X-Ray Studies in the Caryophyllene Series. The Chloride and Bromide from β-Caryophyllene Alcohol.

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A complete X-ray structure determination of the chloride from β-caryophyllene alcohol is described, based on an interpretation of the two principal electron-density projections. Partial phase determination was achieved by the isomorphous replacement method, making use of the bromide and chloride. The complete structure was built up by successive approximations from this basis, as recognisable fragments of the molecule became clear. The space group is $D_2^4 - P2_12_12_1$ and there are four molecules per unit cell.

The structure obtained is in complete agreement with that deduced from chemical evidence by Barton, Bruun, and Lindsey, and enables further stereochemical points to be established regarding the nature of the ring fusions and the shapes of the rings. It also supports the chemical structures assigned to β-caryophyllene alcohol and β-caryophyllene itself.

THE X-ray studies described in this paper commenced in 1950, when the constitution of β-caryophyllene and its derivatives was still in considerable doubt. Since that time infrared spectroscopic work (Šorm, Dolejš, and Plíva, *Coll. Czech. Chem. Comm.*, 1950, **15**, 186) and chemical work (Barton and Lindsey, *J.*, 1951, 2988; Barton, Bruun, and Lindsey, *J.*, 1952, 2210; Aebi, Barton, and Lindsey, *J.*, 1953, 3124) have cleared up the doubtful points, and the conclusions are in agreement with our X-ray work, on which a preliminary note has been published (Robertson and Todd, *Chem. and Ind.*, 1953, 437).

The isomorphous-replacement method of phase determination (Robertson, *J.*, 1935, 615; 1936, 1195) offers the best chance of success with a structure of this degree of complexity. It proved difficult to prepare suitable derivatives from β-caryophyllene itself; but the chloride and bromide of β-caryophyllene alcohol (Wallach and Walker, *Annalen*, 1892, **271**, 285; Tuttle, *N. Jahrb. Min., Geol. u.s.w.*, 1894—95, Beil.-Bd., **9**, 451; *Z. Krist.*, 1897, **27**, 526) are nicely crystalline and known to be isomorphous. These derivatives proved suitable for a complete structure determination of the tricyclic molecule, and the results, taken in conjunction with the chemical evidence of Barton, Bruun, and Lindsey (*loc. cit.*), support the constitution which these authors have assigned to β-caryophyllene.

Crystal Data.—β-Caryophyllene alcohol chloride, $C_{15}H_{25}Cl$; *M*, 240·8; m. p. 62—63°; *d*, calc. 1·115, found 1·135. Orthorhombic, $a = 8·27 \pm 0·04$, $b = 10·54 \pm 0·05$, $c = 16·47 \pm 0·08$ Å. Absent spectra, (*h*00) when *h* is odd, (0*k*0) when *k* is odd, (00*l*) when *l* is odd. Space group, $D_2^4 - P2_12_12_1$. Four molecules per unit cell. No molecular symmetry required. Volume of the unit cell = 1436 Å³. Absorption coefficient for X-rays ($\lambda = 1·54$ Å) $\mu = 22·2$ per cm. Total number of electrons per unit cell = F(000) = 528.

β-Caryophyllene alcohol bromide, $C_{15}H_{25}Br$; *M*, 285·3; m. p. 60—61°; *d*, calc. 1·292, found 1·293. Orthorhombic, $a = 8·35 \pm 0·04$, $b = 10·75 \pm 0·05$, $c = 16·41 \pm 0·08$ Å. Absent spectra, (*h*00) when *h* is odd, (0*k*0) when *k* is odd, (00*l*) when *l* is odd. Space group, $D_2^4 - P2_12_12_1$. Four molecules per unit cell. No molecular symmetry required. Volume of the unit cell = 1467 Å³. Absorption coefficient for X-rays ($\lambda = 1·54$) $\mu = 38·6$ per cm. Total number of electrons per unit cell = F(000) = 600.

For both substances the crystals were usually tabular with (001) well developed. Occasionally, small prismatic rhombs were obtained, elongated along *c*. The crystals have been described by Tuttle (*loc. cit.*) and his figures for the axial ratios are in very good agreement with our measurements.

Structure Analysis. Patterson Syntheses.—Our work on this structure has been confined to a study of the three axial zones of reflections from each crystal, and the corresponding two-dimensional projections. There are naturally some difficulties in resolving all the atoms by these methods; but although the accuracy finally attained is not very

high (about ± 0.1 Å in bond lengths) it is sufficient to solve the structure completely as regards the configuration of the molecule.

There is no centre of symmetry in the space group $P2_12_12_1$, the elements being three mutually perpendicular sets of non-intersecting screw axes. The general origin ("International Tables for X-Ray Crystallography," 1952, Kynoch Press, Birmingham) is equidistant from three pairs of these axes. All co-ordinates given in this paper are referred to this origin. The projections along the three principal axes are centrosymmetrical, however, at the points where the screw axes intersect the projection planes, and it is convenient to use these points as origins for the calculation of structure factors (Tables 4 and 5). These origins are not spatially coincident, and the ones chosen are related to the general origin as follows : zone $(0kl)$ origin at $(\frac{1}{4}0\frac{1}{4})$, zone $(h0l)$ origin at $(\frac{1}{4}0\frac{1}{4})$, zone $(hk0)$ origin at $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$.

