$

The space group is $P2_1/a$, uniquely determined as in Photodrin.

$$d \text{ obs.} \approx 1.75 \text{ gm. cm.}^{-3}$$

$$d \text{ calc.} = 1.86 \text{ gm. cm.}^{-3}$$

There are 8 molecules per unit cell and, therefore, 2 per asymmetric unit.

7. Zorin Iodoacetate ($C_{32}H_{53}O_3I$) Mol. wt. = 612.69

Monoclinic; Laue symmetry $2/m$.

$$\left. \begin{array}{l} a = 8.38 \\ b = 11.52 \\ c = 14.86 \end{array} \right\} \text{ \AA}$$

$$\beta = 92^\circ$$

The systematic absences found were 0 k 0 when $k=2n+1$, which, with the optical activity of the molecule, led to the conclusion that the space group is $P2_1$:

$$d \text{ obs.} = 1.425 \text{ gm. cm.}^{-3}$$

$$d \text{ calc.} = 1.42 \text{ gm. cm.}^{-3}$$

There are 2 molecules in the unit cell. Hence one molecule per asymmetric unit.

III. Intensity measurement.

Two distinct sets of three - dimensional data were collected around two different axes for both B I T and C J. The intensity photographs were taken in the usual way using packs of four "Ilford Industrial "G" films with one sheet of black paper between each. Two different exposure times (approximately 15 : 1) for each layer were used to enable a wide range of intensities to be recorded. For each pack of films new developer and fixer were

used. The photographs were developed for 5 minutes at 65°F and fixed for one hour.

All the intensities for B I T and C C were measured visually, by comparing the intensities with those on a step wedge made with the same type of film and same crystal. Having obtained up to eight different estimates of the intensity of each reflection the film-to-film ratios were determined and used to convert all the estimates to the scale of the densest film. The mean value of these estimates for each reflection was taken as the intensity on an arbitrary scale. Changes in spot-shape were not very large, so no systematic spot-shape correction was applied. An effort was, however, made to compensate for this factor when measuring the intensities visually.

IV. Lorentz and polarization corrections

Before use, the observed intensities must be corrected for certain geometrical factors. The intensity ($I_{\text{obs.}}$) of a reflection is given by the expression

$$(I \text{ obs.}) \propto F^2 L p A T$$

ere F is the structure factor, L the Lorentz factor, p the polarization factor, A the absorption factor and T the temperature factor. The process of diffraction causes partial polarization of the diffracted beam. The polarization correction is given by,

$$p = \frac{1}{2} (1 + \cos^2 2\theta)$$

Thus, the intensities decrease down to a minimum at $\theta = 45^\circ$.

The Lorentz factor expresses the length of time any crystal plane spends in the reflecting position and also depends upon the type of photograph. For equi-inclination photos

$$L = \frac{2}{\xi} \sqrt{4 \cos^2 \gamma - \xi^2}$$

where $\frac{\pi}{2} - \gamma =$ the angle between the X-ray beam and the oscillation axis

and $\xi =$ the radial cylindrical

co-ordinate of the reciprocal lattice point. It is usual to combine these two corrections for practical purposes i.e. the correction becomes

$$(L p)^{-1} = \frac{\xi \sqrt{4 \cos^2 \gamma - \xi^2}}{1 + \cos^2 2\theta}$$

The Lorentz and polarization factors for B I T were first determined by Cochran's⁽³⁰⁾ method for the zero layer only, and applied by hand to the mean intensity estimates. Afterwards the program ZK43 of Smits was used for correcting all the data in the layers around both the main and subsidiary axes.

In the case of C C the data was processed using the data - reduction program, D R O-4, written by Dr. C.K. Prout for the Mercury computer. The program applies the Lorentz - polarization correction and scale factor.

V. Absorption correction

All crystals absorb x-rays to some extent. The linear absorption co-efficient is given by

$$\mu = \rho \sum p_j \mu_j,$$

where atoms of type j have mass absorption co-efficient μ_j and represent a fraction p_j of the molecular weight; ρ is the density of the crystal.

The absorption co-efficient of the crystal depends on a factor of the form $\int e^{-\mu l} dv$ where l denotes the path length to and from a diffracting volume dv inside the crystal. Both for a sphere

and a cylinder it can be expressed in terms of the radius. The correction has been tabulated and is easy to apply. But it is customary to try to avoid having to make any correction by choosing a specimen of small enough radius. This was done for all the specimens used in this work.

The linear absorption co-efficient of B I T is 36.4 cm^{-1} , but the crystal did not take kindly to sphere grinding, so blocks roughly $\frac{1}{2}$ mm square were cut from plates about $\frac{1}{3}$ mm thick. For such a small irregular, near - cubic shape the corrections are virtually only a function of $\sin \theta$, so it was thought justifiable not to apply an absorption correction.

In the case of C C the crystals used for taking intensity photographs were hexagonal prisms, 0.687 mm long and 0.375 mm wide when oscillating about the θ axis, and 0.484 mm long and 0.424 mm wide when oscillating about the a axis. It has a linear absorption co-efficient of 29.2 cm^{-1} , so again no absorption correction was applied.

VI. Determination of scaling and temperature factor

Wilson⁽³¹⁾ showed that, if the atoms lie randomly in the cell, and no one or two atoms dominate the scattering, the average observed intensity is given by

$$\langle I_0 \rangle = \langle KI \rangle = K \sum f_j^2 \exp\left(-\frac{2B \sin^2 \theta}{\lambda^2}\right)$$

If this is re-written as

$$\ln\left(\frac{\langle I_0 \rangle}{\sum f_j^2}\right) = \ln K - \frac{2B \sin^2 \theta}{\lambda^2}$$

one can see how, by plotting $\ln\left(\frac{\langle I_0 \rangle}{\sum f_j^2}\right)$ against $\sin^2 \theta$

one should get a straight line from which both K and B can be found. In practice the reflections are divided into groups

covering suitable ranges of $\sin^2 \theta / \lambda^2$, the mean of the observed intensities is evaluated for each group.

The graph of $\ln\left(\frac{\langle I_0 \rangle}{\sum f_j^2}\right)$ versus $\sin^2 \theta$ is linear only if $\sum f_j^2$ is based on f data appropriate to the structure.

Strong curvature at low $\sin^2 \theta$ has often been found. The linear

extrapolation back to $\theta = 0$ can then give rise to considerable

error in the scaling factor. If $\ln\left(\frac{\langle I_0 \rangle}{\sum Z_j^2}\right)$ is also

plotted (Rogers⁽³²⁾) these two curves will have a common intercept,

from which a better value of the scaling factor can be obtained.

The latter function is often the more linear of the two for structures consisting wholly of light atoms.

C H A P T E R 3

Crystallographic Functions and their Computation

If an electron is located in the path of an X-ray beam, it is forced into oscillation by the electric component of the X-rays, thus becoming a source of radiation, i.e. the electron scatters the impinging radiation. If the electron density at the point x, y, z is $\rho(x, y, z)$, a volume element $dx dy dz$ at this point contains a charge of $\rho(x, y, z) dx dy dz$ electrons. The structure factor, F , is the resultant of the scattering from the whole cell, due allowance being made for the phase differences caused by differing path lengths. Thus

$$F(h, k, l) = \iiint \rho(x, y, z) \exp[i\pi(hx + ky + lz)] dx dy dz \quad \text{---(i)}$$

This is an exact, but not very practical, expression. An obvious objection to calculating the structure factor in this way is that it requires an integration over the whole cell contents. As, to a first approximation, the electron density distribution in atoms is spherically symmetrical, the integration over each type of atom can be done once and for all. The result is the atomic scattering factor, and values have been tabulated for a wide variety of atoms and ions. The structure factor can now be computed much more quickly by adding vectors, one for each atom. Thus,

$$F(h, k, l) = \sum_{n=1}^N f_n \exp[2\pi i(hx_n + ky_n + lz_n)] \quad \text{---(ii)}$$

where f_n = scattering factor of the n th atom,

x_n, y_n, z_n = fractional coordinates of the n th atom, and

N = No. of atoms in the unit cell.

We often write this as $F_{hkl} = A_{hkl} + iB_{hkl}$

For all the space groups, except $P1$, the atoms occur in crystallographically equivalent sets whose positions are related by the space group symmetry. Thus if there is centre of symmetry in the space group and this is chosen as origin, every atom at x, y, z has a counterpart at $\bar{x}, \bar{y}, \bar{z}$, and the structure factor expression becomes real,

$$F(h, k, l) = 2 \sum_{n=1}^{N/2} f_n \cos [2\pi(hx_n + ky_n + lz_n)] \quad \text{--- (iii)}$$

$$\text{i.e. } A_{hkl} = F_{hkl},$$

$$B_{hkl} = 0.$$

The space group of BIT is $P2_1$ in the monoclinic system. The only symmetry element in this space group is a 2_1 screw axis. The origin of the unit cell is chosen arbitrarily at some point on the 2_1 screw. The equivalent points in the cell are then,

$$x, y, z; \quad \bar{x}, 1/2+y, \bar{z}$$

By substituting these in equation (ii) and simplifying gives:

$$A = 2 \cos 2\pi(hx+lz+k/4) \cos 2\pi(ky - k/4), \text{ and}$$

$$B = 2 \cos 2\pi(hx+lz+k/4) \sin 2\pi(ky-k/4).$$

These can be further simplified by considering different

types of reflections.

Thus when $k = 2n$,

$$A = 2 \cos 2\pi(hx + lz) \cos 2\pi ky$$

$$B = 2 \cos 2\pi(hx + lz) \sin 2\pi ky = 0 \text{ if } k=0;$$

and when $k=2n+1$,

$$A = -2 \sin 2\pi(hx+lz) \sin 2\pi ky$$

$$B = 2 \sin 2\pi(hx+lz) \cos 2\pi ky.$$

The systematic absences follow from this, thus $A = B = 0$ for reflections of the type $0k0$ when

$$k = 2n + 1.$$

It follows that

$$\begin{aligned} |F(h, k, l)| &= |F(\bar{h}, \bar{k}, \bar{l})| = |F(h, \bar{k}, l)| \neq |F(\bar{h}, k, l)| \\ |F(\bar{h}, k, l)| &= |F(h, k, \bar{l})|, \end{aligned}$$

These relations are shown in stereogram (3.1). The four reflections having identical intensity ($|F|^2$) are related by symmetry $2/m$. This is the Laue symmetry common to all monoclinic space groups. These four reflections, however, have a variety of phases. Thus,

$$\text{for } k = 2n, \alpha(h, k, l) = -\alpha(\bar{h}, \bar{k}, \bar{l}) = -\alpha(h, \bar{k}, l) \neq \alpha(\bar{h}, k, l)$$

$$\alpha(\bar{h}, k, l) = \alpha(h, k, \bar{l}),$$

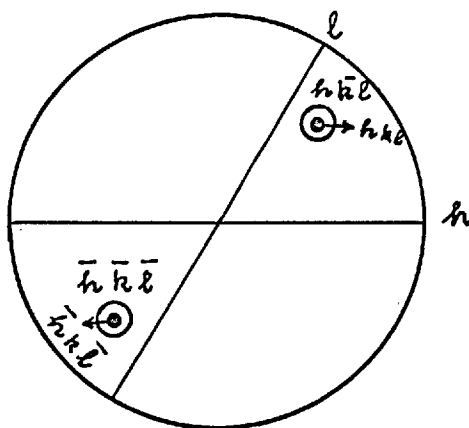
$$\text{and for } k = 2n + 1, \alpha(h, k, l) = -\alpha(\bar{h}, \bar{k}, \bar{l}) = \pi - \alpha(h, \bar{k}, l) \neq \alpha(\bar{h}, k, l)$$

$$\alpha(\bar{h}, k, l) = \pi + \alpha(h, k, \bar{l})$$

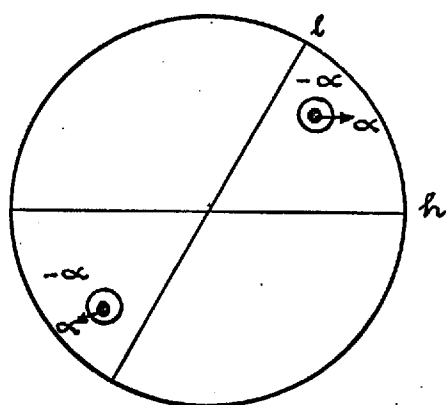
as shown in stereograms (3.2).

The chlorohydrin space group is $P3_1$. The origin of the space group is chosen at an arbitrary point on the 3_1 screw. The equivalent points in the cell are:

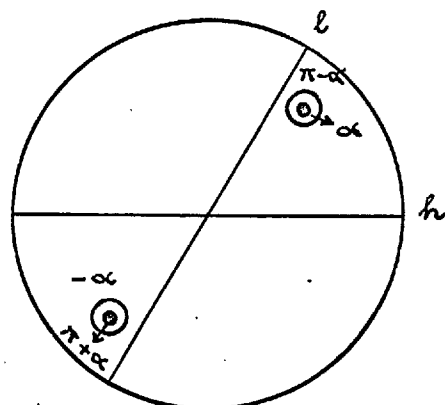
$$x, y, z; \quad \bar{y}, x-y, 1/3+z; \quad y-x, \bar{x}, 2/3+z.$$



STEREOGRAM 3.1



$$k = 2n$$



$$k = 2n + 1$$

STEREOGRAM 3.2

As there are three equivalent positions in the space group the atoms may be considered in groups of three and thus:

$$F(h, k, l) = \sum_{n=1}^{\sqrt{3}} f_n \sum_{j=1}^3 \exp \left[2\pi i (hx_{jn} + ky_{jn} + lz_{jn}) \right]$$

By substituting the 3 equivalent points and simplifying we have the real part of the structure factor

$$A = \cos 2\pi(hx+ky+lz) + \cos 2\pi(hx+iy+lz+1/3) \\ + \cos 2\pi(ix+hy+lz-1/3),$$

and the imaginary part

$$B = \sin 2\pi(hx+ky+lz) + \sin 2\pi(hx+iy+lz+1/3) \\ + \sin 2\pi(ix+hy+lz-1/3)$$

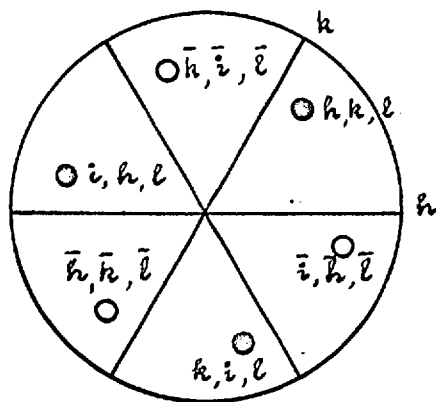
Thus $A = B = 0$ if $h = k = 0$ and $l = 3n \pm 1$,

i.e. the 001 reflections are systematically absent for $l \neq 3n$.

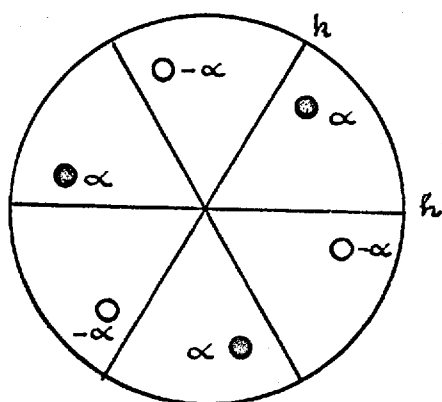
We can also deduce from these equations that the 6 reflections in stereogram (3.3) have the same $|F|$ i.e. their intensities conform to have symmetry $\bar{3}$. But their phase vary as shown in stereograms (3.4). The phase sequence on all ℓ layers can be expressed as:

$h \ k \ \ell$	$k \ i \ \ell$	$i \ h \ \ell$
α	$\alpha + 2\pi\ell/3$	$\alpha - 2\pi\ell/3$
$\bar{h} \ \bar{k} \ \bar{\ell}$	$\bar{h} \ i \ \bar{\ell}$	$\bar{i} \ \bar{h} \ \bar{\ell}$
$-\alpha$	$-(\alpha + 2\pi\ell/3)$	$-(\alpha - 2\pi\ell/3)$

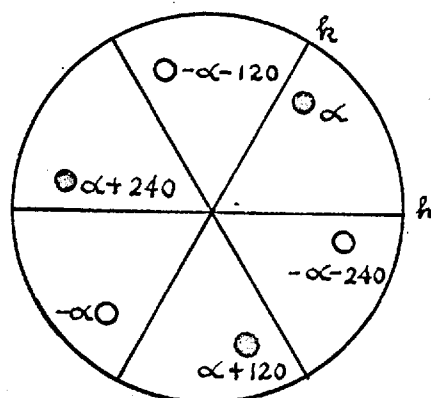
The structure factor expression derived above does not take account of the thermal motion of the atoms, which makes the atom occupy a larger volume and so lowers the electron density peak of the atom. This means that the scattering factor of the atom falls off more rapidly with $\sin \theta$. Thus if the motion is isotropic



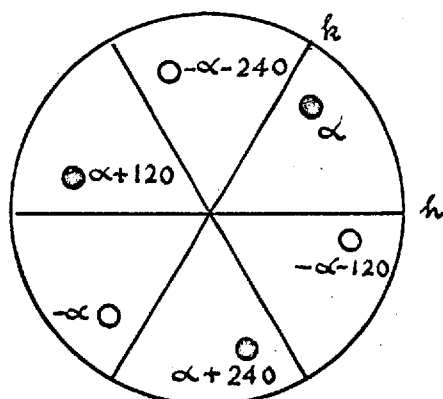
STEREOGRAM 3.3



$$l = 3n$$



$$l = 3n+1$$



$$l = 3n+2$$

STEREOGRAM 3.4

attenuation may be allowed for by a factor of the form

$$\exp (-B \sin^2 \theta / \lambda^2)$$

where B = temperature factor

θ = Bragg angle

and λ = wave length of the radiation used.

It may be shown that $B = 8\pi^2 \overline{u^2}$ where $\overline{u^2}$ is the mean square displacement of the atom from its mean position.

The calculation of anisotropic temperature factors is more complicated. The temperature factor is given by the expression:

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

where the B_{ij} 's are the coefficients of the tensor-ellipsoid with respect to the h , k and l axes. The above calculations are only practicable with a computer.

Fourier Synthesis

The structure factor $F(h, k, l)$ is the value at the point h, k, l in the reciprocal space of the Fourier transform of the electron density. Conversely ρ is the Fourier transform of the structure factors in the reciprocal space. This can be seen more clearly from the Fourier expression for the electron density.

$$\rho(x, y, z) = 1/v \sum_h \sum_k \sum_{l=-\infty}^{\infty} F(h, k, l) \exp \left[-2\pi i (hx + ky + lz) \right],$$

where v = volume of the unit cell.

A few of the early 2-D Fourier's were done by hand using Beavers-Lipson strips, but the rest of the 2-D and 3-D Fourier's were done

on the Mercury computer using a program written by Dr. O.S. Mills. This requires the input of only the unique set of reflection data, followed by the symmetry relations. The electron density can be calculated at intervals of $n/240$ of each cell edge and is output as integers in an adjustable layout approximating to the required Fourier map.

A program on these lines was not available for the trigonal problem, so this had to be treated as triclinic i.e. half the terms in reciprocal space had to be supplied; This meant duplicating some of the reflection data, taking due care of the phase changes. This is easy for the Patterson function, and a program for doing this was written by Dr. R. Diamand. If h, k, l, F^2 is input for each reflection, the program generates the extra terms needed.

No comparable program was available for changing the phases of the structure factors, so the "extra" F -data were calculated as independent reflections by the structure-factor program. Checks were made to ensure the $|F|$'s and phases were correctly linked.

Patterson Synthesis

The Patterson synthesis can be derived from the Fourier expression for the electron density integrating the product of the electron densities at two points at the ends of a constant vector which ranges all over the unit cell. Contributions to this integral occur only when the vector joins two atoms. The

expression simplifies to

$$P(u,v,w) = 1/v \sum_h \sum_k \sum_{l=-\infty}^{\infty} |F(h,k,l)|^2 \cos 2\pi(hu+kv+lw),$$

because $|F(h,k,l)| = |F(\bar{h},\bar{k},\bar{l})|$ by Friedel's law.

In this expression there is no unknown phase associated with $|F(h,k,l)|^2$. In B I T the symmetry of the Patterson function is $2/m$ and the Patterson expression reduces to

$$P(u,v,w) = 4/v \sum_h \sum_k \sum_{l=0}^{\infty} \left[|F(h,k,l)|^2 \cos 2\pi(hu+lw) + |F(\bar{h},k,l)|^2 \cos 2\pi(hu-lw) \right] \cos 2\pi kv.$$

In the case of CC the symmetry of the Patterson function is $\bar{3}$, but has to be evaluated as $\bar{1}$. For this the expression reduces to

$$P(u,v,w) = 2/v \sum_h \sum_k \sum_{l=0}^{\infty} \left\{ |F(h,k,l)|^2 \cos 2\pi(hu+kv+lw) + |F(\bar{h},k,l)|^2 \cos 2\pi(-hu + kv + lw) + |F(h,\bar{k},l)|^2 \cos 2\pi(hu - kv+lw) + |F(h,k,\bar{l})|^2 \cos 2\pi(hu + kv - lw) \right\}$$

These also were calculated using Dr. O.S. Mill's Fourier-summation program.

Least - Squares Calculations

The S F L S program used was written for Mercury by Dr. J.S. Rollett. It calculates the structure factors and compares these with the observed values. The function minimized is:

$$R = \sum w(k) |F_o| - |F_c|)^2 / \sum w |F_o|^2$$

The parameters which can be refined are:

- (i) the F_o scale factor, k ,
- (ii) atomic coordinates, (x_i, y_i, z_i) ,
- (iii) the average vibration parameters of the whole structure, $\bar{B}$,

- (iv) the individual atomic isotropic vibration parameters, B_n ,
- (v) the six components, B_{ij} , of the individual atomic anisotropic vibrations.

F_o is a nonlinear function of the coordinates and B's, so we must start from a good model and proceed by successive approximations. Experience has shown that in a "good model" the atoms should lie within about one atom diameter of their true position if the structure is to be refined successfully. The program requires a list of (h,k,l) and $|F_o|$ for the independent X-ray reflections and a set of parameters for the atomic positions and vibrations of the non-equivalent atoms. The program uses a block-diagonal approximation to the normal equations, i.e. a 3 x 3 matrix for each atomic position, a 6 x 6 matrix for each atomic vibration, and a 2 x 2 matrix for the overall scaling and temperature factors. At the end of a cycle the normal equations are solved for the shifts in the parameters, and these shifts are applied, wholly or in part in readiness for the next cycle.

Ideally each reflection should be given a weight inversely proportional to its standard deviation. Usually no good estimate of this can be made and the weights usually used are simple functions of the F_o or O .

In this program three alternative weighting schemes are available

$$\sqrt{W} =$$

$$1) \quad |F_o|/F^* \quad \text{if} \quad |F_o| < F^*$$

$$\begin{aligned}
 & \bar{F}/|F_0| \text{ if } |F_0| \geq \bar{F}^*, \\
 2) \quad & 1 \text{ if } |F_0| < \bar{F}^* \\
 & \bar{F}/|F_0| \text{ if } |F_0| \geq \bar{F}^*, \\
 3) \quad & \sqrt{\frac{2}{1 + \left\{ (|F_0| - b)/\bar{a}^2 \right\}}}
 \end{aligned}$$

where a , b and $\bar{F}$ are pre-set parameters. For both structures, weighting scheme 2 was used.

C H A P T E R 4.

The solution of the crystal structure of Bromoisotenulin (B I T)

1. Introduction

The parent compound tenulin, $C_{17}H_{22}O_5$, was isolated by Clark⁽³³⁾ from several Helenium species. Its properties were studied by him⁽³⁴⁾ and later on by Ungnade et al.^(35, 36) Clark's work revealed that tenulin is isomerised by mild alkali to isotenulin. Both compounds can be smoothly hydrogenated to dihydro-derivatives, and both give dibromides which easily evolve one molecule of hydrogen bromide.

Pyrolysis of tenulin first gives anhydrotenulin, $C_{17}H_{20}O_4$, and then pyrotenulin, $C_{15}H_{16}O_3$. Treatment of isotenulin with sulphuric acid gives desacetyl-isotenulin and one molecule of acetic acid. Oxidation of tenulin or isotenulin with alkaline hydrogen peroxide gives tenulinic acid, $C_{15}H_{20}O_7$. On acetylation this acid gives acetyltenulinic acid, $C_{17}H_{22}O_8$, which can also be obtained by direct oxidation of tenulin and isotenulin with potassium permanganate. On the basis of these

experiments Clark represented the functional groups of tenulin as (4.1).

Ungnade and his collaborators reported that the ultraviolet absorption spectra of tenulin and isotenulin showed them to be α,β - unsaturated ketones. They showed that isotenulin consumed two molecules of alkali, one for hydrolysis of an acetate residue and the other for opening a lactone ring.

Although much work was done on these compounds, little progress was at first made toward elucidating their structures. Barton and de Mayo⁽³⁷⁾ and later Braun et al⁽³⁸⁾ studied them extensively.

Barton and de Mayo established from chemical work, that these substances are α,β - unsaturated cyclopentenones, and γ - methyl - δ - lactones. Since tenulin has the formula, $C_{17}H_{22}O_5$, these facts would appear to account for three of the oxygen atoms. Isotenulin contains a true acetyl group, which accounts for its other two oxygens. The infra-red and ultraviolet spectra of tenulin, however, disclosed the presence of a hydroxyl function, and it was also observed that this molecule

does not afford acetic acid on acid hydrolysis as does a true acetate. Tenulin (4.2) was, therefore, considered to contain a masked acetyl group and was formulated as (4.3). This is then converted to a true acetyl in isotenulin, (4.4).

The work of Braun et al duplicated the work of Barton and de Mayo; but they proposed structures (4.5) for tenulin and (4.6) for isotenulin, both differing in one detail from those proposed by Barton and de Mayo.

The difference between the two structures lay in the position of the carbonyl group in the unsaturated five -
(39)
membered ring. Barton and de Mayo based their argument in favour of (4.7) on the isolation of a new compound desacetylneotenulin, which is formed when tenulin is treated with aqueous sodium bicarbonate. This contains $-C(=O)-C(Me)=C<$, since on ozonolysis it affords acetic acid; it also furnishes neotenulin on acetylation. This led Barton and de Mayo to propose (4.3), (4.4), and (4.9), for tenulin, isotenulin and desacetylneotenulin respectively.

Braun et al were in favour of (4.8), as they had observed

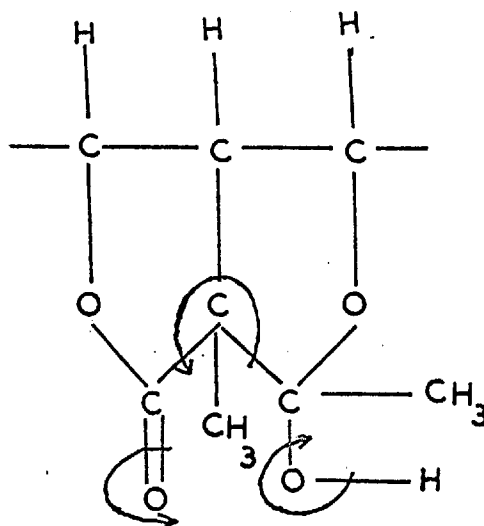
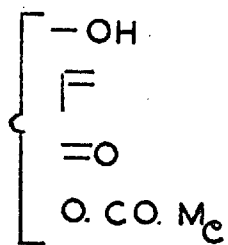
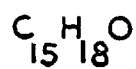


FIG. 4.1

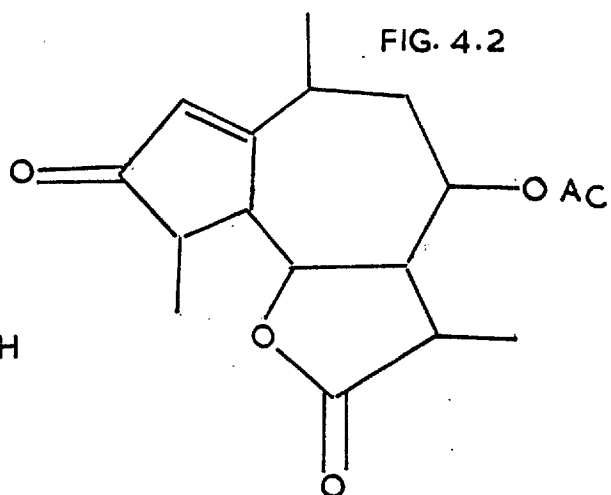
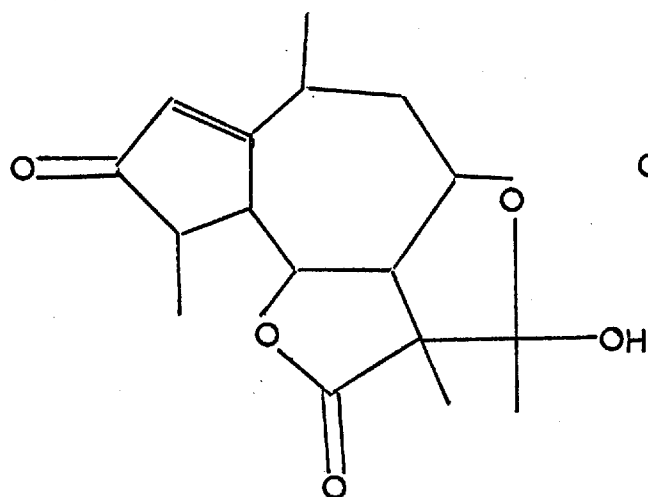


FIG. 4.2

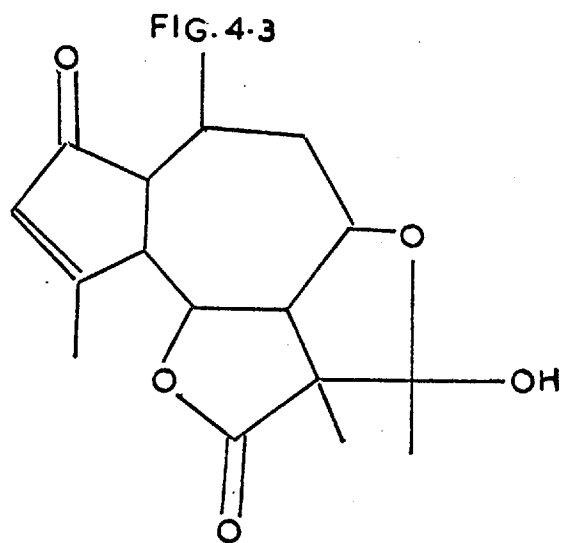


FIG. 4.3

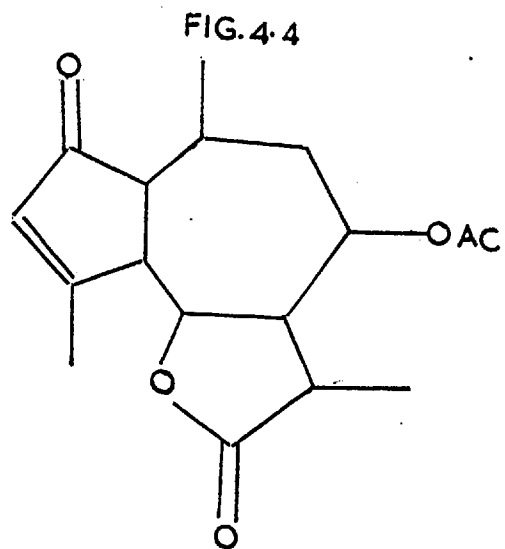


FIG. 4.4

F .4.5

FIG. 4.6

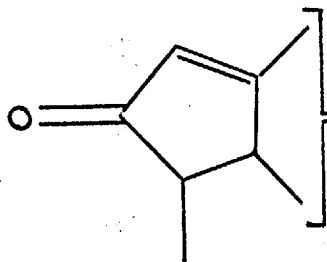


FIG. 4.7

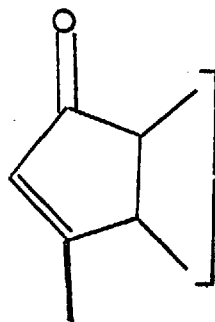


FIG. 4.8

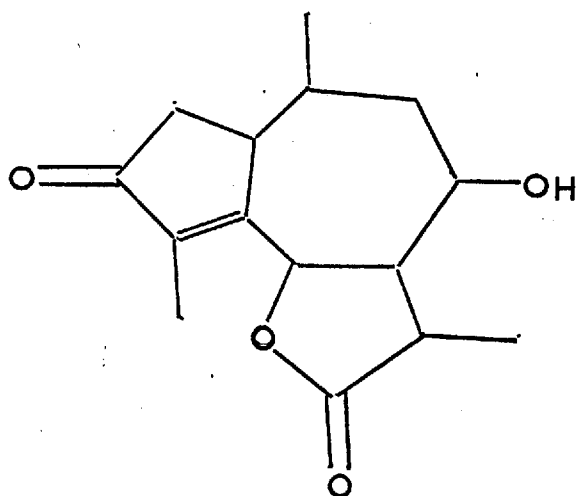


FIG. 4.9

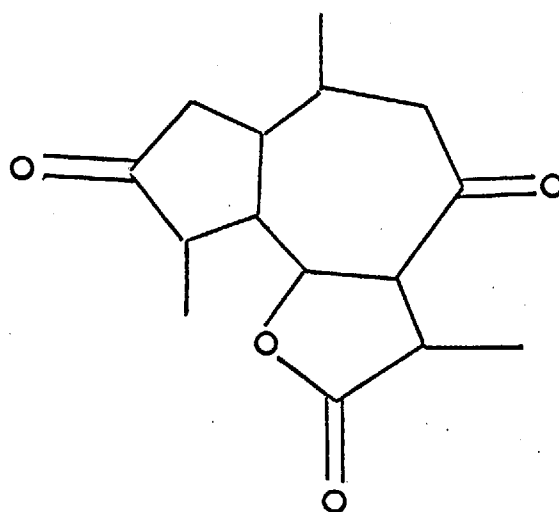


FIG. 4.10

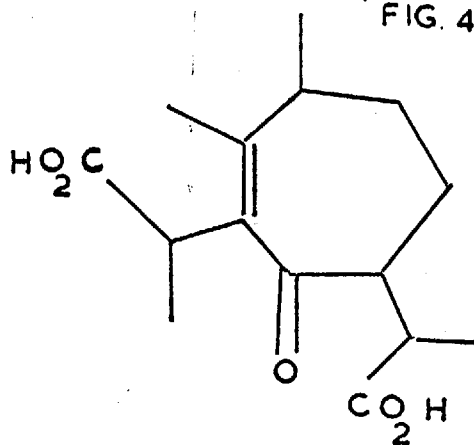


FIG. 4.11

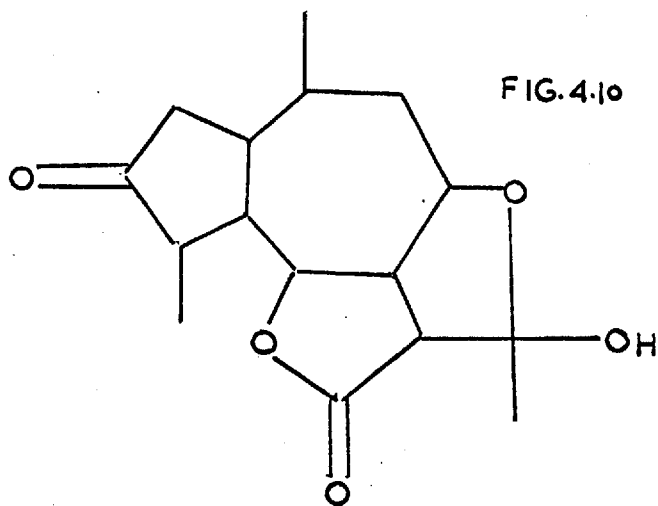


FIG. 4.12

that dehydridesacetyldihydroisotenulin (4.10) is cleaved by alkali to a dicarboxylic acid (4.11) containing an $\alpha\beta$ -unsaturated ketone grouping. The rest of their work tends to support the position of the lactone rings in (4.3) and (4.4) or (4.5) and (4.6).

The point of difference was cleared to some extent in favour of (4.3) by two independent lines of evidence described (40) by Djerassi et al.

- (i) In the nuclear magnetic resonance spectra of tenulin (4.3) and dihydrotenulin (4.12) or isotenulin (4.4) and dihydroisotenulin (4.13) the peak corresponding to the hydrogen atoms in the "cyclopentenone" methyl group remained constant. This is consistent with partial structure (4.7), since hydrogenation of the double bond in the alternative (4.8) would lead to (4.14), which would exhibit three more H-H peaks in the N.M.R. spectrum.
- (ii) The rotatory dispersion curves of tenulin and isotenulin also support a cyclopentenone chromophore of type (4.7).

In view of this confusion, and the lack of any stereochemistry, there was ample justification for a new approach to the problem.

The only heavy-atom derivative available at that time was bromoisotenulin, first described by Clark.⁽⁴¹⁾ Despite the presence of two unrelated molecules in its asymmetric unit, this was accepted for the X-ray study.

After the work was started, however, some N.M.R. studies⁽⁴²⁾ were published by Herz et al which threw doubts on the correctness of formulae (4.3) and (4.4). They showed that parthenin (4.15) and ambrosin (4.16) were not guianolides. This raised doubts for the first time about the carbon skeletons of tenulin and other sesquiterpene lactones of the Helenium species.

