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The Determination of the Crystal Structure of Methyl Melaleucate Iodoacetate

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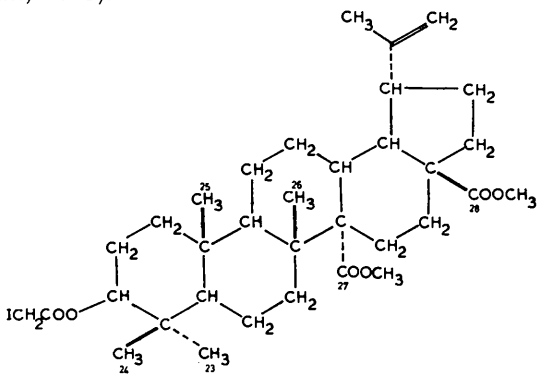
The crystal structure of methyl melaleucate iodoacetate ($C_{34}H_{51}O_6I$), a derivative of melaleucic acid, was determined from phases calculated by anomalous dispersion methods (Ramachandran & Raman, 1956) and refined by block diagonal least squares to a final R index of 0·079 for 1342 measurable reflexions. The unit cell is orthorhombic, space group $P2_12_12_1$ with $a=15{\cdot}719$, $b=24{\cdot}533$ and $c=8{\cdot}618$ Å. 48 of the 51 H atoms were located in a 3–D difference synthesis enabling a close study of the packing and associated steric hindrance in the structure. Abnormally high C–C bond lengths of up to 1·66 Å are attributed to strain resulting from this hindrance.

Introduction

Methyl melaleucate iodoacetate is a derivative of melaleucic acid, a plant product isolated along with betulinic acid from the paper-like barks of *Melaleuca rhaphiophylla* Schau., *M. viminea* Lindl. and *M. cuticularis* Labill. Melaleucic acid was suggested by Arthur, Cole, Thieberg & White (1956) to have the constitution 3β-hydroxylup-20(29)-ene-25,28-dioic acid. Subsequent investigation showed that the more hindered carboxyl group was not at C(25), and with the study of a number of derivatives by nuclear magnetic resonance spectra, Chopra, Fuller, Thieberg, Shaw, White, Hall & Maslen (1963) suggested that it was 3β-hydroxylup-20(29)-ene-27,28-dioic acid. Methyl melaleucate iodoacetate (I) was prepared with the aim of using X-ray diffraction techniques to provide an independent check of the molecular formula and the position of the carboxyl at C(27). Preliminary structure analysis confirming the suggested constitution has already been reported (Chopra *et al.*, 1963).



(I)

Since the derivative contained an iodine atom it was intended to solve the structure by normal heavy-atom techniques. However, during the collection of intensity data large differences between the intensities of the hkl and the $\bar{h}\bar{k}\bar{l}$ reflexions were observed, indicating the possibility of using anomalous dispersion phasing methods.

Two techniques have been proposed for the solution of structures from anomalous dispersion measurements. They are, the direct phase method suggested by Ramachandran & Raman (1956) and the sine-Patterson methods proposed by Okaya, Saito & Pepinsky (1955). Geurtz, Peerdeman & Bijvoet (1963) have indicated in a comparison of these two methods that the results from the sine-Patterson function are less clear than those of the direct phase method. In view of this and the possible difficulties in deconvoluting the sine-Patterson function, the direct phase method was chosen to solve this structure.

It is interesting to note that the majority of previous structures solved by the direct phase methods such as L(+)-lysine hydrobromide dihydrate (Raman, 1959), Factor Vla (Dale, 1962) and cystine hydrobromide (Geurtz *et al.*, 1963) contained centrically arranged anomalous scatterers which may have presented problems of artificial symmetry if solved by normal methods. However, although no such difficulties arose in the solution of methyl melaleucate, as the iodine is acentrically placed, the direct phase method was chosen as a superior technique.

Experimental

Crystal data

Methyl melaleucate iodoacetate ($C_{34}H_{51}O_6I$).
M.W. 682·7.

$$a=15{\cdot}719\pm5,\ b=24{\cdot}533\pm7,\ c=8{\cdot}618\pm5\ \text{Å}.$$
$$V=3323{\cdot}3\ \text{Å}^3.$$

Space group: $P2_12_12_1$ (D_2^4), acentric with 4 molecules per unit cell. $F(000)=1428$ electrons. Crystal form: colourless orthorhombic needles with long axis in c direction. Crystallized from methanol. Density:

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measured = 1·37 ± 1, calculated = 1·366 ± 1. Linear absorption coefficient for Cu $K\alpha$: 80·7 cm^{-1}.

Intensity data collection

Crystals of methyl melaleucate iodoacetate were supplied by C. Chopra, Department of Chemistry, University of Western Australia, who prepared specimens suitable for X-ray photography by slow crystallization from methanol. The crystals, which are stable at room temperature, were in the form of colourless needles, elongated in the *c* direction and of a generally rectangular cross-section. A crystal was mounted about the long axis and a series of photographs was taken with a Buerger precession camera. From these the unit-cell dimensions, corrected for film shrinkage, were measured.

Systematic absences in the $0k0$, $00l$ and $h00$ reflexions on these photographs uniquely determined the space group as $P2_12_12_1$ (D_2^4), which is acentric with four equivalent positions per unit cell. The theoretical density, assuming one molecule per asymmetric unit, was calculated as 1·366 ± 1 and this compares favourably with the value of 1·37 ± 1 measured by the flotation method.

Two crystal specimens were prepared for X-ray diffraction studies. The first specimen, which had the approximate dimensions 0·29 × 0·27 × 1·00 mm^3, was mounted along the *c* axis and aligned on an oscillation camera. With Cu $K\alpha$ radiation (1·5418 Å) a series of photographs of the layers $l=0$ to 7 was then taken by multi-film, multi-exposure equi-inclinational Weissenberg techniques. The intensity data were limited by an apparently high overall temperature factor so that only a few reflexions were observed with Bragg angles (θ) greater than 50°. To ensure the maximum number of measurable reflexions, exposure times of up to 96 hours at 40 kV and 25 mA were necessary. Intensity spot shapes were generally uniform and therefore no spot integration was required.

The second crystal specimen was prepared by slicing a block of dimensions 0·27 × 0·25 × 0·22 mm^3 from a needle crystal and mounting it about the *a* axis. Intensity data of layers $h=0$, 1 and 2 were collected with procedures similar to those used for the first specimen.

Intensity correlation

The intensities of the hkl and $\bar{h}\bar{k}\bar{l}$ reflexions, which are non-equivalent because the iodine atom is an anomalous scatterer to Cu $K\alpha$ radiation, were measured separately by visual comparison with a calibrated intensity strip. This excluded the $0kl$, $h0l$ and $hk0$ reflexions which, since the projections in space group $P2_12_12_1$ are centric, are equivalent to $0\bar{k}\bar{l}$, $\bar{h}0\bar{l}$ and $\bar{h}\bar{k}0$ reflexions and therefore were only measured once. The indexing of the hkl and $\bar{h}\bar{k}\bar{l}$ reflexions on the Weissenberg films was carried out by the procedure suggested by Peerdeman & Bijvoet (1956). Only 1342 hkl reflexions of the 3795 theoretically observable independent reflexions in an octant of the Cu $K\alpha$ sphere were observed. This was primarily because the intensity data did not extend beyond the Bragg angle of 50°.

Lorentz and polarization factors were applied to all reflexions (hkl and $\bar{h}\bar{k}\bar{l}$) and cylindrical and spherical absorption factors were applied to the *c*- and *a*-axis data respectively. Although the linear absorption coefficient for Cu $K\alpha$ is high (80·7 cm^{-1}), these absorption factors were considered to be a sufficiently accurate approximation for the solution and the initial refinement of the structure. Correlation in the latter stages of refinement showed that errors in these factors were considerably less than the errors in the measurement of the visual intensity data. The application of general absorption factors involving the exact crystal shape was therefore unnecessary.