The first step in the analysis is the determination of the positions of the replaceable halogen atoms, of which there are four in the unit cell. This was accomplished without difficulty by an application of the Patterson method. Fig. 1 shows a portion of the vector map obtained for the a-axis projection of β-caryophyllene bromide. Large peaks

FIG. 1. *Asymmetric portion of Patterson projection along a axis for β-caryophyllene bromide.*
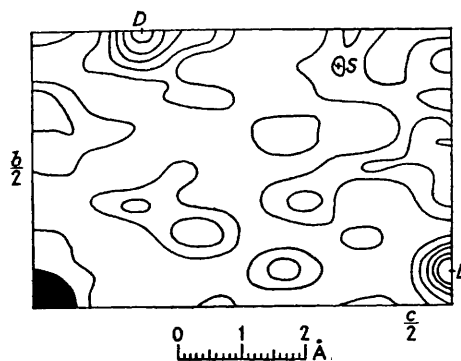
such as D, at $y = \frac{1}{2}$ and $z = \frac{1}{2}$, are formed by the superposition of two equivalent vectors related to each other by the centre of symmetry in this projection, whereas a peak such as S is due to a unique vector crossing the centre of symmetry.

Similar syntheses were applied to the $(h0l)$ and $(hk0)$ data. Solution of the vector sets was effected without difficulty and the co-ordinates obtained for the bromine atom are given in Table 1.

TABLE 1.

	Bromine co-ordinates		
Zone	x/a	y/b	z/c
$0kl$	—	0·218	0·567
$h0l$	0·290	—	0·563
$hk0$	0·292	0·218	—
Average	0·291	0·218	0·565

The position of the chlorine atom in the chloride was found to be closely similar, and the co-ordinates obtained, after the structure had been fully refined, are included in Table 2. The bromide was utilized for phase determination, and a number of preliminary projections of the structure were obtained which established its close isomorphism with the chloride. All the later work on the refinement of the structure was, however, carried out on the chloride, and we do not feel justified in reporting any further co-ordinates for the bromide; in the preliminary studies they were not found to differ significantly from those obtained for the chloride.

Isomorphous-replacement Method and Preliminary Structure.—The positions of the halogen atoms having been determined, it was possible to calculate their contribution to each reflection and assess their effectiveness for phase determination. If we assume strict isomorphism, then for any plane we can write the following relation between the structure factors F for the bromide and chloride :

$$F(C_{15}H_{25}Br) - F(C_{15}H_{25}Cl) = F(Br) - F(Cl) = \Delta F$$

The contributions from the atoms other than halogen cancel out, and the difference, ΔF, may be calculated from the atomic scattering curves (f) for bromine and chlorine, and the purely geometrical factor s which depends upon their known co-ordinates :

$$\Delta F = s(f_{Br} - f_{Cl})$$

If the value of ΔF is large enough to be significant with the accuracy available, then it can be used to determine the signs of the two structure factors $F(C_{15}H_{25}Br)$ and $F(C_{15}H_{25}Cl)$ without ambiguity.

The difficulties which attend the practical application of this method are mainly concerned with making reliable absolute determinations of the F values, and with uncertainties regarding the strictness of the isomorphism. In this investigation we did not make any direct absolute measurements. Instead, the relative F values were put on an approximately absolute scale by making use of various modifications of Wilson's statistical methods (*Nature*, 1942, **150**, 152). A check on these results was made for certain special planes, *e.g.*, when the reflection from one of the isomorphs, say the chloride, is absent or near zero, then

$$F(C_{15}H_{25}Br) - 0 = s(f_{Br} - f_{Cl})$$

and this value can be calculated. Again, reflections for which the halogen contribution is near zero should have approximately the same absolute value in the case of the two isomorphs, and this enables the relative scaling factor to be determined.

Reasonably consistent results were obtained by these methods, but phase determination remained uncertain for many reflections with small halogen contribution. However, preliminary electron-density projections of the structure were now prepared for the bromide. For the projection along the a axis, 80 structure factors in the $(0kl)$ series were used, and for the projection along the b axis, 73 structure factors in the $(h0l)$ series. No useful projection could be obtained along the c axis.

TABLE 2. *Co-ordinates. Origin equidistant from three pairs of non-intersecting screw axes.*

| Atom	x/a	y/b	z/c	$X(\text{Å})$	$Y(\text{Å})$	$Z(\text{Å})$
Cl	0·285	0·207	0·564	2·36	2·18	9·29
C(1)	0·411	0·068	0·557	3·40	0·72	9·18
C(2)	0·438	0·017	0·467	3·62	0·18	7·70
C(3)	0·323	0·053	0·395	2·67	0·56	6·51
C(4)	0·475	0·051	0·341	3·93	0·54	5·62
C(4')	0·466	0·165	0·276	3·85	1·74	4·54
C(4'')	0·525	−0·080	0·296	4·34	−0·84	4·88
C(5)	0·577	0·090	0·419	4·77	0·95	6·90
C(6)	0·744	0·038	0·438	6·15	0·40	7·22
C(7)	0·744	−0·065	0·511	6·15	−0·68	8·42
C(8)	0·710	−0·004	0·598	5·87	−0·04	9·85
C(8')	0·863	0·038	0·638	7·14	0·40	10·51
C(9)	0·632	−0·103	0·655	5·23	−1·09	10·79
C(10)	0·468	−0·139	0·624	3·87	−1·46	10·28
C(11)	0·345	−0·023	0·614	2·85	−0·24	10·12
C(12)	0·590	0·110	0·590	4·88	1·16	9·72