The N.M.R. spectra of helenalin, tenulin, baldulin and some other sesquiterpene lactones isolated from the Helenium species indicated the presence of four "vinyl" protons and a tertiary methyl group. This led to the conclusion that the carbon skeleton of these substances would be similar to that

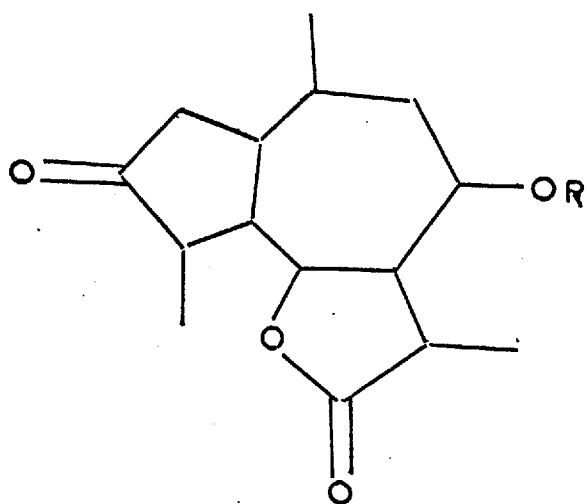


FIG. 4.13

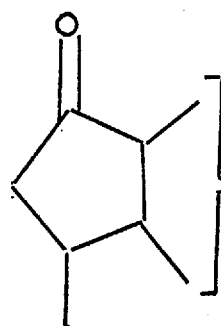


FIG. 4.14

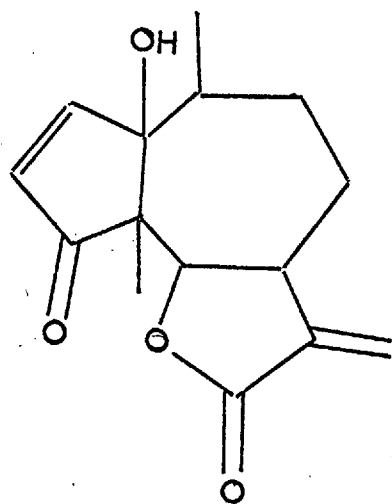


FIG. 4.15

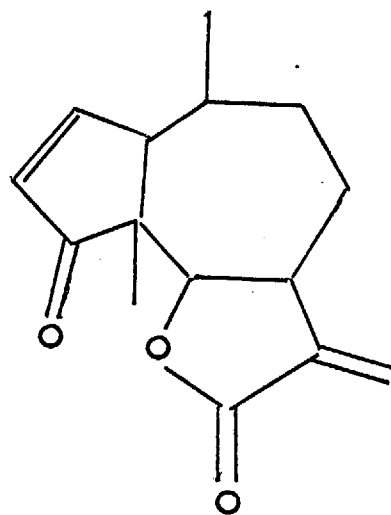
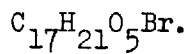


FIG. 4.16

of parthenin and ambrosin. This was the position when, in September, 1962, we deduced the structure of B I T.

(43)

Meanwhile, further work by Herz et al led them to propose exactly the same structure in a paper which appeared in the 20th October issue of the J.A.C.S. Although they could say nothing as to the stereochemistry of the molecule, their constitutional formula agreed precisely with that derived in this x-ray study.

Bromoisotenulin

$$\text{M. wt.} = 385$$

$$\mu = 36.4 \text{ cm.}^{-1}$$

$$\text{M. Pt.} = 213^{\circ}\text{C.}$$

$$F(0\ 0\ 0) = 792$$

Monoclinic:

Laue symmetry 2/m.

$$\left. \begin{array}{l} a = 8.75 \\ b = 23.15 \\ c = 10.28 \end{array} \right\} \begin{array}{c} \text{\AA} \\ \text{\AA} \end{array}$$

$$\beta = 121^{\circ}$$

$$Z = 4 \text{ molecules/cell.}$$

$$d_{\text{obs.}} = 1.457 \text{ gm. cm.}^{-3}$$

$$d_{\text{calc.}} = 1.451 \text{ gm. cm.}^{-3}$$

Absences: $0\ k\ 0$ when $k=2n+1$ Space group $P2_1$

2. Crystallographic data for B I T ($C_{17}H_{21}O_5Br$)

A summary of the crystallographic data obtained in Chapter 2, and other relevant details are set out on page (44).

Weissenberg photographs from the zero to the 7th layer were taken by oscillating about the a axis.

Intensities were measured visually. No absorption correction was applied for reasons explained in Chapter 2. The Lorentz and polarization corrections were applied using ZK43 on the Zebra computer. All the h layers were correlated with the (h k 0) reflections by comparing the common reflections in the usual way. The scaling and temperature factors were determined by Wilson's method.

3. Solution of the structure.

While the 3-D data was being collected, an attempt was made to solve the structure from the $[100]$ projection. The 2-D Patterson was calculated, which showed clear Br - Br peaks Fig. (4.17a). From this, the bromine coordinates were calculated and are shown in Fig. (4.17b). The bromine positions found are given below,

2-D Patterson
(Location of Br-Br peaks only)

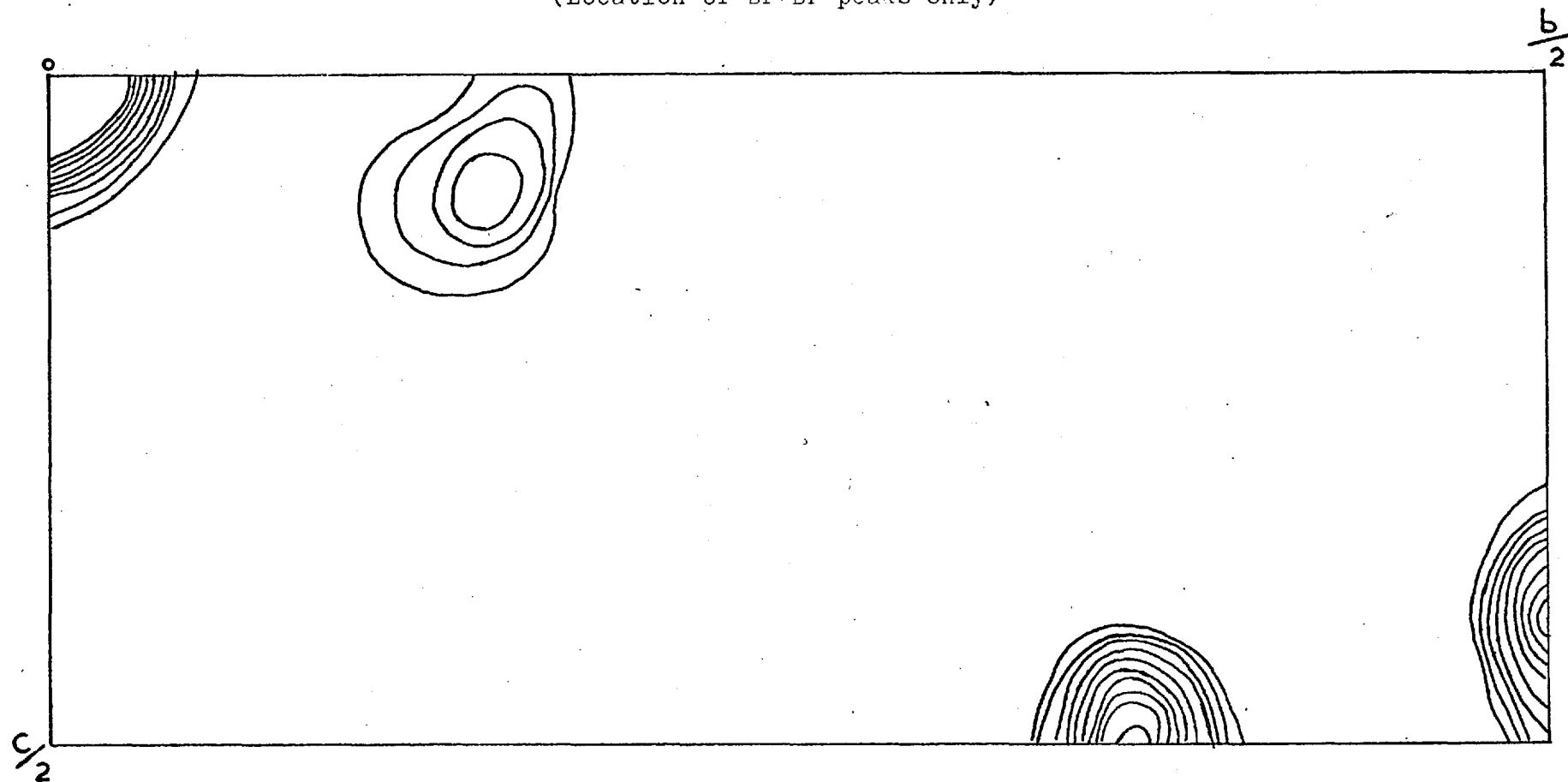


Fig. (4.17a)

Bromine positions deduced from the 2-D Patterson

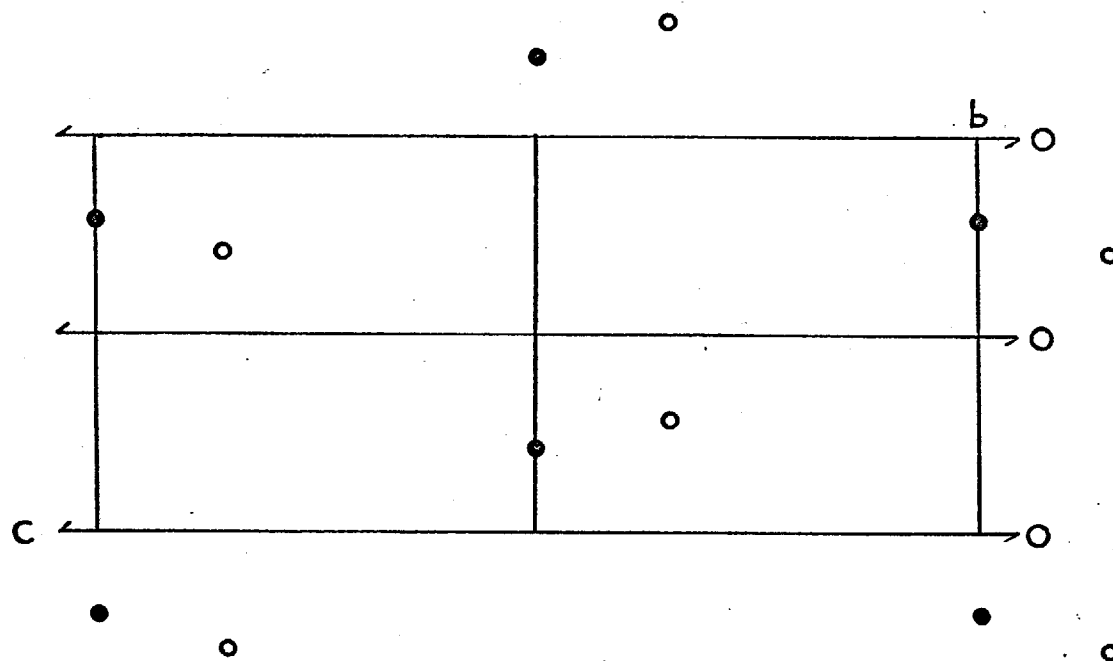


Fig. (4.17b)

	y	z
Br ₁	0.000	0.205
Br ₂	0.144	0.295

from which it was noted that $Z_1 + Z_2 \approx 0.5$, a very odd relationship, i.e. they are unrelated in b but seem to pair off approximately $c/2$ apart in the c direction.

Partial structure factors for bromine were calculated using program ZK20 on Zebra. A 2-D Fourier was computed using ZK1. Because of extensive overlap of atoms it was impossible to derive any more atomic positions from this Fourier map.

A 3-D Patterson was computed using Mills' Fourier program for Mercury. The Br - Br peaks are shown in Fig. (4.18a). Sections through these peaks gave the bromine positions as

	x	y	z
Br ₁	-0.358	0.000	0.208
Br ₂	0.025	0.146	0.295

i.e. the origin is chosen on the 2₁ screw on the level of Br₁. The positions of these two sets of bromines are shown in Fig. (4.18b).

3-D Patterson
(Location of Br-Br peaks only)
x coordinates shown for each peak.

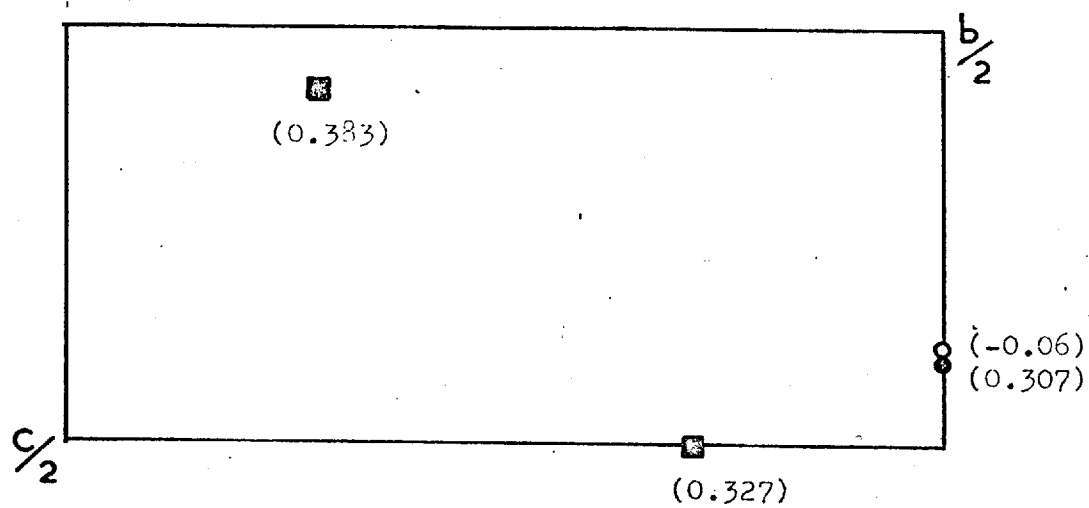


Fig. (4.18a)

Bromine positions deduced from the 3-D Patterson

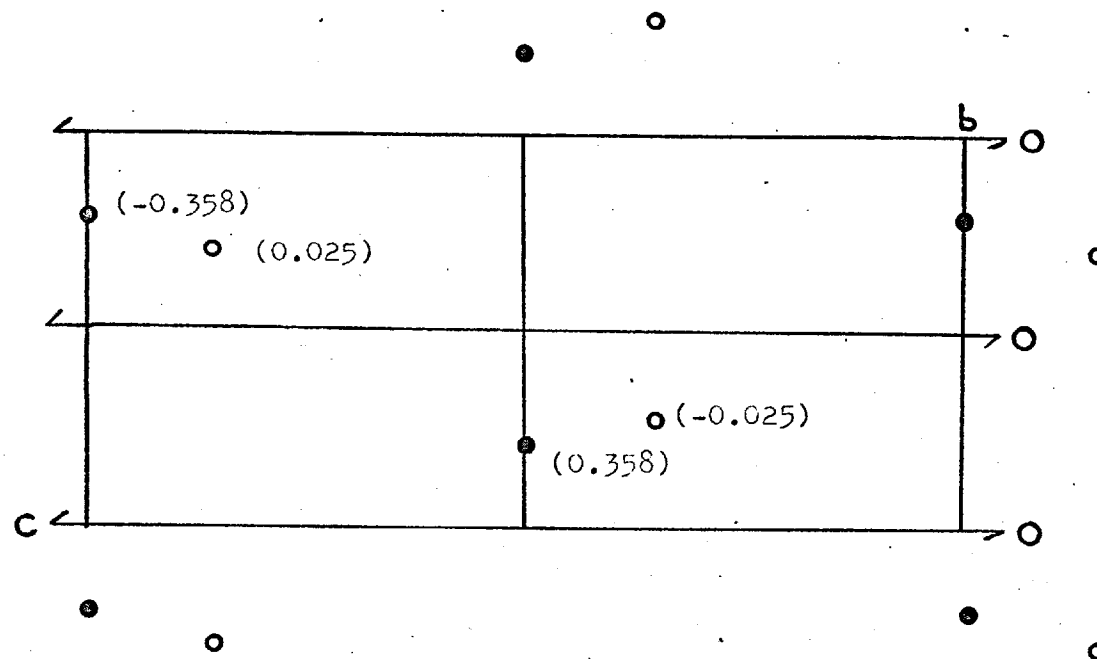


Fig. (4.18b)

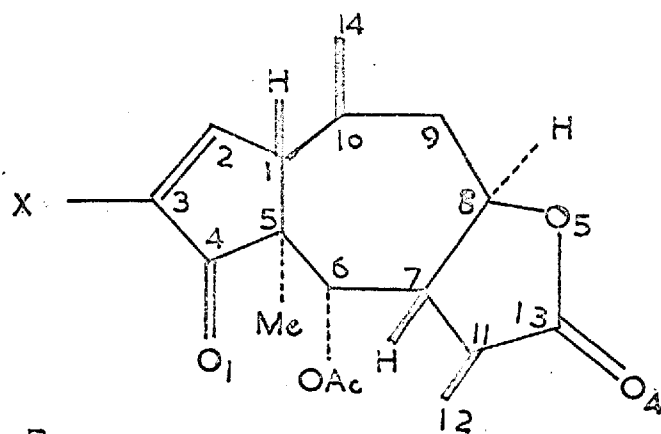
The bromine contribution to the structure factors was calculated for about 2300 h k l reflections using Rollett's program for Mercury. An arbitrary criterion of $|F_{Bs}| \geq 0.4 |F_0|$ was used for selection of the terms for the first Fourier. This criterion rejected approximately 80 terms, an unusually low proportion even for bromine. This is a consequence of having 2 independent sets of bromines. The Fourier transform of the 2 sets has considerably fewer regions of low amplitude than for each set alone.

Thus the first Br - phased Fourier used well over 2000 terms. The result was much more encouraging than had been expected. It showed about 50 peaks per asymmetric unit apart from the bromines.

For the interpretation of this Fourier, reductions of each section were drawn on perspex sheets with a chinagraph pencil and the sheets were stacked one above the other. This revealed all the main features of the structure. A wire-and-bead model was constructed on a cork mat. Each molecule was built up by starting at the Br atom, and locating the remaining atoms, one at a time, using a "Dreiding" carbon tetrahedron to check on the chemical plausibility of each Fourier peak. The two independent molecules

lay in quite different orientations in the cell, but both were in good agreement with each other. Most atoms were equally well defined in both, but a few were only well defined in one or other of the two molecules. It was a great help having the two molecules for comparison. In fact it was only the acetate group and C₁₂ that were rather poorly defined for both molecules. Their peaks, though rather diffuse, never-the-less made reasonable chemical sense and so these atoms were accepted for the structure-factor calculations.

There were a few extra "peaks" left. None was higher than any of those attributed to the atoms of the structure, and all were either too far from a molecule, or lay in a chemically improbable position. They were, therefore, ruled out. In this way all the C and O atoms of both the unrelated molecules were recognised. All the positions made good chemical sense, and both molecules were in good agreement. The stereochemistry is shown in Fig. (4.19). It was easy to build a Dreiding model and flex it to agree with the bead- and-spoke model. Its plausibility was further checked by calculating the inter-atomic distances and angles for both molecules using Dr. Sparks' program.



419 : X = Br

420 : X = H

FIG. 4.19, 20

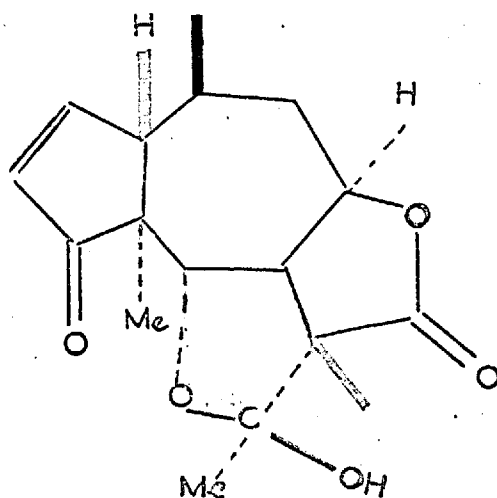


FIG. 4.21

This gave reasonable bond lengths and angles..

A first set of structure factors was calculated for all the atoms of both molecules. A second 3 - D Fourier and difference Fourier were computed using all the phases obtained from the above calculations. This revealed the structure very clearly and the difference Fourier showed no peak ≥ 3 electrons / Å³.

The R value at this stage was 0.35 which was considered promising. The coordinates of all the atoms of the two unrelated molecules were determined by Sparks' "19 - point program", which used the electron - density at a set of 19 points around each peak in the Fourier. The inter-atomic distances and angles were computed and showed general improvement. At this stage it was decided to refine the structure by the least-squares method.

C H A P T E R 5

Refinement of the crystal structure of Bromoisotenulin (BIT)

The last Fourier revealed a marked anisotropy on bromine as well as the light atoms. The first cycle of refinement was treated anisotropically and gave $R = 0.349$, and $\sum w \Delta^2 \times 10^{-5} = 12471$. The second cycle was treated isotropically and brought R down to 0.322, and $\sum w \Delta^2 \times 10^{-5}$ to 11524. (For converting the vibrations from anisotropic temperature factors, B_{ij} , to the equivalent B , Spark's program was used. This gives the three axes a , b and c of the vibrational ellipsoid and their direction cosines. The radius of the equivalent sphere, $r = (abc)^{\frac{1}{3}}$, but unless the anisotropy is severe, a convenient and acceptable alternative is the mean of a , b and c . The result is the r.m.s. value of the equivalent isotropic displacement, i.e. $(\overline{u^2})^{\frac{1}{2}}$, and this is readily converted to the equivalent $B = 8 \pi^2 \overline{u^2}$). In the third cycle the bromines were refined anisotropically and the rest of the atoms, . isotropically. This gave R of 0.219 and $\sum w \Delta^2 \times 10^{-5}$ of 5073. After this four cycles of anisotropic least squares were done, with R and $(\sum w \Delta^2 \times 10^{-5})$ changing from 0.197 (3918), 0.169 (2935), 0.158 (2445) and 0.155 (2351). At this stage all the cyclic carbon had settled down well and for these the shifts per cycle were $\leq 0.01\text{\AA}$, and the bond lengths and angles were satisfactory. But C_{12} and the atoms of the acetate group in both molecules were still shifting

considerably and one acetate group seemed rather distorted. Their temperature factors were rather higher than for the rest of the molecule, and the interatomic distances and angles were not so satisfactory. A difference Fourier was computed, which revealed only a misplacement of $0.12\text{\AA}$ in the position of C_{17} in the first molecule. As a check it was decided to calculate the structure factors for a new Fourier excluding C_{12} and the acetate groups of both the molecules. From this the position of these atoms were found. Least-squares calculations were resumed excluding the rest of the molecules from the refinements. Two cycles of isotropic least-squares gave an R of 0.274 and 0.175, and $\sum w \Delta^2 \times 10^{-5}$ of 7643 and 2721. After this two cycles of anisotropic refinement on the same short list of atoms were done, with R and $(\sum w \Delta^2 \times 10^{-5})$ changing to 0.154 (2474) and 0.152 (2351). The refinement then had to be stopped, and at this stage the shifts can be summarised as follows:

	$ \Delta x $	$ \Delta y $	$ \Delta z $
Mean $ \Delta x $, etc.	0.00143	0.00034	0.00117
Max. $ \Delta x $, etc.	0.03014(C_{17})	0.00261(C_{17})	0.00537(C_{17})
Maximum Shift (C_{17})	$= 0.0767\text{\AA}$		

The final positions are given in Table 5.1 and the B_{ij} coefficients in Table 5.2.

The final positions were used for the calculation of molecular geometry using Spark's program. The interatomic distances and their standard deviations are given in Table 5.3, and the angles and their

standard deviations in Table 5.4.

The final positions were used for the calculation of structure factors for the final Fourier. The observed and calculated structure factors are given in Appendix 1.A, and calculated structure factors for the unobserved reflections are given in Appendix 1.B.

An agreement analysis was done on the above structure factors using Dr. G.C.Mair's program. Part of the output of this program is given in Table 5.5, which shows the variations in R with ranges of intensity, $\sin^2 \theta$ and each of the layers. The final R value is 0.152 and $\sum w \Delta^2 \times 10^{-5} = 2241$.

The final Fourier was computed using the last set of structure factors. Sections (0-12/24) were calculated up the a axis and are given in Fig 5.1. No fresh difference Fourier was thought necessary.

T A B L E 5.1

Final Coordinates

Atom	<u>Molecule 1</u>			<u>Molecule 2</u>		
	x	y	z	x	y	z
Br	-0.0318	0.6450	0.7032	0.3492	0.4999	0.7889
C ₁	0.1259	0.8198	0.7258	0.4399	0.6303	0.5494
C ₂	0.0975	0.7639	0.7877	0.4339	0.6059	0.6816
C ₃	0.0144	0.7222	0.6790	0.3594	0.5499	0.6532
C ₄	-0.0474	0.7451	0.5307	0.3014	0.5361	0.4964
C ₅	-0.0222	0.8121	0.5486	0.3033	0.5912	0.4139
C ₆	0.0725	0.8325	0.4549	0.3555	0.5784	0.3006
C ₇	0.1643	0.8885	0.5080	0.4522	0.6297	0.2648
C ₈	0.00994	0.9347	0.5725	0.3484	0.6908	0.2499
C ₉	0.1893	0.9282	0.7561	0.4376	0.7218	0.4077
C ₁₀	0.1016	0.8750	0.7893	0.3985	0.6959	0.5798
C ₁₁	0.1985	0.9211	0.4055	0.45802	0.6259	0.1309
C ₁₂	0.3612	0.9018	0.3816	0.6229	0.5903	0.1477
C ₁₃	0.2123	0.9839	0.4579	0.4608	0.6898	0.0893
C ₁₄	0.1757	0.8724	0.9607	0.4956	0.7312	0.6676
C ₁₅	-0.2001	0.8348	0.4936	0.1018	0.6099	0.3499
C ₁₆	-0.0853	0.8195	0.1764	0.2007	0.5068	0.0849
C ₁₇	-0.2141	0.8279	0.0231	0.0445	0.4926	-0.0545
O ₁	-0.0989	0.7194	0.4184	0.2459	0.4869	0.4365
O ₂	-0.0952	0.8441	0.2944	0.2054	0.5636	0.1612

Atom	Molecule 1			Molecule 2		
	x	y	z	x	y	z
O ₃	0.0336	0.78961	0.1844	0.3416	0.4798	0.1446
O ₄	0.2775	1.0247	0.4153	0.4989	0.7063	-0.0033
O ₅	0.1831	0.9877	0.5539	0.3988	0.7221	0.1569

T A B L E 5.2

Molecule 1

Atom	B ₁₁	B ₂₂	B ₃₃	B ₂₃	B ₃₁	B ₁₂
Br	0.00027	0.00711	0.00234	0.04589	0.04922	0.02998
C ₁	-0.00983	0.00143	0.00258	0.02972	0.05968	0.07076
C ₂	0.00437	0.00499	0.00241	0.02786	0.06489	0.03223
C ₃	-0.00491	0.00172	0.00324	0.02859	0.02407	0.01580
C ₄	0.00039	-0.00361	0.00124	0.02076	0.03827	0.01268
C ₅	0.00406	0.00172	0.00121	0.01680	0.05468	0.02096
C ₆	-0.00220	0.00179	0.00216	0.01303	0.01197	0.00306
C ₇	0.00324	0.00152	0.00217	0.02020	0.02761	0.02937
C ₈	-0.00356	-0.00063	0.00184	0.03023	0.00476	0.01079
C ₉	-0.00006	0.00027	0.00285	0.02226	0.02726	0.01151
C ₁₀	-0.00087	0.00220	0.00285	0.01897	0.06534	0.04219
C ₁₁	-0.00021	0.00163	0.00213	0.01627	0.00995	-0.00310
C ₁₂	-0.00504	-0.00008	0.00289	0.05184	0.11652	0.12093
C ₁₃	-0.00161	0.00252	0.00292	0.01598	0.02676	0.01429
C ₁₄	0.00010	-0.00191	0.00390	0.01978	0.04489	0.02742
C ₁₅	0.00085	-0.00229	0.00168	0.03774	0.03219	0.04424
C ₁₆	-0.01190	-0.00104	0.00295	0.04372	0.06157	-0.02224
C ₁₇	-0.04694	-0.00103	0.00640	0.02275	0.21196	0.01371
O ₁	-0.00070	0.00015	0.00145	0.01932	0.01994	0.00799
O ₂	-0.00472	-0.00456	0.00260	0.02785	0.02986	0.02489
O ₃	0.00023	-0.00578	0.00530	0.03252	0.05691	0.04017
O ₄	-0.01115	0.00492	0.00267	0.03034	0.05612	0.01179
O ₅	-0.00345	0.00057	0.00182	0.02452	0.05464	0.04398

T A B L E 5.2Molecule 2

Atom	B ₁₁	B ₂₂	B ₃₃	B ₂₃	B ₃₁	B ₁₂
Br	-0.00983	0.00143	0.00376	0.02401	0.08313	0.04555
C ₁	-0.00070	0.00015	0.00145	0.01932	0.01994	0.00799
C ₂	-0.00169	-0.00013	0.00249	0.02406	0.01074	0.01862
C ₃	-0.00736	-0.00146	0.00393	0.01895	0.01639	0.02192
C ₄	-0.00674	0.00153	0.00220	0.04696	0.01803	0.04424
C ₅	-0.00434	-0.00304	0.00219	0.02290	0.01579	0.01322
C ₆	0.00116	0.00106	0.00208	0.02133	0.02897	0.03274
C ₇	0.00442	0.00296	0.00272	0.01708	0.01896	0.02483
C ₈	0.00482	0.00063	0.00225	0.01745	0.02457	0.01446
C ₉	0.00015	-0.00080	0.00170	0.02298	0.01988	0.2658
C ₁₀	0.00253	0.00378	0.00186	0.01712	0.02513	0.00000
C ₁₁	-0.00682	-0.00060	0.00358	0.00879	0.03585	0.01961
C ₁₂	0.00228	-0.00128	0.00409	0.02317	0.03409	0.00892
C ₁₃	0.00579	-0.00249	0.00355	0.01235	0.01787	-0.00093
C ₁₄	0.00228	-0.00191	0.00151	0.02934	0.04212	0.00680
C ₁₅	0.00033	0.00429	0.00257	0.04971	0.01544	0.01698
C ₁₆	-0.02492	-0.00475	0.00581	0.04284	0.11616	0.10429
C ₁₇	-0.02501	-0.00114	0.00892	0.02864	0.05518	-0.00005
O ₁	-0.00679	-0.00157	0.00248	0.01801	0.06039	0.03366
O ₂	-0.01626	-0.00537	0.00424	0.00934	0.06673	0.02830
O ₃	-0.00168	-0.00693	0.00460	0.04783	0.05907	0.06503
O ₄	-0.00507	0.00079	0.00475	0.01687	0.05654	0.04594
O ₅	0.00226	0.00492	0.00254	0.02006	0.03948	0.01781

T A B L E 5.3

Bond	Molecule 1		Molecule 2	
	Bond length (Å)	ϵ (Å)	Bond length (Å)	ϵ (Å)
Br ₁ -C ₃	1.878	0.032	1.849	0.030
C ₁ -C ₂	1.515	0.046	1.497	0.041
C ₁ -C ₅	1.612	0.074	1.572	0.052
C ₁ -C ₁₀	1.500	0.045	1.555	0.033
C ₂ =C ₃	1.369	0.066	1.413	0.042
C ₃ -C ₄	1.432	0.058	1.454	0.060
C ₄ -C ₅	1.563	0.034	1.538	0.042
C ₄ =O ₁	1.164	0.049	1.266	0.040
C ₅ -C ₆	1.631	0.035	1.485	0.037
C ₅ -C ₁₅	1.453	0.061	1.592	0.056
C ₆ -C ₇	1.473	0.039	1.606	0.035
C ₆ -O ₂	1.566	0.051	1.399	0.056
C ₇ -C ₈	1.514	0.034	1.646	0.038
C ₇ -C ₁₁	1.448	0.036	1.406	0.040
C ₈ -C ₉	1.635	0.059	1.565	0.051
C ₈ -O ₅	1.49	0.030	1.437	0.033
C ₉ -C ₁₀	1.579	0.047	1.487	0.037
C ₁₀ -C ₁₄	1.534	0.064	1.538	0.059
C ₁₁ -C ₁₂	1.627	0.069	1.593	0.053
C ₁₁ -C ₁₃	1.535	0.037	1.543	0.041
C ₁₃ =O ₄	1.290	0.035	1.220	0.034
C ₁₃ -O ₅	1.144	0.026	1.313	0.033
C ₁₆ -C ₁₇	1.401	0.114	1.418	0.115
C ₁₆ -O ₂	1.382	0.052	1.522	0.058
C ₁₆ =O ₃	1.217	0.062	1.228	0.089

T A B L E 5.4

Molecule 1			Molecule 2		
	Angle ^o	σ^o		Angle ^o	σ^o
C ₂ -C ₁ -C ₅	99.8	3.6		102.8	2.2
C ₂ -C ₁ -C ₁₀	116.9	2.9		115.6	2.1
C ₅ -C ₁ -C ₁₀	112.0	3.9		113.2	3.1
C ₁ -C ₂ -C ₃	113.1	4.1		112.8	2.9
Br ₁ -C ₃ -C ₂	128.7	3.4		127.9	2.9
Br ₁ -C ₃ -C ₄	120.3	3.0		125.0	2.3
C ₂ -C ₃ -C ₄	111.0	3.0		106.9	2.6
C ₃ -C ₄ -C ₅	106.8	3.1		109.4	2.7
C ₃ -C ₄ -O ₁	127.4	2.6		124.4	3.0
C ₅ -C ₄ -O ₁	125.7	3.2		126.1	4.0
C ₁ -C ₅ -C ₄	103.0	2.9		102.1	3.1
C ₁ -C ₅ -C ₆	106.2	3.1		114.2	2.5
C ₁ -C ₅ -C ₁₅	118.5	2.9		112.7	2.5
C ₄ -C ₅ -C ₆	107.6	2.0		111.2	2.2
C ₄ -C ₅ -C ₁₅	104.8	3.2		97.5	2.4
C ₆ -C ₅ -C ₁₅	115.7	3.0		116.9	3.7
O ₂ -C ₆ -C ₅	100.7	2.6		110.3	2.9
O ₂ -C ₆ -C ₇	106.1	2.4		105.9	2.7
C ₅ -C ₆ -C ₇	112.5	2.2		116.3	2.2
C ₆ -C ₇ -C ₈	121.9	2.5		109.0	2.1

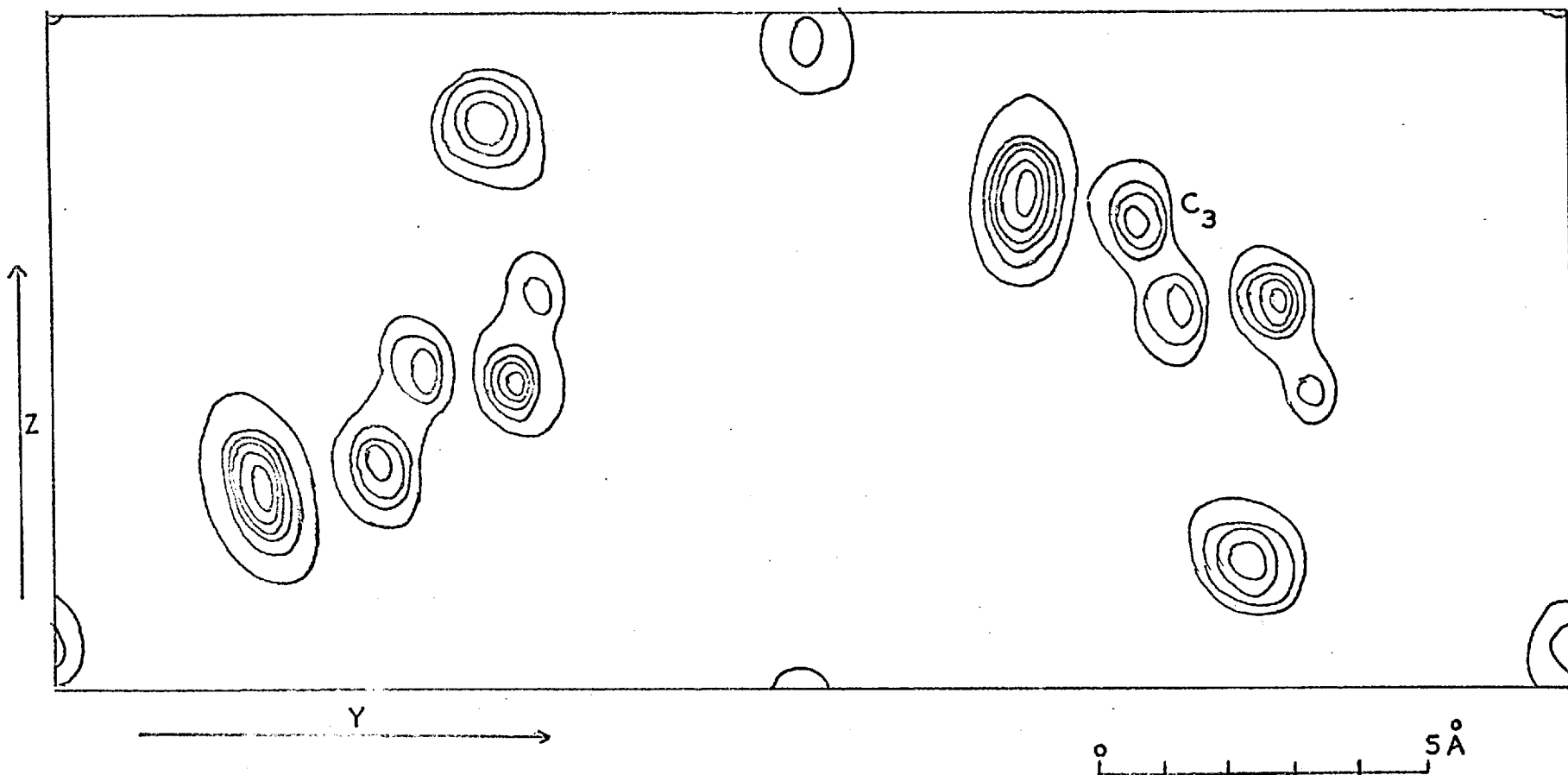
	Angle [°]	σ [°]	Angle [°]	σ [°]
C ₆ -C ₇ -C ₁₁	117.8	2.9	117.9	2.7
C ₈ -C ₇ -C ₁₁	102.4	2.1	105.0	2.6
C ₇ -C ₈ -C ₉	112.0	2.8	109.9	2.9
C ₇ -C ₈ -O ₅	101.9	1.8	98.7	1.9
C ₉ -C ₈ -O ₅	104.3	2.7	107.4	2.4
C ₈ -C ₉ -C ₁₀	108.8	3.3	115.4	2.4
C ₁ -C ₁₀ -C ₉	112.2	2.7	114.9	2.0
C ₁ -C ₁₀ -C ₁₄	113.3	3.6	111.8	3.1
C ₉ -C ₁₀ -C ₁₄	108.3	3.8	108.8	2.5
C ₁₂ -C ₁₁ -C ₇	119.5	3.1	114.4	3.6
C ₁₂ -C ₁₁ -C ₁₃	113.3	2.8	112.7	2.5
C ₇ -C ₁₁ -C ₁₃	104.3	2.8	103.1	2.2
C ₁₁ -C ₁₃ -O ₄	122.9	1.9	124.4	2.5
C ₁₁ -C ₁₃ -O ₅	111.3	2.2	109.2	2.1
C ₄ -C ₁₃ -O ₅	124.9	2.9	126.1	2.9
C ₁₇ -C ₁₆ -O ₂	123.6	5.0	118.5	5.8
C ₁₇ -C ₁₆ -O ₃	108.6	4.8	125.8	5.1
O ₂ -C ₁₆ -O ₃	127.8	6.2	115.4	6.4
C ₁₆ -O ₂ -C ₆	114.0	3.4	120.1	4.1
C ₈ -O ₅ -C ₁₃	113.0	2.5	114.7	2.1