The observed structure factors were correlated by comparing the common row lines of the *c*- and *a*-axis layers, in addition to calculating absolute scaling factors by Wilson (1942) plots for each layer. The final layer scales obtained by a combination of these methods proved quite accurate and did not require adjustment during the complete refinement. The comparison of common row lines also provided a convenient check on the indexing of the hkl and $\bar{h}\bar{k}\bar{l}$ reflexions. After the application of the layer scales, common row reflexions in the *c*- and *a*-axis data were consistent to within 7%, the accuracy expected of good visual data.

Location of the iodine atom

A Patterson synthesis was calculated for the projection down [001]. This projection has the plane group symmetry *pgg* and vectors between identical atoms related by this symmetry give rise to three peaks per asymmetric unit at $2x, 2y$; $\frac{1}{2}, \frac{1}{2}-2y$ and $\frac{1}{2}-2x, \frac{1}{2}$. Peaks corresponding to the iodine–iodine vectors were readily identified and the atom was located at

$$x/a = 0{\cdot}116 \quad \text{and} \quad y/b = 0{\cdot}203 \, .$$

Similarly a Patterson synthesis calculated for the projection down [100] gave pronounced peaks corresponding to the iodine positions of $y/b = 0{\cdot}204$ and $z/c = 0{\cdot}133$. These coordinates compare reasonably well with the final coordinates of the iodine atom,

$$x/a = 0{\cdot}1211, \; y/b = 0{\cdot}2044 \quad \text{and} \quad z/c = 0{\cdot}1239 \, ,$$

the largest deviation from the initial position being less than 0·1 Å.

Solution of the Structure

Structure factor phase determination by anomalous dispersion methods has been developed by Ramachandran & Raman (1956) with special reference to the case of centrically placed heavy atoms. The method

may be presented in a slightly more convenient form, particularly for the solution of structures containing acentrically placed heavy atoms.

The departure from Friedel's Law (1913) is due to an atom in the structure being excited by the incident X-radiation and the resulting diffracted wave having both a real and an imaginary component. These components are usually expressed as corrections to the normal scattering factor f^0. The total scattering factor may then be written in the form

$$f=f^0+\Delta f'+i\Delta f''=f'+i\Delta f''$$

where $\Delta f'$ is the real and $\Delta f''$ the imaginary correction to the atomic scattering factor. These corrections give rise to the real and imaginary components F'_A and F''_A respectively, in the total structure factor F_H as seen

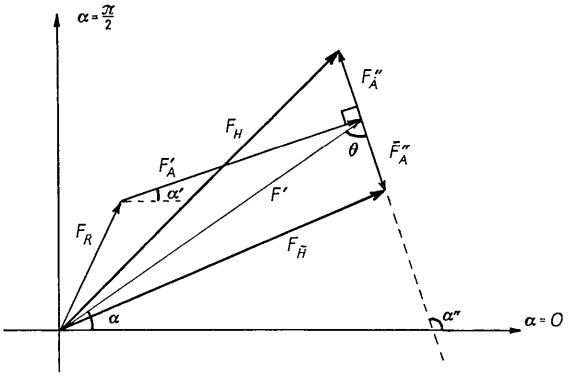

Fig. 1. Structure factor phase diagram for a structure containing one type of acentrically placed anomalous scatterer.

in the phase diagram (Fig. 1). Fortunately the imaginary component provides a means of estimating the mean phase α without any knowledge of the non-anomalous scatterers (which contribute F_R in Fig. 1) from the simple relationship

$$\alpha=\alpha''-\theta \qquad (1)$$

where α'' is the phase of F''_A and θ is the difference in phase between F''_A and F', the total structure factor without the imaginary component. The phase difference θ may be calculated from the trigonometrical expression

$$\cos\theta=\Delta F_o^2/4F'.|F''_A| \qquad (2)$$

where ΔF_o^2 is the Bijvoet inequality $(F^2_{ohkl}-F^2_{o\bar{h}\bar{k}\bar{l}})$. The magnitude of F' may be deduced from

$$F'=\sqrt{(\tfrac{1}{2}(F^2_{ohkl}+F^2_{o\bar{h}\bar{k}\bar{l}})-F''^2_A)}\,. \qquad (3)$$

When only one type of anomalous scatterer is present in the structure, the phase α'' may be replaced by $\alpha'+\pi/2$, where α' is the phase of F'_A. This latter form is preferable since the errors in α' should be much smaller than α'' because of the relative magnitudes of the real f' and the imaginary $\Delta f''$ components of the atomic scattering factor. If more than one type of anomalous scatterer is present in the structure α'' may have any value relative to α'. In this case therefore α'' must be used in equation (1).

The evaluation of θ from equation (2) poses an ambiguity in sign which permits the value of the phase α to be expressed as either $\alpha_1=\alpha'+\pi/2-\theta$ or $\alpha_2=\alpha'+\pi/2+\theta$. The problem of which phase is the correct one is overcome by choosing the phase closest to the heavy atom phase α'. Since the anomalous scatterer usually represents a high proportion of the scattering power, this criterion is generally a valid one, the true phase normally lying closer to α' than to $\alpha'+\pi$.

Consider the general case of N anomalous scatterers acentrically arranged in the unit cell. The components F'_A and F''_A may be expressed as

$$F'_A=\sum_{j=1}^{N} f'_j\cos 2\pi H.x_j+i\sum_{j=1}^{N} f'_j\sin 2\pi H.x_j \qquad (4)$$

$$F''_A=-\sum_{j=1}^{N}\Delta f''_j\sin 2\pi H.x_j+i\sum_{j=1}^{N}\Delta f''_j\cos 2\pi H.x_j\,. \qquad (5)$$

For the case of one anomalous scatterer only the phase α' and magnitude F''_A need be calculated from these equations for the evaluation of the direct phase, though the value of F'_A is necessary if an R index is required.

Application

The first phase calculations were programmed on an IBM 1620 computer as a modification of F. R. Ahmed's structure factor program (I.U.Cr. *World List of Computer Programs*, 1962). It was necessary in drafting these modifications to incorporate a logical routine to deal with reflexions where inaccuracies in intensity measurement or the anomalous scatterer position give rise to meaningless results when applied to equation (2).

The following criteria were adopted in this logical routine for the treatment of doubtful reflexions.

(i) If $\cos\theta>1$, θ is put equal to zero. This results in the direct phase being put equal to $\alpha'=\pi/2$, differing from the heavy atom phase by $\pi/2$. Other alternatives to this criterion are either to exclude the reflexion completely or to put the direct phase equal to the heavy atom phase. A series of Fourier synthesis sections were calculated with data in which the unreliable reflexions were treated according to each of the three alternatives. The accepted criterion, putting $\theta=0$, gave the most pronounced peaks at the atomic sites and was therefore chosen as that providing the most reliable phase.

(ii) If F' or $F''_A=0$, α is put equal to α'.

(iii) If $2F''^2_A>F^2_{ohkl}+F^2_{o\bar{h}\bar{k}\bar{l}}$ in the calculation of F', α is put equal to α'. This criterion is only necessary in smaller structures where Σf_o is of the same order as $\Sigma\Delta f''$.

The output of the modified structure factor program was in the form of two sets of components, one set

having the direct phase α and the other the heavy atom phase α'. The first set were used to calculate a three-dimensional F_o Fourier synthesis with sections along the c axis, since it was expected, from the crystal form, that the molecule would lie roughly parallel to this plane. By superimposing the Fourier sections, the molecule was detected as a region of high density running approximately parallel to the a axis. A section down the z direction in the plane of the high density region enabled the basic ring system to be identified and 40 of the 41 non-hydrogen atoms were readily positioned. The peaks at the atomic sites were generally well resolved with peak heights ranging from 3 to 6 e.Å^{-3}. As a comparison, sections of the Fourier F_o-synthesis perpendicular to the b axis were calculated using both the direct phase and the heavy atom phase. Fig. 2(a) and (c) shows the sections at $y/b=18/120$ and these illustrate the general superiority of the anomalous dispersion phased synthesis. The former is very similar to the section of the final F_o-Fourier synthesis (Fig. 2(d)).