The interpretation of these preliminary maps proved difficult, as there were several unresolved regions on both projections.* At this date (1950) one of the few features of the β-caryophyllene structure that had been definitely established from chemical evidence was the existence of a four-membered ring with a *gem*-dimethyl group (Rydon, *J.*, 1936, 593; 1937, 1340). These atoms could be located on the two projections with some certainty, but attempts to build the complete structure from this basis were at first unsuccessful. It was realised, however, that, although the chemical structure of β-caryophyllene was in doubt, all the possibilities indicated the presence of a six-membered ring in the tricyclic alcohol and its derivatives It was also clear that with the position assigned to the *cyclo*butane ring in the two projections, the *cyclo*hexane ring would be badly resolved,

* These preliminary electron-density projections have been reproduced in the Third Henderson Memorial Lecture (*Roy. Inst. Chem. Monographs*, 1954, No. 6).

and in the *a*-axis projection in particular would provide only an end-on view. This interpretation of one of the unresolved regions enabled a trial structure to be set up, and structure-factor calculations on this basis led to an immediate improvement in the agreements obtained with the observed values.

From this point onwards the refinement of the structure proceeded steadily. All the later work was based on the intensities obtained from the chloride, which could be measured more accurately than those of the bromide, owing to the smaller absorption coefficient. The electron-density maps were also easier to interpret because diffraction effects from the heavy atom were less serious. In the later refinement work considerable use was made of the method of difference synthesis. At one stage these methods showed that the methyl group, $C_{(8')}$, had been wrongly placed, and after correction the structure-factor

FIG. 2. *Electron-density projection on* (100). *Contours at intervals of* 1 eÅ^{-2}, *except on chlorine, with one-electron line dotted. This projection is based on* 115 (0*kl*) *structure factors.*
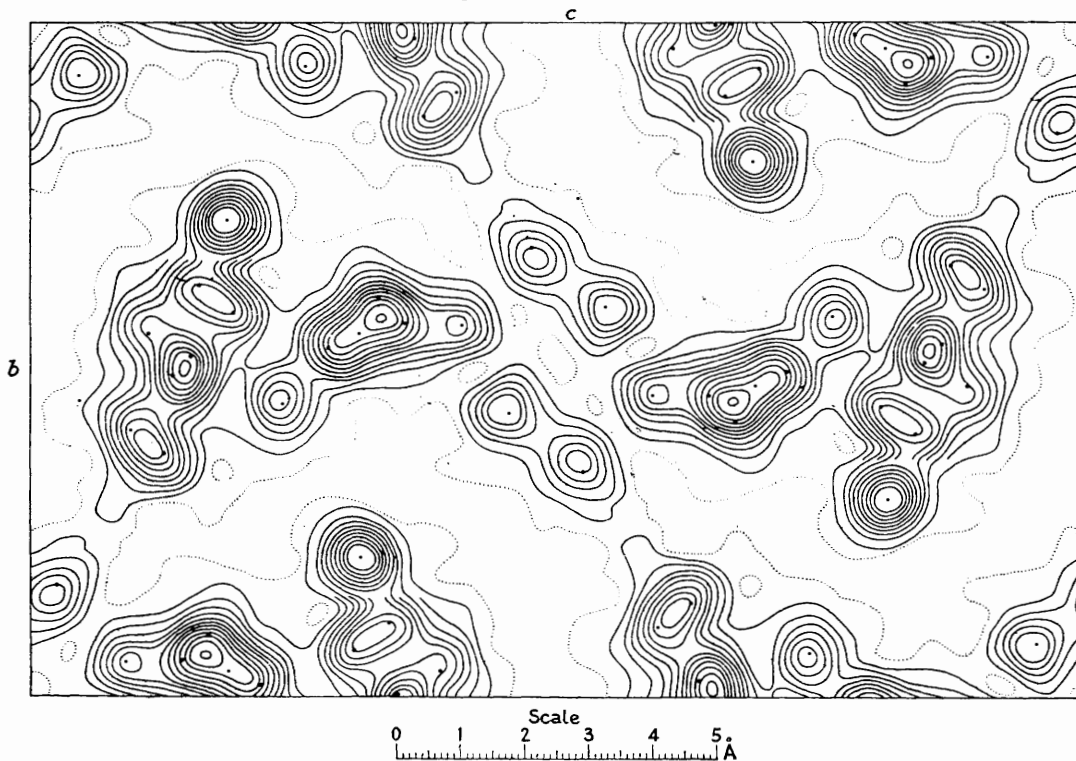

agreements showed further large improvements. In all, some 40 two-dimensional syntheses were made in the course of this work.