T A B L E 5.5

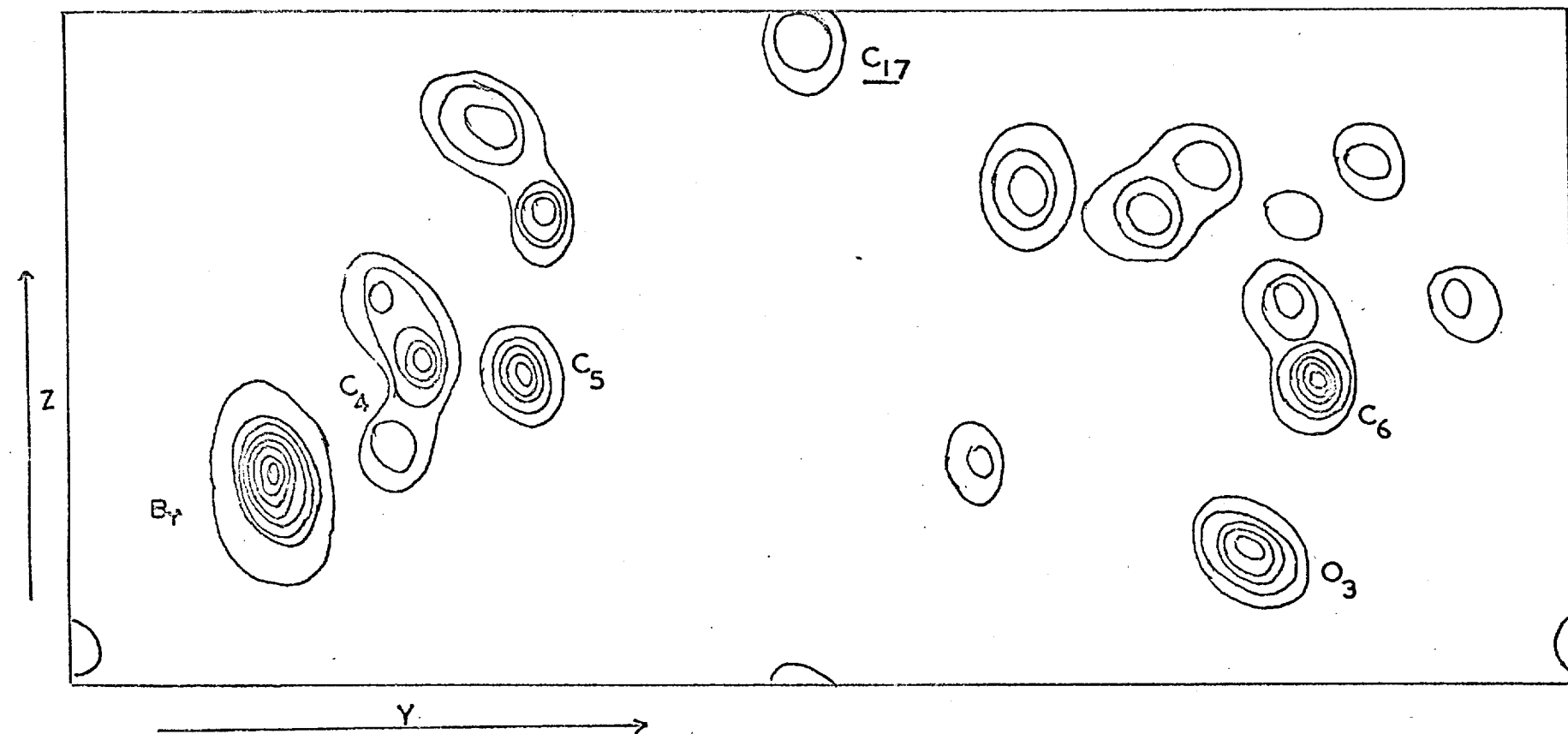
$F_{\text{obs.}} (\text{e})$	R (%)	$\text{Sin}^2 \theta$	R (%)	layer	R (%)
2.50	240.61	0.0-0.1	15.86	ok1	10.68
3.75	47.99	0.1-0.2	15.19	1k1	13.91
6.25	26.98	0.2-0.3	13.86	2k1	14.05
8.75	22.33	0.3-0.4	13.91	3k1	16.52
12.50	14.67	0.4-0.5	13.81	4k1	17.74
17.50	11.82	0.5-0.6	16.06	5k1	17.46
22.50	12.62	0.6-0.7	17.47	6k1	19.87
27.50	10.28	0.7-0.8	18.57	7k1	23.63
32.50	12.43	0.8-0.9	22.05		
37.50	14.21	0.9-1.0	35.69		
42.50	14.44				
47.50	15.81				
52.50	10.94				
57.50	11.55				
62.50	18.96				
67.50	12.37				
72.50	14.74				
77.50	20.37				
82.50	13.64				
87.50	5.69				
92.50	14.45				
97.50	19.64				
125.00	12.04				
175.00	4.09				

Fig. 5.1

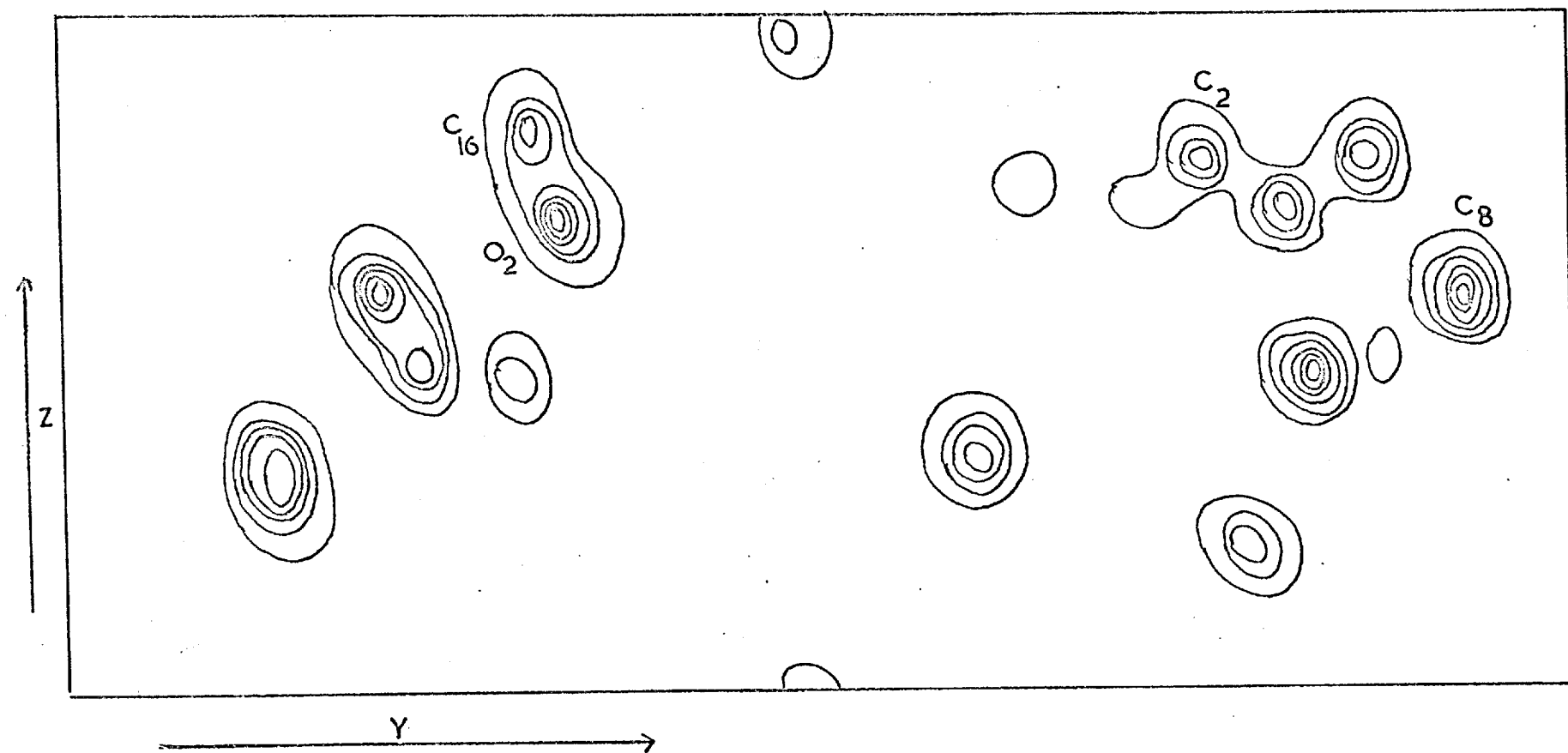
B I T final 3-D Fourier. Sections $a = 0/24$
to $12/24$. Contours at $5e/\text{\AA}^{-3}$ for Br and
 $1e/\text{\AA}^{-3}$ for C and O starting at $1e/\text{\AA}^{-3}$