Calculation of the structure factor scale ($\Sigma F_c/\Sigma F_o$) earlier had shown that the F_o values were twice absolute. This error, which occurred during correlation, might have been expected to have significantly affected the calculation of the direct phases, since equation (2) requires that F_o and ΔF_o^2 are absolutely scaled. The direct phases were therefore recalculated with the correct scale and another three-dimensional F_o Fourier synthesis was evaluated. Fig. 2(b) is a section of $y/b=18/120$ of this synthesis. It appears to be essentially the same as the section calculated with the incorrectly scaled direct phases, except that Fig. 2(a) has slightly more pronounced spurious peaks. It appears therefore that the direct phase is relatively insensitive to errors in the scale of F_o and ΔF_o^2. A possible explanation of this is that the direct phase α may be considered as corrected by the addition of the factor $(\pi/2-\theta)$. If the scale in the calculation of θ is not grossly incorrect, the value of α will always tend to be closer to the true phase than α'. Since $\cos\theta$ which is a slow varying function for small θ for the majority of reflexions has a value close to zero, the resulting corrections $(\pi/2-\theta)$ are generally small. During the first direct phase calculation the scale and consequently $\cos\theta$ were in error by a factor of two, resulting in the maximum of number of reflexions *versus* correction factor $(\pi/2-\theta)$ occurring at about 24°. When the correct scale was used to calculate θ, the equivalent maximum was at about 13°, a difference of only 11° from the former value. Moreover a number of the absurdities resulting from the wrong scale had been rectified by the 'logical routine' procedure of setting θ equal to zero when $\cos\theta$ exceeds one, the number of reflexions with low θ is relatively small, and the data of methyl melaleucate contain 552 centric reflexions which necessarily have the heavy atom phase. Fig. 2(a) and (b) might therefore be expected to be fairly similar. On the other hand the

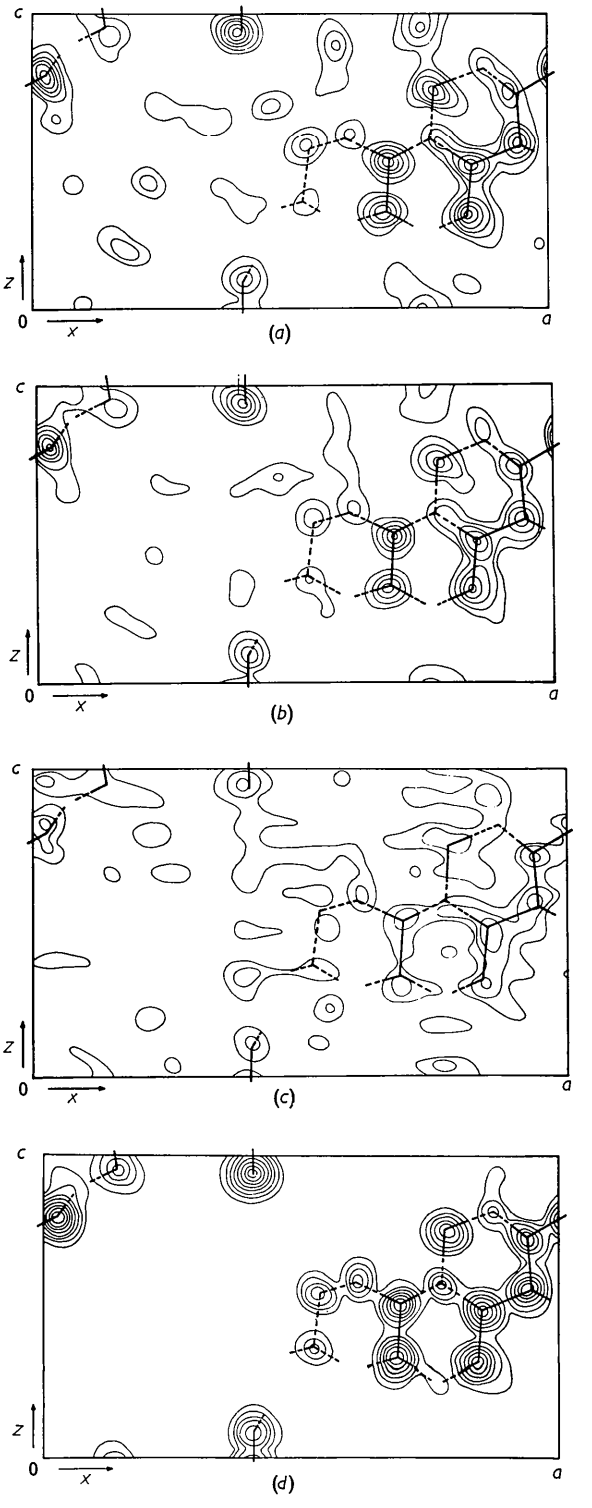

Fig. 2. F_o Fourier sections at $y/b=18/120$ from structure factors phased from (a) anomalous dispersion calculations using the incorrect scale, (b) anomalous dispersion calculations using the correct scale, (c) heavy atom structure factor calculation and (d) final structure factor calculation involving all atoms. Contours from 1 e.Å^{-3} at intervals of 1 e.Å^{-3}.

reflexions which have low θ-values, although few in number, provide the greatest difference from the pure heavy atom phasing and as these are considerably in error the degree of correspondence between the maps with the correct and incorrect phases is surprising. There are a number of possible explanations for this anomaly and a detailed analysis of these has been undertaken. The results of this investigation will be reported in a later paper.

Structure factors on all non-hydrogen atoms, except the oxygen atom O(2), were evaluated with a mean isotropic temperature factor coefficient of 4·9 Å^2 obtained during the Wilson plot scaling and the atomic scattering factors calculated by Freeman (1959) for oxygen and carbon. The resulting reliability index was 0·24, a drop of 0·14 from the structure factors calculated on the iodine atom alone.

In order to locate the oxygen atom O(2), a three-dimensional difference Fourier synthesis, phased on the other non-hydrogen atoms, was calculated. The oxygen was readily identified on a peak of height 4 e.Å^{-3}. This had a pronounced elliptical shape indicating strong anisotropic thermal motion, which was confirmed by the subsequent refinement. Its high temperature factor probably accounts for the difficulty in locating this atom in the initial Fourier synthesis. The three-dimensional difference synthesis also enabled coordinate and temperature factor corrections to be made on most other atoms, especially the iodine where there was also strong evidence for thermal anisotropy.

Another round of structure factors was calculated, an anisotropic temperature factor being given to the iodine and isotropic temperature factors to all other non-hydrogen atoms. The resulting R value of 0·19 indicated that the structure was basically correct.

Refinement of the structure

Depending on the accuracy and the size of the structure, one of two methods may be adopted in the calculation of the structure factors of a structure containing anomalous scatterers. The first, for use with accurate data, involves all the structure factor components, real and imaginary, in the calculation. The second method is an approximation which disregards the contribution of the imaginary correction to the scattering factor and is more appropriate for the refinement of a large structure with visual data.

The first method involves the general structure factor equations

$$F_{hkl}=F_H=\sum_{j=1}^{N}(f_j'+i\Delta f_j'')\exp(2\pi iH.x_j)+\sum_{j=1}^{M}f_j^0\exp(2\pi iH.x_j) \quad (6)$$

and

$$F_{\overline{hkl}}=F_{\overline{H}}=\sum_{j=1}^{N}(f_j'+i\Delta f_j'')\exp(-2\pi iH.x_j)+\sum_{j=1}^{M}f_j^0\exp(-2\pi iH.x_j) \quad (7)$$

where N is the number of anomalous and M the number of non-anomalous scatterers per unit cell. During refinement normally only one set of observed structure factors (F_{o_H}) is compared with the values calculated from equation (6), but it is also possible to use both F_{o_H} and $F_{o_{\overline{H}}}$ since this is effectively equivalent to having two sets of independently measured data. Although this increases the length of the structure factor calculation, the reliability of the structure determination will be improved.