The Final Structure. Co-ordinates and Dimensions.—When the refinement work on the chloride had been completed, the final discrepancies between calculated and observed structure factors in the different zones, expressed as percentages of the total of the measured structure factors in the usual way, were as follows : (0*kl*) zone, 15·7%; (*h*0*l*) zone, 12·3%; (*hk*0) zone, 24·0%; overall, 17·5%. Electron-density maps were not prepared for the (*hk*0) zone, but difference-synthesis refinements were carried out. Hydrogen-atom contributions were not included in any of the structure factor calculations (Table 4). The discrepancy figures show that a reasonably accurate picture of the structure has now been obtained.

The final electron-density projections along the *a* and *b* axes are shown in Figs. 2 and 4, and corresponding views of the atomic positions in Figs. 3 and 5. Reasonably good

resolution of most of the carbon atoms is achieved in Fig. 4, but only a few are separately resolved in Fig. 2. It is clear, however, that the plotted positions of the atoms in Fig. 3 and Fig. 5 explain all the features of the electron density maps. A more detailed picture of the structure could only be obtained from a full three-dimensional analysis.

The co-ordinates of the atoms were individually adjusted from a study of a large number of successive difference syntheses on the three principal zones, and very good agreement was finally obtained for the co-ordinate common to any two zones. After

FIG. 3. *The atomic arrangement in the* (100) *projection.*
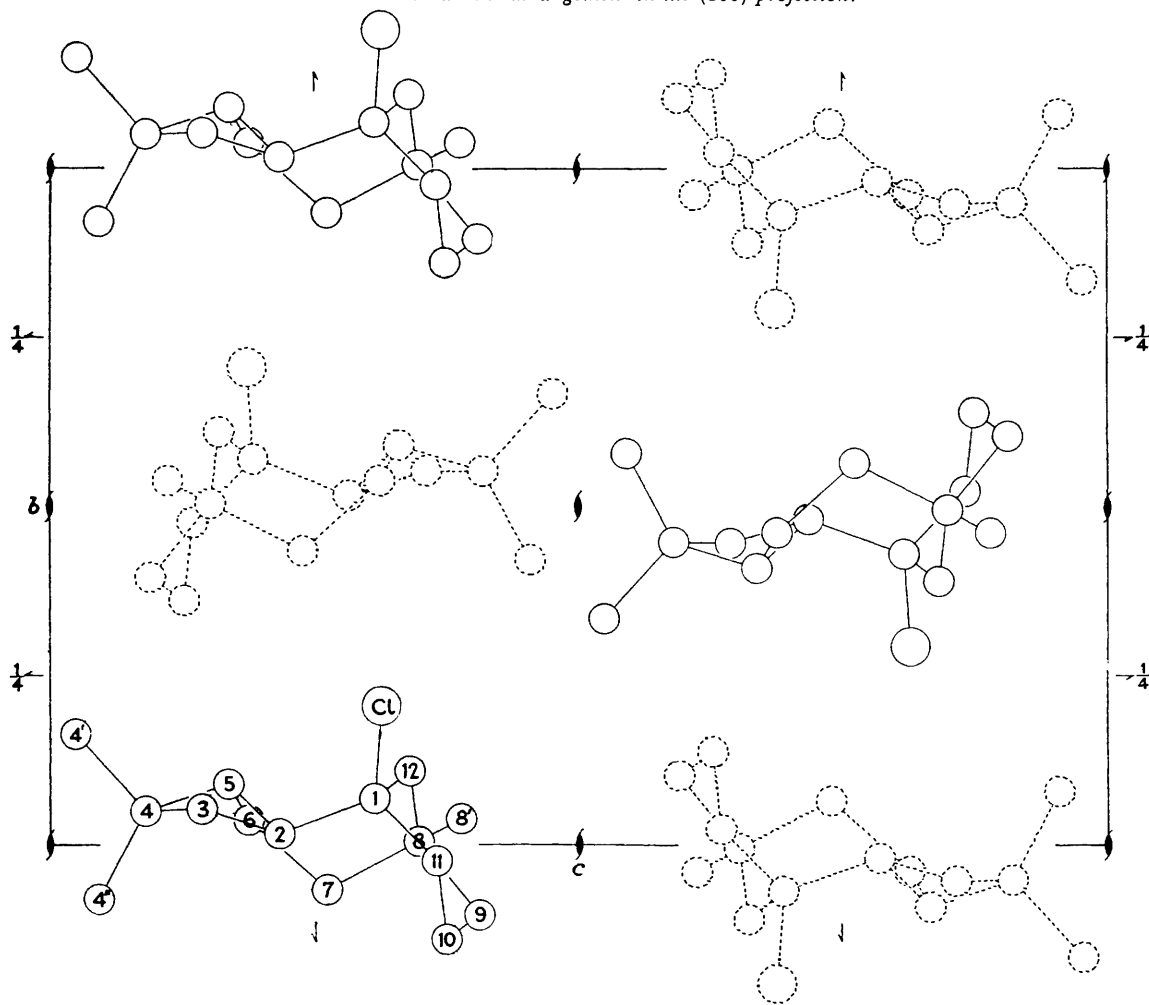
averaging, the final values are given in Table 2, with the atoms numbered as shown in the diagrams.