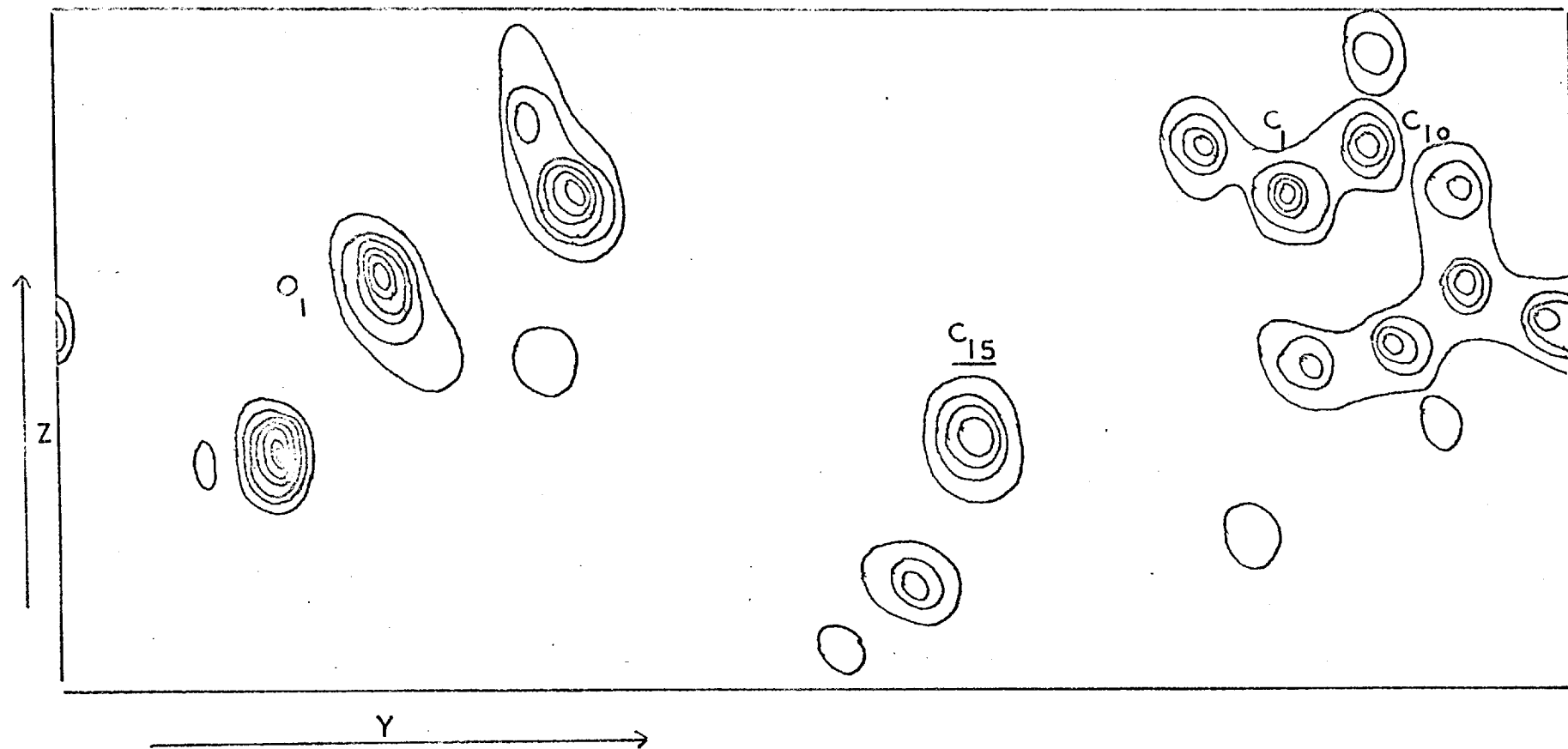
SECTION $X = \frac{0}{24}$



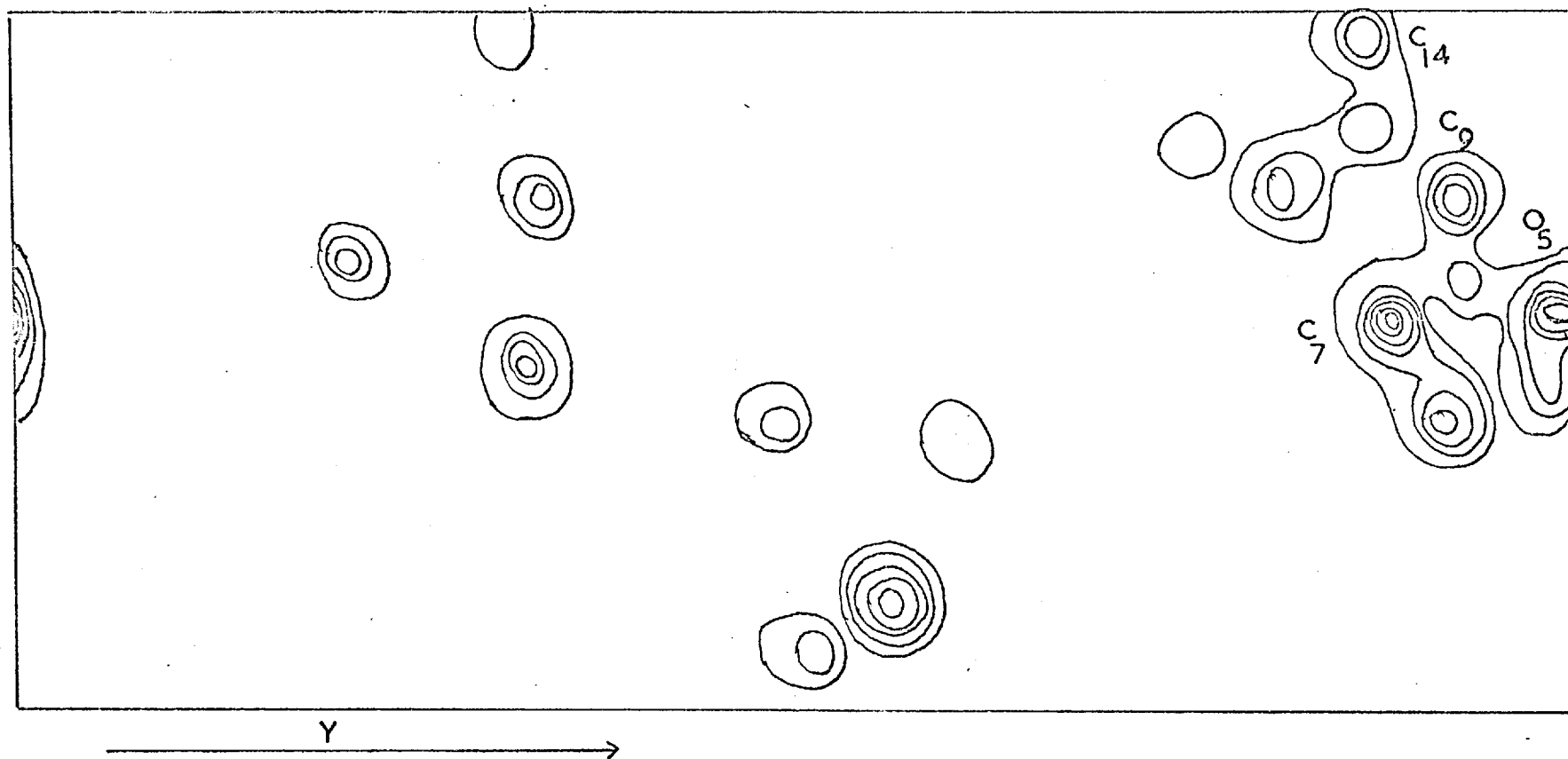
SECTION $X = \frac{1}{24}$



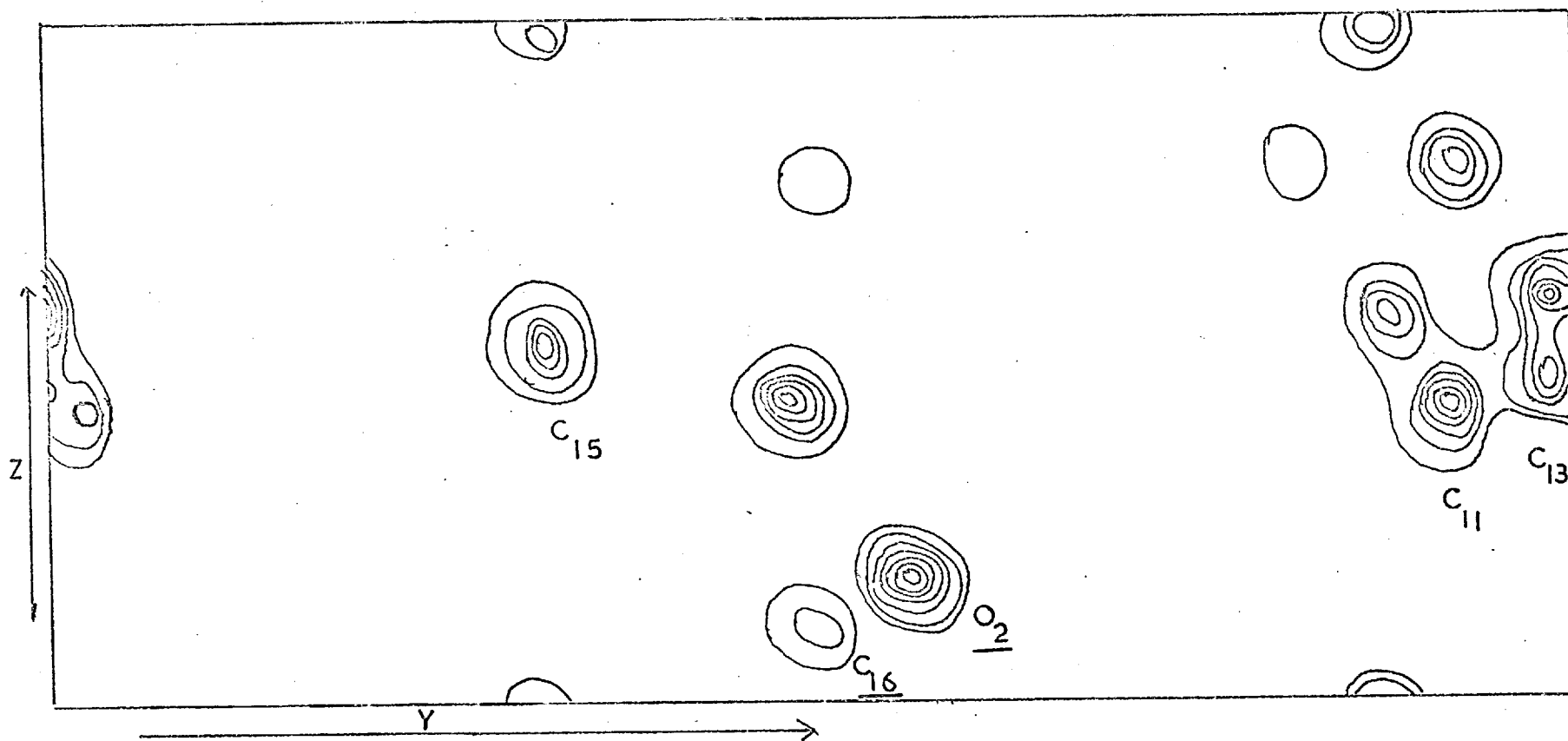
SECTION $X = \frac{2}{24}$



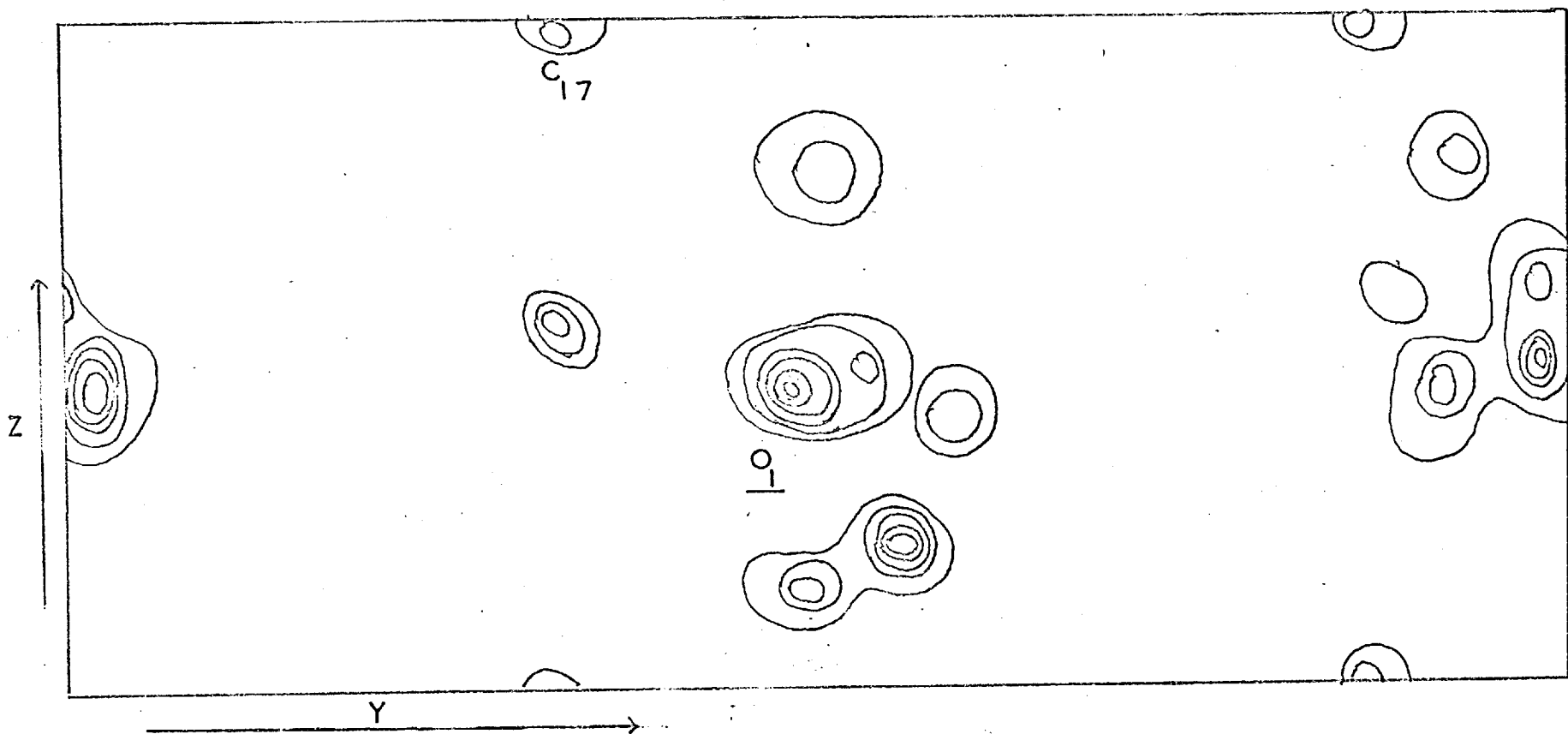
SECTION $X = \frac{3}{24}$



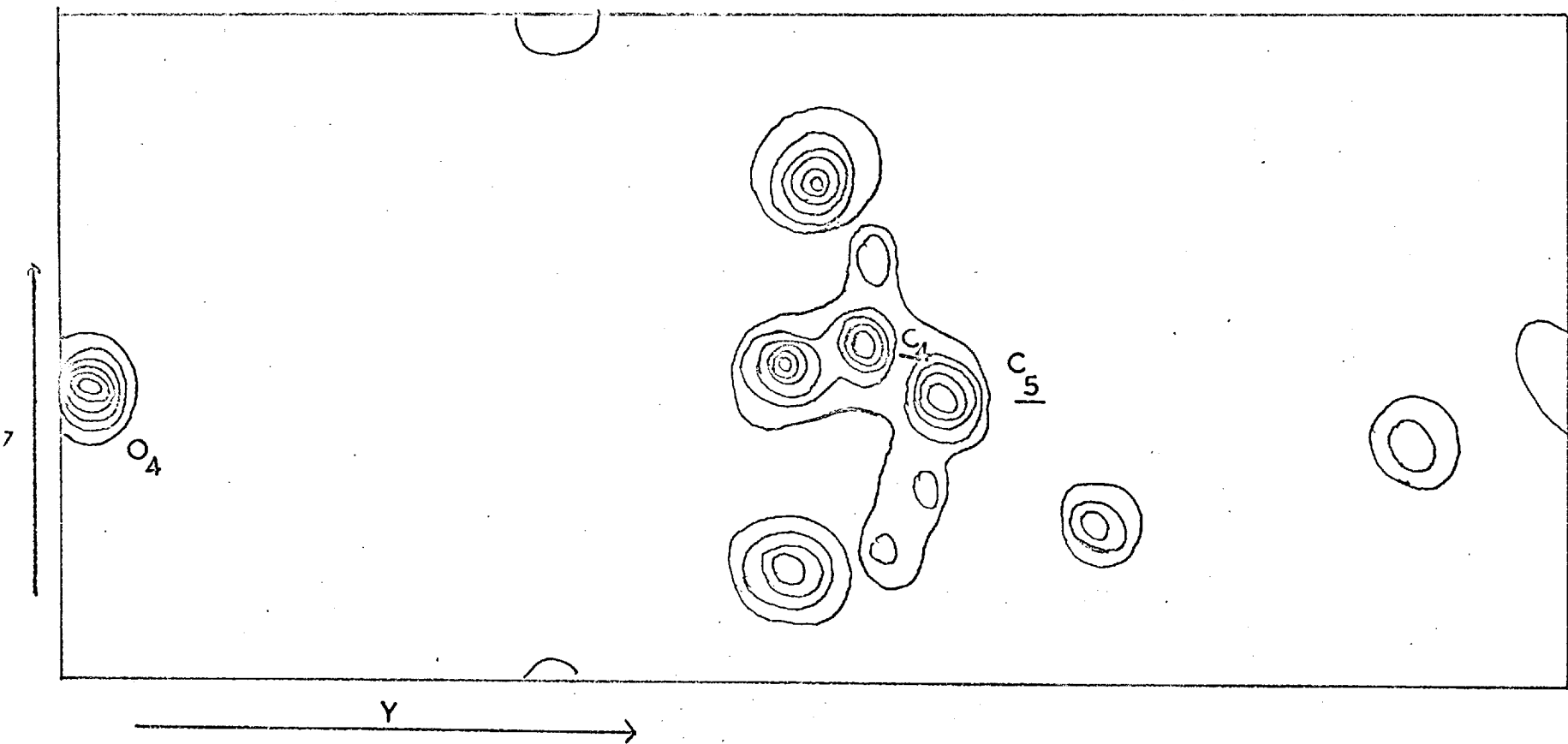
SECTION $X = \frac{4}{24}$



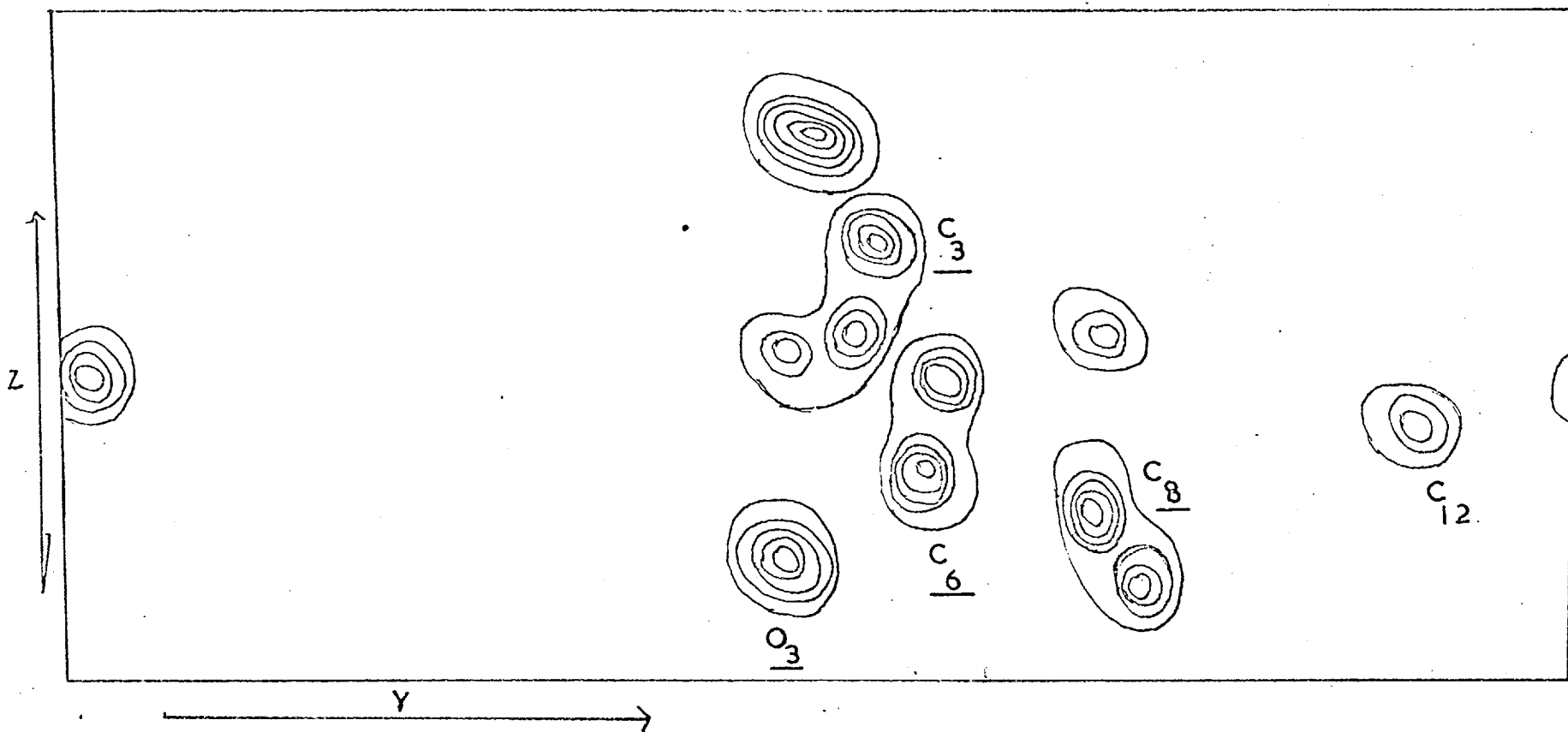
SECTION $X = \frac{5}{24}$



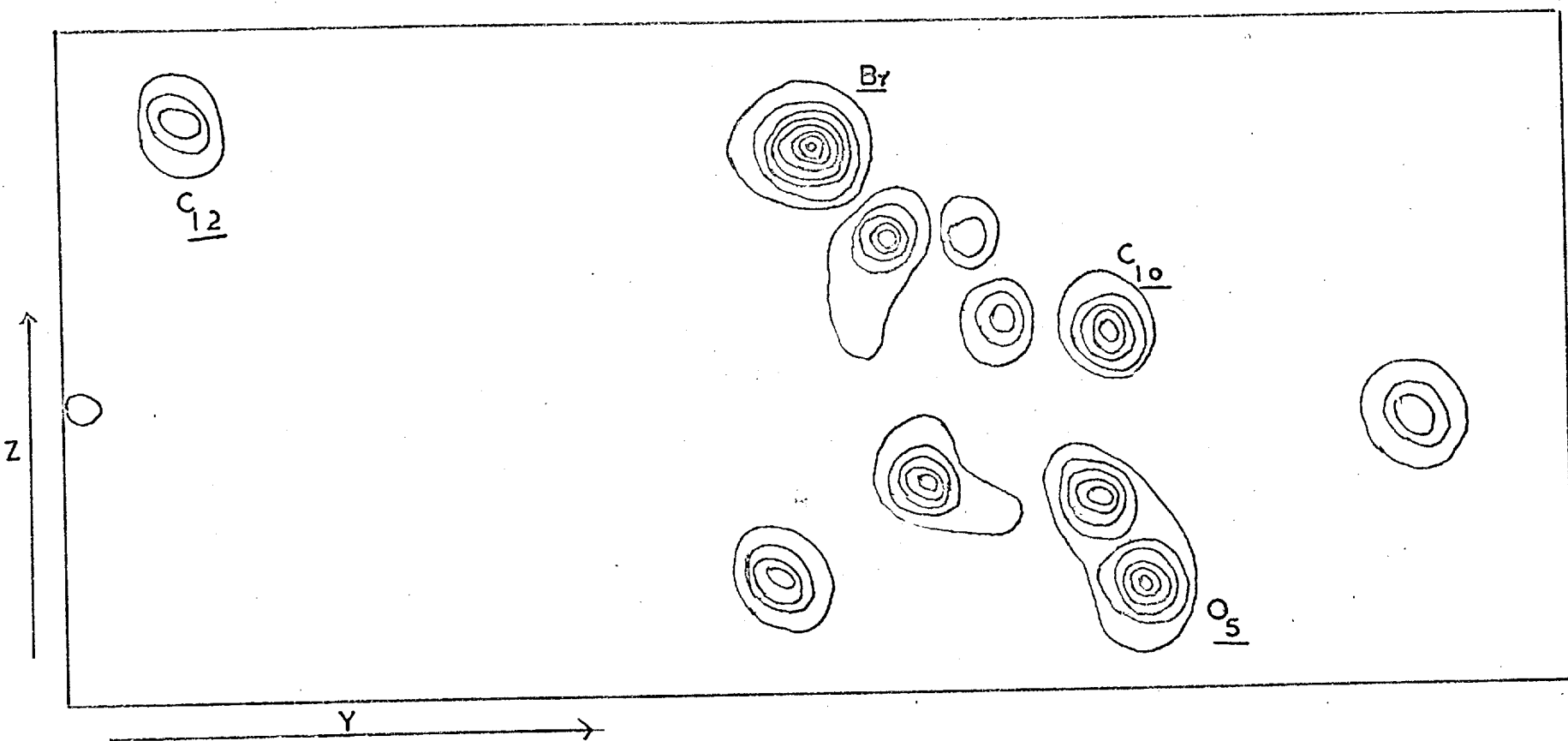
SECTION $X = \frac{6}{24}$



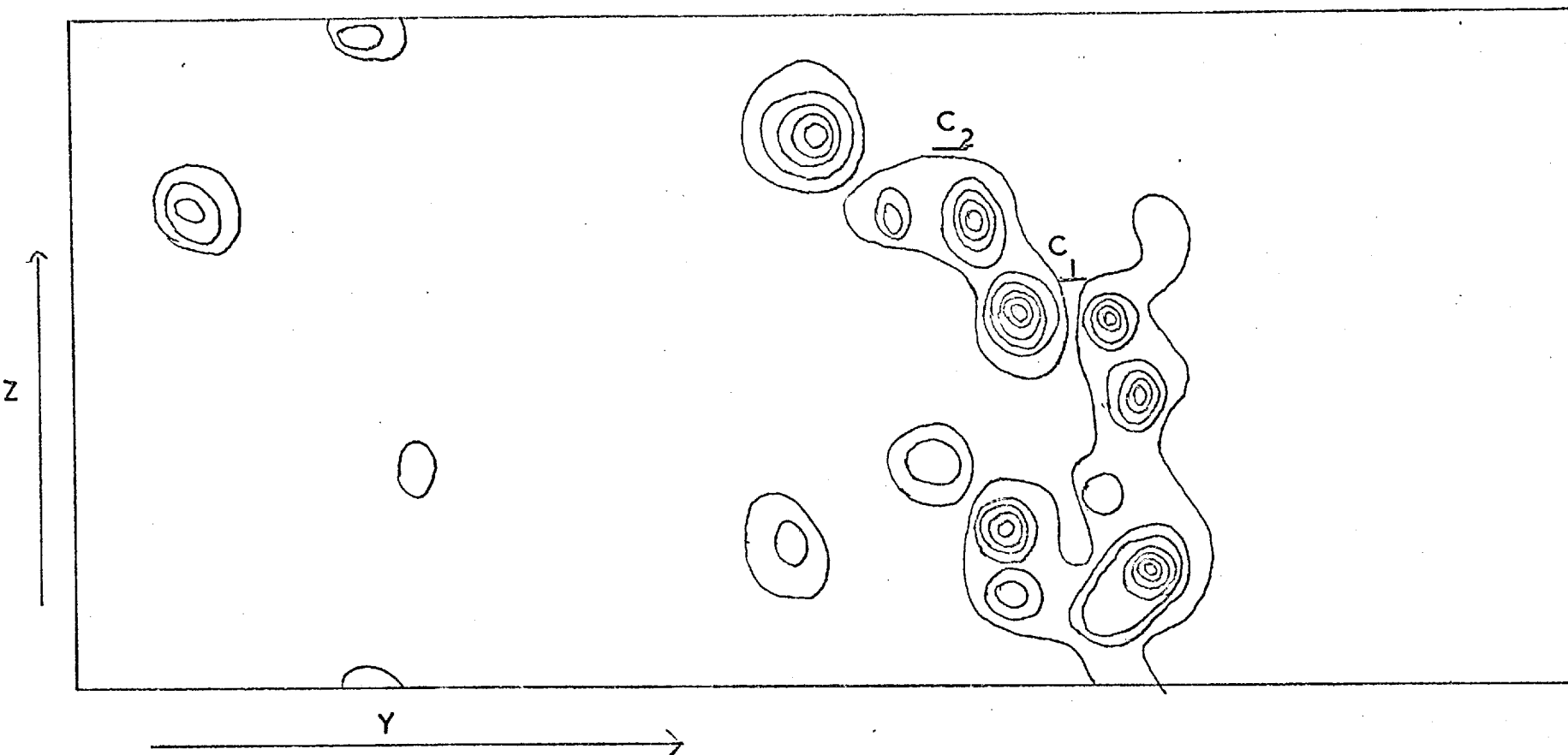
SECTION X = $\frac{7}{24}$



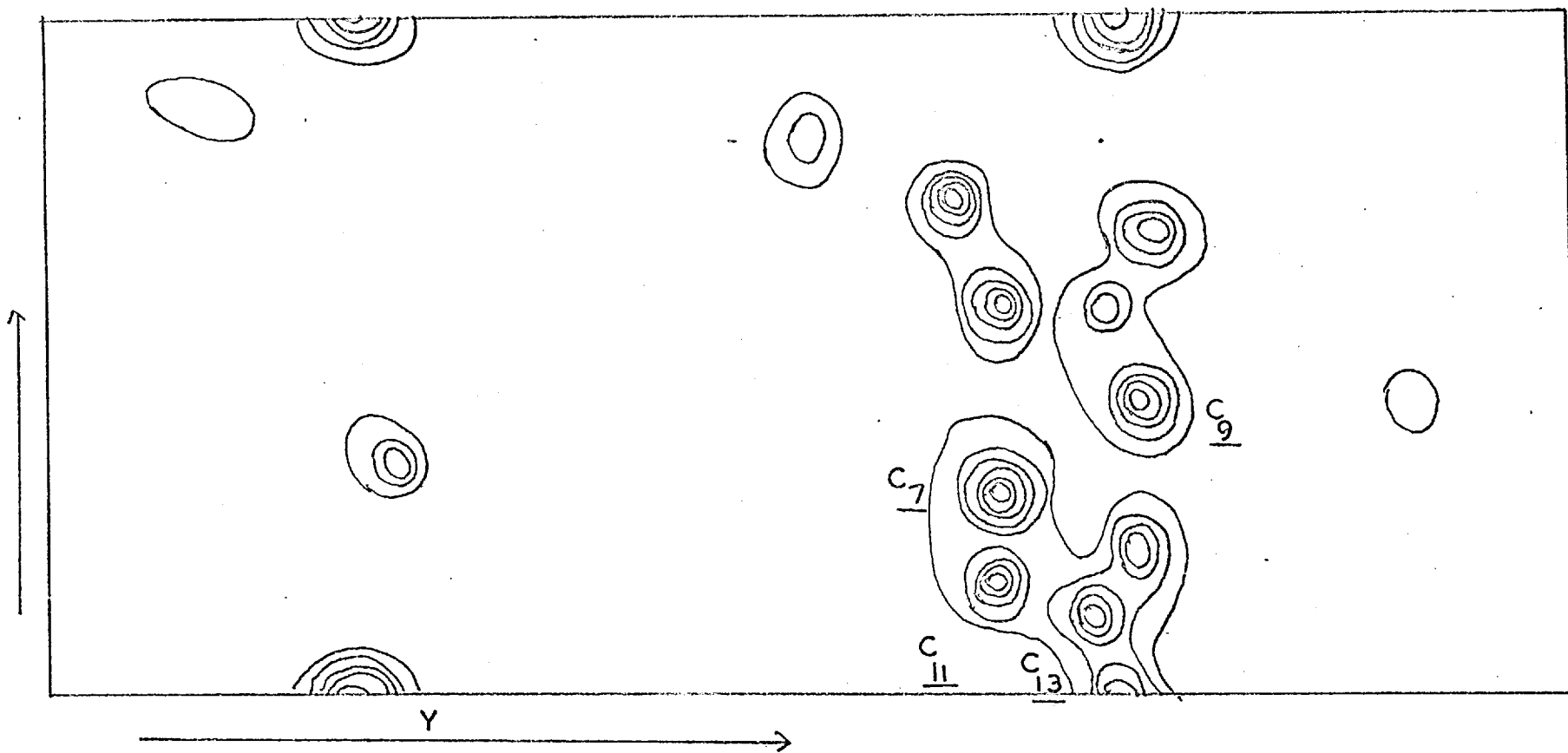
SECTION $X = \frac{8}{24}$



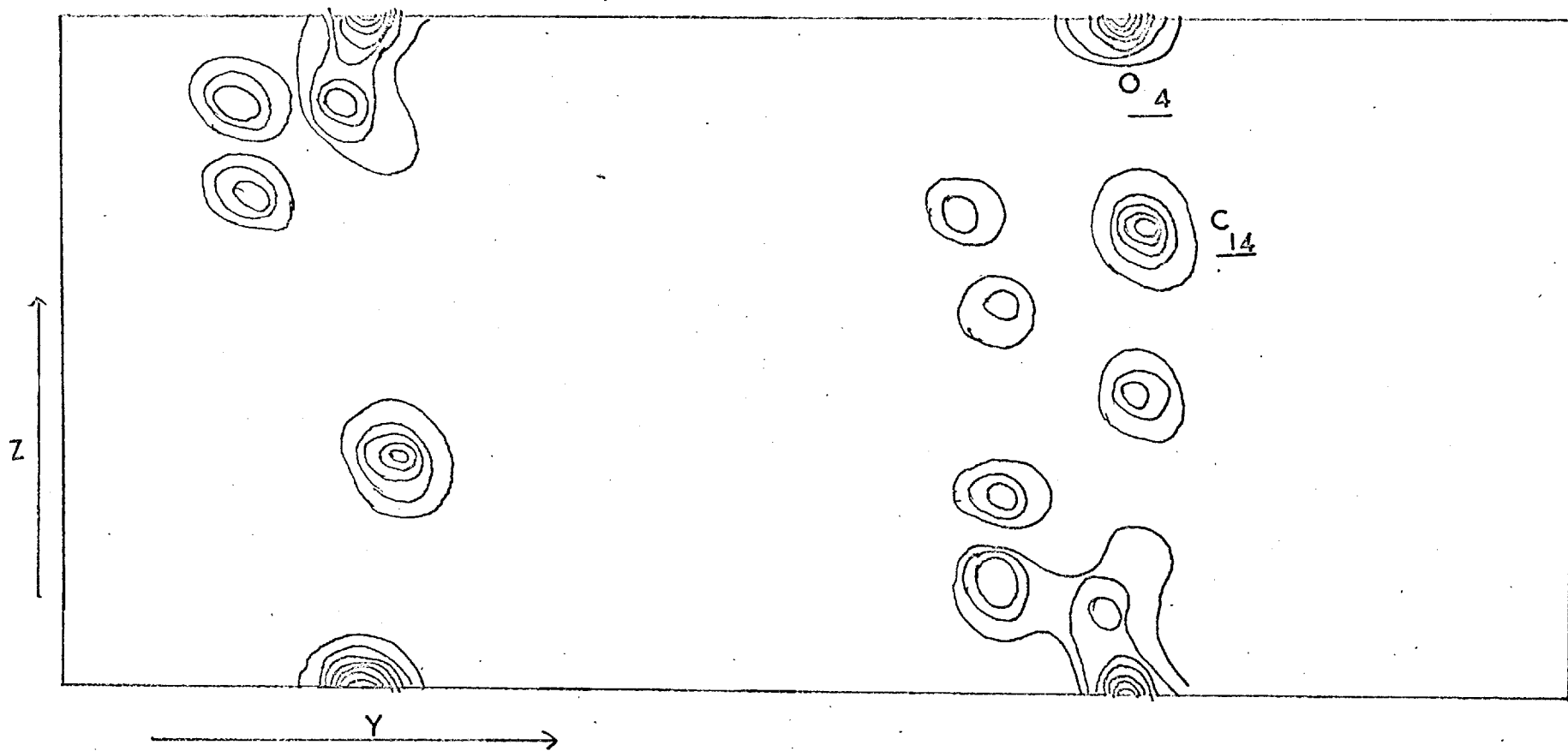
SECTION $x = \frac{9}{24}$



SECTION X = $\frac{10}{24}$



SECTION $X = \frac{11}{24}$



SECTION X = $\frac{12}{24}$

C H A P T E R 6

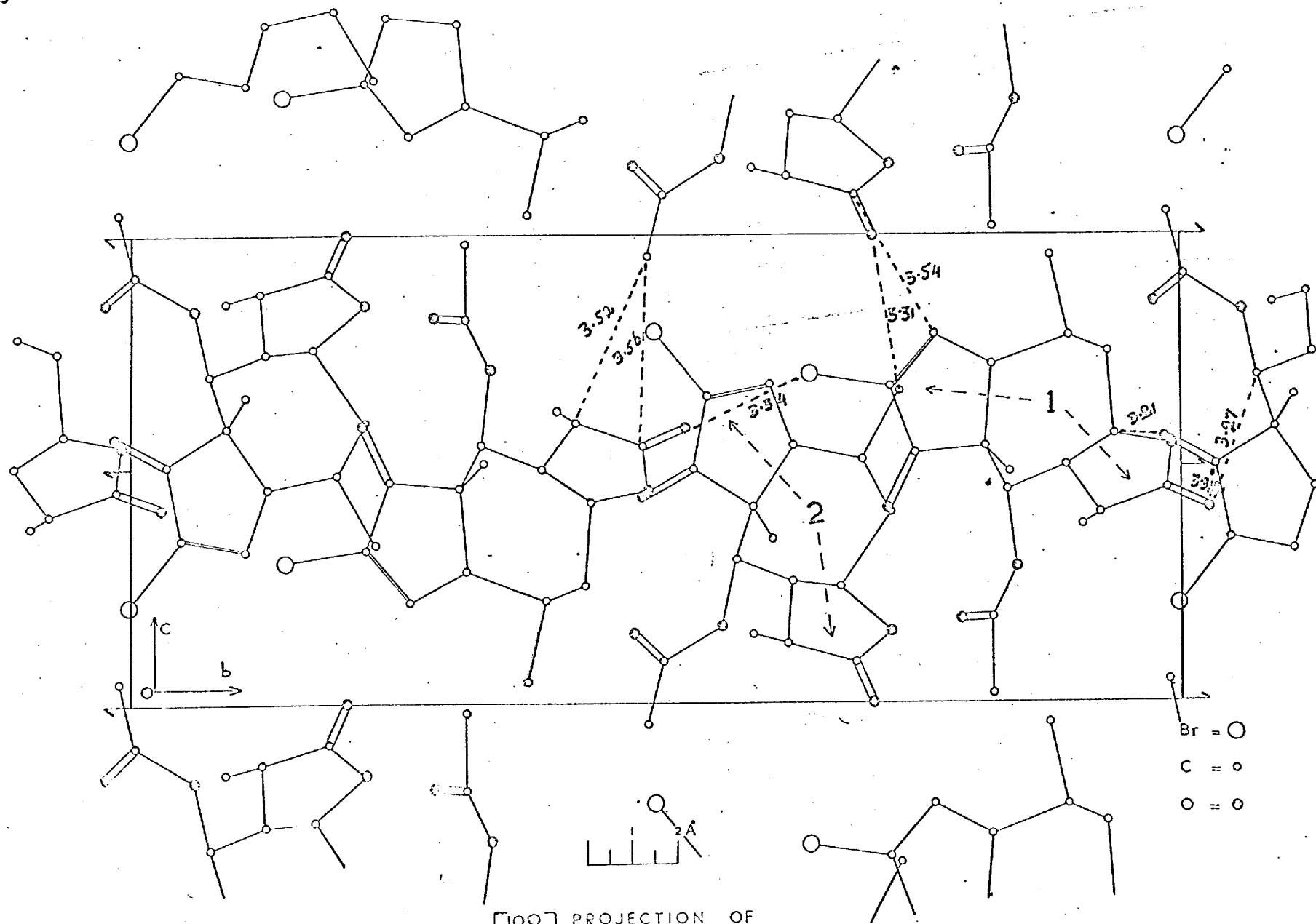
Discussion of the structure of Bromoisotenulin (BIT)

Constitution and stereochemistry:

Both isotenulin and bromoisotenulin are $\alpha\beta$ -cyclopentenones exhibiting very similar properties. We must therefore represent isotenulin by (4.20). The skeleton is ^{biogenetically} abnormal; a methyl group has migrated from position 4 to 5. On dehydrogenation it is not extruded but migrates back to give chamuzulene⁽⁴⁴⁾ in which the methyl group is at position 4. In the structure of BIT both the five-membered rings are trans-fused to the seven-membered ring. The lactone ring and the acetate group are interchanged compared with Barton and deMayo's structure (4.4). Non-bonded repulsion between the angular methyl (α to C₅) and hydrogens on C₈ and C₁₀ cause the molecule to be appreciably bent. A Dreiding model shows this interaction clearly and readily flexes into the form found. The position of the acetate group in isotenulin readily explains the isomerisation to tenulin /^(4.21) Both molecules in the unit cell have identical stereochemistry and similar absolute configuration, and their [100] projection is shown in Fig (6.1).

Related Structures:

The structure and relative stereochemistry of BIT found here has played a key role in determining the stereochemistry of the four Helenium constituents represented by, dihydroisotenulin,



[100] PROJECTION OF
 BROMISO TENULIN
 FIG. 61

tetrahydrohelenalin, dihydromexacanthin C and tetrahydro baldulin.
 Herz et al⁽⁴⁵⁾ showed by a variety of chemical and N.M.R. evidence that in all these the configurations at C_1 and C_{10} are the same, and they were also able to draw up a table of the relative configurations at C_5 , C_6 , C_7 , C_8 and C_{11} . Using the X-ray results for bromoisotenulin they were then able to assign stereochemistry to each of the other congeners. The results seem to be uniformly acceptable in explaining the observed chemical properties throughout the group.

Absolute configuration:

Herz et al⁽⁴⁵⁾ using optical rotatory dispersion measurements, concluded that BIT is probably the mirror image of the structure we deduced. We decided to check this by Bijvoet's⁽⁴⁶⁾ fluorescence method, using Mo $K\alpha$ radiation to excite the bromine atoms. Weissenberg photographs of the 0kl and 1kl layers were recorded and very carefully indexed. Just over 30 (0kl and $0\bar{k}l$, 1kl and $1\bar{k}l$) were noted with varying degrees of intensity difference. The twenty four strongest gave unanimous evidence for a reversal of the structure of BIT. The remainder were indecisive, either because of the smallness of the intensity difference, or because of the near parallelism of the F_{Br} and F_{BIT} structure factors.

Accuracy

The final standard deviations are listed in table (5.3, 5.4), and are generally of the order of 0.03-0.05 $\text{\AA}$ in bond lengths, and 1.8-4.0 $^\circ$ for valence angles. But the accuracy in the acetate group

is rather lower ($0.1\text{\AA}$ and 6°), though remarkably consistent between the two molecules. This consistency seems to rule out disorder, and leaves extra large thermal motion as the main cause of the lower accuracy in the acetate groups.

Comparasion of the molecules:

The bonds and angles are summarised in tables (5.3) and (5.4) and also in Figs. (6.2) and (6.3). Agreement between the two molecules is generally good. The average discrepancy in bond lengths $\approx 0.07\text{\AA}$, and for the non-bonded interatomic distances (less than $3.6\text{\AA}$) the average discrepancy is $0.05\text{\AA}$. The angles agree well in the five-membered rings, but disagree slightly in the seven-membered ring; this is apparently connected with a slight difference in the folding of the molecule.

Intermolecular distances:

The intermolecular contacts are shown in Fig. (6.1). The contacts less than $3.6\text{\AA}$ are:-

- a) three C-C contacts (3.52 - $3.56\text{\AA}$),
- b) one Br-O contact ($3.34\text{\AA}$),
- c) sixteen C-O contacts, of which only the following four are less than $3.35\text{\AA}$:
 - i) $3.21\text{\AA}$; $\text{C}_8(1) - \text{O}_1 = \text{C}_4(2)$
 - ii) $3.27\text{\AA}$; $\text{C}_6(2) - \text{O}_4 = \text{C}_{13}(1)$
 - iii) $3.31\text{\AA}$; $\text{C}_{14}(2) - \text{O}_4 = \text{C}_{13}(2)$
 - iv) $3.32\text{\AA}$; $\text{C}_4(2) - \text{O}_4 = \text{C}_{13}(1)$
- d) there are, curiously, no short O-O contacts.

None, of these, can be regarded as unusually short.

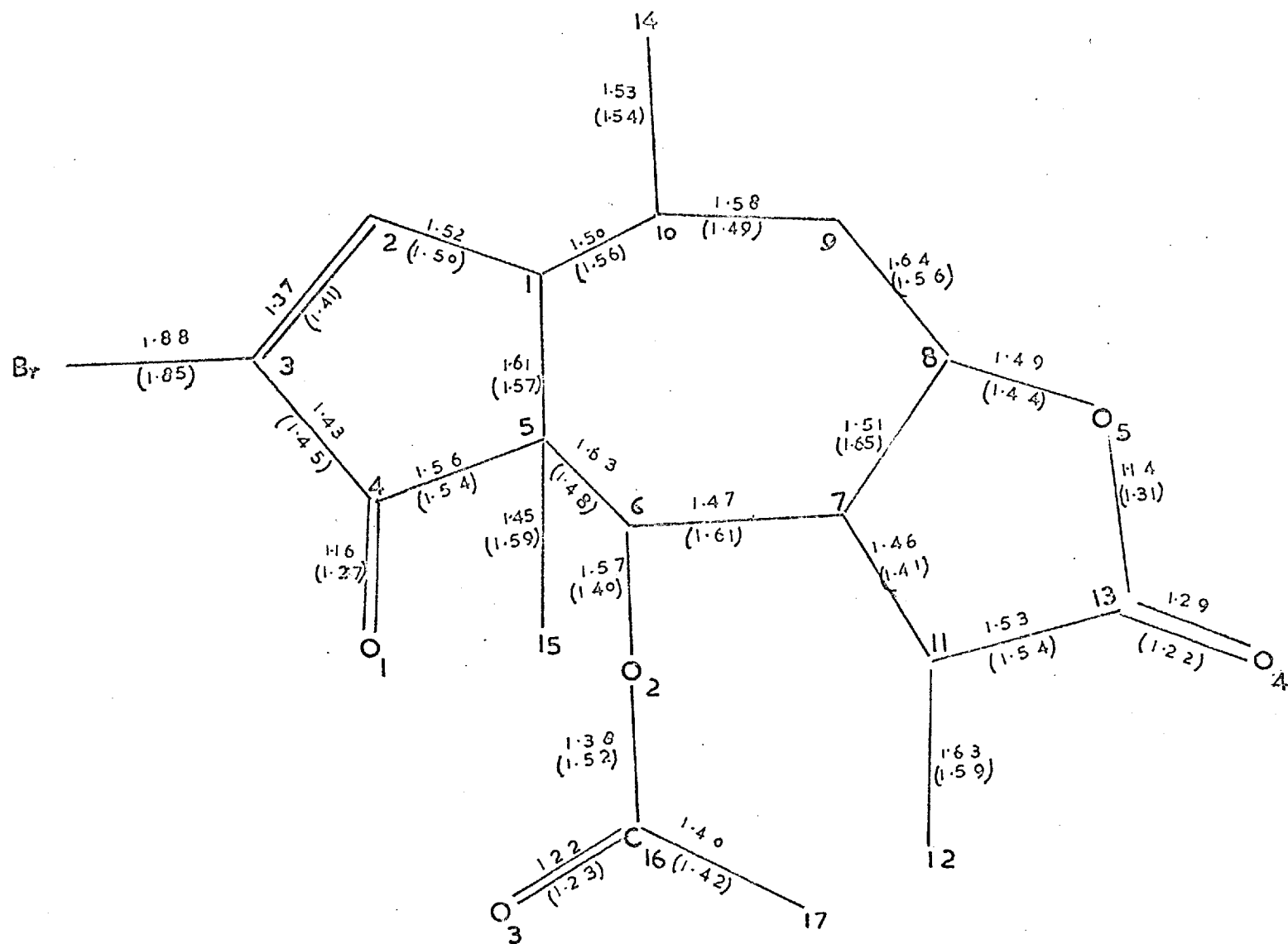


FIG. 6.2

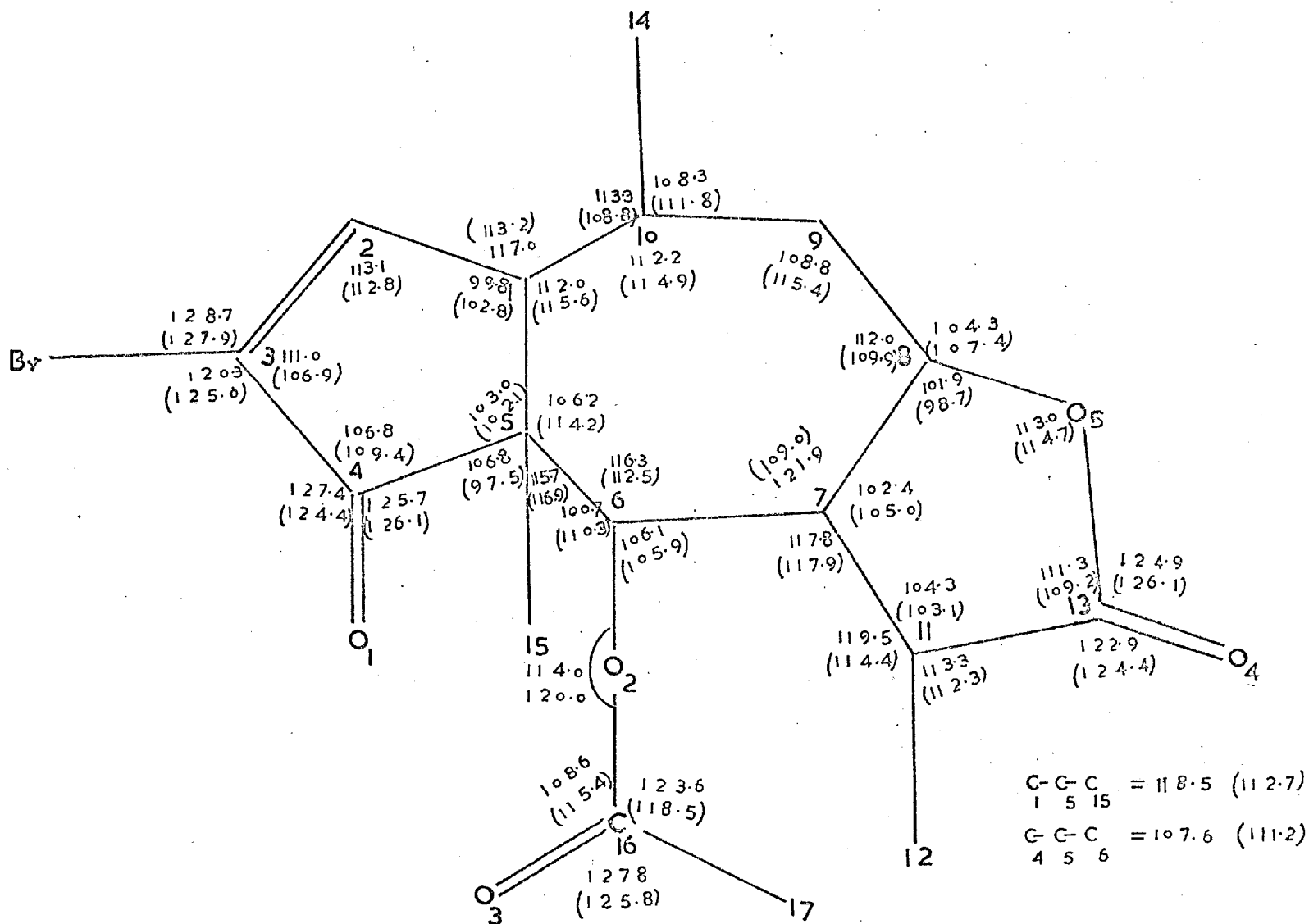


FIG. 6.3

The acceptance of two molecules and two independent sets of bromines was a great help when solving the first 3-D Fourier. On the other hand it was rather^aburden having two molecules throughout the refinement, but their comparison after each cycle was helpful.

This study provides another example for the assurance of organic chemists, that X-ray studies can be duplicated. Here two independent, but apparently identical molecules were found in one study.

C H A P T E R 7

The solution of the crystal structure of caryophyllene chlorohydrin

Introduction:

Caryophyllene, the oldest known sesquiterpene, was first
 observed by Ettling⁽⁴⁷⁾ in clove oil, and later confirmed by other
 investigators.⁽⁴⁸⁾ Church⁽⁴⁹⁾ was the first to show it to have the
 composition $C_{15}H_{24}$ and Brühl⁽⁵⁰⁾, from a consideration of its physical
 constants, suggested that it was a dicyclic hydrocarbon containing
 two ethylenic linkages. A detailed study of the sesquiterpene was
 made by Wallach and Walker,⁽⁵¹⁾ who prepared a number of crystalline
 derivatives and showed that the hydrocarbons present in oil of
 cloves and copaiba oil were identical.

Deussen⁽⁵²⁾ concluded after extensive investigations that
 caryophyllene contains two, and very probably three, hydrocarbons,
 α -caryophyllene, β -caryophyllene, and γ -caryophyllene or
 isocaryophyllene. Numerous other investigations led to several
 proposed formulae (Simonsen and Barton)⁽⁵³⁾, but as pointed out by
 Ramage and Simonsen⁽⁵⁴⁾ much of the early work on caryophyllene is of
 doubtful value because only liquid products of unauthenticated
 homogeneity were obtained.

Barton and Lindsey⁽⁵⁵⁾ gave evidence for a nine-membered ring
 in caryophyllene and proposed three alternative formulae as shown
 in Fig (7.1). Barton et al⁽⁵⁶⁾ favoured formulae (7.1.c) after

studying the properties of the dicarboxylic acid, $C_{12}H_{18}O_4$.

(57)
Aebi et al found that β -caryophyllene reacts much faster with perphthalic acid than does isocaryophyllene, so on this basis β -caryophyllene is the transisomer (7.2), and isocaryophyllene is the cis-isomer (7.3). (58)
Barton and Nickon also proposed the stereochemistry and absolute configuration.

(59)
Robertson and Todd by X-ray work, showed that the chloride and bromide of β -Caryophyllene alcohol are represented by (7.4). They then assigned formulae (7.5) and (7.6) respectively to the alcohol and to β -caryophyllene itself. Their structure (7.4) confirmed that the cyclobutane ring is trans-fused to the larger ring, as proposed by Barton, etc., and this suggests that the configuration at C_1 and C_4 in β -caryophyllene are retained in the alcohol and halides.

(60)
Treibs had shown that autoxidation of caryophyllene furnished in good yield a crystalline oxide, $C_{15}H_{24}O$, m.p. 64° . On further oxidation by $KMnO_4$ in acetone this is converted to a mixture of two isomeric oxidoglycols, $C_{15}H_{26}O_3$, (α -, m.p. 14° ; β -, m.p. 119°) and an oxidoketone, $C_{14}H_{22}O_2$, m.p. $61-62^\circ$. He proposed formula (7.7) for the oxidoketone.

(9)
Barton and Lindsey, however, gave three possible formulae Fig (7.8) for Treib's, $C_{14}H_{22}O_2$, oxidoketone corresponding to formulae (7.1) for caryophyllene. Later they favoured formulae (7.1.C) for caryophyllene and thus (7.8.C) for the oxidoketone.

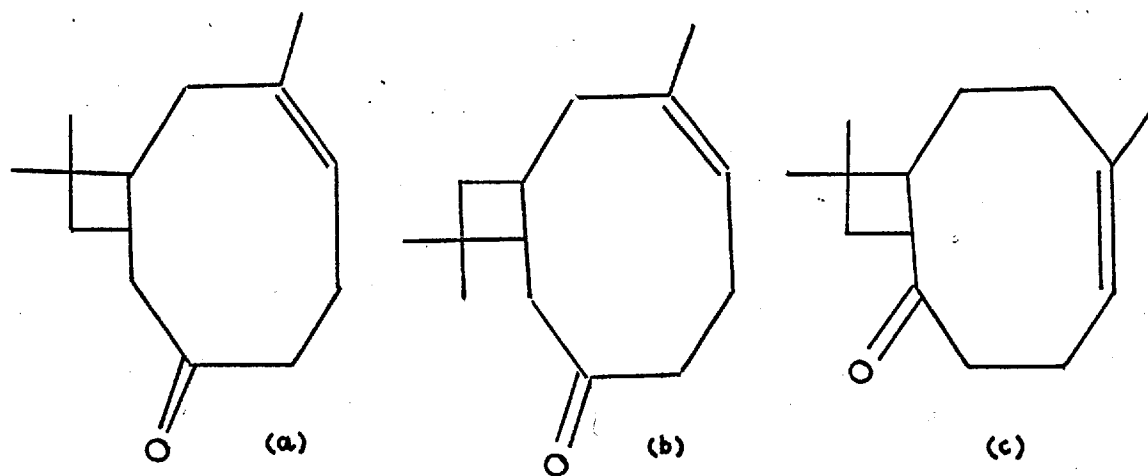


FIG - 7.1

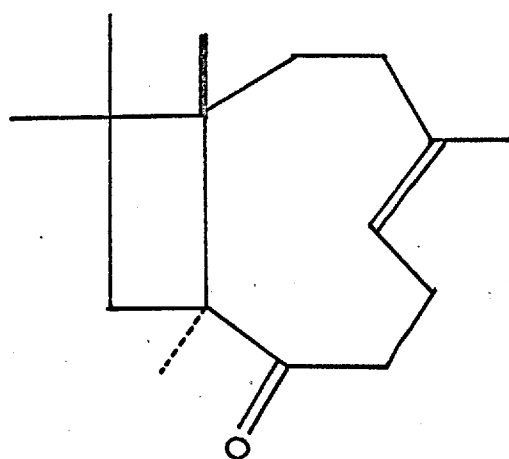


FIG. 7.2

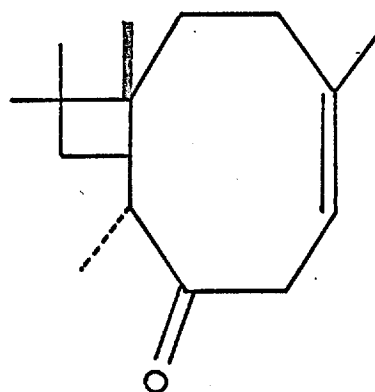
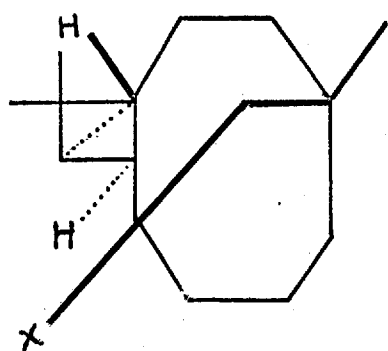


FIG. 7.3



X = Cl, Br

FIG. 7.4

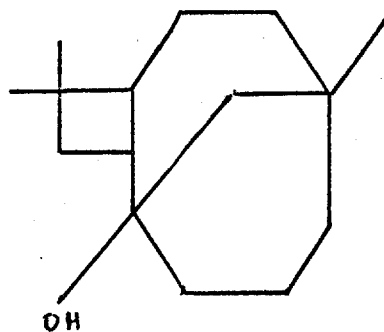


FIG. 7.5

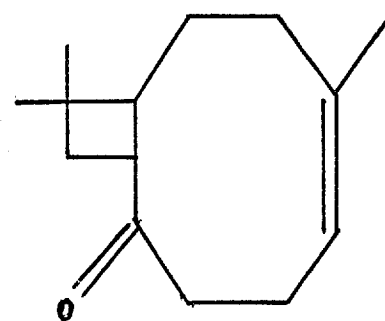


FIG. 7.6

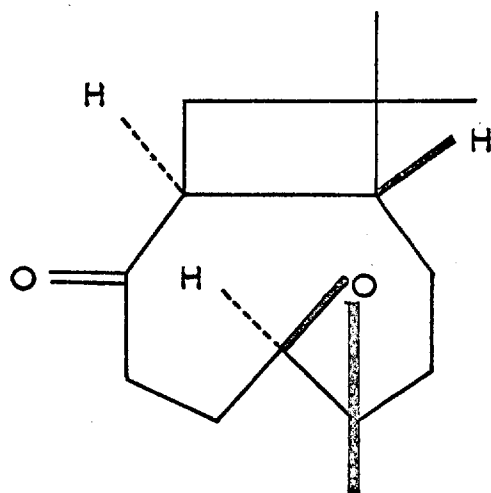


FIG. 7.7

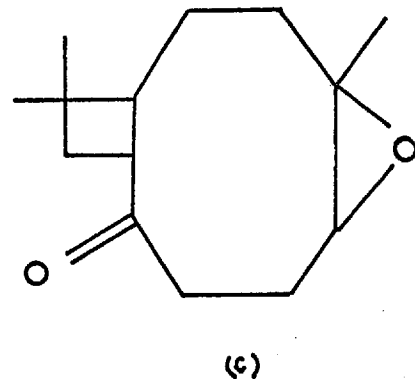
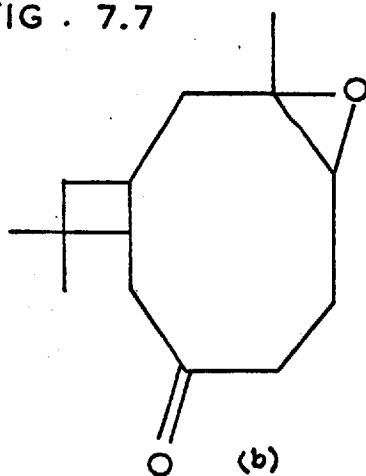
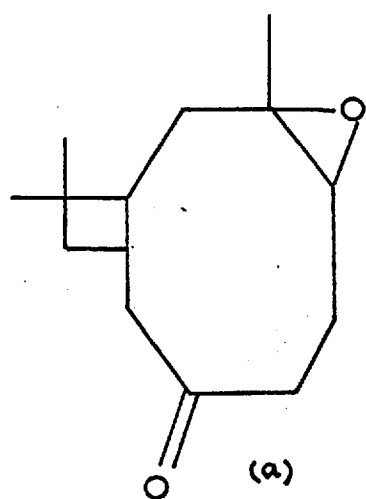


FIG. 7.8

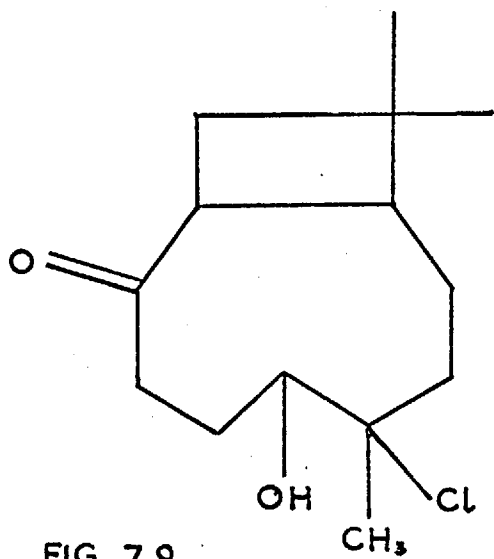


FIG. 7.9

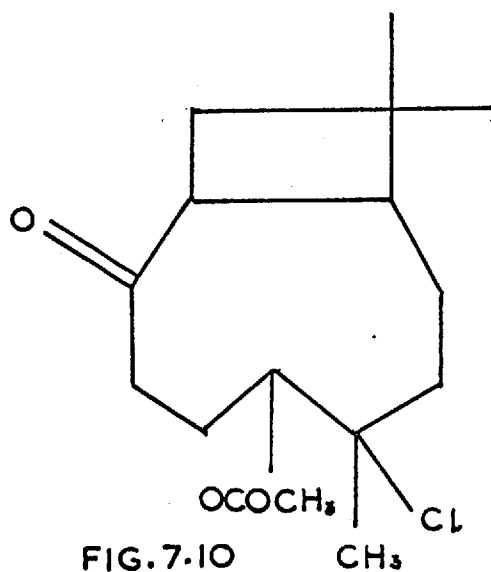


FIG. 7.10

They also showed that when the oxidoketone is treated with hydrogen chloride in chloroform at room temperature for 15 minutes a crystalline chlorohydrin was obtained. This was postulated as (7.9).