In the second method, the imaginary component is ignored. Equation (6) therefore simplifies to

$$F_H'=\sum_{j=1}^{N}f_j'\exp(2\pi iH.x_j)+\sum_{j=1}^{M}f_j^0\exp(2\pi iH.x_j). \quad (8)$$

In the refinement F_H' is compared with the mean observed structure factor F_{o_M} which is derived from $\sqrt{((F_{o_H}^2+F_{o_{\overline{H}}}^2)/2)}$. The equivalence of F_H' and F_{o_M} follows since F_H' is the calculated version of F' from equation (3), and this is equal to F_{o_M} if the imaginary component F_A'' is small in comparison. The condition that F_A'' is small holds for large structures where $\Sigma\Delta f''$ is small compared with Σf^0 and $\Sigma f'$.

The structure factors for methyl melaleucate iodoacetate were therefore evaluated by the use of equation (8). In the following text the calculated and observed structure factors refer to F_H' and F_{o_M} respectively.

The structure was refined mainly by least-squares methods (Hughes, 1941), though a number of Fourier

Table 1. *Progress of structure refinement*

R = Reliability index $M=\Sigma w(F_o-F_c)^2\times10^{-2}$

2–D Patterson synthesis* down [001] and [100]
Direct phase SF calculation ($R=0{\cdot}38$)
Direct phase F_o Fourier synthesis
SF calculation ($R=0{\cdot}24$), 40 non-hydrogen atoms
Difference Fourier synthesis. Location of atom O(2)
SFLS (1) calculation ($R=0{\cdot}19$; $M=285$), 41 non-H atoms
SFLS (2) calculation ($R=0{\cdot}18$; $M=177$), 41 non-H atoms
SFLS (3) calculation ($R=0{\cdot}13$; $M=130$)
SFLS (4) calculation ($R=0{\cdot}123$; $M=91$)
Empirical secondary extinction corrections ($R=0{\cdot}114$)
SFLS (5) calculation ($R=0{\cdot}104$; $M=74$)
Difference Fourier synthesis. Location of hydrogen atoms
SFLS (6) calculation ($R=0{\cdot}093$; $M=68$), 41 non-H atoms and 51 H atoms (SF only)
SFLS (7) calculation ($R=0{\cdot}084$; $M=50$)
SFLS (8) calculation ($R=0{\cdot}081$; $M=45$)
SFLS (9) calculation ($R=0{\cdot}080$; $M=43$)
SFLS (10) calculation ($R=0{\cdot}079$; $M=41$)
SFLS (11) calculation ($R=0{\cdot}079$; $M=40$)
SF calculation ($R=0{\cdot}079$)

* This calculation was carried out on the SILLIAC Computer, University of Sydney. All subsequent calculations were performed on an I.B.M. 1620 computer, University of Western Australia.

and difference syntheses were calculated in the course of refinement. The progress of refinement is shown in Table 1. A block diagonal approximation of the least-squares matrix was used in the solution of the normal equations because of the limited computing facilities available. A least-squares program written by G. A. Mair, of The Royal Institution, London, allowed the simultaneous refinement of the positional parameters and the isotropic and anisotropic temperature factors. Each reflexion was weighted in this calculation by the scheme,

$$\sqrt{w} = 1/\sqrt{(1+((F_o-b)/a)^2)}$$

which was suggested by Mills & Rollett (1960). This gave maximum weight to the terms for which $|F_o-F_c|$ was least. The values of a and b were calculated for each round of least squares by plotting $\sqrt{((F_o-F_c)^2-1)}$ *versus* F_o.

All 41 of the non-hydrogen atoms except iodine were initially refined with isotropic temperature factor coefficients. In later rounds, atoms which showed high and diverging values were then assigned an-

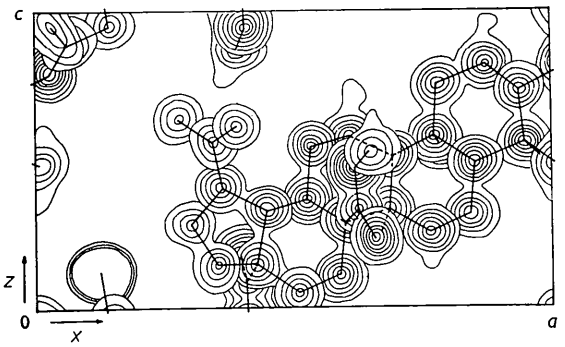

Fig. 3. Composite electron density map projected along the b axis. Contours are from 1 e.Å^{-3} at intervals of 1 e.Å^{-3}.

isotropic coefficients. All atoms listed in Table 2(b), except the iodine atom, showed this behaviour during the refinement. It is interesting to note that all these atoms are in positions in the molecule which give them a relatively high degree of freedom.

Secondary extinction

After four rounds of least-squares refinement the observed and calculated structure factors were compared individually. The high values of F_c were generally larger than the corresponding F_o's, suggesting that these reflexions were subject to secondary extinction. A graphical plot of $\log_e(I_c/I_o)$ *versus* I_c confirmed this, showing a consistent relationship between I_c and I_c/I_o. Since the crystal used in collecting these intensity data was roughly cylindrical an attempt was made to relate the degree of secondary extinction to the Bragg angle θ, as suggested by Hamilton (1957). The presence of a general coefficient ε was evident though no consistent variation

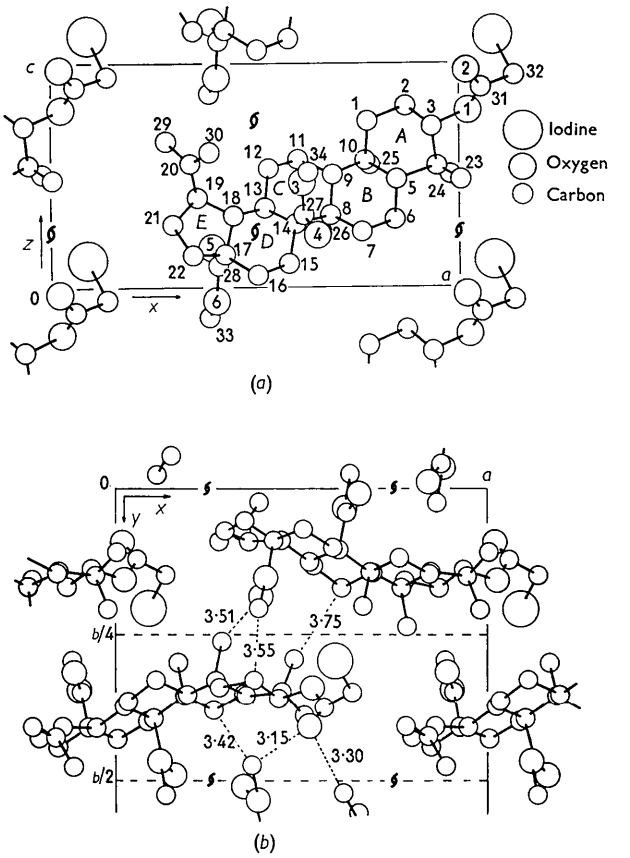

Fig. 4. The structure of methyl melaleucate iodoacetate excluding all hydrogen atoms, (a) projected down the b axis, (b) projected down the c axis.

of ε with θ was detected. The value of ε was estimated by a least-squares calculation including all reflexions above a minimum I_o value, weighted according to I_c. As a check on this calculation, values of I_c and $\log_e(I_c/I_o)$ were averaged for about 30 discrete ranges of I_c and plotted manually. Results from both these methods were in good agreement, the final value of ε being $1{\cdot}1\times10^{-5}$. Correction of the observed structure factors using the equation $F_o^2 = F_{o_1}^2 \exp(\varepsilon . I_c)$, where F_o and F_{o_1} are the corrected and uncorrected observed structure factors respectively, improved the agreement of the stronger reflexions and lowered the overall R value by 0·01.