The interatomic distances calculated from these co-ordinates are given in Table **3**. All the carbon–carbon bond lengths are found to lie in the range 1·45—1·64 Å, with a mean

TABLE 3. *Interatomic distances* (Å).

C(1)–Cl = 1·79	C(2)–C(3) = 1·57	C(5)–C(6) = 1·52	C(8)–C(8′) = 1·50
C(1)–C(12) = 1·64	C(3)–C(4) = 1·54	C(6)–C(7) = 1·61	C(9)–C(10) = 1·50
C(1)–C(11) = 1·45	C(4)–C(5) = 1·59	C(7)–C(8) = 1·59	C(10)–C(11) = 1·60
C(1)–C(2) = 1·59	C(4)–C(4′) = 1·62	C(8)–C(12) = 1·56	
C(2)–C(5) = 1·60	C(4)–C(4″) = 1·62	C(8)–C(9) = 1·55	

FIG. 4. *Electron-density projection on* (010). *Contours at intervals of* 1 eÅ⁻², *except on chlorine, with one-electron line dotted. This projection is based on* 84 (h0l) *structure factors.*
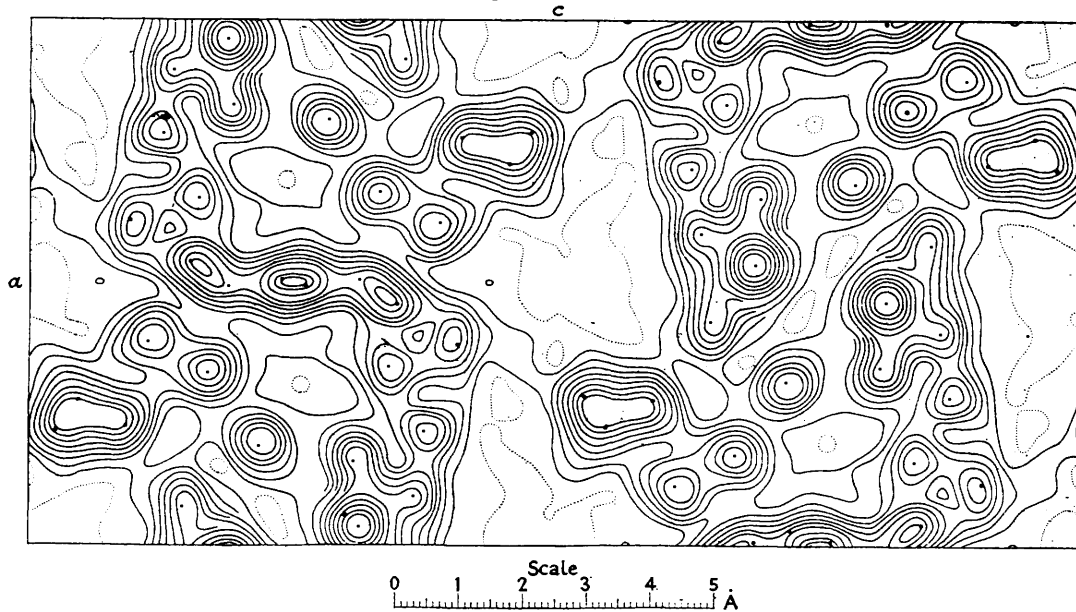
FIG. 5. *The atomic arrangement in the* (010) *projection.*
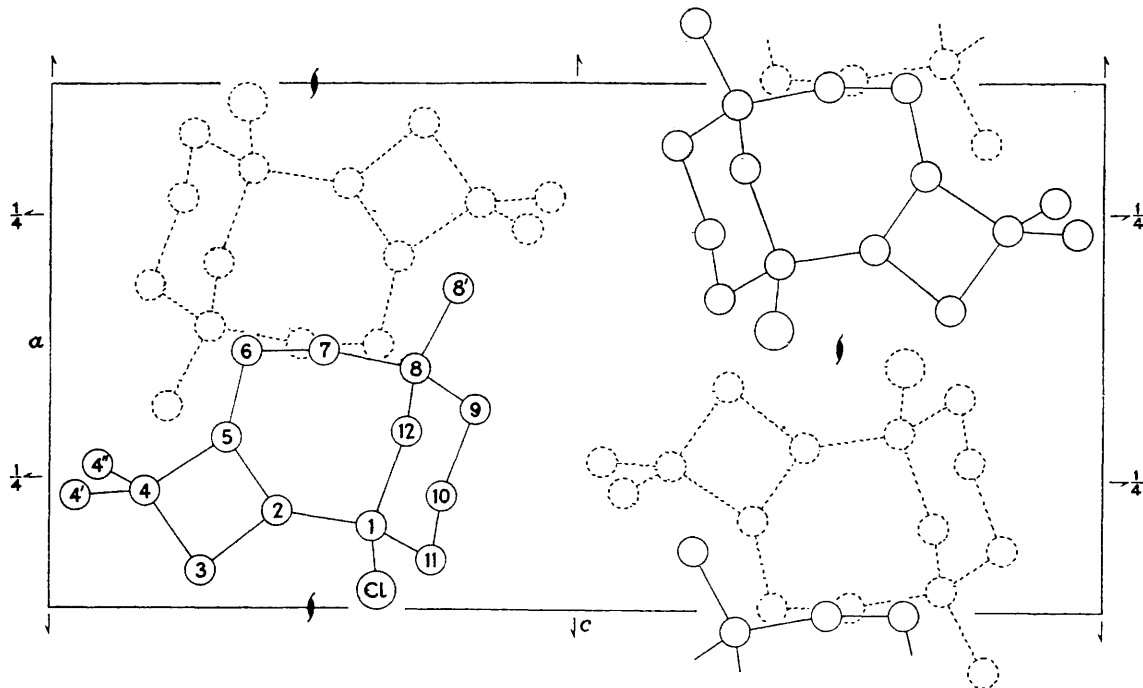
value of 1·57 Å. If we exclude the bonds from atom C(1), where the co-ordinates are more likely to be inaccurate because of the proximity of the chlorine atom, the carbon–carbon bonds lie in the range 1·50—1·62 Å, and provide clear evidence for the existence of single bonds throughout the molecule. The probable error of about ±0·06 Å is of the order to be expected at the present stage of refinement for a structure of this complexity, when no account is taken of the hydrogen atoms. We have not made a complete survey of the intermolecular approach distances, but the minimum appears to be slightly over 4·0 Å as in most saturated hydrocarbons.