Recently a monoacetate (7.10) was prepared by treatment of chlorohydrin with acetic anhydride in pyridine.

The chlorohydrin when treated with lithium in ammonia gave a diol, postulated as (7.11), which was oxidised in pyridine to form a ketol thought to be, (7.12).

However, no C-Me other than $>C \text{ Me}_2$ was shown by any of these compounds in their N.M.R Spectra. In view of this doubt as to its constitution, and the lack of knowledge of its stereochemistry, it was decided to examine C C by X-ray diffraction.

Crystallographic data for Caryophyllene Chlorohydrin ($C_{14}H_{23}O_2Cl$)

A summary of the crystallographic data obtained in chapter 2, is set out with other relevent details on page (98).

The crystals originally available were very fine hairs. All attempts to grow them thicker at room temperature failed. After trying many solvents trigonal prisms were obtained accidentally from a solution in acetone which evaporated slowly at subzero temperatures during a Christmas vacation.

Weissenberg photographs for layers $l = 0$ to 6 were taken by oscillating the crystal about the C axis and for layers $k = 0$ to 2 around the subsidiary axis a_2 .

The intensities were measured visually. No absorption

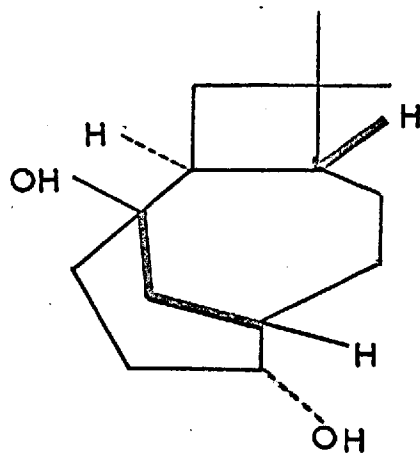


FIG. 7.11

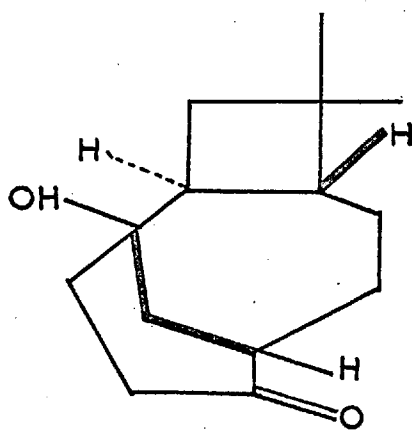


FIG. 7.12

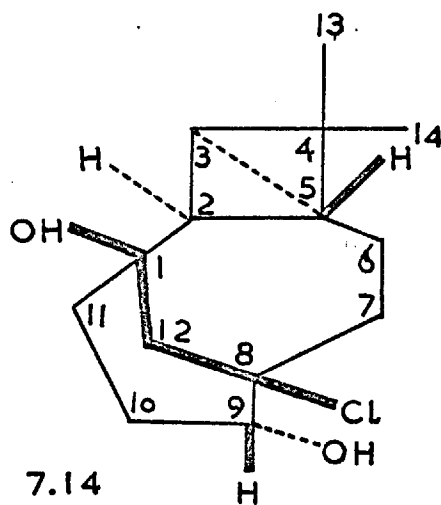


FIG. 7.14

corrections were applied, for reasons explained in chapter 2. The Lorentz and polarization corrections were applied using Mercury program DRO 4 of Dr. C.K.Prout. All the 1 layers were correlated with reflections in layersh = 0, 1, 2 by comparing the common reflections. After this the rest of the reflections needed for the Fourier program (see page 31) were generated using Dr. R.Diamond's program. The scaling and temperature factors were determined by Wilson's method.

Solution of the structure

Before calculating the Patterson the data was sharpened by applying the function:

$$1/f_{Cl}^2 \exp(2 \sin^2 \theta),$$

which past experience has shown to sharpen well, but without introducing too much diffraction ripple.

A three-dimensional Patterson was computed by using Dr.O.S.Mill's Fourier program for Mercury. The Chlorine positions were deduced from the Harker section Fig. (7.13) and are quoted for all three chlorines in the table below and are also shown in Fig (7.15).

	x	y	z
Cl ₁	0.828	0.787	0
Cl ₂	0.213	0.041	1/3
Cl ₃	-0.041	0.172	2/3

Partial structure factors were calculated using Dr.J.S.Rollett's program for the chlorine atoms. An arbitrary criterion of $|F_{Cl}| \geq 0.5 |F_o|$ was used for the inclusion of the terms in the first

Harker section ($Z=1/3$) of Cc

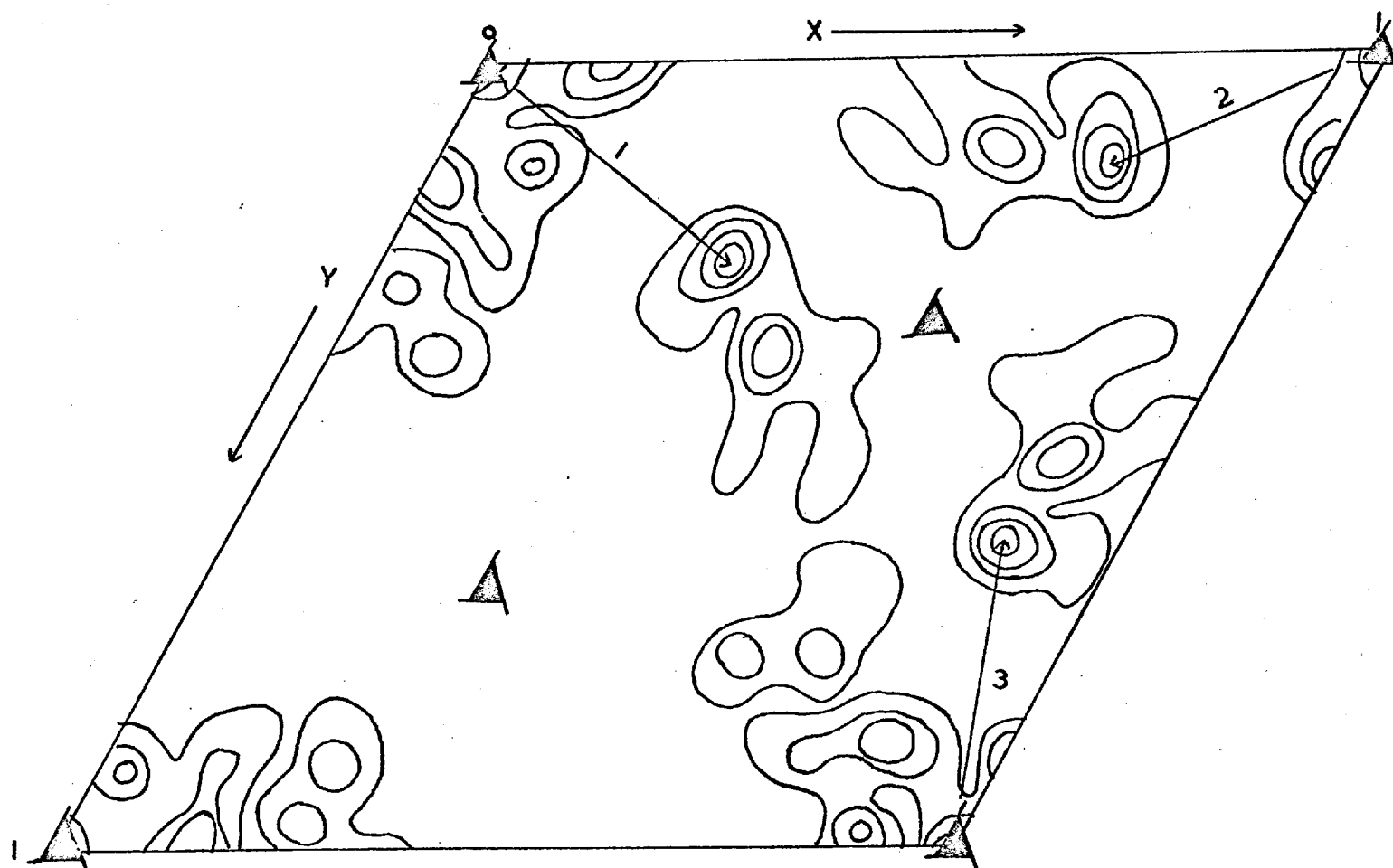


Fig (7.13)

Chlorine positions in C C from the Harker section

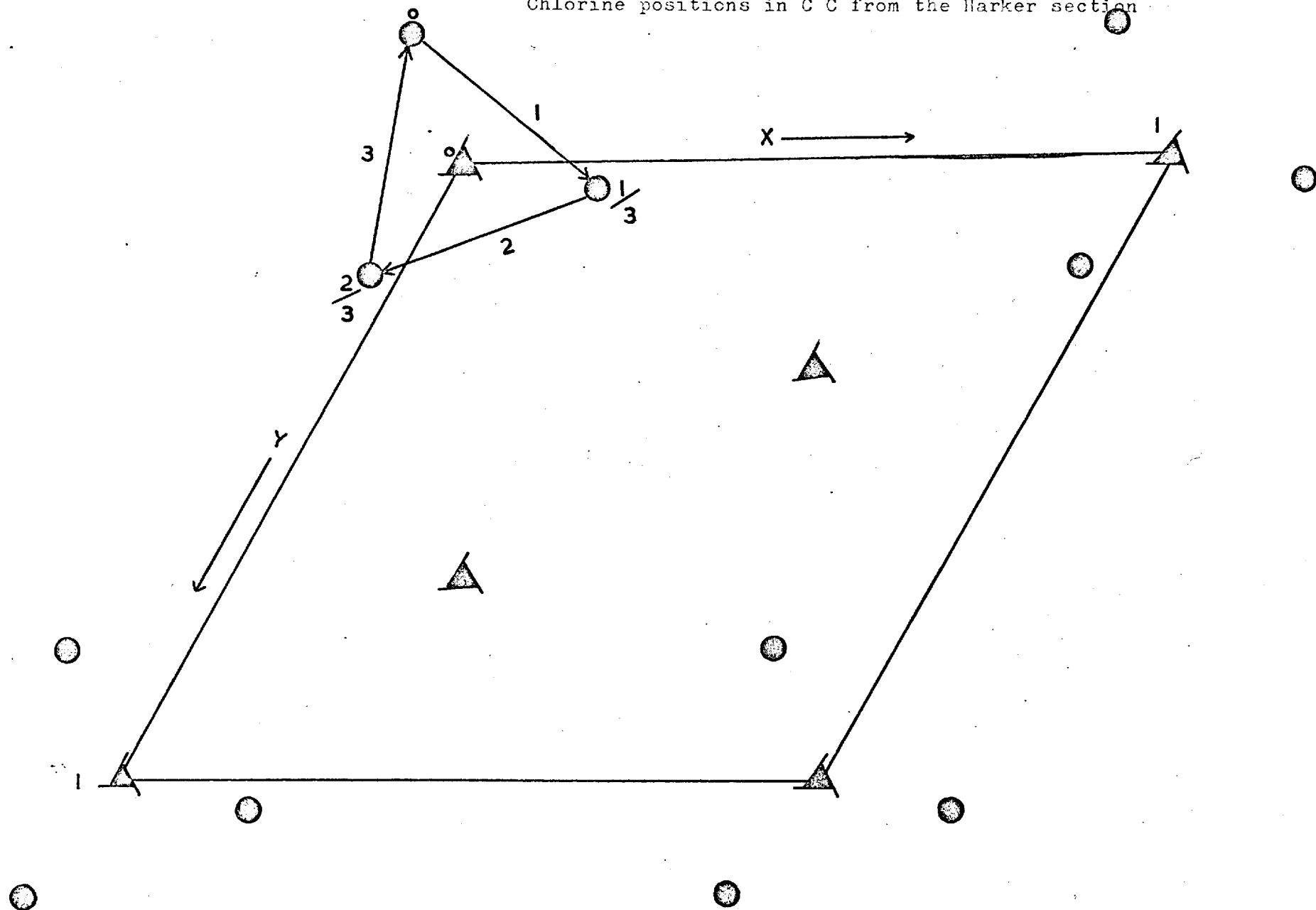


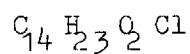
Fig (7.15)

Fourier. For selecting these terms a program was written by Dr. R.Diamand.

The chlorine-phased Fourier gave a few extra peaks, but it was not possible to make any sensible interpretation of it. An attempt was therefore made to solve the structure by the "superposition" method. In this, three copies of the Patterson are superimposed keeping them in parallel orientation, but shifting them to put the Cl - Cl peaks at the true positions of the chlorines in the cell. Each copy of the Patterson contains 3 images of the structure as seen from the three halogens as well as a large number of other superimposed images. The "superposition technique" will bring one image of the structure from each Patterson into coincidence. If therefore we can find peaks common to all three Pattersons, there are possibly the atoms of the desired structure. 8 "atoms" of varying probability were found in this way, but no immediate action was taken on these as it had been discovered in the meantime that there were discrepancies in the computed chlorine-phased structure factors mentioned above. Some of the symmetry-related structure factors did not agree as they should, so several were checked by hand. The discrepancies were eventually traced to the fact that the computer did not correctly interpret the symmetry directives as given below,

X.	Y.	Z.
-X+Y.	-X.	1/3+Z
-Y.	X-Y.	2/3+Z

When $Y-X$ was put instead of $-X+Y$, the calculations were performed correctly. Another Fourier was then calculated and revealed ten possible peaks. When compared with the eight from the superposition procedure only five of them agreed. The five atoms and chlorine were then used for the calculation of a full set of partial structure factors for the next Fourier. This revealed a considerable number of possible atoms, but only ten were selected for the next set of structure factors because they made good chemical sense. The remaining atoms were found from four more successive Fouriers. The structure is shown in Fig (7.14) with its stereochemistry. The positions indicated by the last Fourier were used to calculate the inter-atomic distances and angles. These results seemed good enough to act as a sound basis for refinement.

CARYOPHYLLENE CHLOROHYDRIN

M. Wt. = 258.5

$$\mu = 29.2 \text{ cm}^{-1}$$

M. Pt. = 147°C

F(000) = 420

Trigonal Laue Symmetry $\bar{3}$

$$\left. \begin{array}{l} a = 13.12 \\ c = 7.11 \end{array} \right\} \begin{array}{c} \text{\AA} \\ \text{\AA} \end{array}$$

Z = 3 mol/cell

$$d \text{ obs.} = 1.209 \text{ gm. cm}^{-3}$$

$$d \text{ calc.} = 1.21 \text{ gm. cm}^{-3}$$

Absences: 001 when $l \neq 3n$

Space group: $P\bar{3}_1$ or $P\bar{3}_2$
 $P\bar{3}_1$ adopted arbitrarily.

CHAPTER 8

Refinement of the crystal structure of Caryophyllene Chlorohydrin (C C)

Least-squares refinement

It was obvious from the last Fourier that only chlorine showed any sign of anisotropy. It was decided, therefore, to begin refining the structure using Rollett's isotropic least-squares program. In the beginning a B value of 3 was given to all atoms. Nine cycles of refinement were done, with R and $(\sum w \Delta^2 \times 10^{-4})$ changing from 0.298 (18462), 0.257 (8160), 0.199 (5483), 0.198 (5124), 0.178 (4396), 0.175 (4178), 0.171 (3936), 0.172 (3914) and 0.171 (3864). The isotropic refinement was stopped when the shifts became negligible. The positions and temperature factors resulting from the last isotropic cycle are given in Table 8.1 and compared with the values assumed before commencing refinement. The temperature factors of C₃, C₄, C₅, C₆, C₁₃ and C₁₄ are higher than those of the other atoms of the molecule, the values for C₁₃ and C₁₄ being especially high. The later cycles of least squares were mainly concerned with adjustments of these atoms.

The positions from the 9th cycle were used to calculate structure factors for a difference Fourier, and this was examined for evidence of misplacement of atoms, of anisotropy and for the location of some hydrogens. The only discernible features in this

Fourier were:

- i) Some peaks and holes (not exceeding $1.2e/\text{\AA}^3$) indicating anisotropy of chlorine,
- ii) similar, but smaller, signs of anisotropy for C_5 , C_8 , C_9 , C_{14} and O_1 .
- iii) A few "peaks", presumably hydrogens, the strongest of which reached $0.6e/\text{\AA}^3$. At this stage it was decided to start using Rollett's anisotropic least-squares program. Two cycles of least-squares brought the R value down to 0.144 and $\sum W \Delta^2 \times 10^{-4}$ to 2786.

Positions of 15 hydrogens (i.e. all except those in the 2 methyl groups) were calculated using the program of R.A.Sparks, and these are quoted in Table (3.2). Twelve of them agreed with fairly well defined "peaks" in the difference Fourier, and left nothing in the difference Fourier unexplained.

The 15 hydrogens were then included in the structure factor calculations. The calculated coordinates were used, and 10 were given an isotropic B, $1.0\text{\AA}^2$ greater than that of the isotropic equivalent of the carbon atom to which it is attached. The remaining hydrogens were attached to atoms with large B factors and so were given the same value of B; their contribution is virtually negligible. In the third cycle of least-squares the hydrogens were excluded from refinement; and this gave an R value of 0.127, and $\sum W \Delta^2 \times 10^{-4}$ of 2217. The refinement had then to be stopped, and at this stage the shifts can be summarised as follows:

	$ \Delta x $	$ \Delta y $	$ \Delta z $
Mean $ \Delta x $, etc	0.00067	0.00051	0.00180
Max. $ \Delta x $, etc	0.00225(C_6)	0.00152(C_{14})	0.00722(C_{14})
Maximum Shift (C_{14}) = 0.0027 Å			

The final positions are given in Table 8.2, and the B_{ij} coefficients are given in Table 8.3.

The final positions were used for calculating the interatomic distances and angles using Dr. R.Sparks' program. The interatomic distances and their standard deviations are given in Table 8.4, and the angles and their standard deviations are given in Table 8.5.

The above positions were used for the calculations of the structure factors for Final Fourier. The observed and calculated structure factors are given in Appendix II.A, and the calculated structure factors for the unobserved reflections are given in Appendix II.B.

An agreement analysis was done on the above structure factors using Dr. G.C.Mairs' program. Part of the output of this program is given in Table 8.6, which shows the variations in R with ranges of intensity, $\sin^2\theta$ and each of the layers. The final R value is 0.122 and $\sum w\Delta^2 \times 10^{-4}$ 2071.

The final Fourier was computed using the last sets of structure factors. Sections (0-7/24) were calculated up the C axis and are given in Fig 8.1. No fresh difference Fourier was thought necessary.

T A B L E 8.1.

Atom	<u>Coordinates before the refinement</u>				<u>Coordinates after the last isotropic cycle</u>			
	<u>x</u>	<u>y</u>	<u>z</u>	B($\text{\AA}^2$)	<u>x</u>	<u>y</u>	<u>z</u>	B($\text{\AA}^2$)
C1	0.959	0.171	0.666	3	0.9607	0.1734	0.6685	5.66
C ₁	0.798	0.246	0.242	3	0.7926	0.2425	0.2493	3.11
C ₂	0.904	0.327	0.117	3	0.8959	0.3298	0.1195	3.75
C ₃	0.914	0.433	0	3	0.8938	0.4229	-0.0064	5.79
C ₄	1.033	0.500	0.0416	3	1.0252	0.4989	0.0236	7.53
C ₅	1.006	0.422	0.200	3	1.0039	0.4261	0.2197	5.71
C ₆	1.083	0.404	0.283	3	1.0905	0.3961	0.3059	7.48
C ₇	1.048	0.283	0.333	3	1.0444	0.2687	0.3321	4.59
C ₈	0.925	0.202	0.441	3	0.9231	0.1875	0.4324	3.54
C ₉	0.861	0.075	0.345	3	0.8577	0.0630	0.3501	3.27
C ₁₀	0.804	0.058	0.158	3	0.8049	0.0595	0.1617	3.96
C ₁₁	0.733	0.116	0.179	3	0.7263	0.1197	0.1637	3.94
C ₁₂	0.846	0.231	0.441	3	0.8419	0.2378	0.4384	3.62
C ₁₃	1.063	0.631	0.0625	3	1.0681	0.6339	0.0691	9.05
C ₁₄	1.087	0.483	-0.126	3	1.0999	0.4934	-0.1399	10.29
O ₁	0.929	0.006	0.333	3	0.9341	0.0155	0.3242	3.92
O ₂	0.715	0.303	0.279	3	0.7153	0.2889	0.2784	3.76

T A B L E 8.2.Final Coordinates

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
C1	0.9601	0.1735	0.6685	O ₂	0.7152	0.2893	0.2804
C ₁	0.7932	0.2433	0.2478	H ₂	0.9216	0.2829	0.0418
C ₂	0.8953	0.3278	0.1201	H ₅	0.9775	0.4619	0.3183
C ₃	0.8933	0.4224	-0.0058	H ₉	0.8025	0.0020	0.4403
C ₄	1.0285	0.4987	0.0217	H ₃₁	0.8521	0.4585	0.0591
C ₅	1.0033	0.4242	0.2149	H ₃₂	0.8787	0.3943	-0.1399
C ₆	1.0871	0.3964	0.3045	H ₆₁	1.1188	0.4380	0.4285
C ₇	1.0429	0.2674	0.3303	H ₆₂	1.1632	0.4300	0.2265
C ₈	0.92296	0.1878	0.4318	H ₇₁	1.1067	0.2565	0.3922
C ₉	0.8589	0.0633	0.3492	H ₇₂	1.0477	0.2325	0.2110
C ₁₀	0.8039	0.0595	0.1652	H ₁₀₁	0.0756	-0.0242	0.1192
C ₁₁	0.7265	0.1194	0.1646	H ₁₀₂	0.8691	0.0998	0.0661
C ₁₂	0.8413	0.2367	0.4369	H ₁₁₁	0.6534	0.0701	0.2405
C ₁₃	1.0691	0.6328	0.0610	H ₁₁₂	0.7007	0.1243	0.0343
C ₁₄	1.0978	0.4907	-0.1352	H ₁₂₆	0.7762	0.1907	0.5278
O ₁	0.9346	0.0158	0.3255	H ₁₂₇	0.8842	0.3180	0.4948

T A B L E 8.3

<u>Atom</u>	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
C1	0.02460	0.02031	0.02952	-0.01006	-0.01616	0.03186
C ₁	0.01018	0.00946	0.03049	0.00193	0.00316	0.01370
C ₂	0.01341	0.00917	0.02351	0.00064	0.00449	0.01135
C ₃	0.01606	0.01799	0.04202	0.02072	0.00164	0.01590
C ₄	0.02248	0.01237	0.06433	-0.00141	-0.00136	0.01360
C ₅	0.01057	0.01709	0.05412	0.01229	0.00429	0.00634
C ₆	0.01189	0.02228	0.08025	0.02877	-0.00196	0.00864
C ₇	0.00812	0.01302	0.05809	0.00542	0.00168	0.01144
C ₈	0.01351	0.00976	0.02158	-0.00628	0.00028	0.01354
C ₉	0.01164	0.00902	0.0236	-0.00012	-0.00111	0.01163
C ₁₀	0.01210	0.00933	0.04118	-0.00628	-0.00470	0.01110
C ₁₁	0.01034	0.01202	0.03572	-0.00059	-0.01113	0.01137
C ₁₂	0.01096	0.01281	0.02889	-0.00396	0.00121	0.01445
C ₁₃	0.02676	0.01022	0.11570	0.00950	0.03151	0.01458
C ₁₄	0.02417	0.02692	0.11295	-0.00738	0.04420	0.01934
O ₁	0.01418	0.01061	0.03452	-0.00112	0.00385	0.01669
O ₂	0.00951	0.01339	0.03907	-0.00139	-0.00133	0.01618

T A B L E 8.4

<u>Bond</u>	<u>Bond</u>	<u>σ ($\text{\AA}$)</u>	<u>Bond</u>	<u>Bond</u>	<u>σ ($\text{\AA}$)</u>
	<u>length</u>			<u>length</u>	
	<u>($\text{\AA}$)</u>			<u>($\text{\AA}$)</u>	
C1-C ₈	1.788	0.016	C ₄ -C ₁₄	1.476	0.043
C ₁ -C ₂	1.538	0.029	C ₅ -C ₆	1.466	0.030
C ₁ -C ₁₁	1.528	0.030	C ₆ -C ₇	1.500	0.040
C ₁ -C ₁₂	1.506	0.022	C ₇ -C ₈	1.563	0.032
C ₁ -O ₂	1.442	0.017	C ₈ -C ₉	1.532	0.029
C ₂ -C ₃	1.542	0.027	C ₈ -C ₁₂	1.499	0.020
C ₂ -C ₅	1.506	0.037	C ₉ -C ₁₀	1.484	0.023
C ₃ -C ₄	1.552	0.047	C ₉ -O ₁	1.421	0.017
C ₄ -C ₅	1.621	0.035	C ₁₀ -C ₁₁	1.565	0.021
C ₄ -C ₁₃	1.587	0.042			

T A B L E 8.5

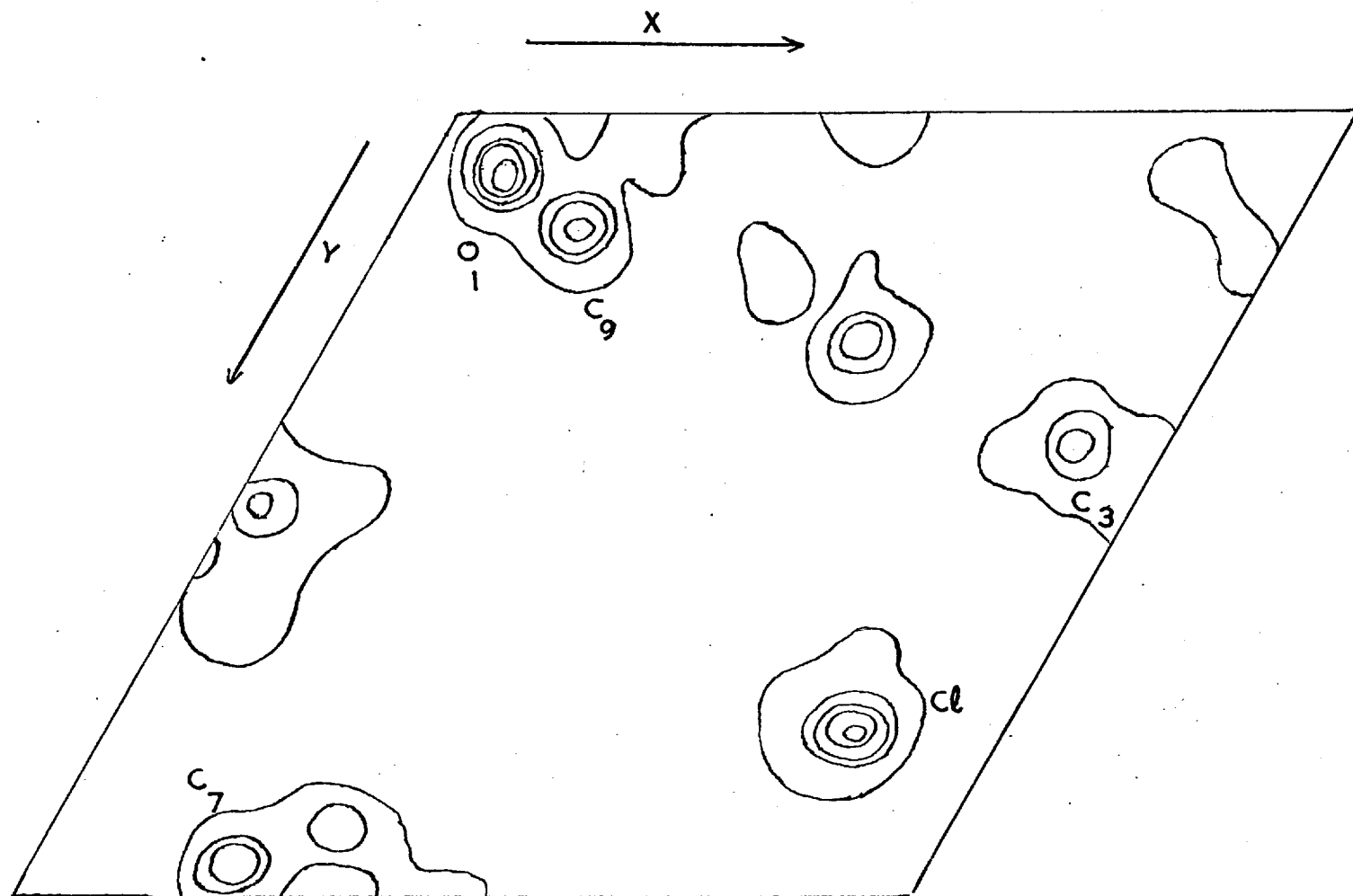
	<u>Angle</u> [°]	<u>σ</u> [°]		<u>Angle</u> [°]	<u>σ</u> [°]
C ₂ -C ₁ -C ₁₁	111.6	1.3	C ₂ -C ₅ -C ₆	119.5	2.2
C ₂ -C ₁ -C ₁₂	109.2	1.7	C ₄ -C ₅ -C ₆	124.5	2.4
C ₂ -C ₁ -O ₂	109.8	1.3	C ₅ -C ₆ -C ₇	114.8	2.7
C ₁₁ -C ₁ -C ₁₂	108.5	1.5	C ₆ -C ₇ -C ₈	120.2	1.5
C ₁₁ -C ₁ -O ₂	110.9	1.6	C1 -C ₈ -C ₇	105.6	1.3
C ₁₂ -C ₁ -O ₂	106.7	1.1	C1 -C ₈ -C ₉	106.4	1.13
C ₁ -C ₂ -C ₃	124.3	1.5	C1 -C ₈ -C ₁₂	108.2	1.0
C ₁ -C ₂ -C ₅	117.1	1.5	C ₇ -C ₈ -C ₉	111.6	1.3
C ₃ -C ₂ -C ₅	88.3	1.8	C ₇ -C ₈ -C ₁₂	114.9	1.6
C ₂ -C ₃ -C ₄	88.4	1.7	C ₉ -C ₈ -C ₁₂	109.7	1.7
C ₃ -C ₄ -C ₅	83.9	2.1	C ₈ -C ₉ -C ₁₀	111.8	1.4
C ₃ -C ₄ -C ₁₃	112.3	2.0	C ₈ -C ₉ -O ₁	112.5	1.6
C ₃ -C ₄ -C ₁₄	113.9	2.7	C ₁₀ -C ₉ -O ₁	108.4	1.2
C ₅ -C ₄ -C ₁₃	111.9	2.1	C ₉ -C ₁₀ -C ₁₁	114.4	1.3
C ₅ -C ₄ -C ₁₄	123.0	2.0	C ₁ -C ₁₁ -C ₁₀	111.3	1.7
C ₁₃ -C ₄ -C ₁₄	109.5	3.0	C ₁ -C ₁₂ -C ₈	114.4	1.3
C ₂ -C ₅ -C ₄	87.1	1.8			

T A B L E 8.6

$r_{\text{obs.}} (\text{\AA})$	R(%)	$\sin^2 \theta$	R(%)	Layer	R(%)
2.50	32.94	0.0-0.1	11.70	hk0	10.99
3.75	18.33	0.1-0.2	10.58	hk1	10.59
6.25	13.14	0.2-0.3	9.21	hk2	11.98
8.75	12.32	0.3-0.4	10.12	hk3	14.00
12.50	10.02	0.4-0.5	12.47	hk4	10.93
17.50	6.95	0.5-0.6	13.25	hk5	12.33
22.50	8.17	0.6-0.7	14.62	hk6	19.22
27.50	15.13	0.7-0.8	18.14		
32.50	9.67	0.8-0.9	23.38		
37.50	9.16	0.9-1.0	38.98		
42.50	11.90				
47.50	10.64				
52.50	8.04				
57.50	6.14				

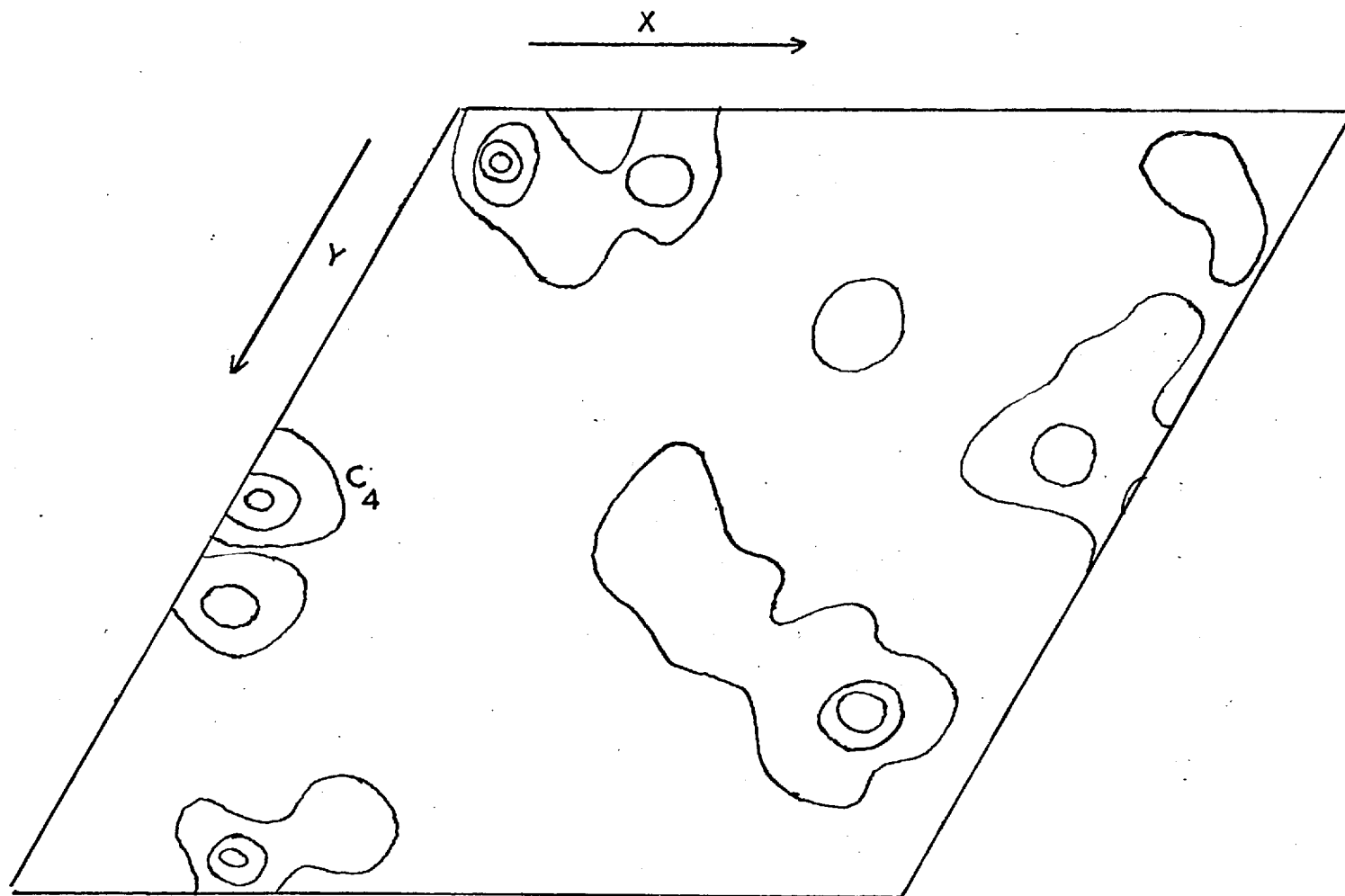
Fig. 8.1

C C final 3-D Fourier. Sections $z = 0/24$ to $7/24$. Contours at $5e/\text{\AA}^{-3}$ for C1 and $2e/\text{\AA}^{-3}$ for C and O starting at $0e/\text{\AA}^{-3}$.