Location of hydrogen atoms

After another round of least-squares refinement with the data corrected for secondary extinction, there were still a number of marked discrepancies in the low order terms. This was expected to result from contribution of the hydrogen atoms. A three-dimensional difference synthesis was calculated in an attempt to locate the 51 hydrogen atoms in the structure. 34 of the 51 can be approximately positioned from the knowledge of the basic skeleton, 28 being

Table 2(*a*). *Coordinates and isotropic thermal parameters of the non-hydrogen atoms*

	x/a	*y/b*	*z/c*	*B*		*x/a*	*y/b*	*z/c*	*B*
I	0·1211	0·2044	0·1239		C(15)	0·5849	0·1016	0·1042	3·2
O(1)	0·0244	0·1556	0·7913	5·0	C(16)	0·5076	0·0701	0·0528	5·6
O(2)	0·0267	0·0856	0·9582		C(17)	0·4282	0·0896	0·1501	3·5
O(3)	0·6165	0·0333	0·4691	4·2	C(18)	0·4475	0·0865	0·3256	3·1
O(4)	0·6553	0·0113	0·2306	5·3	C(19)	0·3597	0·0954	0·4019	4·5
O(5)	0·3951	0·1869	0·1755	5·0	C(20)	0·3403	0·0714	0·5590	5·6
O(6)	0·4054	0·1510	−0·0596	5·4	C(21)	0·2995	0·0703	0·2782	6·7
C(1)	0·7814	0·1572	0·7514	4·3	C(22)	0·3501	0·0556	0·1420	4·5
C(2)	0·8705	0·1692	0·8137	4·8	C(23)	0·0045	0·1088	0·4830	4·7
C(3)	0·9352	0·1388	0·7278	4·0	C(24)	0·9798	0·2073	0·5133	5·0
C(4)	0·9475	0·1493	0·5559	2·6	C(25)	0·7835	0·2337	0·5544	3·6
C(5)	0·8503	0·1415	0·4881	2·5	C(26)	0·6690	0·1994	0·2487	4·0
C(6)	0·8427	0·1456	0·3101	4·1	C(27)	0·6245	0·0434	0·3272	5·7
C(7)	0·7650	0·1187	0·2549	2·9	C(28)	0·4061	0·1469	0·0903	5·5
C(8)	0·6842	0·1428	0·3276	2·2	C(29)	0·2760	0·0919	0·6342	
C(9)	0·6926	0·1457	0·5046	1·7	C(30)	0·3880	0·0252	0·6126	
C(10)	0·7723	0·1695	0·5732	2·6	C(31)	0·0577	0·1230	0·8911	7·8
C(11)	0·6097	0·1684	0·5769	3·7	C(32)	0·1380	0·1473	0·9519	
C(12)	0·5330	0·1318	0·5412	2·7	C(33)	0·3917	0·2053	−0·1270	
C(13)	0·5214	0·1244	0·3662	3·1	C(34)	0·6440	−0·0215	0·5246	
C(14)	0·6017	0·1035	0·2830	3·0					

Table 2(*b*). *Anisotropic thermal parameters*

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
I	0·00833	0·00420	0·01664	−0·00080	−0·00007	−0·00116
O(2)	0·01094	0·00593	0·07849	0·02575	−0·04645	−0·00868
C(29)	0·01365	0·00456	0·02805	−0·00311	0·01406	0·00103
C(30)	0·00702	0·00327	0·02283	0·00550	0·00188	−0·00312
C(32)	0·00607	0·00442	0·02419	−0·00770	−0·00714	−0·00331
C(33)	0·01002	0·00214	0·02502	0·00732	−0·00466	0·00189
C(34)	0·01945	0·00096	0·02673	0·00075	−0·01761	0·00661

tetrahedrally bonded to the basic ring system and another 6 existing in a *gem*-dimethyl configuration. These are referred to below as group I hydrogen atoms. Of the remaining 17, 15 were in five methyl groups and their positions are restricted to the circumference of a circle of radius 1·03 Å centred at the intersection of the produced C–C bond and a plane perpendicular to it. The other two hydrogen atoms H(50) and H(51) in the vinylidene group have their positions restricted to a plane containing the C(20)–C(29) double bond. These 17 atoms will be referred to below as the group II hydrogen atoms.

The group I hydrogen positions were calculated assuming the carbon–hydrogen bond distance of 1·09 Å and an ideal tetrahedral configuration. As shown in Fig. 5, a summary of the three-dimensional difference synthesis, most atoms of this group were clearly indicated by positive peaks or areas, ranging from 0·1 to 0·7 e.Å^{-3}. Exceptions were atoms H(16) and H(30) which were in negative regions. These two atoms were positioned purely from stereochemical considerations, while the positions of the other hydrogens are a compromise between the shape of the positive regions in the difference synthesis and the calculated tetrahedral sites. The atomic coordinates of the group I hydrogen atoms are indicated by an asterisk in Table 4.

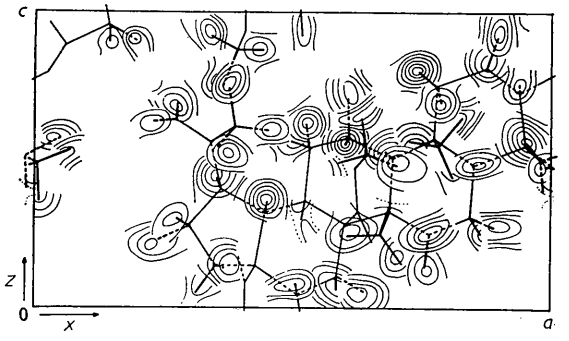

Fig. 5. A summary of a three-dimensional difference synthesis projected along the *b* axis to locate the hydrogen atoms. Contours from 0·1 e.Å^{-3} at intervals of 0·1 e.Å^{-3}.

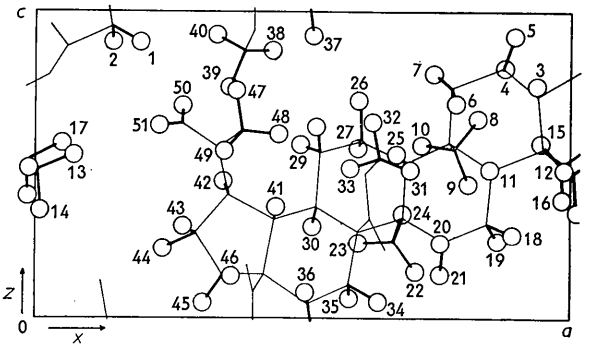

Fig. 6. Diagrammatic representation of the structure showing the hydrogen atoms as positioned from the difference synthesis (see Fig. 5).

Table 3. *Observed and calculated structure factors* ($\times 10$)

α = the final structure factor phase
α_0 = the phase initially calculated by anomalous dispersion methods*
α_0' = the heavy atom phase*