DISCUSSION

The structure now reached in this analysis for the chloride of β-caryophyllene alcohol has been obtained directly from the X-ray data and is independent of the chemical evidence. It is true that in the early stages of the analysis chemical evidence for the existence of a four-membered ring with *gem*-dimethyl groups in β-caryophyllene, and the existence of a six-membered ring in the alcohol derivative, enabled us to interpret the early electron-density maps and facilitated the final solution. The maps themselves, however, are based
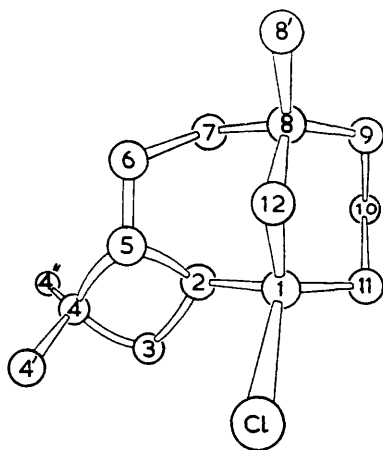
FIG. 6. *Perspective drawing of the β-caryophyllene chloride molecule.*

on *measured* structure amplitudes, and the great majority of the phases are also obtained directly by the isomorphous substitution method. Additional phases derived from trial structures incorporating the chemical features mentioned above played an important part in solving the projections; but the process of successive approximation involved renders the final results independent of these particular chemical assumptions. That is to say, initial chemical postulates differing in quite material respects would lead to the same final solution. This is generally true in X-ray structure analysis; but very interesting evidence of the fact was obtained in the present instance when it was found that one of the methyl groups (8′) had been placed in a position which was quite wrong in one of our trial structures.

The molecular model which results from the co-ordinates in Table 2 is shown in Figs. 3 and 5, and the stereochemical aspects are shown more fully in Fig. 6. The chemical constitution which corresponds with this model (I) is in complete agreement with that deduced from chemical evidence by Barton, Bruun, and Lindsey (*J.*, 1952, 2210, formula XIX). In addition, the X-ray evidence enables certain stereochemical points to be elucidated, which are difficult to settle conclusively from the chemical evidence alone. Thus, the *trans*-fusion of the *cyclo*butane ring to the larger ring is established; and the hydrogen atom attached to $C_{(5)}$, although not resolved on the electron-density maps, must clearly lie on the same side of the molecule as the methylene bridge, $C_{(12)}$. The six-membered carbon ring has the usual staggered *trans*-configuration, with very little distortion, while the adjacent seven-membered ring is boat-shaped, with atoms 5 and 6 *cis* to atom 12. The four-membered ring is somewhat distorted from a planar configuration, as would be expected from the nature of the fusion with the larger ring.

TABLE 4. *Caryophyllene chloride. Measured and calculated values of the structure factor.*