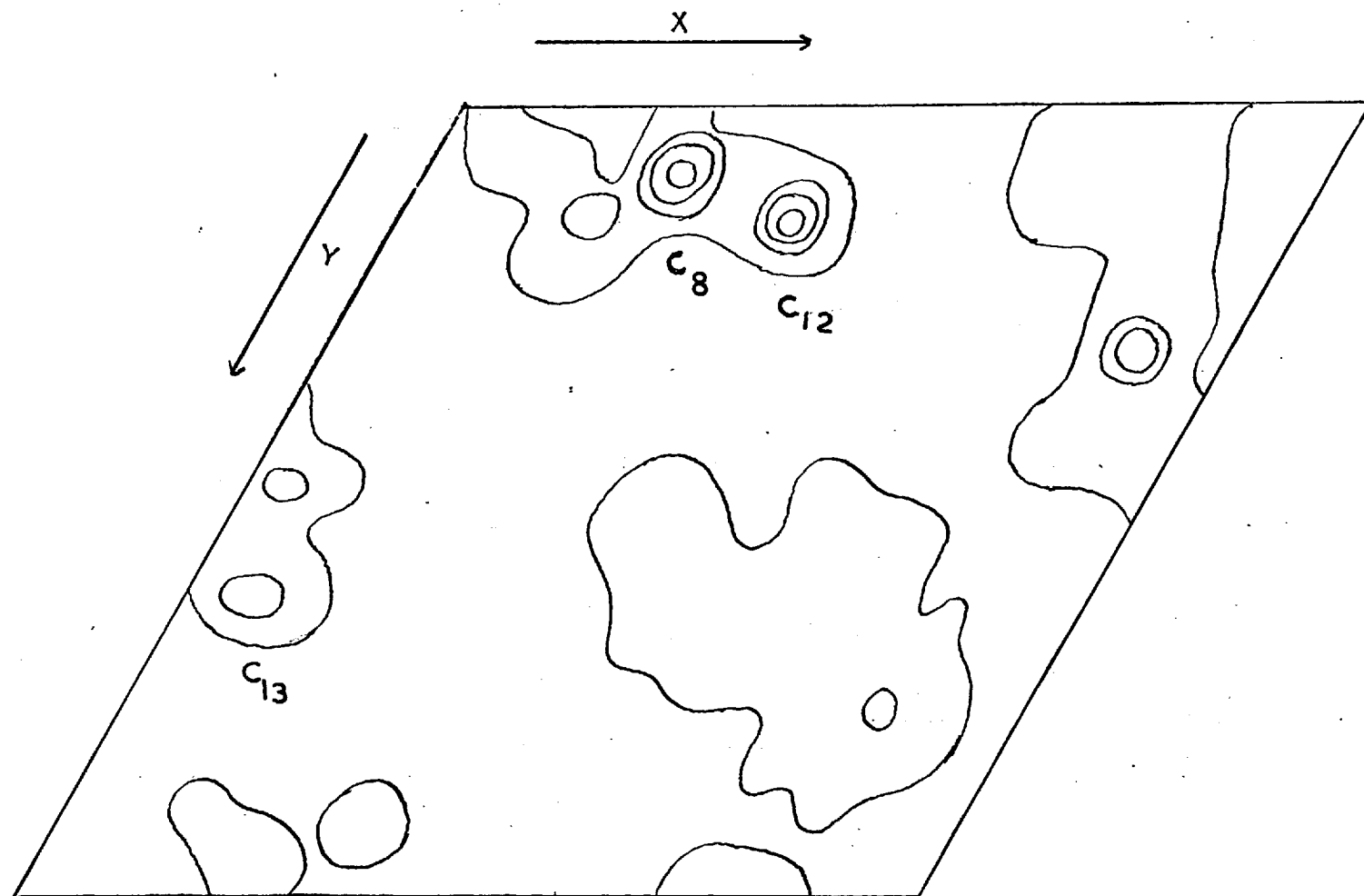


Section $Z = 0/24$

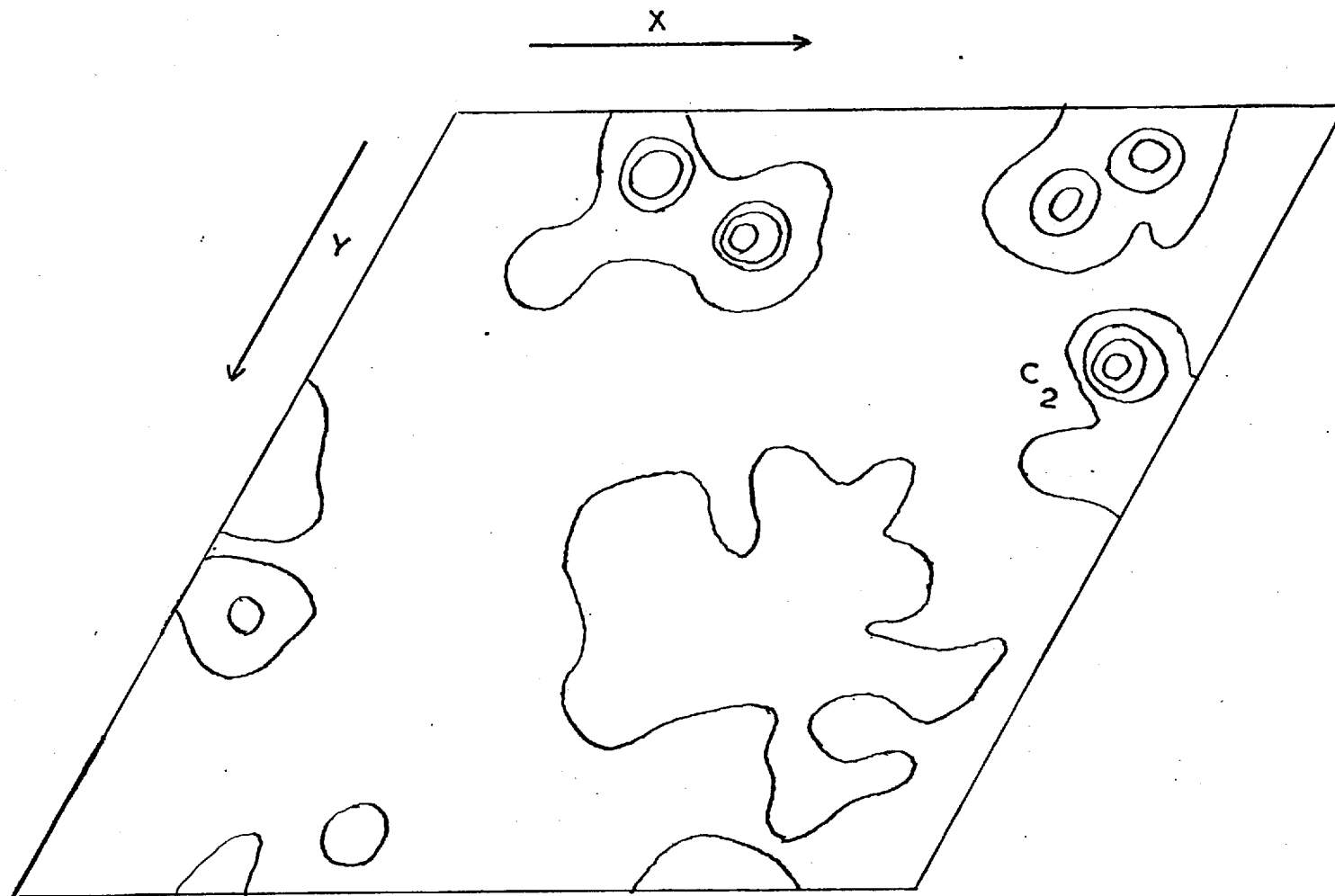




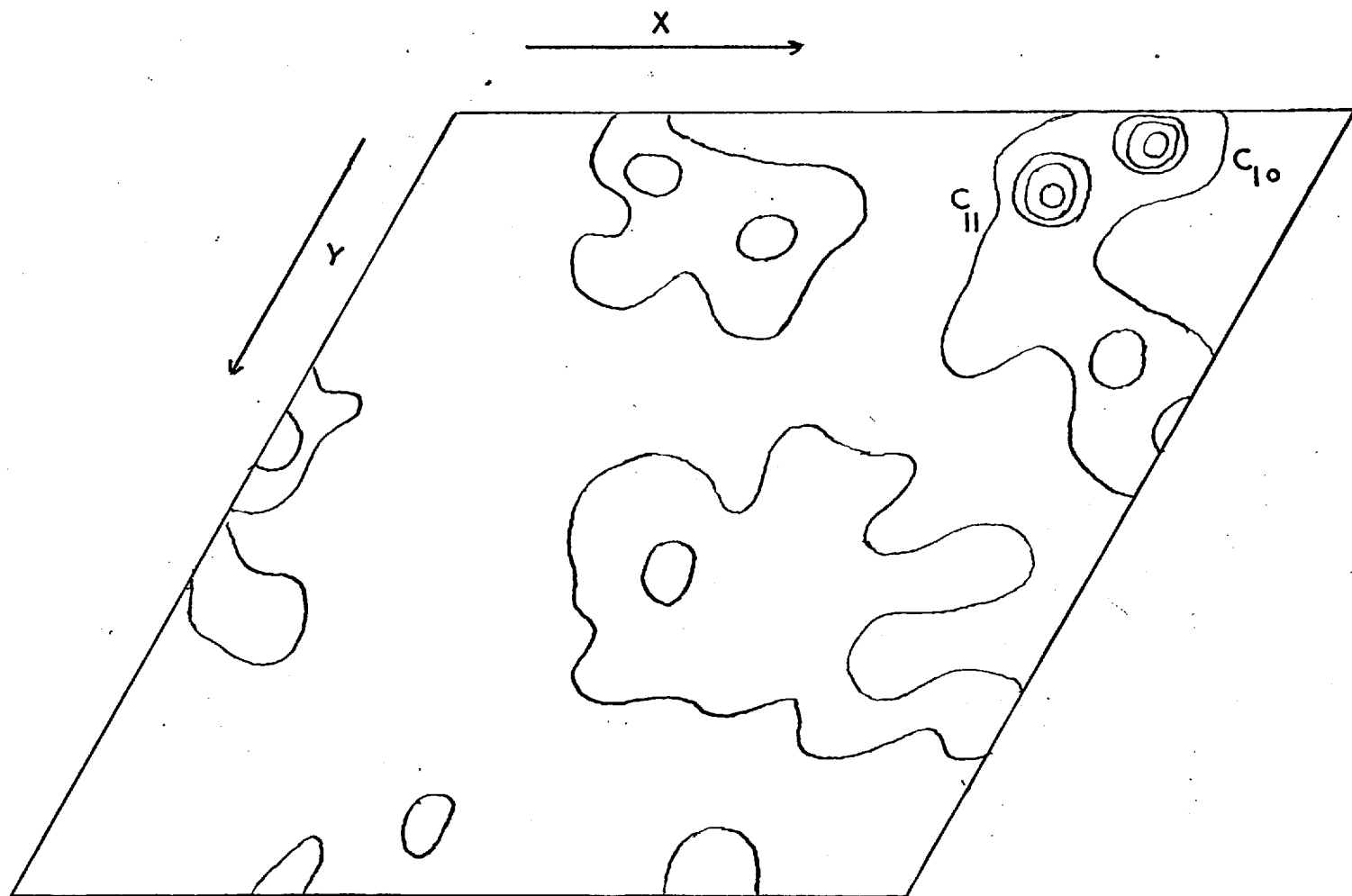
Section $Z = 1/24$



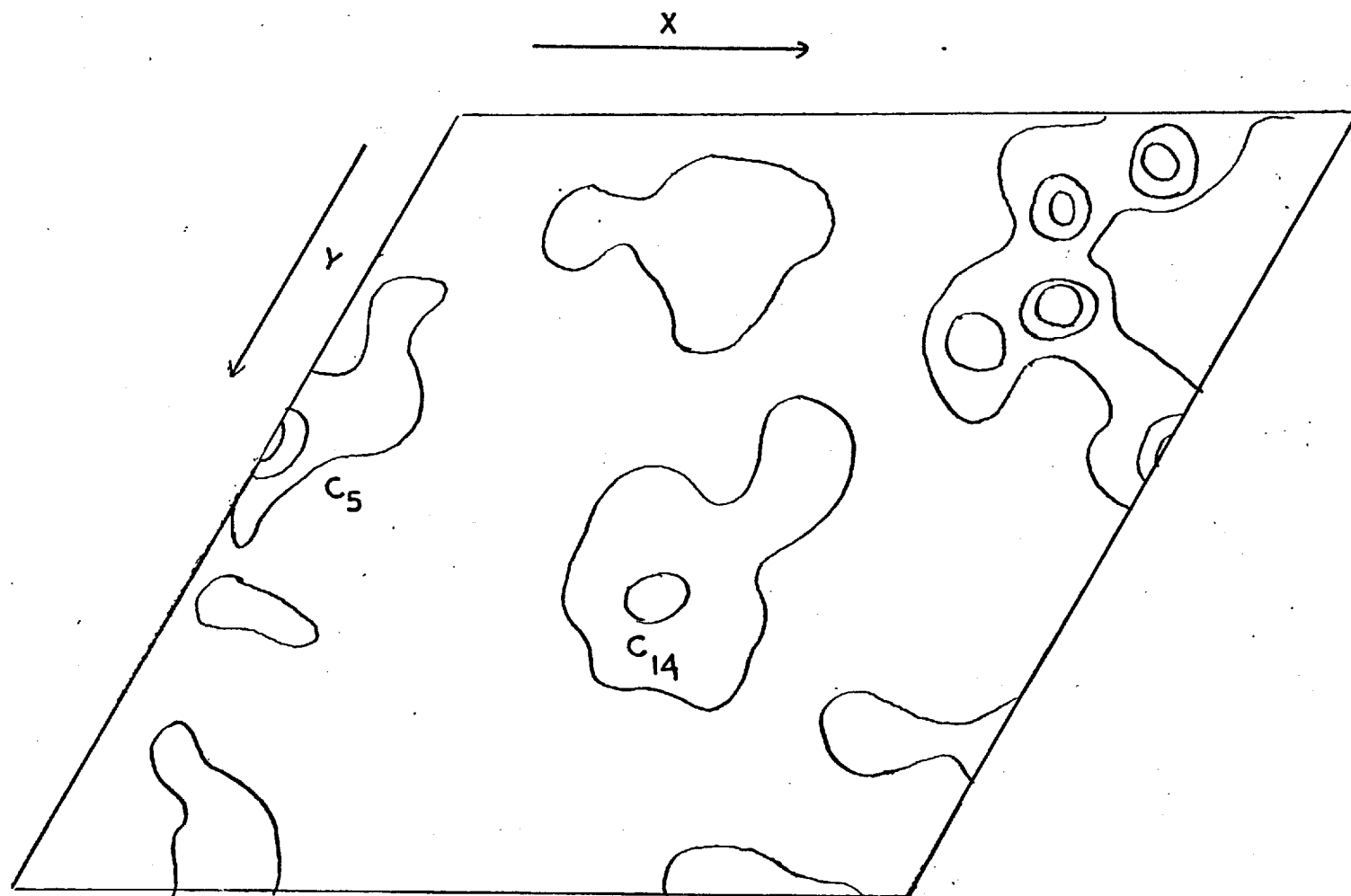
Section $Z = 2/24$



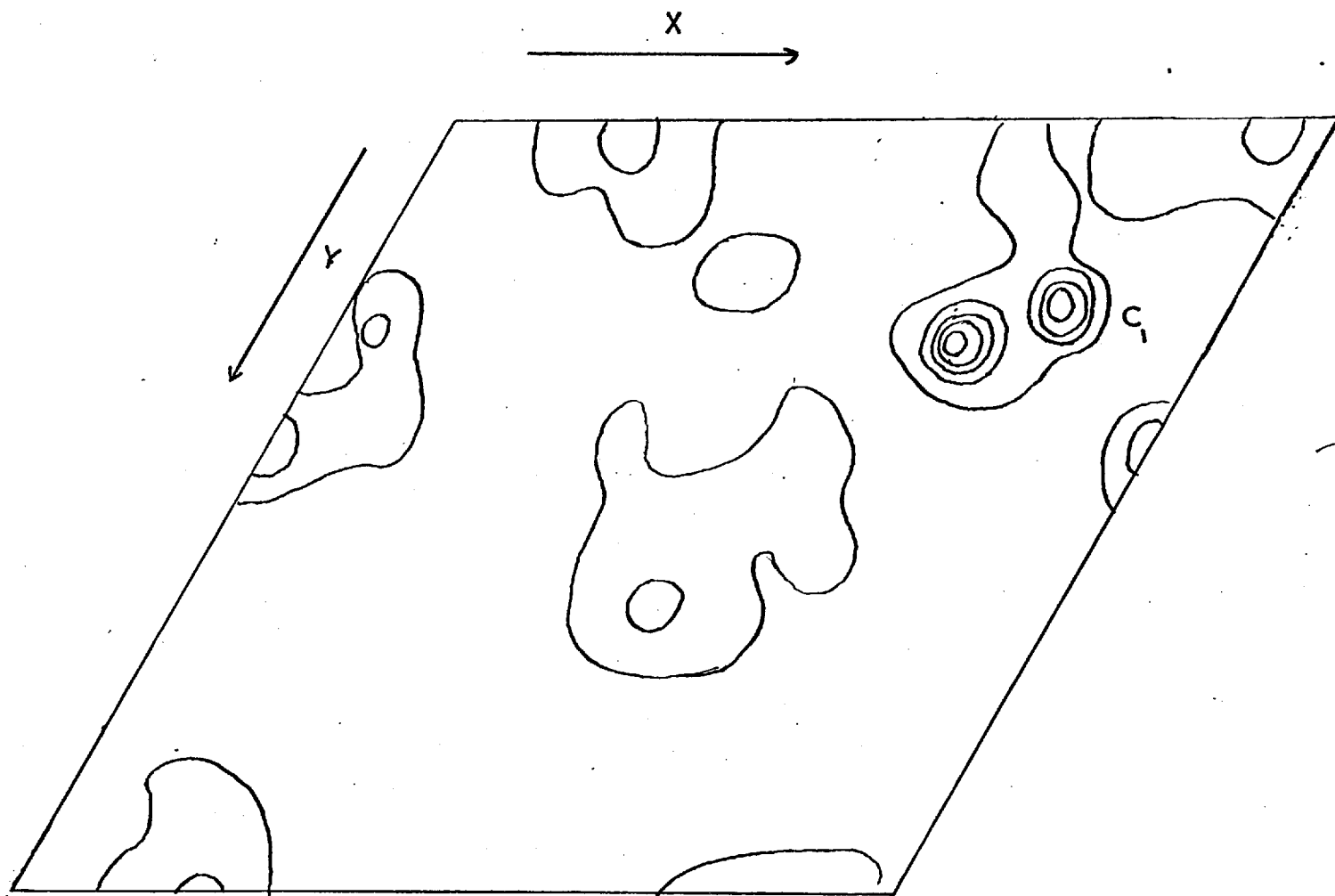
Section $Z = 3/24$



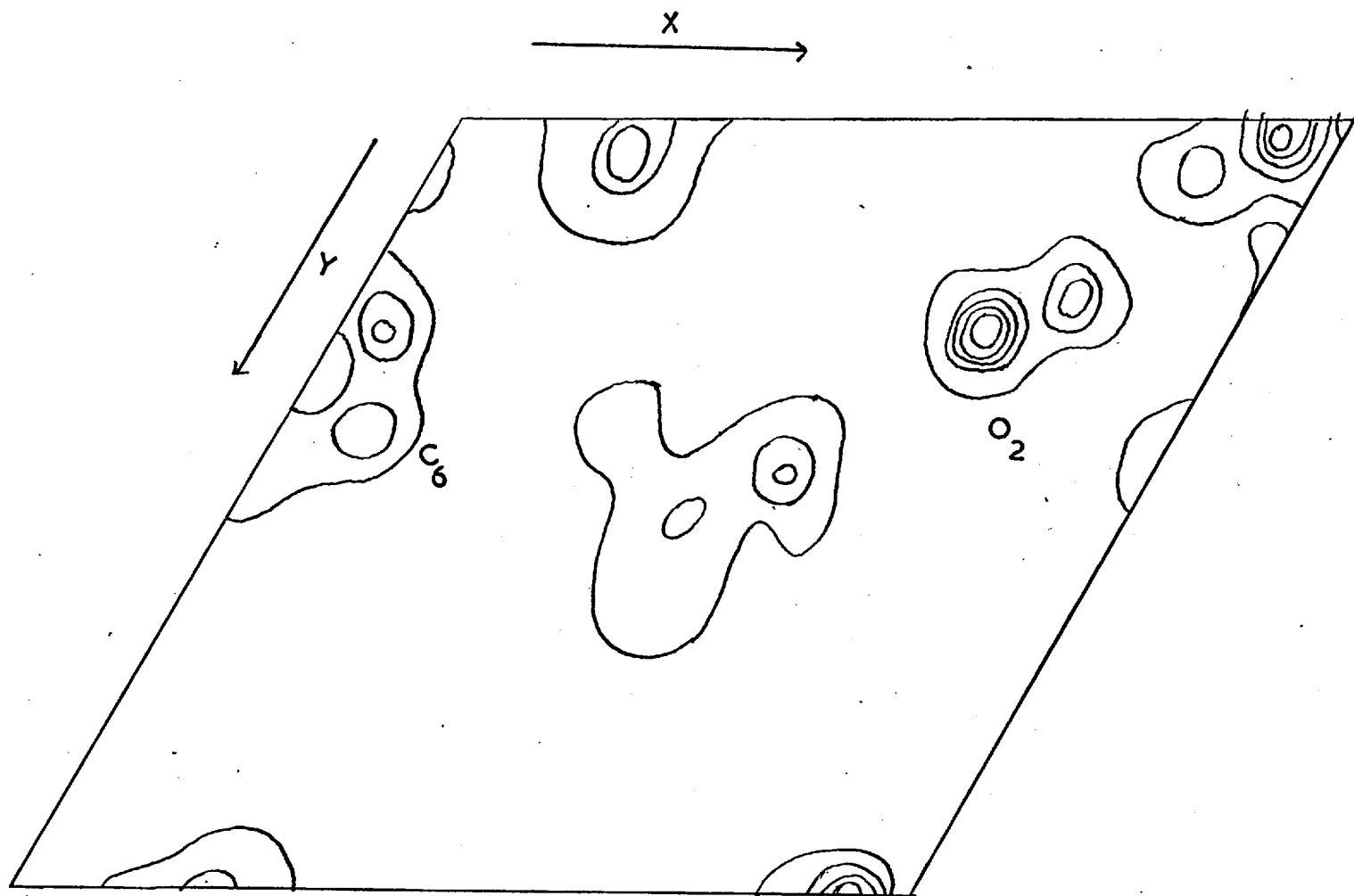
Section Z = 4/24



Section $Z = 5/24$



Section $Z = 6/24$



Section $Z = 7/24$

C H A P T E R 9

Discussion of the structure of Caryophyllene Chlorohydrin (CC)

Constitution and Stereochemistry:

The constitution differs radically from anything proposed by the organic chemists (7.9) upto the start of our work. But similar conclusions were reached independently by Greenwood et al⁽⁶¹⁾ of this department by chemical and N.M.R. studies, and these have been submitted for publication along with our paper⁽⁶²⁾, which also describes the stereochemistry (see Fig 7.14).

Apart from its substituents this bears a remarkable resemblance to the structure and stereochemistry of the caryophyllene halides determined by 2-D Fourier refinement by Robertson and Todd⁽¹⁰⁾, Fig (7.4). The present study in 3-D is of course much more accurate, but it is especially interesting to note that even the details of the buckling of the cyclobutane ring are reproduced. This is discussed in more detail later.

The preparations of these two compounds from caryophyllene involve two quite different cyclisations, though neither interferes with the cyclobutane ring. There was, therefore, no need for this close correspondence, but it certainly speaks well of Robertson and Todd's work.

This stereochemistry confirms Barton's formula for the oxidoketone (7.7).

An attempt is to be made to find the absolute configuration as soon as we can get access to a source of Cr radiation.

Crystal Structure

If Barton and Nickon's absolute configuration is accepted, Fig (9.1) has to be drawn as shown and this fixes the space group as $P3_1$. The figure also shows how the molecules are linked via hydrogen bonds in spirals around two screws. There is a large "cylindrical" cavity (6-7Å in diameter) around the third screw. There is nothing in this hole in our map, and the B factors show that the free ends of the molecules i.e. C₃, C₅, C₆, C₁₃ and C₁₄ are oscillating vigorously mainly parallel to c. The holes are only big enough to accommodate very small chains, and only if these can bend to follow the contours of the cavity. This hole probably explains the difficulties met in growing the crystals.

Accuracy

The final standard deviations are given in table (8.4, 8.5), and are generally of the order 0.017-0.03Å in bond lengths, and 1.0-2.0° for the angles, but the accuracy in the cyclobutane ring and the two methyls is rather lower (i.e. 0.047Å and 3.0°), probably due to their large thermal motion.

Diagrams (9.2) and (9.3) show the bond lengths and angles of C C.

1) Although there is some scatter in the magnitude of the bond lengths, none can be regarded as significantly different from experimental values. The bond C₄-C₅ is the only notably large

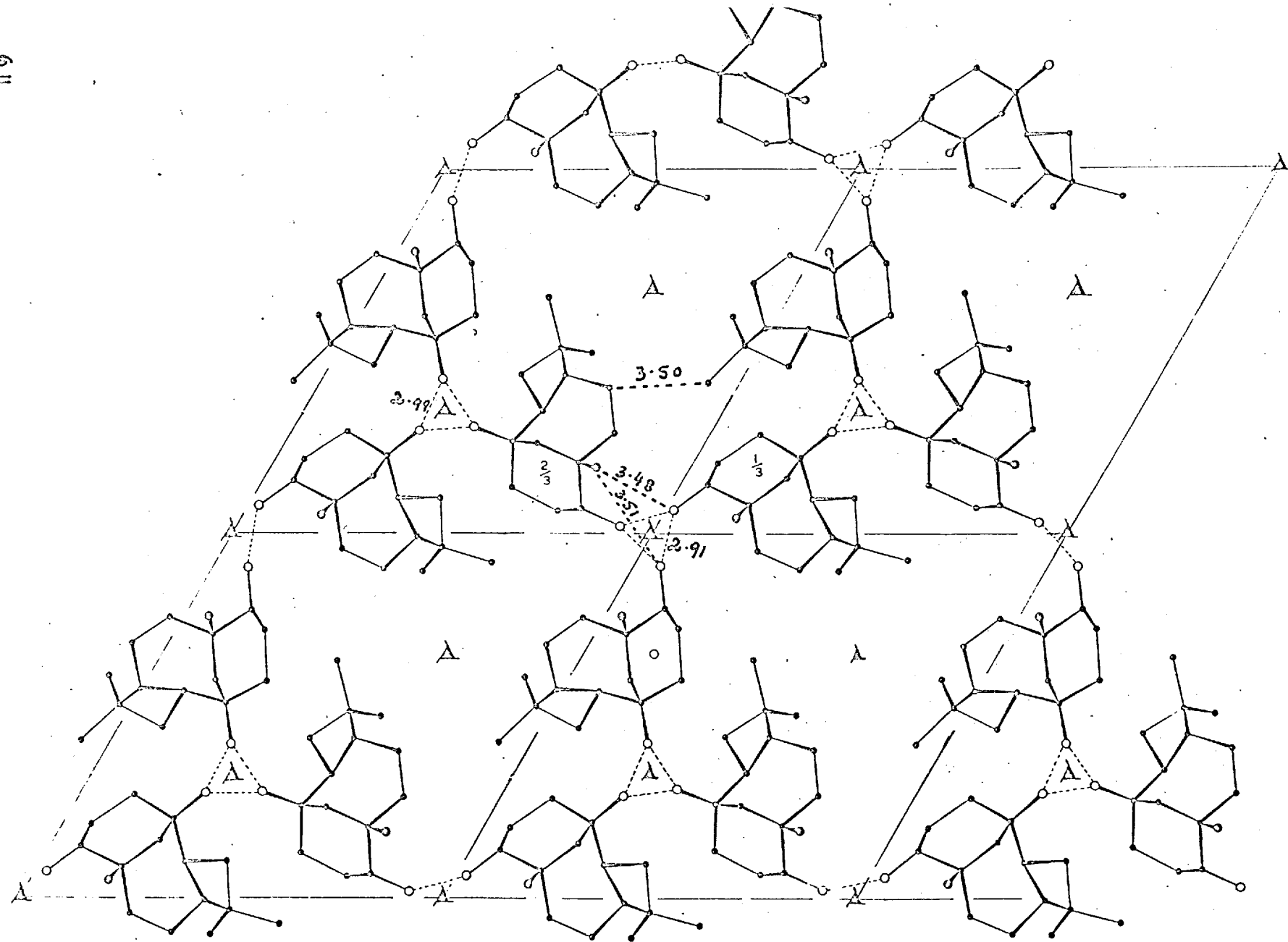


FIG. 9.1

one ($1.62\text{\AA}$). It is conceivable that it is under tension from non-bonded repulsion between C_6 and methyl group, C_{14} , (at $3.34\text{\AA}$), but the present accuracy ($\sigma = 0.035\text{\AA}$) does not justify us in regarding it as significantly long.

2) A few angles depart significantly from 109.5° . These are mainly associated with the strain of the cyclobutane ring.

a) All four angles in this ring are less than 90° (average deficit = 3.05°), therefore, it is not planar.

b) The angles at both C_2 , C_5 are severely splayed and roughly the same deformation occurs at each atom.

c) One angle at C_4 ($C_{14}-C_4-C_5$) is splayed to 123.0° while all the others outside the cyclobutane ring are relatively undistorted. Fig (9.4) shows the non-bonded repulsion between C_6 and C_{14} , and suggests an explanation of both this enlarged-angle at C_4 , and the "stretched" bond C_{4-5} .

d) One other largish ring angle at C_7 is probably due to reflected strain from the fused cyclobutane ring.

3) Intermolecular distances:

Only one C-C contact is less than $3.8\text{\AA}$, namely C_6-C_{13} ($3.5\text{\AA}$). There are in addition two hydrogen bonds per molecule linking OH'S at ($2.91\text{\AA}$) and ($2.99\text{\AA}$). Apart from these the chlorine has two shortish contacts with OH'S, at 3.48 and $3.51\text{\AA}$. These are all shown in Fig (9.1). The very loose packing is mainly controlled by the O-O hydrogen bonding.

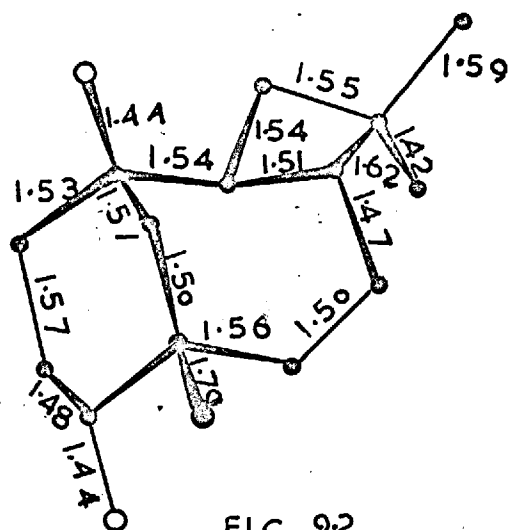


FIG. 9.2

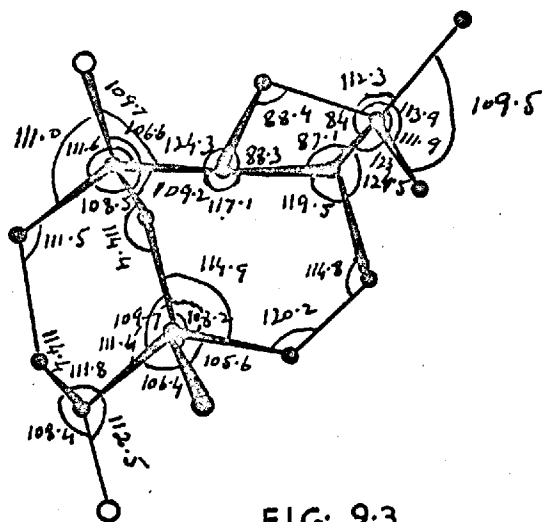


FIG. 9.3

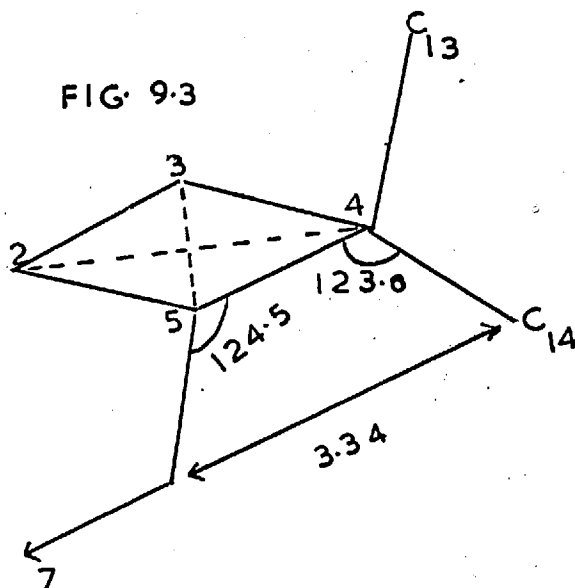


FIG. 9.4

Appendix I.A

B I T observed and calculated structure
factors.

Layout of data

* k l

h

F_{OA}

F_{OB}

F_{CA}

F_{CB}

* O -7				* I 4				
7 -984	0 -227			0 0 -4121	830	-3724	750	
* O -8				I -2409	4160	-1856	3205	
2 -447	0 -2792			0 2 -1895	4466	-1603	3780	
3 -626	0 -799			0 3 -980	-88	-1010	-91	
5 -1900	0 -1631			0 4 -503	188	-506	189	
6 1408	0 1616			0 5 -1017	154	-1046	159	
7 447	0 845			0 * I 5				
* O -9				0 0 -2012	976	-1737	842	
3 1610	0 1621			0 I -175	-991	-290	-1639	
4 1006	0 834			0 2 726	993	818	1119	
5 -1654	0 -995			0 3 81	463	80	460	
7 -939	0 -1155			0 4 766	-653	834	-711	
* O -10				* I 6				
4 -537	0 -681			0 0 1160	3313	942	2691	
7 -581	0 -356			0 I 961	-3330	858	-2972	
* O -11				2 823	-1663	716	-1447	
5 335	0 217			* I 7				
* I 0				0 0 -1768	1217	-1399	963	
I 4999	-5756	6066	-6085	I 665	927	455	635	
2 -6289	13670	-5810	12629	2 -1084	155	-1274	182	
3 3350	-2271	2144	-1453	* I 8				
4 -5922	-1477	-4241	-1057	0 1311	-1811	1140	-1575	
5 -718	1263	-618	1087	I -197	1440	-190	1390	
6 -1311	1282	-1396	1365	* I 9				
7 468	-39	236	-20	0 0 -9	-872	-8	-800	
* I I				* I -1				
0 -223	3929	-254	4487	I 3410	-3062	5922	-5318	
I -7589	-3404	-7270	-3261	2 4157	-4560	6620	-7262	
2 42	-737	11	-195	3 1465	-6523	1572	-6998	
3 -1983	7755	-1238	4841	4 3793	-237	3763	-235	
4 -2610	712	-1751	478	5 1297	-604	1842	-858	
5 -357	371	-444	461	6 1452	-1226	1577	-1332	
7 -378	-314	-179	-149	7 1036	-174	831	-139	
* I 2				* I -2				
0 5432	-4011	5817	-4295	I -1726	4318	-1693	4235	
I -1812	7498	-1269	5253	2 -4545	-2809	-5875	-3631	
2 5174	-4269	4275	-3527	3 -907	436	-1428	687	
3 2499	1148	2342	1076	4 -1203	347	-2154	622	
4 2874	-2054	1905	-1362	5 -771	-681	-1037	-917	
5 1421	-2007	1883	-2659	7 -153	-676	-155	-688	
6 564	-215	520	-198	* I -3				
* I 3				I -4806	4352	-3949	3577	
0 4796	-6352	4148	-5493	2 -2632	-3306	-3355	-4214	
I 943	2844	734	2213	3 -1171	1200	-1827	1873	
2 655	-2231	712	-2428	4 -773	493	-1584	1011	
3 -1479	-1937	-1562	-2045	5 -389	-104	-1337	-359	
4 94	619	151	992	6 -184	944	-178	909	
5 -706	980	-603	838	7 -227	679	-398	1191	

*	3	2				*	3	-2					
2		2478	766	2742	848	6		1302	1621	1515	1887		
3		822	1983	733	1768	7		190	1170	88	541		
4		944	639	988	669	*	3	-3					
5		101	753	87	646	1		-926	-3455	-773	-2884		
6		-362	891	-372	915	2		-3531	-7629	-4162	-8992		
*	3	3				3		57	-758	46	-618		
0		281	-1449	299	-1542	4		-1557	-968	-1857	-1154		
1		1870	7183	1597	6135	5		-1984	-1635	-2784	-2294		
2		-4219	2008	-3407	1621	6		-641	-943	-786	-1156		
3		2266	-955	1645	-693	7		-710	-1031	-744	-1080		
4		441	3122	337	2388	*	3	-4					
5		51	-512	40	-404	1		497	-302	615	-374		
*	3	4				2		-1656	2604	-1392	2189		
0		470	-5211	398	-4409	3		314	3069	328	3207		
1		-455	-1118	-509	-1250	4		124	-1538	174	-2159		
2		23	-402	31	-533	5		1274	25	1811	36		
3		-386	-3421	-333	-2957	6		287	1080	398	1500		
4		-1066	-886	-997	-829	7		548	-253	625	-288		
*	3	5				*	3	-5					
0		-1493	1447	-1144	1109	1		996	-2587	836	-2171		
1		141	-1446	150	-1536	2		728	4752	533	3483		
2		1539	1683	1518	1661	3		-2876	-3598	-2628	-3288		
3		470	3	832	6	4		1181	847	1407	1008		
*	3	6				5		-387	1769	-393	1798		
0		-475	4581	-485	4681	6		522	-807	694	-1073		
2		-104	663	-110	706	7		-513	620	-370	448		
3		-197	895	-290	1314	*	3	-6					
*	3	7				1		-8	-671	-8	-651		
0		-71	-1787	-69	-1730	2		-132	817	-157	976		
1		235	1457	218	1347	3		-763	-3929	-728	-3749		
2		154	-1400	161	-1469	4		-688	1651	-575	1379		
*	3	8				5		-535	-540	-209	-211		
0		188	-1102	231	-1356	6		-217	-312	-74	-106		
*	3	9				7		-236	-298	-178	-225		
0		481	-183	351	-134	*	3	-7					
*	3	-1				1		-388	2790	-277	1987		
1		-2061	6006	-2562	7467	2		507	-1338	441	-1165		
2		1749	5591	1801	5760	3		-95	1159	-58	711		
3		-1585	1762	-852	948	3		-95	1159	-58	711		
4		-1440	7874	-1132	6190	4		-700	626	-871	778		
5		1244	1776	1337	1909	5		802	-2372	668	-1977		
6		-148	-1018	-110	-754	6		-243	-601	-278	-690		
7		462	486	340	357	7		279	200	488	509		
*	3	-2				*	3	-8					
1		2113	6029	1931	6334	2		1541	-1113	1249	-902		
2		2467	-5680	3059	-7042	3		568	2896	505	2572		
3		2050	167	3219	262	6		-657	2043	-491	1527		
4		2779	584	2582	542	7		804	-744	785	-727		
5		115	-774	135	-912								

*	3	-9			
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1	-347	155	-432	194		3	-390	-830	-370	-788	
2	-768	-500	-657	-428		4	-681	429	-696	438	
3	-309	-438	-459	-651		5	-760	-28	-924	-34	
4	-349	378	-330	357		* 24	-5				
* 23	-7					1	109	-270	209	-517	
2	329	-303	347	-319		2	1008	-429	1063	-453	
3	367	-256	500	-349		3	840	125	748	111	
5	-105	-640	-115	-701		4	59	-398	57	-386	
* 24	0					5	202	-802	232	-923	
0	-1182	245	-1058	219		* 24	-6				
1	-1527	219	-1591	228		1	-226	360	-308	491	
2	-1133	259	-1349	308		3	-56	421	-65	491	
4	-425	9	-661	14		* 24	-7				
* 24	1					2	-70	374	-90	484	
0	715	-18	780	-20		3	-594	107	-704	127	
1	960	47	1060	51		* 25	0				
3	497	132	631	168		1	-38	-916	-35	-856	
4	537	275	809	414		4	439	-593	568	-769	
* 24	2					* 25	1				
0	913	-422	836	-387		0	939	16	963	16	
1	1608	-389	1469	-355		1	474	-409	581	-502	
2	567	130	581	133		2	1001	-445	1117	-496	
* 24	3					4	368	-212	438	-252	
0	-1343	343	-1378	352							

* 27	-1			
I	-330	-635	-432	-831
2	-372	-663	-329	-587
3	-244	-528	-341	-737
* 27	-2			
I	711	579	798	650
* 27	-3			
I	-176	624	-186	659
2	79	913	93	1071
3	118	841	131	931
4	-128	521	-211	862
* 27	-4			
I	-601	-751	-574	-717
2	-307	-571	-449	-836
4	-37	-603	-60	-981
* 27	-5			
I	226	-216	371	-354
3	-129	-405	-198	-619
* 28	0			
0	699	235	793	267
I	870	52	1073	65
2	564	272	536	258
3	319	207	694	450
* 28	1			
0	-32	424	-27	355
I	-759	35	-322	15
2	-689	78	-973	111
* 28	2			
0	-824	-615	-995	-742
* 28	3			
0	178	94	465	245
* 28	-1			
I	-725	230	-843	267
2	287	-372	291	-377
3	116	362	150	458
* 28	-2			
3	-661	-497	-800	-602
* 28	-3			
I	396	-73	766	-141
* 28	-4			
I	276	460	400	667
* 29	1			
* 4	2			
5	367	479	342	447
6	-692	-29	-1177	-50
* 4	3			
0	-8254	-2443	-8283	-2451
I	-6138	-4485	-5292	-3867
2	3855	-4411	3097	-3544
3	-3513	-1963	-2954	-1651
4	173	-3349	202	-3913
5	-805	-21	-820	-22
* 29	1			
0	-391	545	-498	692
* 29	-1			
I	316	112	563	199

Appendix I.B.