H	K	L	F_o	F_c	α	α_c	α_o
0	2	0	1466	1392	180	180	180
	4		2474	2374	180	0	0
	6		1103	1052	0	0	0
	8		467	550	180	180	180
	10		591	611	0	0	0
	12		618	658	180	180	180
	14		765	831	0	0	0
	16		567	552	180	180	180
	18		408	463	180	180	180
	20		382	413	0	0	0
	22		160	198	180	180	180
1	3	0	159	41	270	270	270
	4		2164	2316	270	270	270
	5		260	323	90	90	90
	6		330	363	90	90	90
	7		2115	2239	270	270	270
	8		529	510	270	270	270
	9			261	90	90	90
	10		309	395	90	90	90
	11		506	470	90	90	90
	12		276	206	270	90	90
	13		311	281	270	270	270
	14		356	324	270	270	270
	15		616	618	90	90	90
	16		282	283	90	90	90
	17		276	258	270	270	270
	18		304	254	270	270	270
	19		132	123	90	90	90
	20		277	248	90	90	90
2	0	0	829	869	0	0	0
	1		733	793	180	180	180
	3		1218	1414	0	0	0
	4		832	914	180	0	0
	5		257	283	180	180	180
	6		300	267	180	0	0
	7		352	324	180	180	180
	9		793	777	0	0	0
	10		273	315	0	0	0
	11		1459	1465	180	180	180
	12		233	223	180	180	180
	13		559	538	0	0	0
	15		83	89	0	180	180
	16		156	148	180	180	180
	17		130	105	0	180	180
	21		164	182	180	180	180
	23		181	184	0	0	0
3	1	0	525	511	90	90	90
	2		446	391	90	270	270
	3		1605	1864	270	270	270
	4		1206	1364	90	90	90
	5		1226	1433	90	90	90
	6		183	200	270	270	270
	7		849	879	270	270	270
	8		269	334	90	90	90
	9		317	380	90	90	90
	11		152	110	90	90	90
	14		257	272	90	90	90
	15		386	433	90	90	90
	16		157	154	270	270	270
	17		245	307	270	270	270
	22		159	189	90	270	270
4	0	0	2763	2725	180	180	180
	1		308	270	180	180	180
	2		772	850	0	0	0
	3		660	582	180	0	0
	4		1176	1260	180	180	180
	5		442	421	180	180	180
	6		1334	1184	180	180	180
	7		429	427	0	180	180
	8		1102	1032	0	0	0
	9		125	134	0	0	0
	10		883	806	180	180	180
	12		739	762	0	0	0
	14		231	188	180	180	180
	15		360	334	0	180	180
	16		306	293	0	0	0
	17		162	163	0	180	180
	18		299	323	0	0	0
	19		370	390	180	0	0
	20		330	354	180	180	180
5	2	0	295	295	90	270	270
	3		1015	1042	90	90	90
	4		488	539	90	90	90
	5		488	540	270	270	270
	6		580	647	270	270	270
	7		798	776	90	90	90
	8		606	632	90	90	90
	9		340	280	270	270	270
	10		136	139	270	270	270
	11		231	212	90	270	270
	12		370	342	90	270	270
	13		337	371	90	90	90
	14		660	659	90	90	90
	15		379	387	270	270	270
	16		579	632	270	270	270
6	1	0	1008	1004	0	0	0
	2		502	479	0	0	0
	3		814	873	180	180	180
	4		120	125	0	180	180
	5		734	738	0	0	0
	7		412	418	0	0	0
	9		807	758	180	180	180
	10		183	168	180	180	180
	11		639	606	0	0	0
	14		316	338	0	180	180
	15		160	142	0	0	0
	16		267	231	0	0	0
	17		286	196	180	0	0
7	1	0	160	144	270	270	270
	2		507	535	90	90	90
	3		1004	1153	90	90	90
	4		749	774	270	270	270
	5		1241	1249	270	270	270
	6		110	75	90	90	90
	7		138	125	90	90	90
	8		521	456	270	270	270
	9		526	520	270	270	270
	11		304	332	90	270	270
	12		202	177	90	90	90
	15		741	771	270	270	270
	16		393	347	90	90	90
	17		407	471	90	90	90
	18		368	354	270	270	270
8	0	0	1398	1380	0	0	0
	1		314	333	180	0	0
	2		569	581	180	180	180
	4		542	527	0	0	0
	5		475	470	0	0	0
	6		362	339	0	0	0
	8		687	673	180	180	180
	9		264	260	180	180	180
	10		641	641	0	0	0
	11		128	145	0	0	0
	12		517	509	180	180	180
	14		189	224	180	0	0
9	2	0	187	172	90	90	90
	3		360	302	270	270	270
	4		555	486	270	270	270
	5		121	140	90	90	90
	6		569	544	90	90	90
	7		344	395	270	270	270
	8		676	742	270	270	270
10	1	0	468	490	180	180	180
	2		344	338	180	180	180
	7		159	164	180	180	180
	8		160	154	180	180	180
	9		162	184	0	0	0
	11		189	181	180	180	180
	13		316	309	0	0	0
11	2	0	621	719	270	270	270
	4		641	672	90	90	90
	5		546	533	90	90	90
	8		164	180	270	90	90
	9		190	188	90	90	90
	12		189	159	90	270	270
	15		182	244	90	90	90
	16		179	147	270	270	270
	17		150	182	270	270	270
12	0	0	475	417	180	180	180
	1		585	581	180	180	180
	2		313	339	0	0	0
	3		379	388	180	0	0
	4		218	231	180	180	180
	5		251	253	0	180	180
	6		164	151	180	180	180
	7		134	139	0	180	180
	8		190	256	0	0	0
13	1	0	165	124	270	270	270
	6		368	396	270	270	270
	7		284	268	90	90	90
	8		365	409	90	90	90
	9		280	247	270	270	270
14	0	0	209	89	180	180	180
0	1	1	416	415	90	90	90
	2		1204	1392	180	180	180
	3		865	1059	270	270	270
	4		273	234	180	0	0
	5		280	299	90	90	90
	6		1162	1322	180	180	180
	7		757	688	90	90	90
	8		1235	1406	0	0	0
	9		1196	1267	270	270	270
	10		494	438	180	180	180
	11		548	585	90	90	90
	12		838	704	180	180	180
	13		416	386	270	270	270
	14		651	651	0	0	0
0	15	1	188	195	90	90	90
	16		445	439	180	180	180
	18		143	153	0	0	0
	21		289	292	90	90	90
1	0	1	1089	1256	270	90	90
	1		887	1018	317	298	287
	2		1889	1954	212	241	242
	3		868	919	93	114	140
	4		2076	2340	34	42	29
	5		661	671	352	3	353
	6		606	519	165	165	168
	7		620	615	240	213	206
	10		582	611	126	114	102
	11		307	198	92	259	272
	12		739	752	307	257	255
	13		427	417	164	151	126
	14		312	316	38	37	44
	16		192	221	172	162	186
	17		171	165	156	165	192
	18		286	293	360	327	327
	21		177	172	174	258	258
2	0	1	904	1023	90	90	90
	1		834	880	146	178	161
	2		995	1080	283	269	265
	3		752	836	21	12	355
	4		207	188	151	164	74
	5		1442	1704	174	180	180
	6		660	597	258	159	127
	7		667	634	348	354	3
	8		598	548	327	282	278
	9		814	817	192	203	189
	10		912	1010	76	112	92
	11		659	568	283	166	110
	12		425	412	227	237	268
	13		451	387	22	6	352
	14		496	474	108	81	81
	15		347	342	150	161	180
	16		275	200	14	215	215
	17		323	341	354	356	0
	19		309	270	191	184	184
3	0	1	392	360	270	270	270
	1		1210	1310	227	255	259
	2		1469	1660	152	141	130
	3		609	607	61	75	53
	4		1121	1178	13	343	341
	5		816	868	165	184	191
	6		545	576	177	180	187
	7		756	673	353	356	323
	8		209	176	56	85	36
	9		819	771	102	104	111
	10		417	357	228	224	252
	11		408	379	254	253	269
	12		405	345	68	84	113
	13		373	397	60	66	66
	14		476	444	325	322	329
	15		115	131	219	190	212
	16		458	445	166	167	180
	17		415	408	331	329	343
	18		368	335	25	9	22
	19		230	212	135	123	123
4	0	1	181	173	270	90	90
	1		1649	1849	276	278	266
	2		1079	1104	11	5	343
	3		1012	1114	99	103	73
	4		859	901	169	174	175
	5		594	559	61	219	206
	6		929	997	358	8	0
	7		204	238	277	298	298
	8		369	395	187	187	190
	9		561	548	101	88	99
	10		162	162	44	39	39
	11		846	751	297	281	270
	12		307	243	339	293	329
	13		492	520	72	59	80
	14		228	177	136	142	171
	16		330	300	344	356	360
	18		383	366	180	186	186
	21		237	208	281	284	273
	22		196	225	344	291	291
5	0	1	889	882	270	270	270
	1		449	422	124	140	116
	2		827	825	96	79	72
	3		367	362	258	258	333
	4		783	699	232	228	222
	5		1103	1153	180	166	176
	6		810	758	321	341	342
	7		1062	996	357	358	16
	8		483	422	112	89	118
	9		587	551	243	225	225
	10		116	108	324	341	277
	11		279	208	90	107	83
	12		304	279	78	80	80
	13		412	420	333	329	320
	14		621	599	237	251	238
5	16	1	174	134	29	10	10
	18		280	240	166	133	133
	19		174	152	117	172	211
	21		242	245	18	29	70
	22		204	216	68	74	88
	23		159	129	265	302	302
6	0	1	208	165	270	270	270
	1		837	848	311	290	313
	2		596	623	100	107	76
	3		221	232	219	215	165
	4		192	106	340	260	228
	5		844	793	40	15	360
	6		125	52	232	322	338
	7		1015	879	158	183	189
	8		494	446	186	174	113
	9		407	368	356	20	28
	10		634	573	257	269	276
	11		261	183	312	263	277
	12		579	533	67	48	82
	13		432	386	129	124	156
	14		422	382	275	244	244
	15		250	222	328	335	353
	16		233	217	214	22	11
	17		230	212	180	180	180
	18		170	177	114	138	126
	19		237	234	58	61	17
	20		156	158	268	262	282
7	0	1	558	595	90	90	90
	1		969	964	70	87	84
	2		555	519	286	294	325
	3		935	891	235	233	246
	4		560	574	202	192	169
	5		699	616	320	289	19
	6		959	931	356	358	3
	7		644	579	108	100	127
	8		333	291	223	202	203
	9		299	303	285	256	283
	10		256	215	124	115	60
	11		178	154	51	80	89
	12		311	237	338	37	307
	13		237	241	262	276	255
	14		285	186	109	144	160
	15		287	225	137	74	47
	16		174	110	270	331	360
	17		190	167	138	80	152
	18		243	203	243	211	193
8	0	1	371	407	90	270	270
	1		716	684	75	81	81
	2		397	357	169	150	146
	3		630	600	239	225	238
	4		484	480	315	312	350
	5		253	214	219	17	13
	6		393	424	154	172	184
	7		281	241	97	131	138
	8		380	342	335	18	22
	9		350	312	262	261	288
	10		433	406	211	240	240
	11		147	143	168	135	89
	12		185	205	126	110	127
	13		448	429	293	255	244
	14		446	428	27	352	341
	15		392	316	122	46	36
	16		123	167	239	202	180
	17		177	222	138	159	159
	18		197	168	281	324	12
	19		170	225	317	298	298
	20		143	152	110	128	218
9	0	1	670	600	90	90	90
	1		199	197	318	37	314
	2		316	308	224	244	261
	3		386	309	114	147	165
	4		364	270	39	53	60
	5		487	474	353	349	360
	6		283	244	191	189	148
	7		123	128	195	161	187
	8		183	161	342	315	286
	9		395	306	77	42	27
	10		475	425	107	97	94
	11		276	218	243	255	277
	12		307	286	251	265	265
	13		123	168	165	187	156
	14		403	354	42	60	72
	17		217	236	164	161	180
	18		168	131	277	223	296
	19		130	121	42	286	16
10	1	1	271	234	117	109	117
	2		495	512	256	235	245
	3		199	177	10	292	334
	4		217	191	47	32	32
	5		409	383	201	184	176
	7		468	388	355	7	15
	8		326	302	293	308	308
	9		143	132	243	223	223
	10		293	242	92	96	100
	13		217	161	312	306	321
	14		297	253	65	37	48