hkl	F (meas.)	F (calc.)	hkl	F (meas.)	F (calc.)	hkl	F (meas.)	F (calc.)	hkl	F (meas.)	F (calc.)
000	—	528	290	10	11	605	10	−11	04,12	7	− 5
200	12	14	490	7	7	606	11	−11	04,14	7	4
400	31	30	790	6	4	607	7	− 8	04,15	7	− 8
600	11	11	2,10,0	10	8	608	13	−15	051	11	−14
020	105 [1]	123	6,10,0	7	4	60,11	9	11	052	9	− 5
040	9	18	2,11,0	12	− 8	60,13	10	10	053	21	27
060	15	−10	5,11,0	4	− 4	60,17	2	− 4	054	12	17
080	21	−18	2,12,0	7	8	701	19	−18	055	18	−15
002	87	−96				702	12	−13	056	7	7
004	73	−76	101	— [2]	9	704	6	−12	059	20	22
006	56	57	103	16	15	70,12	7	8	05,10	13	6
008	25	−22	104	47	−49	805	8	−13	05,11	8	− 7
00,10	11	10	105	24	−21	806	8	9	05,12	13	15
00,14	12	−16	106	33	33	807	9	− 9	05,14	13	−10
00,18	7	− 8	107	30	−35	80,11	12	12	05,15	4	− 4
			109	18	−16	902	5	− 8	061	45	−45
110	26	32	10,10	9	11	903	7	− 4	065	11	14
210	41	−38	10,11	16	−16	904	7	−10	066	8	7
310	15	−18	10,12	5	− 7	905	7	− 4	067	8	−10
510	13	15	10,13	14	−10	909	6	5	068	11	13
610	9	− 5	10,14	11	10				069	29	30
710	18	−22	10,17	13	12	011	9	−10	06,11	17	−18
810	10	−10	10,19	4	2	013	64	62	06,12	8	− 9
120	29	−43	201	8	− 5	014	56	−57	06,14	5	7
220	5	−13	202	79	79	015	36	31	06,15	6	9
320	34	21	203	31	−30	016	39	37	072	14	− 7
420	10	16	204	10	− 7	017	22	−26	073	10	− 7
620	8	0	205	17	15	019	10	−13	074	7	4
10,20	5	5	206	31	−29	01,10	24	−26	075	31	33
130	5	−11	208	9	−14	01,12	12	14	077	22	−23
230	25	24	20,11	10	13	01,14	14	−15	078	7	−11
330	33	−19	20,12	7	10	021	62	−62	079	8	5
430	16	17	20,13	20	23	022	29	−28	07,10	5	− 7
530	21	24	20,15	12	9	023	24	22	07,11	12	15
630	20	−26	20,16	12	14	024	47	−45	07,12	9	9
730	11	5	20,17	11	−10	025	54	45	07,13	11	−10
830	8	9	20,18	5	6	026	10	−16	07,15	4	1
10,30	6	− 6	20,19	8	− 5	027	59	−58	07,16	6	− 4
140	24	−23	20,20	3	2	028	25	26	081	11	10
240	44	−53	302	46	−40	029	23	23	082	7	6
340	28	21	303	24	−23	02,10	20	−16	083	6	−12
440	10	10	305	33	−28	02,13	13	−13	085	19	−23
740	7	5	306	40	−34	02,14	10	11	087	9	14
840	6	− 2	307	23	−22	02,16	10	−11	088	10	12
150	17	13	309	10	−14	02,20	5	3	08,15	5	− 5
250	29	−44	30,10	11	11	031	15	7	091	13	−11
550	7	5	30,12	8	10	032	58	−61	092	13	−17
650	8	− 9	30,13	8	10	033	63	−49	093	10	13
750	12	− 8	402	13	10	034	51	39	094	11	14
.850	6	4	404	24	27	035	18	24	096	9	−11
160	26	−26	405	17	−19	037	28	−30	099	9	8
260	11	6	407	23	−16	038	15	13	09,11	7	− 6
460	17	− 6	408	19	−16	03,11	16	19	09,15	4	1
560	21	−22	409	8	− 7	03,12	10	− 8	0,10,1	5	− 6
960	7	5	501	6	3	03,13	11	− 9	0,10,2	6	− 8
170	8	− 9	502	9	− 7	03,14	6	− 5	0,10,3	6	− 3
270	13	− 6	503	10	−12	03,18	4	− 5	0,10,5	7	− 6
470	21	23	504	31	−27	041	4	− 8	0,10,6	9	10
670	11	− 6	505	11	7	042	40	−37	0,10,8	11	− 6
870	7	9	507	9	9	043	18	−14	0,11,4	4	− 6
180	14	−22	509	15	−16	045	35	34	0,11,8	6	3
380	14	17	50,11	19	−18	046	9	9	0,12,3	4	5
480	10	−10	602	29	27	047	18	15	0,13,5	4	0
580	7	4	603	8	−12	048	16	− 7			
880	4	− 1	604	13	14	049	8	7			

[1] Value probably low owing to extinction.   F = 123 used in Fourier synthesis.
[2] Intensity difficult to estimate because of spot shape.

It also follows that the constitution of β-caryophyllene alcohol (II), from which the chloride is derived, is in agreement with the chemical evidence, the tertiary hydroxyl group being replaced without inversion or rearrangement. Finally, from the arguments given by Barton, Bruun, and Lindsey (*loc. cit.*) it is clear that the present work supports the constitution (III) for caryophyllene. A further discussion of the stereochemistry of caryophyllene has recently been given by Aebi, Barton, and Lindsey (*J.*, 1953, 3124), from whose paper formula (III) is taken.
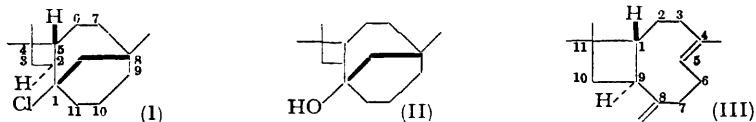
EXPERIMENTAL

β-*Caryophyllene Alcohol.*—β-Caryophyllene, purified by fractional distillation, was hydrated by Asahina and Tsukamoto's method (*J. Pharm. Soc. Japan*, 1922, 463). β-Caryophyllene alcohol thus obtained was purified by steam-distillation and crystallisation from acetone, and had m. p. 92°.