B I T structure factors for unobserved reflections.

Layout of data

* k l

h F_{OA} F_{OB} F_{CA} F_{CB}

N.B. F_{OA} and F_{OB} correspond to that of the weakest spot on the wedge.

*	I	-11				*	2	-13				
6		-79	-332	-41	-173	4		111	-37	78	-26	
7		-21	102	-80	382	5		-52	23	-113	50	
*	I	-10				6		116	146	238	300	
I		-325	68	-163	34	7		47	27	225	128	
2		24	328	66	902	*	2	-12				
4		285	136	254	121	2		-179	-63	-140	-49	
7		-99	-50	-220	-111	3		-268	-9	-378	-13	
*	I	-9				4		214	-94	349	-153	
3		-302	255	-53	45	5		75	-52	184	-127	
6		170	311	180	330	6		-258	-127	-677	-332	
7		30	103	60	204	7		49	-74	166	-254	
*	I	-7				*	2	-11				
7		88	-9	561	-55	I		-212	-154	-173	-126	
*	I	-4				2		-172	-223	-39	-51	
6		-11	110	-80	837	3		-235	-260	-137	-151	
*	I	-2				4		-173	229	-228	302	
6		-173	98	-477	270	6		-297	154	-521	270	
*	I	I				7		-11	-104	-24	-226	
6		-254	-214	-489	-411	*	2	-10				
*	I	2				I		-315	104	-717	237	
7		95	-50	350	-183	2		291	153	385	202	
*	I	3				7		89	-65	76	-55	
6		-344	97	-310	88	*	2	-9				
7		67	72	34	36	I		-270	-248	-402	-368	
*	I	4				6		-276	222	-192	155	
6		-241	-224	-99	-92	7		16	106	74	481	
7		-29	73	-140	352	*	2	-8				
*	I	5				2		-21	328	-33	515	
5		-79	73	-356	329	3		351	117	505	169	
6		217	-163	502	-378	*	2	-7				
*	I	6				7		65	-60	62	-57	
3		278	280	744	750	*	2	-3				
5		87	28	230	73	5		-38	-4	-161	-16	
*	I	7				7		19	-60	213	-681	
3		-162	332	-253	518	*	2	2				
4		-200	150	-530	397	7		107	-5	184	-9	
*	I	8				*	2	3				
2		-156	275	-24	42	6		-234	266	-101	114	
3		76	-294	110	-423	7		-58	79	-91	123	
4		-94	123	-167	220	*	2	4				
*	I	9				6		-48	-325	-67	-459	
I		-40	-320	-20	-156	7		57	-50	293	-253	
2		59	246	130	540	*	2	5				
3		177	-5	347	-10	4		270	-164	626	-381	
*	I	10				5		101	-37	342	-125	
0		-111	282	-105	266	6		268	-18	192	-13	
I		-95	-224	-152	-358	*	2	6				
*	I	11				3		-392	49	-144	18	
0		-80	189	-287	678	5		-65	64	-453	446	

*	2	7				*	3	1				
	3	-230	286	-466	579		6	325	-83	522	-133	
	4	242	20	714	59	*	3	2				
*	2	8					7	71	81	280	321	
	3	2	-300	2	-311	*	3	3				
	4	-49	-143	-117	-339		6	273	-225	684	-564	
*	2	9					7	-97	13	-655	87	
	1	-230	-226	-426	-417	*	3	4				
	2	-191	-161	-86	-73		5	-78	-87	-575	-640	
	3	172	27	112	18		6	-308	-97	-369	-116	
*	2	10					7	39	-65	210	-348	
	0	215	-214	45	-45	*	3	5				
	1	94	221	59	138		4	94	302	241	768	
	2	-60	56	-217	202		5	67	84	172	215	
*	2	11					6	41	259	92	575	
	0	-202	-14	-349	-24	*	3	6				
*	3	-13					1	125	321	146	374	
	4	-38	-94	-115	-288		5	-62	-63	-55	-55	
	5	16	-51	66	-212	*	3	7				
	6	118	136	204	235		3	157	331	89	188	
	7	2	-51	9	-267		4	-238	-51	-131	-28	
*	3	-12				*	3	8				
	2	41	-182	136	-598		1	-218	290	-394	524	
	3	-111	238	-187	400		2	-289	-121	-287	-120	
	4	-39	231	-119	695		3	-289	-80	-300	-83	
	5	-3	-92	-16	-446		4	-44	139	-38	122	
	6	256	125	188	92	*	3	9				
	7	-81	-28	-341	-117		1	-240	211	-142	125	
*	3	-11					2	123	214	267	462	
	1	64	251	94	368		3	147	-73	250	-123	
	2	-194	199	-299	306	*	3	10				
	3	-291	-184	-253	-160		0	-99	284	-150	431	
	4	243	153	441	278		1	-128	-199	-206	-320	
	5	30	-103	115	-393	*	3	11				
	6	318	-106	226	-75		0	87	179	123	253	
	7	38	94	195	481	*	4	-13				
*	3	-10					4	61	-17	118	-33	
	1	172	-280	188	-307		5	-40	31	-254	196	
	2	-194	265	-541	738		6	137	-97	318	-225	
	4	199	245	261	322		7	44	-6	341	-44	
	7	-108	-24	-243	-54	*	4	-12				
*	3	-9					2	139	-114	398	-327	
	5	117	6	489	25		3	-258	26	-671	67	
	6	340	-98	498	-144		4	226	30	596	78	
*	3	-8					5	-30	83	-216	606	
	1	163	325	323	646		6	-252	-126	-239	-119	
	4	88	-280	21	-66		7	-24	82	-58	194	
	5	93	54	563	325	*	4	-11				
*	3	1					1	-166	195	-261	308	
	5	-43	-84	-178	-349		2	209	-179	741	-633	

*	4	-11				*	5	-13				
	3	-289	181	-849	531		6	-14	154	-25	281	
	4	38	-282	32	-240		7	9	-30	66	-218	
	6	-297	-148	-172	-86	*	5	-12				
	7	-81	61	-69	52		2	-13	-170	-36	-458	
*	4	-10					3	241	67	123	34	
	1	-324	-55	-118	-20		4	-138	177	-378	484	
	2	244	-216	612	-541		5	51	-73	261	-374	
	6	-96	-344	-105	-375		6	17	274	18	289	
*	4	-9					7	-58	-58	-114	-115	
	1	357	69	445	86	*	5	-11				
*	4	-7					1	23	249	75	828	
	5	93	31	656	216		2	-100	249	-134	333	
*	4	0					3	-216	-260	-345	-415	
	7	-107	3	-652	19		4	6	281	13	554	
*	4	2					6	135	-300	43	-95	
	7	48	-96	157	-318		7	17	100	90	515	
*	4	3				*	5	-10				
	6	-317	-158	-44	-22		1	-30	-321	-15	-162	
	7	-48	82	-312	530		2	-270	176	-226	147	
*	4	4				*	5	-9				
	5	114	26	902	208		1	-141	-335	-259	-617	
	6	193	-258	415	-554		2	284	195	578	397	
	7	57	46	23	19		5	-111	-38	-320	-110	
*	4	5					6	-14	357	-26	657	
	4	193	251	206	268	*	5	-6				
	5	-65	85	-84	110		7	79	-33	379	-161	
	6	-238	102	-61	26	*	5	1				
*	4	6					7	-19	-109	-57	-335	
	5	-87	-18	-161	-34	*	5	2				
*	4	7					7	-107	-6	-645	-34	
	1	100	-353	115	-404	*	5	3				
	2	-337	-51	-625	-95		6	328	-134	618	-253	
	3	-334	-143	-745	-319		7	69	-65	372	-351	
	4	236	42	492	88	*	5	4				
*	4	8					6	-264	180	-213	145	
	1	-311	182	-370	217		7	-67	19	-136	39	
	3	61	284	37	173	*	5	5				
	4	-130	40	-248	77		3	-144	364	-86	217	
*	4	9					5	5	107	18	412	
	1	-298	106	-443	158		6	44	-249	66	-376	
	2	-235	-61	-337	-88	*	5	6				
	3	108	102	96	91		2	-334	-85	-544	-138	
*	4	10					5	-85	11	-188	25	
	0	152	-251	208	-344	*	5	7				
	1	-229	47	-227	46		3	138	329	91	216	
*	4	11					4	157	-173	170	-187	
	0	162	98	155	93	*	5	8				
*	5	-13					1	332	139	228	96	
	5	9	-43	37	-186		2	123	277	126	283	

* 5 8					* 6 4				
3 -149	-246	-93	-153		5 100	-61	110	-67	
* 5 9					6 -80	306	-86	330	
1 -263	-163	-274	-169		7 -66	3	-839	36	
2 -113	208	-241	441		* 6 5				
3 -50	-109	-216	-470		4 -304	74	-415	101	
* 5 10					5 -101	24	-377	90	
0 -164	240	-242	354		6 243	38	137	22	
1 44	-220	110	-555		* 6 6				
* 5 11					5 85	2	256	5	
0 -7	180	-24	615		* 6 7				
* 6 -13					3 -325	-139	-100	-43	
5 -32	1	-597	26		4 230	19	390	32	
6 21	-118	27	-155		* 6 8				
* 6 -12					1 -349	-77	-385	-85	
2 36	154	82	348		3 -128	250	-141	277	
3 -164	-180	-234	-257		* 6 9				
4 172	134	394	309		1 -304	39	-718	93	
5 -52	67	-33	43		2 -230	-20	-146	-13	
6 140	230	58	95		* 6 10				
7 61	-51	134	-112		0 158	237	227	341	
* 6 -11					1 -195	-97	-195	-98	
1 -82	-226	-245	-675		* 6 11				
2 260	33	811	103		0 164	-13	382	-31	
3 -326	-61	-821	-153		* 7 -12				
4 -195	199	-322	328		2 -19	-138	-104	-772	
6 -309	91	-439	129		3 138	185	202	271	
7 37	-91	230	-563		4 -107	183	-78	133	
* 6 -10					5 -14	-81	-18	-105	
1 -272	-168	-707	-436		6 259	-6	114	-3	
2 311	70	500	113		7 31	-73	31	-74	
6 -47	351	-27	200		* 7 -11				
* 6 -9					1 110	203	195	362	
1 29	-359	9	-112		2 255	18	186	13	
* 6 -7					3 96	-311	263	-854	
5 67	76	216	247		4 -96	254	-151	400	
* 6 -2					5 -58	-87	-154	-232	
5 47	55	361	421		6 314	-59	127	-24	
7 -9	94	-52	556		7 19	96	69	356	
* 6 0					* 7 -10				
7 -91	-56	-333	-205		1 -219	-219	-344	-343	
* 6 2					2 -270	164	-482	294	
6 -41	-355	-71	-612		7 -82	69	-77	65	
7 -51	91	-282	505		* 7 -9				
* 6 3					5 -88	-76	-218	-189	
4 -110	279	-77	194		6 338	116	413	142	
6 185	295	441	703		* 7 -6				
7 76	-52	873	-595		7 -49	-81	-238	-392	
* 6 4					* 7 -3				
4 17	-316	11	-208		7 -13	88	-51	347	

* 7	-2					* 8	-11			
7	-36	91	-151	385		7	58	75	59	75
* 7	1					* 8	-10			
5	49	92	155	291		1	-9	303	-14	446
* 7	2					2	120	-289	125	-301
5	108	-37	466	-161		6	252	239	183	174
6	-355	37	-136	14		7	-107	5	-194	8
7	-57	-88	-244	-378		* 8	-9			
* 7	3					1	181	-308	218	-372
5	-34	-112	-304	-993		* 8	-8			
6	-27	-343	-41	-515		7	98	45	294	136
7	7	88	62	778		* 8	-7			
* 7	4					6	-55	-327	-79	-473
3	-108	357	-178	590		* 8	-6			
5	16	113	86	608		7	-16	97	-17	105
6	44	303	82	563		* 8	-3			
* 7	5					3	-244	-35	-348	-50
3	-249	-306	-100	-124		* 8	-2			
5	-47	-90	-209	-398		7	37	94	62	160
6	-7	-234	-14	-467		* 8	0			
* 7	6					7	98	51	876	452
3	-285	269	-416	393		* 8	1			
5	74	-36	117	-57		7	-73	-83	-385	-436
* 7	7					* 8	2			
3	-348	-45	-349	-45		6	319	160	498	249
4	119	186	288	451		7	-40	93	-218	504
* 7	8					* 8	3			
1	120	330	208	571		6	-297	-168	-366	-207
3	180	203	266	300		7	85	-11	827	-107
* 7	9					* 8	4			
1	292	-71	440	-107		6	-244	170	-220	153
2	-217	42	-239	46		* 8	5			
* 7	10					4	-253	-178	-274	-193
0	-273	-28	-136	-14		5	-63	79	-278	349
1	-93	-187	-278	-556		6	-175	-135	-76	-58
* 7	11					* 8	6			
0	105	96	121	111		2	325	-115	56	-20
* 8	-12					5	-11	-75	-41	-280
3	-215	4	-125	2		* 8	7			
4	118	-160	215	-292		1	-41	364	-72	632
5	-66	43	-222	144		2	231	238	475	488
6	-218	-114	-441	-231		3	-332	-77	-308	-71
7	76	-3	306	-11		4	58	207	100	353
* 8	-11					* 8	8			
1	-216	-31	-163	-24		1	-151	-313	-137	-283
2	239	72	94	28		3	-254	-50	-648	-127
3	-189	254	-393	528		* 8	9			
4	-174	-204	-264	-310		1	-292	-37	-690	-87
5	95	36	998	380		2	35	209	42	252
6	-303	91	-382	114						

*	8	10				*	9	4				
	0	181	194	361	385		5	-110	-15	-336	-45	
	1	159	109	413	284		6	-245	-150	-760	-464	
*	8	11				*	9	5				
	0	-85	-5	-428	-27		0	322	-50	335	-52	
*	9	-12					5	78	60	552	425	
	3	79	176	82	185		6	177	105	87	52	
	4	105	154	203	298	*	9	6				
	5	-12	-75	-34	-208		3	200	326	271	442	
	6	6	234	6	235		5	-36	-63	-76	-131	
	7	-68	-14	-227	-47	*	9	7				
*	9	-11					3	293	-156	348	-185	
	1	120	163	510	692		4	-138	152	-524	581	
	2	-4	-237	-5	-315	*	9	8				
	3	20	-303	47	-710		3	-195	-151	-108	-84	
	4	-73	249	-130	443	*	9	9				
	5	-52	-83	-114	-180		1	203	-195	132	-127	
	6	294	-86	475	-138		2	178	-82	247	-114	
	7	34	85	188	470	*	9	10				
*	9	-10					0	-231	104	-206	93	
	1	-63	-290	-29	-133		1	-103	-136	-173	-229	
	2	-157	259	-285	470	*	10	-12				
	7	-5	-104	-10	-203		3	-132	-98	-318	-236	
*	9	-9					4	168	-43	462	-118	
	2	81	332	181	741		5	-58	39	-191	128	
	6	238	266	154	172		6	-78	200	-39	101	
	7	-7	-110	-22	-359		7	62	12	219	43	
*	9	-8				*	10	-11				
	7	-41	103	-88	221		1	-110	151	-229	315	
*	9	-7					2	200	102	783	398	
	6	125	311	249	619		3	-289	33	-859	97	
*	9	-5					4	-7	-253	-18	-612	
	1	134	-272	51	-104		5	47	-32	299	-208	
*	9	-4					6	-248	157	-187	118	
	6	-281	63	-559	126		7	-76	-46	-173	-104	
*	9	-2				*	10	-10				
	3	27	-248	85	-780		1	-273	79	-707	205	
*	9	0					2	155	-250	388	-626	
	7	-103	-41	-434	-173		3	283	218	40	31	
*	9	1					5	97	53	146	79	
	4	-195	180	-220	203		6	161	294	220	400	
	7	96	-49	118	-60	*	10	-9				
*	9	2					1	35	343	14	141	
	5	43	-109	297	-759		5	-117	3	-615	16	
	7	93	32	444	152		7	-110	8	-166	12	
*	9	3				*	10	-8				
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	5	-80	-85	-528	-563		7	-91	63	-292	203	
	6	-159	-295	-38	-71	*	10	-7				
	7	-82	-7	-443	-39		7	-56	92	-226	370	

* IO	-7					* II	-11				
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* IO	-6					7	-21	83	-72	282	
6	-51	325	-15	100		* II	-10				
* IO	0					1	157	-226	337	-484	
7	31	106	96	328		2	166	235	385	544	
* IO	1					5	4	107	21	570	
7	107	10	181	17		6	-41	-326	-60	-476	
* IO	2					* II	-9				
5	-102	-58	-392	-223		1	52	-328	167	-1046	
6	354	-8	144	-3		2	234	231	263	259	
7	-71	67	-250	235		5	80	85	202	214	
* IO	3					6	-150	320	-131	280	
4	-19	312	-37	610		7	103	-31	171	-52	
6	-204	-257	-309	-389		* II	-8				
7	-47	-64	-164	-223		5	13	-116	48	-442	
* IO	4					* II	-7				
3	-3	392	-2	337		2	-287	-173	-269	-162	
4	-316	-6	-498	-9		7	1	111	2	195	
6	138	245	184	326		* II	-6				
* IO	5					7	76	-75	76	-75	
5	-93	-19	-264	-55		* II	-1				
* IO	6					7	-62	-92	-326	-484	
5	-57	-33	-137	-80		* II	0				
* IO	7					7	103	-41	681	-275	
1	327	167	469	239		* II	1				
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4	32	-187	94	-550		* II	2				
* IO	8					6	68	341	170	850	
0	-363	-24	-69	-5		7	51	80	261	406	
1	-216	-252	-355	-413		* II	3				
3	-93	-211	-111	-252		3	-50	-369	-57	-418	
* IO	9					5	-92	-72	-518	-407	
1	-217	164	-295	223		6	-302	-105	-448	-155	
2	36	176	93	453		7	-21	-70	-146	-490	
* IO	10					* II	4				
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1	-139	28	-455	92		5	20	106	78	409	
* II	-12					6	163	-205	482	-607	
3	76	40	263	138		* II	5				
4	110	99	187	168		0	302	159	242	127	
5	-29	-56	-148	-282		4	75	-284	195	-745	
6	-13	192	-16	241		5	-38	83	-168	371	
7	-34	37	-66	72		* II	6				
* II	-11					2	181	-290	295	-473	
1	-22	157	-85	614		3	60	362	84	505	
2	51	205	64	255		5	-43	42	-77	75	
3	-81	-269	-58	-193		* II	7				
4	-117	210	-366	657		1	-143	334	-221	514	
5	-66	-63	-431	-410		3	188	246	363	476	

* II	7				* I 2	3			
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* II	8				* I 2	4			
0	-173	-312	-143	-258	4	-183	-254	-59	-82
1	263	192	288	210	6	-240	68	-153	43
2	199	166	391	326	* I 2	5			
3	157	-132	395	-331	5	-74	42	-240	137
* II	9				* I 2	6			
0	309	-13	247	-10	2	-334	24	-553	40
1	-94	-238	-126	-317	3	55	-353	79	-512
2	-84	134	-231	366	* I 2	7			
* II	10				3	-294	-44	-546	-81
0	-39	224	-33	188	4	50	-140	64	-176
* I 2	-12				* I 2	8			
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5	50	20	158	63	2	48	-242	8	-41
6	-158	0	-244	0	3	100	146	348	509
* I 2	-11				* I 2	9			
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3	-199	-171	-169	-144	1	-207	123	-139	83
4	-121	-193	-292	-467	2	-117	-3	-230	-5
5	78	34	380	167	* I 2	10			
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7	62	-49	263	-207	* I 3	-11			
* I 2	-10				2	132	103	204	159
1	-259	11	-824	36	3	242	-22	338	-31
2	80	-263	129	-425	4	-106	187	-250	439
6	-86	307	-135	482	5	-73	-38	-509	-265
* I 2	-9				6	246	42	258	44
1	-197	259	-4	5	7	-12	72	-69	396
4	12	309	11	282	* I 3	-10			
5	-60	-97	-128	-207	1	68	-233	11	-39
* I 2	-6				2	-170	200	-481	563
7	-43	102	-185	441	4	268	-18	208	-14
* I 2	-5				6	-103	-289	-158	-443
7	96	49	381	194	7	83	40	298	143
* I 2	-2				* I 3	-9			
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7	-82	75	-455	417	6	341	18	179	9
* I 2	-1				* I 3	-7			
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6	-302	-172	-190	-109	5	-33	-112	-105	-361
* I 2	1				* I 3	-6			
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* I 2	2				* I 3	-5			
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7	-5	-88	-8	-134	* I 3	-4			
* I 2	3				7	3	-111	7	-292
5	-7	-114	-29	-454	* I 3	-1			
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* 13	1				* 14	-3			
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6	-231	268	-168	195	* 14	-1			
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* 13	2				* 14	1			
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7	58	-63	155	-167	* 14	2			
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4	-150	278	-277	512	6	-215	-240	-155	-174
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6	-70	289	-84	349	* 14	3			
* 13	4				6	87	268	81	251
5	87	51	164	96	* 14	4			
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* 13	5				6	-33	-200	-18	-110
4	-55	-269	-66	-326	* 14	5			
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* 13	6				4	-250	-88	-456	-161
3	-339	61	-280	51	5	13	-72	96	-530
* 13	7				* 14	6			
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* 13	8				3	305	-130	512	-218
2	5	-231	10	-474	* 14	7			
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* 13	9				2	154	239	407	631
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* 13	10				* 14	8			
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* 14	-11				* 14	9			
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4	147	-125	227	-193	* 14	10			
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6	-142	178	-113	142	* 15	-11			
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* 14	-10				4	29	171	34	197
1	-214	-57	-302	-81	5	-18	-64	-151	-530
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6	289	53	275	51	7	48	16	293	98
7	-85	-9	-555	-57	* 15	-10			
* 14	-9				1	196	-8	147	-6
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* 14	-7				6	18	-274	36	-545
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6	209	-289	79	-109	* 15	-9			
7	110	12	297	32	1	-121	-257	-136	-290
* 14	-5				4	-105	-264	-264	-666
6	-154	-319	-202	-416	6	-258	188	-145	105

* 15	-8				* 16	-11			
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* 15	-7				6	-151	34	-371	85
3	-200	-341	-57	-96	* 16	-10			
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7	92	56	29	18	2	-37	-202	-43	-234
* 15	-6				5	50	-69	115	-161
3	160	-358	185	-414	6	-36	250	-90	631
* 15	-5				7	-41	-60	-306	-456
1	-29	359	-26	325	* 16	-9			
* 15	-4				1	260	52	226	45
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7	24	108	96	432	4	-95	258	-77	208
* 15	-2				6	169	-256	202	-306
7	25	108	127	547	7	-7	-88	-2	-29
* 15	-1				* 16	-8			
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6	338	-114	269	-90	6	-151	-299	-147	-290
7	-77	-75	-365	-354	7	24	95	80	320
* 15	0				* 16	-7			
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7	98	-8	342	-29	5	117	-7	299	-19
* 15	1				6	-14	347	-3	70
7	-88	-10	-737	-86	* 16	-6			
* 15	2				1	-315	193	-655	401
6	245	-190	519	-402	* 16	-5			
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* 15	3				* 16	-4			
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4	-263	170	-384	249	* 16	-3			
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* 15	4				* 16	-1			
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* 15	6				7	-95	5	-361	18
1	348	-93	271	-73	* 16	1			
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3	181	259	433	620	* 16	2			
* 15	7				6	251	-154	206	-127
1	-326	-39	-126	-15	* 16	3			
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* 16	6					* 17	1				
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* 16	8					6	205	-1	359	-2	
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2	-93	154	-208	347		* 17	5				
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5	-75	-10	-309	-39		4	107	190	204	364	
6	99	-205	243	-502		* 17	6				
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* 17	-9					2	270	99	160	59	
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* 17	-4					6	262	14	480	26	
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* 17	-3					4	260	-107	466	-191	
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* 17	1					7	43	85	19	38	
3	-390	-41	-385	-40		* 18	-5				
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* 18	-5				* 19	-8			
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* 18	-2				* 19	-7			
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* 18	-1				7	60	65	382	418
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* 18	0				7	-16	93	-14	83
5	-81	-80	-468	-458	* 19	-5			
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7	-69	45	-160	105	* 19	-4			
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6	-244	-55	-425	-95	7	-89	-22	-474	-118
* 18	3				* 19	-1			
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* 18	6				* 19	1			
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2	186	-87	388	-180	* 19	2			
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* 18	9				* 19	4			
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* 19	-10				* 19	5			
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* 20	-6				7	-47	-19	-395	-162
5	-83	68	-146	119	* 21	-7			
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* 20	-5				5	-54	-74	-238	-330
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* 20	-4				* 21	-6			
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* 20	-3				5	-35	95	-98	265
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* 20	-2				7	35	71	318	646
7	82	23	61	17	* 21	-5			
* 20	-1				5	-101	38	-59	22
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7	-2	-76	-17	-695	* 21	-4			
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* 20	1				* 21	-3			
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6	-244	31	-155	20	* 21	-2			
* 20	2				4	-176	-255	-180	-261
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* 20	3				* 21	-1			
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* 21	2					* 22	-2			
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* 21	4					6	156	161	339	348
4	-130	124	-682	650		* 22	1			
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2	129	-225	115	-199		5	-54	-66	-502	-608
3	46	-226	27	-132		* 22	2			
* 21	6					3	-97	-337	-47	-163
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2	181	-75	231	-96		5	22	66	45	131
* 21	7					* 22	3			
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* 21	8					3	-261	179	-330	227
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* 22	-8					* 22	4			
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3	69	-233	118	-398		3	-103	248	-178	430
4	104	166	204	326		* 22	5			
5	-51	47	-370	336		3	47	-181	199	-769
6	-176	39	-376	83		* 22	6			
* 22	-7					2	3	155	11	542
1	102	231	188	429		* 22	7			
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6	-76	-224	-12	-35		* 23	-8			
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* 22	-6					3	57	188	157	521
3	54	-334	74	-455		4	163	20	169	21
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6	-133	-226	-333	-569		* 23	-7			
7	-11	-65	-54	-326		1	163	144	128	113
* 22	-5					4	-175	125	-130	93
6	36	279	70	545		5	-12	-75	-115	-701
7	-64	34	-287	154		6	-61	180	-85	251
* 22	-4					* 23	-6			
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7	71	17	360	84		5	-79	31	-427	167
* 22	-3					6	144	-184	211	-270
3	86	-373	30	-129		* 23	-5			
5	104	6	79	4		3	4	-341	3	-221
6	226	-178	391	-309		6	-130	213	-257	420
7	-38	58	-208	318		* 23	-4			
* 22	-2					4	11	-278	18	-487
5	86	-53	93	-57		5	70	-64	138	-127
6	-209	-179	-530	-454		6	86	-244	56	-158

* 23	-4				* 24	0			
7	6	-57	65	-582	3	-341	15	-350	15
* 23	-3				5	-51	-52	-117	-117
3	-218	299	-418	572	* 24	1			
5	-52	-83	-125	-197	2	-27	-302	-18	-202
6	-248	-74	-528	-157	5	55	-14	70	-18
* 23	-2				* 24	2			
2	-229	-236	-481	-495	3	5	-297	6	-333
3	193	315	116	190	4	121	-146	308	-371
5	-66	68	-99	103	* 24	4			
6	216	118	555	303	3	54	-169	131	-410
* 23	-1				* 24	5			
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6	117	-192	261	-428	* 24	6			
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5	-42	-74	-196	-351	1	125	68	364	197
* 23	1				* 25	-7			
5	-38	62	-30	49	3	170	-34	435	-87
* 23	2				* 25	-6			
4	57	214	130	490	2	204	-56	259	-72
* 23	3				4	182	-40	366	-81
0	346	-35	267	-27	* 25	-5			
3	257	-129	300	-151	1	-209	-148	-393	-277
4	25	172	31	214	2	-217	123	-535	304
* 23	6				4	-36	-212	-39	-230
1	191	55	579	166	* 25	-4			
* 24	-7				4	-165	166	-360	361
1	-134	-106	-634	-500	* 25	-3			
4	158	-93	203	-120	3	7	-322	9	-456
5	-60	0	-239	1	* 25	-2			
* 24	-6				1	136	292	178	383
2	228	86	470	177	2	-86	-284	-128	-424
4	163	149	47	43	4	-73	229	-135	423
5	53	54	431	442	* 25	-1			
6	87	158	158	285	5	-67	18	-593	156
* 24	-5				* 25	0			
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* 24	-4				3	62	-310	65	-322
1	-278	151	-267	145	5	54	19	591	209
6	-220	-46	-500	-105	* 25	1			
* 24	-3				3	290	-65	210	-47
3	-273	221	-351	284	* 25	3			
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6	194	107	517	285	* 26	-6			
* 24	-2				2	164	-15	239	-22
3	205	288	105	148	* 26	-5			
* 24	-1				2	19	217	45	506
3	-191	294	-247	379	* 26	-4			
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* 26	-3			
4	-212	-2	-213	-2
5	1	-63	6	-259
* 26	-2			
4	139	164	269	317
* 26	-1			
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4	10	-205	8	-160
* 26	0			
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* 26	1			
2	-182	180	-255	252
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* 26	4			
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* 26	5			
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1	2	82	12	470
* 27	-5			
2	149	83	306	170
* 27	-4			
3	-199	117	-306	180
* 27	-2			
2	66	-234	182	-649
3	239	-101	361	-153
4	-164	58	-384	137
* 27	-1			
4	157	-48	92	-28
* 27	0			
1	214	-173	395	-320
3	3	-243	3	-270
* 27	1			
1	90	246	101	277
* 27	2			
3	-126	-43	-282	-96
* 27	3			
1	-3	-212	-3	-214
2	-5	-139	-33	-910
* 27	4			
1	113	91	608	487
* 28	-4			
2	-46	154	-48	160
* 28	-3			
2	88	-172	56	-110
3	106	165	74	114

* 28	-2			
1	-175	-150	-382	-327
2	-175	-107	-133	-81
* 28	1			
3	-22	-35	-322	-499
* 28	2			
1	-59	-190	-137	-443
2	-45	-125	-118	-328
* 28	3			
1	97	112	364	422
* 29	-2			
1	-122	123	-438	441
2	129	79	152	93
* 29	-1			
2	60	-143	92	-217
* 29	0			
1	190	-1	80	0
2	-53	128	-94	226
* 29	1			
1	-149	-84	-809	-456
* 29	2			
0	133	-102	223	-172
1	99	-48	677	-329

Appendix II.A

C C observed and calculated structure
factors.