* Values for α_0 and α'_0 are in the penultimate and last columns respectively throughout the table.

Examination of the circles to which the groups of methyl hydrogen positions should be confined showed, in every case except H(33), three positive peaks approximately 120° apart. The positions of these atoms were deduced accordingly. It had been expected that the hydrogen atoms of the methyl groups attached to C(8) and C(10) would be sufficiently hindered to force them into a staggered configuration with the

Table 3 (*cont.*)

H	K	L	F_o	F_c	α	α_o	α_o'
10	15	1	151	146	92	78	168
	16		136	112	266	276	187
11	0	1	98	126	270	270	270
	1		423	377	235	252	268
	2		401	400	155	165	165
	3		369	369	73	93	80
	4		345	312	356	4	356
	6		355	342	174	167	180
	7		313	280	319	262	287
	8		190	182	0	355	10
	9		252	247	121	95	95
	10		291	255	244	215	215
	11		206	207	237	270	270
	12		222	230	106	137	152
	13		180	188	35	41	84
12	0		369	401	270	90	90
	1			155	221	212	255
	2		143	93	149	287	312
	3		279	268	90	53	43
	4		422	396	102	126	163
	5		191	192	360	203	188
	6		417	382	320	96	6
	7		147	167	334	332	332
	8		295	271	227	229	214
	9		320	346	130	132	118
	10		215	251	87	53	70
	11		200	176	295	234	268
	13		168	160	47	12	58
13	0	1	179	161	270	270	270
	1		449	499	137	172	172
	2		123	119	100	65	88
	3		320	313	23	24	360
	4		229	193	265	265	265
	5		174	166	229	210	180
14	3	1	200	228	143	142	142
	4		174	170	189	201	201
	5		172	163	354	354	354
0	0	2	487	510	0	180	180
	1		685	694	90	90	90
	3		781	794	270	270	270
	4		105	19	180	180	180
	5		1696	1814	90	90	90
	6		252	271	180	180	180
	7		1341	1509	270	270	270
	8		287	283	0	0	0
	9		480	473	90	90	90
	10		463	413	180	180	180
	11		455	391	90	90	90
	12		129	129	180	0	0
	13		326	307	270	270	270
	15		373	386	90	90	90
	16		249	246	180	0	0
	17		188	193	270	270	270
	18		110	119	180	0	0
	19		111	122	90	90	90
1	0	2	1401	1303	180	180	180
	1		761	808	165	170	180
	2		442	456	4	352	356
	3		1345	1330	342	6	6
	4		438	491	159	153	166
	5		326	386	196	236	215
	6		409	404	108	180	214
	7		355	369	124	96	170
	8		1191	1059	315	355	7
	9		518	528	25	15	357
	10		468	491	168	160	180
	11		812	833	175	167	180
	12		839	829	34	8	360
	13		537	577	360	349	3
	14		269	284	193	187	172
	15		247	255	141	168	192
	18		164	201	360	27	12
	19		278	289	40	0	355
	20		156	163	171	180	180
2	0	2	1053	889	0	180	180
	1		240	252	240	42	18
	2		711	646	294	302	271
	3		169	157	174	213	233
	4		1876	1922	100	94	90
	5		360	311	46	95	84
	6		1003	1054	260	265	270
	8		1200	1273	92	104	89
	9		170	150	349	146	146
	10		296	248	345	339	268
	11		94	140	328	90	0
	12		370	369	230	266	272
	14		280	293	72	78	90
	15		214	213	28	47	71
	16		395	410	284	270	270
	17		197	181	281	247	280
	18		392	374	84	85	90
	20		236	219	272	252	269
	21		218	214	28	0	360
	22		92	132	165	191	280
3	0	2	981	1006	180	180	180
	1		886	921	357	0	360
	2		864	873	3	10	3
	3		558	623	185	183	171
	4		1040	1039	175	215	189
	5		322	322	333	330	312
	6		466	413	218	175	157
	7		139	160	343	16	16
	8		843	789	337	345	355
	9		569	563	172	177	184
	10		549	571	197	196	180
	11		601	592	357	352	360
	12		563	588	7	3	0
	13		407	375	140	168	175
	15		190	166	360	328	342
	16		161	194	251	345	39
	18		206	213	287	309	355
	19		215	187	159	156	187
4	1	2	465	439	262	274	274
	2		265	205	185	229	236
	3		729	760	92	100	91
	4		319	305	19	87	79
	5		1297	1317	251	265	270
	6		387	399	223	274	274
	7		853	929	84	96	89
	8		260	291	133	118	112
	9		442	546	290	286	268
	10		540	507	0	331	331
	11		470	361	202	302	303
	12		119	117	102	308	217
	13		416	426	106	98	92
	14		89	85	192	111	71
	15		450	495	276	271	271
	16		261	229	13	256	268
	17		318	309	142	123	90
	18		94	101	21	49	103
	21		170	181	30	84	84
5	0	2	1536	1567	0	0	0
	1		688	719	337	339	0
	2		532	606	173	160	174
	3		509	563	159	175	183
	5		497	535	326	57	23
	6		418	336	47	138	48
	7		323	264	23	8	354
	8		552	507	191	204	190
	9		579	533	174	171	180
	10		149	137	85	90	0
	11		570	578	347	355	0
	12		441	378	168	160	180
	13		560	572	206	200	180
	14		271	273	19	348	348
	15		254	241	348	351	8
	19		166	192	203	190	180
	21		140	177	345	351	360
6	0	2	353	293	0	0	0
	1		330	293	279	226	226
	2		1022	1035	82	93	93
	3		1002	978	134	118	76
	4		1540	1456	252	270	271
	6		752	712	140	100	90
	7		532	488	340	91	98
	8		652	670	273	283	268
	9		120	144	264	350	296
	10		320	288	25	43	82
	12		110	115	167	166	96
	13		129	96	335	68	68
	14		175	157	258	269	272
	15		164	146	129	279	264
	16		312	285	74	67	90
	17		177	199	135	93	93
	18		222	231	258	269	269
	20		174	146	111	106	86
7	0	2	985	1042	0	0	0
	1		364	358	201	266	176
	2		499	482	158	164	180
	3		407	447	61	75	345
	4		379	415	338	4	4
	5		393	353	113	145	117
	6		315	264	276	356	347
	7		285	254	295	296	206
	8		432	437	159	172	180
	9		537	477	360	3	8
	10		579	616	33	8	360
	11		746	688	165	164	180
	12		396	363	170	159	180
	13		214	203	291	260	351
	14		218	181	323	335	0
	16		177	152	115	204	204
	18		105	161	208	231	180
	19		235	191	321	29	13
8	0	2	240	265	0	180	180
	1		271	271	53	25	99
	2		216	189	40	65	72
	3		473	527	269	299	272
	5		764	779	93	103	90