β-*Caryophyllene Chloride.*—β-Caryophyllene alcohol (2·2 g.) and phosphorus pentachloride (2·1 g.) were allowed to react slowly. The product was isolated in the usual way, and after three crystallisations from ethyl alcohol had m. p. 62—63°.

β-*Caryophyllene Bromide.*—β-Caryophyllene alcohol (2·2 g.) and bromine (3·2 g.) with a minimum of acetic acid were boiled with a trace of iodine for 3 hr. Further bromine in acetic acid was then added and boiling continued for a further 3 hr. (Deussen, *J. pr. Chem.*, 1936, **145**, 31). The product was isolated and after five crystallisations from ethyl alcohol had m. p. 60—61°.

Crystal Data and Intensities.—Rotation, oscillation, and moving-film photographs were taken with copper $K\alpha$ radiation, $\lambda = 1.542$ Å. The intensities were estimated visually by the multiple-film technique on moving-film photographs. In all, 232 bromide reflections and 254 chloride reflections were observed on the three principal axial zones, these representing 47% and 51% respectively of the 498 reflections possible for each crystal. The crystals of both substances are volatile and special precautions were necessary to preserve them for the time

TABLE 5.   *Caryophyllene bromide.   List of observed structure factors, with signs determined by replacement method.*

hkl	F	hkl	F	hkl	F	hkl	F	hkl	F	hkl	F
000	600 [1]	203	−65	607	−13	027	−90	048	−57	073	−50
200	70	205	−47	60,13	23	028	84	04,10	27	074	22
400	66	206	−74	701	−32	029	41	04,11	(±)12	075	67
020	81	208	−53	702	−36	02,10	−47	04,15	−21	077	−31
040	67	20,11	34	704	−33	02,13	−24	04,16	11	07,11	32
060	−44	20,13	37	70,12	23	02,14	30	051	−34	07,13	−24
080	(±)23	20,16	29	807	−12	02,16	−30	052	(+)16	081	45
002	−121	20,19	−12	903	−11	031	33	053	60	083	(±)11
004	(±)95	302	−85	904	−19	032	−105	054	(±)21	085	−41
006	121	305	−56	909	11	033	−104	055	−49	087	42
008	−81	306	−70	011	(−)15	034	121	056	35	089	−18
0010	39	307	−62	012	59	035	51	059	44	08,15	(−)13
0014	−35	309	−34	013	87	036	−29	05,11	−34	091	−32
		30,10	35	014	−131	037	−41	05,12	39	092	−25
103	41	30,12	29	015	(±)40	038	(±)14	05,13	18	093	38
104	−73	30,13	26	016	82	039	−14	05,14	−27	094	(±)13
105	−60	402	33	017	(±)29	03,10	32	061	−89	095	−25
107	−74	405	−57	01,10	−67	03,11	35	062	25	09,11	−16
109	−56	407	−38	01,12	47	03,12	−35	063	14	0,10,1	−28
10,10	21	408	−43	01,14	−30	03,13	(−)21	065	32	0,10,3	(+)13
10,11	−26	501	19	021	−85	041	30	067	−42	0,10,7	(−)13
10,12	21	502	−45	022	21	042	−81	068	32	0,10,8	(±)11
10,14	16	504	−81	023	36	043	−35	069	55	0,10,9	(+)11
10,17	28	509	−29	024	(±)52	045	24	06,11	(±)25	0,11,5	(+)11
201	−33	603	−38	025	76	046	45	06,15	(±)20		
202	125	605	−35	026	−56	047	50	072	−28		

[1] Calculated value.

required for the moving-film exposures. Of several methods tried, sealing in narrow lithium borate tubes was most successful, although this added to the background scatter. Crystals of approximately square cross section perpendicular to the rotation axis were employed to minimize absorption errors. The path length of the beam in the crystal, which was completely bathed in the radiation, varied from 0·2 to 0·35 mm. for different specimens of the bromide, and from 0·2 to 0·6 mm. for different specimens of the chloride. Some specimens were dipped in liquid air and rephotographed without noticeable change in intensities. It was concluded that extinction errors were not serious. Structure factors were derived by the usual mosaic crystal formula. The observed values are given in Tables 4 and 5.

Structure Calculations.—The various two-dimensional Fourier syntheses were calculated in the usual way, using the 3-figure strip and stencil method (Robertson, *J. Sci. Instr.*, 1948, **25**, 28). The formulæ for the structure-factor calculations reduce to simple sine and cosine products when the origin is chosen on a two-fold axis, and this was done for all the projections. The signs of the calculated values of the structure factors given in Tables 4 and 5 are related to these non-coincident origins.

The theoretical scattering curves given by James and Brindley (*Phil. Mag.*, 1932, **12**, 81) for chlorine and bromine were employed. The temperature factor was found to be abnormally high, and in the Debye–Waller factor B was given a value of $4·4 \times 10^{-16}$. The carbon scattering curve finally used was that given by McWeeny (*Acta Cryst.*, 1951, **4**, 513) for carbon (valence states) with $B = 3·5 \times 10^{-16}$.

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