Layout of data

* k h

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F_{OA}

F_{OB}

F_{CA}

F_{CB}

*	O	I				*	O	7					
O		2810	-4132	3293	-4843	2		87	593	111	756		
2		2402	698	3969	1153	3		-200	-712	-220	-782		
3		1637	732	2058	920	4		-478	-189	-550	-217		
4		-472	-999	-616	-1305	5		566	127	558	125		
5		268	69	369	95	6		-490	-601	-438	-538		
6		324	107	719	237	*	O	8					
*	O	2				O		-1100	-1639	-1055	-1573		
O		1517	-4191	1388	-3836	1		-403	353	-450	393		
1		-2675	-2547	-2748	-2617	2		-330	505	-416	636		
2		-515	-147	-613	-175	3		-1043	-1299	-1241	-1546		
3		3392	1019	2737	822	4		-743	341	-808	370		
4		-1101	-1770	-1095	-1760	6		-118	-518	-123	-538		
5		-592	649	-655	718	*	O	9					
6		445	62	336	47	O		-206	49	-242	58		
*	O	3				2		256	-351	363	-499		
O		-1185	-573	-1712	-829	3		-120	-595	-124	-616		
1		-2612	1242	-1868	888	4		271	108	338	135		
2		-1421	1374	-1188	1149	5		150	-342	162	-369		
3		595	-2799	547	-2570	6		-55	-254	-62	-287		
4		-1377	-122	-1305	-116	*	O	10					
5		-632	1901	-694	2087	O		590	311	362	191		
6		41	-1314	35	-1115	1		19	702	17	633		
*	O	4				*	O	11					
O		1936	-846	1996	-873	O		87	381	86	375		
1		-1117	1743	-1295	2021	1		350	-312	310	-276		
2		-2152	2734	-2455	3119	2		322	536	366	610		
3		1420	-920	1381	-895	3		-392	229	-364	213		
4		-774	1169	-791	1194	5		212	-10	343	-16		
5		605	1281	581	1232	*	O	12					
6		212	-584	126	-346	O		-8	-177	-9	-186		
*	O	5				1		218	-508	242	-564		
O		1535	-214	1485	-207	2		390	17	516	22		
1		-707	2009	-693	1970	3		-177	16	-289	27		
2		1346	1335	1365	1354	*	O	13					
3		-379	-673	-299	-531	O		-163	-165	-103	-104		
4		-596	911	-589	901	1		-163	-15	-129	-12		
5		596	232	509	198	2		-16	-177	-25	-282		
6		454	135	342	102	3		99	-112	164	-185		
*	O	6				*	O	14					
O		-2573	1497	-2542	1479	O		264	236	275	246		
1		-2509	494	-2489	489	1		-107	255	-124	296		
2		977	1017	951	989	2		-5	-164	-6	-204		
3		95	663	113	791	*	I	0					
4		-673	-761	-722	-818	2		908	-2518	680	-1884		
5		974	699	988	709	3		2315	912	3087	1216		
6		124	486	116	454	4		-215	-1336	-345	-2150		
*	O	7				5		-586	-530	-954	-863		
O		-275	-1342	-267	-1303	6		1004	-33	1530	-51		
1		-38	-1167	-37	-1142								

*	I	I				*	I	7			
0		-2259	4906	-2302	5000	3		-620	-122	-737	-145
1		-5062	2685	-4751	2520	4		-437	-227	-519	-269
2		-1465	148	-1153	116	5		-19	384	-23	463
3		1919	86	1821	82	6		-161	-475	-134	-393
4		-1735	-1125	-2113	-1370	*	I	8			
5		-361	66	-493	90	0		-821	-952	-709	-823
6		296	-105	370	-131	1		-235	-55	-285	-67
*	I	2				2		-285	-162	-245	-139
0		-1624	-2682	-1306	-2157	3		-203	-1235	-202	-1226
1		-1098	-2829	-1290	-3322	4		-470	-240	-576	-295
2		-1379	3113	-1490	3364	5		-382	-44	-415	-47
3		-1859	2173	-1722	2013	6		-32	-327	-36	-369
4		-695	-405	-659	-384	*	I	9			
5		-79	1828	-80	1864	0		-168	-531	-127	-402
6		-900	-304	-746	-251	1		22	259	15	177
*	I	3				2		-418	-6	-387	-5
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1		701	83	938	112	5		300	-7	330	-8
2		-590	1569	-615	1637	*	I	10			
3		964	-360	654	-244	0		173	840	160	777
4		-244	769	-160	505	1		-73	-290	-86	-338
5		-67	874	-49	643	2		411	80	609	118
*	I	4				3		269	-132	296	-145
0		3179	-1943	3420	-2090	5		218	-41	230	-43
1		1387	-783	1528	-862	*	I	11			
2		-1535	1733	-1484	1676	0		356	274	178	137
3		1617	159	1755	173	1		-462	-426	-429	-395
4		307	607	321	635	2		97	378	116	453
5		-781	747	-712	681	*	I	12			
6		872	-255	718	-210	0		-273	-586	-194	-416
*	I	5				1		311	-43	285	-40
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1		-401	1062	-375	995	3		-213	-188	-275	-242
2		1507	300	1523	303	*	I	13			
3		1073	-363	1157	-392	1		-142	-237	-107	-179
4		-581	-522	-594	-534	2		256	-80	345	-109
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2		-57	154	-76	208	3		1743	-3250	1473	-2745
3		5	-712	5	-786	4		-427	619	-315	457
4		-451	-453	-520	-522	5		161	-493	151	-464
5		245	108	117	51	6		-277	-283	-217	-222
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*	I	7				1		-1711	2298	-1249	1678
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1	372	894	284	682	5	-248	484	-296	578
2	2054	383	1692	316	*	2	8		
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4	486	1006	473	979	1	514	270	639	336
5	-35	-795	-34	-784	2	32	130	77	309
6	-367	770	-284	595	3	413	-201	530	-258
*	2	2			4	280	-171	422	-257
0	-39	2377	-39	2374	5	-64	-260	-78	-318
1	1411	421	1418	424	*	2	9		
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3	-264	1542	-194	1132	1	-43	-669	-42	-652
4	1241	1119	1192	1074	3	397	61	575	88
5	-1204	879	-943	688	4	91	99	168	183
6	-124	388	-89	279	*	2	10		
*	2	3			0	489	-652	414	-552
0	541	-1615	565	-1686	1	-278	230	-289	239
1	1323	1259	1348	1283	2	469	16	552	19
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3	-265	-1236	-287	-1339	4	2	-134	5	-261
4	1700	75	2069	91	*	2	11		
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2	-1517	94	-1608	100	3	-1196	-4907	-990	-4062
3	-340	430	-248	314	4	-1004	1036	-925	955
4	-384	-397	-369	-382	5	172	170	227	224
5	-433	-553	-457	-584	6	-316	-598	-240	-454
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2	-129	262	-205	418	4	-451	2852	-454	2871
3	-293	523	-284	507	5	-300	-1103	-304	-1119
4	-257	-747	-252	-730	6	-966	-684	-956	-677
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		3	1020	-632	1172			5	410	-46	455	-51
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		6	300	544	238			1	811	-49	811	-49
		0	2869	-1174	2777			2	585	-175	654	-196
		1	445	1353	470			3	307	2	265	1
		2	1781	-214	1894			4	268	-367	316	-433
*	4	3	-685	-296	-694	*	4	8				
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		5	1580	-532	1566			1	259	-20	303	-23
		0	-508	-2250	-556			2	-52	-436	-68	-572
		1	1542	824	1468			3	187	-224	189	-225
		2	384	703	416			5	244	-87	253	-90
*	4	3	-95	-523	-96	*	4	9				
		4	-864	717	-852			0	-257	549	-201	429
		5	641	-521	633			2	18	-221	16	-197
		6	623	-48	397			3	-193	-229	-209	-247
		0	-1508	-2196	-1426			4	-205	127	-276	171
		1	410	1559	436			5	131	-120	206	-189
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		4	-322	1007	-351			2	359	-75	429	-90
		5	-1533	-802	-1579			3	-227	47	-353	74
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		3	-928	270	-842			3	-163	202	-277	343
		4	-188	969	-224			5	-4			
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		6	-41	-547	-30			2	-33	305	-14	131
*	4	0	402	-15	383	*	5	-3				
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		2	313	-30	505			2	-128	997	-128	996
		3	-394	-681	-382			3	-745	245	-671	221
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		5	319	309	339			5	-55	1537	-50	1397
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		2	313	-30	505			3	-745	245	-671	221
		3	-394	-681	-382			4	-1340	92	-1409	97
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		6	-269	449	-203			3	379	-515	430	-583
		1	-2385	-630	-1975			4	649	96	714	106
		2	-415	1745	-390			5	261	-161	329	-203
*	5	0				*	5	7				
		3	375	1453	335			0	-545	-583	-550	-588
		4	-118	863	-120			1	1116	-155	1145	-159
		5	89	615	94			2	59	435	75	555
*	5	0				*	5	8				
		6	637	-172	663			3	-520	-655	-595	-749
		1	-3930	-123	-4060			4	301	-347	312	-360
		2	2917	-1464	2795			5	298	35	267	31
*	5	0				*	5	9				
		3	1192	228	1185			0	-736	-122	-653	-108
		4	-660	-938	-601			1	550	-388	520	-366
		5	655	619	608			2	314	367	347	405
*	5	0				*	5	10				
		6	589	199	363			3	-416	-521	-468	-587
		1	-2714	727	-2603			5	239	-121	292	-148
		2	535	-1457	537			0	-79	-281	-41	-146
*	5	0				*	5	11				
		3	987	-842	1007			2	174	-270	263	-410
		4	3	-975	2			3	-408	-163	-480	-192
		5	947	4	839			4	119	366	169	517
*	5	0				*	5	12				
		6	223	-666	166			5	-19	-93	-44	-219
		1	-1319	-2070	-1335			0	-91	72	-166	132
		2	-598	2063	-639			1	-20	188	-17	163
*	5	0				*	5	13				
		3	-1115	-1292	-1124			2	4	-379	5	-489
		4	-1028	-141	-1000			3	-201	68	-291	99
		5	21	702	23			0	-25	148	-34	203
*	5	0				*	5	14				
		6	-344	-86	-309			1	244	130	361	193
		1	-1337	-389	-1250			3	168	145	308	265
		2	-553	1695	-510			6	-5			
*	5	0				*	5	15				
		3	-1307	295	-1504			1	-1397	-2627	-1140	-2143
		4	34	841	28			2	-526	-1965	-481	-1796
		5	-1135	277	-1269			3	463	-37	450	-36
*	5	0				*	5	16				
		6	-281	-723	-239			4	-550	-1253	-534	-1215
		1	-98	-250	-70			5	-603	-718	-612	-729
		2	-1224	-369	-1351			6	-4			
*	5	0				*	5	17				
		3	-311	-1327	-342			1	-1090	117	-931	100
		4	-816	1092	-960			2	743	119	853	136
		5	343	-175	322			3	-814	1167	-724	1038
*	5	0				*	5	18				
		3	-1066	-575	-1112			4	773	-340	606	-266
		4	-1224	-369	-1351			5	620	-44	567	-40
		5	343	-175	322			6	26	743	20	561
*	5	0				*	5	19				
		3	-1066	-575	-1112			6	-3			
		4	-1224	-369	-1351			1	2863	-657	2360	-542
		5	343	-175	322							

* 6	-3					* 6	4						
2	113	734	78	504		1	342	-67	391	-76			
3	339	1365	266	1069		2	1021	-769	1228	-926			
4	1172	19	1147	19		3	648	-513	761	-602			
5	-582	698	-569	683		4	-70	-200	-50	-143			
6	288	905	285	895		* 6	5						
* 6	-2					0	-323	-258	-394	-315			
1	174	-203	149	-173		1	447	-534	451	-538			
2	-630	1476	-633	1485		2	349	-113	318	-103			
3	1136	1654	1128	1641		3	708	-447	826	-521			
4	567	-47	634	-53		4	240	73	193	59			
5	-243	395	-217	353		5	211	-18	250	-22			
6	716	-199	464	-129		* 6	6						
* 6	-1					0	463	-34	329	-24			
1	-220	-619	-226	-636		1	188	233	224	277			
2	110	-608	128	-709		2	315	-133	207	-88			
3	781	316	769	311		3	-369	-613	-456	-756			
4	81	-525	70	-449		4	167	89	261	140			
5	31	-535	20	-348		5	208	-254	227	-276			
6	825	-101	798	-98		* 6	7						
* 6	0					0	-342	-299	-298	-260			
1	28	-1705	30	-1813		1	192	306	197	314			
2	571	-502	539	-474		2	-398	53	-424	56			
3	314	-222	548	-388		3	-556	11	-683	13			
4	-1039	-1058	-1091	-1110		4	244	57	297	69			
5	-488	-1	-437	-1		5	-276	-18	-283	-18			
6	146	-253	119	-206		* 6	8						
* 6	1					0	-95	150	-125	198			
0	-1159	1920	-1080	1789		1	57	121	48	102			
1	-438	-1510	-440	-1517		3	-108	375	-128	444			
2	220	-203	241	-222		* 6	9						
3	-524	443	-525	444		0	73	199	81	220			
4	-374	-187	-459	-230		2	268	-178	238	-158			
5	76	567	78	584		3	241	20	336	28			
* 6	2					* 7	-6						
0	1115	-20	1009	-18		1	430	1198	330	921			
1	-217	1092	-179	900		2	-1065	-770	-1010	-730			
2	-188	752	-208	833		3	-1248	716	-1126	646			
3	227	84	282	104		4	-102	571	-78	439			
4	-765	637	-746	621		6	-955	1	-740	1			
5	-454	573	-413	522		* 7	-5						
6	-584	17	-472	13		1	1018	190	705	132			
* 6	3					2	829	-131	674	-106			
0	386	-749	417	-809		3	-977	996	-900	917			
1	333	1422	344	1471		4	-1072	-17	-1002	-16			
2	-1270	1258	-1367	1355		5	640	-360	507	-285			
3	-169	590	-158	554		6	-478	916	-384	736			
4	-77	898	-85	989		* 7	-4						
* 6	4					1	1550	1140	1484	1091			
0	113	-980	88	-766		2	269	-249	318	-295			

*	7	-4				*	7	3					
		3	-800	1275	-691			2	-418	-966	-477	-1103	
		4	707	988	635			3	-286	-186	-192	-125	
		5	359	-37	294			4	-153	-249	-165	-269	
*	7	6	-10	945	-9	*	7	5	-437	-206	-427	-202	
								6	393	-228	419	-243	
		1	2013	624	2012			0	287	-1190	252	-1047	
		2	245	1372	246			2	353	-707	409	-818	
*	7	3	763	1353	692	*	7	3	407	-336	441	-365	
		4	1338	523	1245			4	268	-268	343	-343	
		5	155	256	119			5	303	-682	298	-670	
		6	-307	454	-212			1	381	-993	342	-892	
*	7	-2				*	7	2	-186	-837	-230	-1036	
		1	1445	993	1258			3	-259	397	-245	376	
		2	-918	-900	-930			4	108	-254	136	-321	
		3	74	-638	67			5	-151	-163	-169	-182	
*	7	4	255	45	243	*	7	6					
		5	-153	-686	-155			0	-246	534	-199	433	
								1	180	112	125	78	
		1	490	-47	489			2	-354	7	-517	10	
*	7	2	-1261	-753	-1233	*	7	3	139	282	151	306	
		3	-159	-794	-115			4	93	-285	107	-329	
		4	-265	-324	-184			5	-35	219	-47	297	
		5	-371	-630	-341			0	191	91	152	72	
*	7	6	-416	295	-326	*	7	1	106	157	107	157	
		1	-1294	-328	-1313			2	-279	319	-345	395	
		2	-614	-223	-487			3	156	84	222	120	
		3	-1161	-490	-1121			4	192	130	148	100	
*	7	4	-364	237	-339	*	7	5	87	-204	65	-152	
		5	-57	-654	-57			6	-7				
		6	-416	295	-326			1	695	713	618	634	
								2	341	-435	375	-479	
*	7	1	-1394	836	-1315	*	7	3	269	-162	230	-138	
		0	-1394	836	-1315			4	54	-140	82	-213	
		1	30	-175	33			5	217	318	155	227	
		2	-1110	-382	-1220			6	-112	-761	-93	-631	
*	7	3	-1059	782	-1192	*	7	8	-6				
		4	790	150	775			1	-479	395	-420	347	
		5	-650	-149	-643			2	934	-275	859	-253	
		6	-204	682	-207			3	112	-153	99	-135	
*	7	0	667	772	679	*	7	4	-667	935	-802	1125	
		1	-143	382	-120			5	677	360	653	347	
		2	-319	1041	-360			6	-624	-294	-545	-257	
		3	331	641	278			8	-5				
*	7	4	459	-15	573	*	7	1	-84	2330	-73	2011	
		5	-541	-57	-534								
		6	378	119	325								
		0	1716	439	1669								
*	7	1	-427	381	-425	*	7	3					

* II	-7				* II	0			
2	-420	-751	-463	-828	5	-141	-107	-108	-83
3	299	-223	321	-239	* II	1			
4	354	27	406	31	0	-450	-259	-389	-224
5	-29	-360	-32	-405	1	-518	-24	-520	-24
* II	-6				2	-284	70	-308	76
1	662	-330	607	-303	3	-102	-160	-123	-193
2	-1854	1094	-1760	1038	4	-250	-251	-291	-293
3	5	373	4	286	5	-255	48	-344	65
4	376	-711	333	-628	* II	2			
5	-443	-139	-392	-124	1	-187	-28	-245	-37
6	218	104	197	94	2	-189	202	-176	188
* II	-5				5	145	102	237	166
1	255	-1987	237	-1844	* II	3			
2	-998	866	-919	798	0	601	319	554	294
3	-581	602	-579	601	1	-146	153	-181	189
4	-340	-308	-357	-324	2	279	128	321	147
5	-181	111	-206	126	3	178	-66	198	-74
6	-326	262	-192	154	* II	4			
* II	-4				0	276	189	245	168
1	-658	-1201	-597	-1089	1	-106	370	-108	375
2	-39	1098	-37	1022	3	-37	145	-18	71
3	270	-258	181	-172	* II	5			
4	-413	-115	-397	-110	1	117	-65	160	-89
5	-610	94	-609	94	* I2	-11			
6	-25	407	-20	332	1	415	312	387	292
* II	-3				3	59	330	84	466
1	-432	194	-253	113	* I2	-10			
2	167	220	184	244	2	-252	347	-170	234
3	45	399	48	426	3	201	12	205	13
4	448	33	469	34	* I2	-9			
5	-248	244	-317	311	1	884	857	768	745
6	424	373	351	309	2	371	-225	431	-261
* II	-2				3	-13	-250	-12	-221
1	653	-3	535	-2	4	446	273	515	315
2	81	228	69	195	5	293	-61	311	-65
3	727	330	738	335	* I2	-8			
4	-65	-361	-77	-429	1	1441	-252	1324	-232
5	-108	216	-162	323	2	-224	-613	-206	-563
6	498	-59	551	-66	4	423	30	443	32
* II	-1				5	-219	-36	-178	-30
1	-730	-967	-677	-897	* I2	-7			
2	-110	169	-162	250	1	709	-360	480	-244
3	389	-39	375	-38	2	-495	-81	-507	-83
4	-377	-309	-430	-353	4	172	-80	171	-79
* II	0				5	-134	-177	-169	-224
1	-220	-626	-234	-665	* I2	-6			
2	243	-353	281	-408	1	-820	-69	-708	-60
3	57	-451	48	-378	2	-644	227	-646	228
4	-248	-36	-314	-46	3	365	154	234	99

* I 2	-6					* I 3	-12				
4	-105	-158	-81	-122		1	-281	-141	-231	-115	
5	-208	-169	-167	-136		2	-77	145	-81	154	
6	-220	166	-253	191		3	176	-152	222	-192	
* I 2	-5					* I 3	-11				
1	366	301	397	327		1	-331	144	-378	165	
2	-213	176	-273	225		2	245	172	299	210	
3	-556	152	-560	153		* I 3	-10				
4	253	400	223	353		2	286	-175	331	-203	
5	-259	202	-256	199		* I 3	-9				
6	-139	417	-153	458		2	64	-213	60	-201	
* I 2	-4					3	-1	-232	-1	-365	
1	438	-485	411	-456		* I 3	-8				
2	-37	274	-38	281		1	-320	330	-336	346	
3	190	429	146	329		2	42	457	38	419	
4	290	-456	310	-487		5	-189	-7	-189	-7	
5	-84	303	-68	244		* I 3	-7				
6	167	327	214	419		1	-457	574	-437	550	
* I 2	-3					2	-188	25	-136	18	
1	49	-701	45	-655		3	-734	97	-721	95	
2	-151	-115	-211	-162		4	-219	121	-227	126	
3	456	53	448	52		* I 3	-6				
4	71	-211	74	-221		1	322	334	269	279	
5	205	-86	243	-101		2	355	189	364	194	
6	222	9	302	13		3	-90	330	-103	379	
* I 2	-2					5	35	219	30	187	
1	-638	-79	-484	-60		* I 3	-5				
2	-92	315	-64	217		1	337	129	331	127	
4	-87	-235	-88	-238		2	415	-54	456	-59	
5	5	-232	7	-318		3	-50	534	-45	481	
* I 2	-1					5	252	240	303	288	
1	-374	-360	-391	-376		* I 3	-4				
2	-246	-331	-241	-323		1	513	-263	315	-162	
3	-216	-84	-236	-92		2	173	-77	135	-60	
4	-154	-145	-197	-185		3	246	-106	210	-91	
5	-195	-171	-268	-235		5	145	-37	159	-41	
* I 2	0					* I 3	-3				
3	-131	214	-169	275		1	182	-534	156	-457	
5	-248	155	-329	206		2	154	-326	124	-265	
* I 2	1					3	-161	-168	-142	-148	
0	364	-44	302	-36		4	99	-161	102	-165	
2	24	275	29	330		5	92	-136	189	-280	
3	284	-12	321	-13		* I 3	-2				
* I 2	2					1	-450	-133	-450	-133	
0	298	-27	357	-33		2	-227	-376	-235	-388	
2	200	14	269	19		3	-389	-40	-419	-44	
* I 2	3					4	-227	-106	-250	-117	
0	362	112	403	125		5	-47	-142	-95	-286	
2	318	-80	475	-119		* I 3	-1				
						3	-125	272	-118	258	

* I 3	0			
2	-132	70	-210	111
3	-40	173	-58	249
* I 3	1			
0	261	275	179	189
2	60	120	82	165
* I 3	2			
2	8	-134	14	-254
* I 4	-13			
2	-76	209	-104	284
* I 4	-12			
2	5	150	5	151
* I 4	-11			
1	-80	-158	-141	-277
2	205	172	280	236
3	148	-24	305	-50
* I 4	-10			
1	-145	-169	-153	-179
2	268	94	268	94
3	49	-157	66	-211
* I 4	-9			
2	240	-28	309	-36
3	101	-219	111	-240
* I 4	-8			
1	-443	392	-434	383
2	-375	394	-393	413
* I 4	-7			
1	-256	79	-254	78
3	-305	-607	-357	-711
* I 4	-6			
1	21	428	13	273
2	405	271	471	316
3	-180	-210	-230	-267
* I 4	-5			
1	313	-75	256	-61
2	365	104	400	114
3	-378	30	-375	29
* I 4	-4			
1	-227	-184	-244	-198
2	357	-173	321	-156
3	-232	10	-199	8
* I 4	-3			
1	-238	140	-267	157
2	-198	-287	-213	-309
3	-248	75	-273	82
* I 4	-2			
1	162	24	263	38
2	-20	-250	-26	-318
* I 4	-1			
1	196	81	179	74
2	75	298	90	359
3	238	206	393	340

* 14	0			
2	172	-44	236	-60
* 15	-13			
2	-172	-105	-332	-202
* 15	-12			
2	-200	15	-325	25
* 15	-11			
2	50	195	66	258
* 15	-10			
2	-99	90	-119	108
* 15	-9			
1	55	-155	18	-50
2	7	454	9	582
3	306	24	398	31
* 15	-8			
1	-354	117	-259	86
2	-29	175	-57	340
* 15	-7			
2	87	-193	75	-167
3	178	-163	276	-253
* 15	-6			
3	128	-317	156	-385
* 15	-5			
1	84	-263	51	-159
3	-256	-140	-305	-167
* 15	-4			
1	-207	-46	-198	-44
2	-33	312	-32	299
* 15	-3			
1	-442	-206	-488	-228
2	-164	12	-230	17
* 15	-2			
1	-207	263	-187	237
2	177	-6	302	-9
* 16	-10			
2	-204	87	-268	115
* 16	-8			
1	217	125	149	85
* 16	-7			
1	102	-219	107	-230
* 16	-6			
1	48	-206	54	-234
* 16	-5			
1	30	-175	39	-228

Appendix II.B

C C structure factors for unobserved
reflections.

Layout of data

* k	h				
1		F_{OA}	F_{OB}	F_{CA}	F_{CB}

N.B. F_{OA} and F_{OB} correspond to the weakest
spot on the wedge.

Reflections marked with + were obscured by the back stop.

†*	0	1					*	2	9				
	1	-3	27	-693	67 37			5	49	115	26	62	
*	0	8						6	206	-6	356	-10	
	5	-92	108	-58	69		*	2	10				
*	0	9						5	15	103	19	132	
	1	-69	74	-69	74		*	2	11				
*	0	10						1	-39	-89	-18	-41	
	2	1	-95	2	-181			2	80	-20	61	-15	
	3	18	115	2	13			3	-36	-86	-48	-115	
	4	14	107	37	278			4	-42	-69	-145	-238	
	5	106	71	194	130			5	65	19	130	38	
	6	66	202	10	32		*	2	12				
*	0	11						4	-47	-4	-205	-16	
	4	12	-99	22	-190		*	2	13				
	6	-129	-13	-238	-24			1	24	54	55	127	
*	0	12						2	0	42	0	89	
	4	55	-62	70	-79		*	3	2				
	5	73	-13	85	-15			5	29	-111	58	-216	
*	0	13					*	3	6				
	4	-49	20	-3	1			5	142	3	21	1	
†*	1	0					*	3	7				
	1	-27	2	-1491	129			6	-215	140	-129	84	
*	1	3					*	3	8				
	6	-25	232	-23	210			2	74	-61	64	-53	
*	1	7						5	34	-122	35	-125	
	2	31	77	67	164			6	210	-67	205	-66	
*	1	9					*	3	9				
	6	192	-132	139	-95			5	-45	-103	-15	-34	
*	1	10						6	155	0	194	0	
	4	-63	83	-134	176		*	3	10				
	6	135	123	149	136			1	-59	80	-88	118	
*	1	11						5	28	78	32	89	
	3	-78	-69	-155	-136		*	3	11				
	4	79	-46	112	-65			1	44	-75	31	-52	
	5	47	-81	49	-84			4	-3	61	-6	115	
*	1	12					*	3	12				
	4	-53	-46	-61	-52			1	25	65	33	87	
*	1	13						2	-33	-44	-27	-36	
	3	11	-58	36	-193			3	-18	-45	-6	-14	
*	1	14					*	3	13				
	1	-33	18	-204	112			0	-15	3	-114	22	
*	2	3				†*		4	-1				
	6	168	-189	27	-31			2	-29	42	-969	1409	
*	2	4				*		4	0				
	6	-218	-161	-36	-26			6	118	213	238	431	
*	2	7				*		4	6				
	6	-252	101	-188	75			6	-248	81	-255	83	
*	2	8				*		4	7				
	6	234	82	220	77			5	84	-101	90	-108	
								6	-62	-220	-61	-217	

* 4 8					* 6 8				
4 -41 95 -4 10					4 -78 8 -130 13				
6 -175 -35 -134 -27					5 -22 60 -6 17				
* 4 9					* 6 9				
1 0 -102 -1 -179					1 -59 57 -35 34				
* 4 10					4 -38 31 -12 10				
1 31 -86 40 -113					* 6 10				
4 63 30 140 68					0 43 28 127 82				
* 4 12					1 -60 13 -40 8				
0 -15 38 -50 128					2 42 20 214 104				
1 46 7 185 29					* 7 -6				
* 5 4					5 -126 56 -133 60				
6 -119 -248 -90 -187					* 7 -2				
* 5 5					6 121 257 60 128				
6 -208 157 -99 75					* 7 0				
* 5 6					0 -14 66 -267 1303				
6 -72 -222 -125 -386					* 7 4				
* 5 7					1 38 99 86 225				
4 -69 81 -99 116					5 -74 -108 -99 -144				
6 -144 -115 -128 -103					6 43 -225 33 -169				
* 5 8					* 7 5				
1 -88 55 -69 43					6 -184 15 -159 13				
* 5 9					* 7 7				
4 70 29 248 103					4 -71 39 -89 48				
5 -25 -44 -42 -74					5 49 47 45 44				
* 5 10					* 7 8				
2 41 51 90 113					0 41 54 74 97				
4 33 6 308 60					2 26 65 6 14				
* 5 11					3 27 -71 40 -105				
0 32 34 165 173					4 41 34 36 30				
1 38 -43 33 -37					* 7 9				
2 20 35 48 83					0 -9 52 -22 133				
* 6 -5					2 51 -2 324 -15				
6 267 69 242 63					3 25 23 212 202				
* 6 0					* 8 0				
0 -53 -31 -2542 -1479					0 -41 62 -1055 1573				
* 6 1					* 8 3				
6 -250 -135 -123 -66					6 214 52 239 58				
* 6 3					* 8 4				
5 -83 115 -90 125					4 53 -89 101 -171				
6 21 -275 3 -42					6 165 -68 167 -69				
* 6 4					* 8 5				
5 75 -118 66 -104					3 -32 101 -25 80				
6 246 88 320 114					* 4 39 -85 79 -171				
* 6 5					* 8 6				
6 6 -233 3 -116					3 43 83 56 110				
* 6 6					4 65 -44 142 -97				
6 92 -165 115 -207					5 -2 64 -6 173				
* 6 8					* 8 7				
2 -82 14 -210 36					4 51 -13 180 -44				

* 8	8					* 11	-10				
0	42	36	64	56		6	-155	96	-213	132	
2	34	-38	74	-82		* 11	-9				
3	37	10	306	79		5	-99	77	-53	41	
* 8	9					6	-149	141	-89	84	
0	-5	-14	-94	-286		* 11	-7				
* 9	-2					6	99	206	81	169	
6	-252	-101	-168	-67		* 11	-1				
* 9	-1					5	79	86	120	132	
4	-90	67	-144	107		6	81	-164	113	-229	
5	-121	-69	-89	-51		* 11	0				
* 9	0					0	19	-83	86	-375	
3	-85	79	-126	117		6	-33	-125	-60	-226	
4	-75	84	-186	209		* 11	2				
* 9	1					0	31	70	68	152	
3	-57	102	-40	73		3	89	29	289	93	
6	-176	-153	-160	-140		4	-72	-35	-19	-9	
* 9	2					* 11	3				
6	-200	-47	-56	-13		4	-31	53	-121	211	
* 9	3					* 11	4				
0	21	82	61	245		2	52	33	80	51	
6	45	148	14	45		* 11	5				
* 9	5					0	23	-41	148	-261	
2	74	33	21	10		2	11	-39	43	-149	
3	86	31	35	13		* 12	-11				
5	-51	6	-218	26		2	-81	-37	-337	-154	
* 9	6					4	91	-7	79	-6	
2	-19	67	-39	140		5	-39	-85	-58	-126	
4	47	-15	446	-140		* 12	-10				
* 9	7					1	1	-104	1	-148	
0	53	6	191	23		4	-85	42	-106	53	
2	-43	28	-137	90		5	-17	-102	-1	-7	
3	-16	-30	-80	-146		* 12	-9				
* 9	8					6	39	150	22	85	
0	-9	-12	-23	-31		* 12	-8				
* 10	-9					3	110	24	150	33	
6	-132	193	-81	119		6	-29	176	-25	150	
* 10	-1					* 12	-7				
4	16	111	21	147		3	35	109	56	172	
5	131	26	164	33		6	-141	-119	-122	-103	
* 10	0					* 12	-2				
4	0	-11	3	-236		3	50	-96	89	-172	
* 10	5					* 12	0				
3	53	-45	156	-134		0	-4	78	-9	186	
4	-3	34	-16	198		1	6	-97	13	-196	
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0	-50	-9	-44	-8		4	-82	-12	-176	-27	
2	19	-42	35	-77		* 12	1				
* 10	7					1	-68	-60	-120	-105	
0	2	1	112	35		4	17	-68	20	-79	

* 12	2				* 13	3			
1	31	-77	45	-111	0	-11	10	-66	66
3	60	40	141	95	* 14	-13			
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* 12	3				3	31	-51	130	-213
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* 13	-12				4	-47	-39	-183	-152
4	-55	43	-153	120	* 14	-10			
* 13	-11				4	-12	69	-16	93
3	58	-73	164	-207	* 14	-9			
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* 13	-10				5	-36	36	-129	130
1	-75	65	-55	48	* 14	-8			
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4	81	-30	91	-34	4	-41	67	-150	246
5	76	-32	189	-80	5	-12	62	-40	202
* 13	-9				* 14	-7			
1	17	-100	4	-27	2	-58	59	-130	133
4	45	79	113	197	4	-55	58	-146	154
5	76	54	84	60	5	23	64	99	268
* 13	-8				* 14	-6			
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* 13	-7				* 14	-5			
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* 13	-6				5	51	5	201	21
4	-82	-49	-33	-20	* 14	-4			
* 13	-5				4	-37	-59	-120	-193
4	-31	88	-104	297	* 14	-3			
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4	76	51	169	114	* 14	-2			
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1	-88	25	-127	37	4	-16	-44	-72	-200
2	-68	-34	-80	-39	* 14	0			
4	-9	69	-6	42	0	38	-34	275	-246
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0	-48	48	-103	104	* 14	1			
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* 13	1				1	-36	-60	-47	-79
1	-1	74	-1	52	3	31	-37	225	-269
3	59	-5	204	-16	* 15	-11			
* 13	2				1	76	10	170	23
0	26	-41	78	-123	3	7	-61	19	-173
1	59	-10	227	-37					

* 15	-10			
1	75	-28	126	-47
3	-6	70	-15	169
* 15	-8			
3	-47	60	-70	91
4	-9	52	-72	411
* 15	-7			
1	17	83	27	127
4	52	8	65	10
* 15	-6			
1	78	-27	167	-59
2	-22	66	-61	184
4	47	-13	271	-78
* 15	-5			
2	-16	64	-66	267
* 15	-4			
3	-53	31	-210	120
* 15	-3			
3	-49	1	-164	4
* 16	-12			
1	8	46	4	24
* 16	-11			
1	30	49	157	252
2	-40	-7	-265	-45
* 16	-10			
1	58	-20	113	-39
* 16	-9			
1	-47	46	-47	46
2	-28	42	-138	208
* 16	-8			
2	-41	-30	-210	-151
* 16	-7			
2	-46	-21	-159	-73
* 16	-6			
2	-47	0	-262	-3
* 16	-5			
2	-20	35	-256	455

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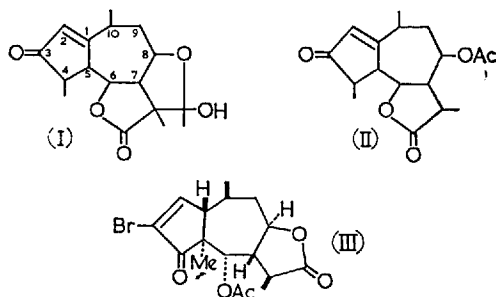
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The Structure of Bromoisotenulin

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TENULIN, which was isolated by Clark¹ from various *Helenium* species and studied by Barton and de Mayo,² was assigned formula (I), that of isotenulin being (II), but nuclear magnetic resonance studies³ have thrown doubt on these formulæ. The correct constitutions and relative stereochemistry have now



been determined by an *X*-ray study of bromoisotenulin⁴ (III).

The carbon skeleton is biogenetically abnormal, a methyl group having migrated from position 4 to 5; both five-membered rings are *trans*-fused to the seven-membered ring; non-bonded repulsions between the angular methyl (α to C-5) and the α -hydrogens on C-8 and C-10 cause the molecule to be appreciably folded. A Dreiding model shows this

interaction clearly and readily folds into the form found.

Bromoisotenulin ($C_{17}H_{21}BrO_5$) crystallises in the monoclinic system with 4 molecules in a cell of dimensions, $a = 8.75$, $b = 23.15$, $c = 10.28$ Å, $\beta = 121^\circ$; the space group being $P2_1$, the asymmetric unit comprises two crystallographically unrelated molecules. Some 2300 independent reflexions were measured visually, and the positions of the two sets of bromine atoms, deduced from the three-dimensional Patterson function, were such as to avoid phase ambiguity. The first electron-density synthesis revealed all 44 carbon and oxygen atoms. Refinement, not yet complete, has reduced R to 0.21 for all observed reflexions, and shows satisfactory agreement between bond lengths in the two molecules and identical stereochemistry. We publish this Communication at this stage partly because of the concordance between the two unrelated molecules in this study, and partly because of a recent chemical study by Herz *et al.*⁵ which, though devoid of stereochemistry, accords with our findings.

We are indebted for assistance and support to Professor D. H. R. Barton, to Dr. J. T. Pinhey, to Woolwich Polytechnic, to the British Council, and to the Department of Scientific and Industrial Research.

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¹ Clark, *J. Amer. Chem. Soc.*, 1939, **61**, 1836; 1940, **62**, 597.

² Barton and de Mayo, *J.*, 1956, 142.

³ Herz, Watanabe, Miyazaki, and Kishida, *J. Amer. Chem. Soc.*, 1962, **84**, 2601.

⁴ Clark, *J. Amer. Chem. Soc.*, 1939, **61**, 1840.

⁵ Herz, Rohde, Rabindran, Jayaraman, and Viswanathan, *J. Amer. Chem. Soc.*, 1962, **84**, 3857.

The Molecular and Crystal Structure of Caryophyllene Chlorohydrin

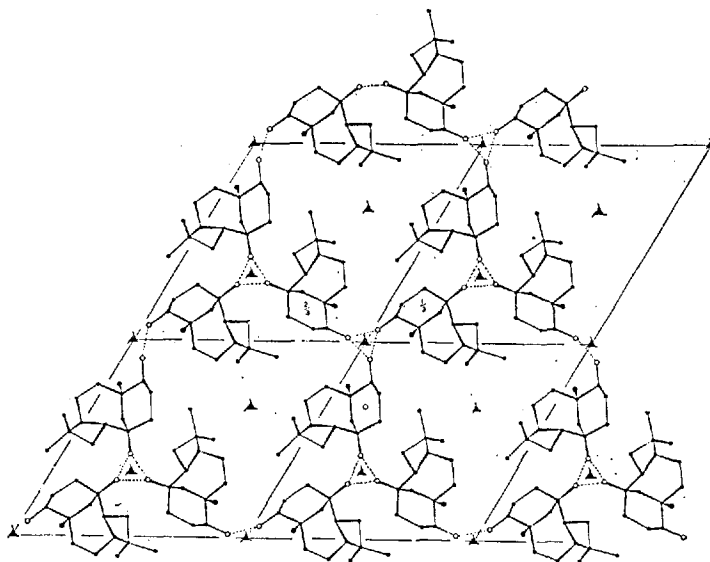
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In the unravelling of the structure of caryophyllene two derivatives played specially important parts: (I) The *X*-ray study by Robertson and Todd¹ of the halides derived from caryophyllene alcohol(I) established the mode of fusion of the cyclobutane ring, and confirmed all the chemical deductions to that date. (2) An elaborate chain of experiment and deduction centring largely around Treibs' epoxyketone² indicated that it has the stereochemistry and absolute configuration of (III).^{3,4} The formation from this of a chlorohydrin was the only inexplicable reaction; both its constitution and its mode of formation were obscure. An *X*-ray study and further chemical work, reported in the next Communication,⁵ have both led to the formulation of the chlorohydrin as (II).

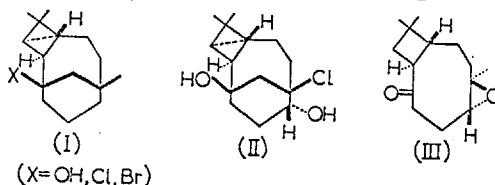
atom located from a sharpened three-dimensional ^{Patterson} Fourier. The other atoms emerged gradually from five successive Fouriers. Refinement, not yet complete, has reduced *R* to 0.17 for all reflections.

The stereochemistry and conformational details of (II) agree very closely with those of (I) deduced by Robertson and Todd. Even the same pattern of buckling occurs in the cyclobutane ring; the diagonals fail to intersect by about 0.25 Å, the upper one being shown dotted in both (I) and (II). The preparations of these compounds from caryophyllene involve two quite different cyclisations, but neither interferes with the cyclobutane ring. It is considered, therefore, that the close similarity of (I) and (II), and the orientation of the hydroxyl group vicinal to the chlorine atom in (II), confirm Barton's formula (III)



The crystals are trigonal prisms with three molecules in a cell of dimensions $a = 13.14$, $c = 7.11$ Å, ($d_{\text{obs}} = 1.209$ g.cm.⁻³; $d_{\text{calc.}} = 1.21$ g.cm.⁻³). The Laue symmetry is $\bar{3}$, the systematic absences are confined to $00l$ for $l \neq 3n$, and the molecules are optically active. The space group is, therefore, $P3_1$ or its enantiomorph, $P3_2$, and the former was initially chosen arbitrarily. The intensities of some 1150 Cu- $K\alpha$ reflections were measured visually, and the chlorine

and also validate all his chain of chemical argument including the deductions of relative configurations.³



¹ Robertson and Todd, *J.*, 1955, 1254.

² Treibs, *Ber.*, 1947, 80, 56.

³ Barton and Lindsey, *J.*, 1951, 2988; Barton, Bruun, and Lindsey, *J.*, 1952, 2210; Aebi, Barton, and Lindsey, *J.*, 1953, 3124; Aebi, Barton, Burgstahler, and Lindsey, *J.*, 1954, 4659.

⁴ Barton and Nikon, *J.*, 1954, 4665.

⁵ Greenwood, Qureshi, and Sutherland, following Communication.

Formulae (I), (II), and (III) have been drawn to comply with Barton and Nickon's assignment of absolute configuration,⁴ and the Figure confirms the space group as $P3_1$. The mode of formation and other chemical implications of formula (II) are discussed by Greenwood *et al.*⁵

The Figure shows how the molecules are linked by hydrogen-bond spirals around two screws leaving a large void around the third screw. The void has an effective diameter of about 6–7 Å, scarcely wide

enough to admit small molecules or chains: it is empty in the electron-density map, and this may explain why the crystals are so difficult to grow.

We are indebted to Dr. J. K. Sutherland for the specimen and for discussion, to the British Council and D.S.I.R. for financial support, and to Dr. O. S. Mills and Dr. J. S. Rollett for the use of their Mercury computer programmes.

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