	6		243	180	148	92	92
	7		640	657	296	287	269
8	9	2	208	196	95	85	85
	10		101	93	35	219	129
	11		120	110	13	232	142
	12		173	164	262	58	58
	13		106	143	268	238	274
	14		107	140	284	207	261
	15		349	348	74	94	91
	18		151	131	215	314	276
9	0	2	368	317	180	180	180
	1		569	545	175	175	180
	2		251	281	339	340	348
	3		355	332	32	11	0
	4		221	218	175	125	141
	5		249	247	196	219	192
	7		181	185	235	196	180
	8		421	357	309	5	20
	9		280	261	15	0	360
	10		115	151	188	270	180
	11		406	404	156	168	180
	12		283	303	5	0	360
	13		274	314	360	0	0
	16		154	166	238	284	284
	17		129	107	80	90	180
10	0	2	166	186	0	180	180
	1		89	118	134	20	62
	2		252	238	286	281	276
	3		254	237	235	268	262
	4		472	487	80	92	92
	6		391	380	277	270	270
	7		378	179	248	267	274
	14		142	188	90	128	93
	16		255	270	262	266	270
11	0	2	379	416	180	180	180
	1		365	335	323	262	352
	2		257	265	5	0	0
	3		124	125	141	54	144
	4		162	173	186	218	180
	5		190	204	292	12	282
	8		192	163	295	0	360
	9		243	260	180	175	198
	10		273	303	170	180	180
	11		191	172	36	90	360
	12		311	357	34	21	0
12	3	2	339	324	89	90	94
	5		422	433	256	279	271
	6		200	186	238	264	271
	7		126	136	135	145	88
	8		111	125	149	96	96
	9		117	130	266	173	263
13	1	2	254	275	14	355	0
	4		174	137	332	283	284
	5		121	157	323	270	0
	8		186	209	141	246	246
	9		129	151	148	158	180
	11		126	155	0	0	0
	13		148	179	173	171	180
14	1	2	121	140	20	297	252
	2		153	148	114	99	99
	3		193	74	93	95	85
	4		130	197	261	273	273
	5		172	134	255	283	269
	7		148	112	360	92	92
0	1	3	1624	1628	270	270	270
	2		113	58	0	180	180
	3		1186	1143	90	90	90
	4		448	487	0	0	0
	5		219	167	90	270	270
	6		578	635	180	180	180
	7		838	737	270	270	270
	8		479	480	0	0	0
	9		658	673	90	90	90
	11		597	602	270	270	270
	12		161	153	180	180	180
	13		352	384	90	90	90
	14		342	290	0	0	0
	16		201	196	180	180	180
	18		339	352	0	0	0
1	0	3	872	991	90	90	90
	1		946	949	247	259	246
	2		809	857	287	313	309
	3		1186	1155	40	32	29
	4		720	723	141	153	160
	5		367	370	184	180	184
	6		881	901	40	17	8
	7		494	455	344	355	342
	8		490	527	218	219	217
	9		495	459	121	124	132
	10		485	442	82	94	73
	11		540	515	280	291	267
	12		317	327	302	299	293
	13		159	148	75	101	43
	14		527	482	149	162	147
	15		138	152	162	174	194
1	16	3	234	186	342	0	360
	19		224	221	175	147	147
	20		144	108	44	19	56
2	0	3	779	760	270	270	270
	1		298	284	262	297	207
	2		548	549	140	109	93
	3		590	538	3	14	7
	4		507	544	256	259	281
	5		873	913	169	180	180
	6		197	176	250	243	243
	7		911	945	358	8	356
	8		236	181	33	54	85
	9		229	230	180	156	166
	10		518	508	266	259	269
	11		239	242	317	237	257
	12		409	419	93	95	92
	13		269	211	15	31	11
	14		224	205	270	276	276
	15		228	226	193	205	180
	16		234	206	105	134	134
	17		278	264	10	11	360
	18		240	202	126	81	81
	19		180	100	158	82	172
3	0	3	1061	998	270	270	270
	1		587	551	243	258	286
	2		725	686	26	12	39
	3		648	636	131	164	139
	4		826	847	220	203	193
	5		311	321	360	29	354
	6		602	685	351	356	356
	7		500	523	208	216	207
	8		836	764	141	155	155
	9		579	592	70	60	60
	10		642	574	270	263	296
	12		313	257	58	23	57
	13		310	275	114	107	124
	14		500	455	225	207	202
	15		230	222	293	307	338
4	1	3	847	871	94	115	93
	2		379	401	4	29	26
	3		382	373	279	279	281
	4		452	412	171	188	188
	5		494	523	147	185	143
	6		696	651	360	8	360
	7		507	458	111	71	71
	8		765	705	186	165	165
	9		789	795	268	264	264
	10		352	332	45	310	310
	11		504	456	95	90	90
	12		230	210	31	21	43
	13		221	231	264	256	277
	14		255	265	192	167	194
	16		161	122	360	314	0
	17		224	247	44	360	50
5	0	3	669	678	270	270	270
	1		402	453	100	348	54
	2		739	752	114	116	116
	3		269	240	211	187	199
	4		514	474	304	332	330
	5		415	449	23	21	4
	6		678	622	190	214	192
	7		231	217	165	180	169
	8		537	466	40	69	51
	9		516	497	290	314	326
	10		381	356	274	259	259
	11		467	435	95	93	85
	12		287	305	95	80	104
	13		155	140	255	162	209
	14		201	215	325	314	314
6	0	3	281	313	90	90	90
	1		158	173	68	148	58
	2		533	510	254	274	280
	3		340	357	201	213	202
	4		659	607	96	211	121
	5		570	577	7	19	3
	6		240	217	7	360	32
	7		537	519	180	167	167
	8		177	200	252	230	254
	9		342	316	335	309	322
	10		524	445	79	80	86
	11		134	154	141	44	86
	12		389	363	268	270	275
	13		331	292	176	214	214
	15		387	360	356	0	10
	16		254	255	334	25	343
	17		316	297	168	149	176
7	0	3	489	519	90	90	90
	1		459	433	99	99	99
	2		451	438	233	231	205
	3		537	524	339	336	303
	4		557	507	28	24	7
	5		278	284	153	132	167
	6		528	518	163	177	180
	7		224	239	328	311	41
	8		555	566	352	16	345

carbon atoms of the adjacent ring system. This was not found to be the case and the reasons for this are discussed below. The positions of the vinylidene hydrogen were also clearly indicated on the difference synthesis. Fig. 6 shows a diagrammatic representation of all hydrogen atoms in the structure, viewed down the *b* axis.

Structure factors were calculated involving all 92 atoms, each hydrogen atom being given an isotropic temperature factor coefficient 1·5 times that of the carbon atom to which it was bonded. The resulting *R* value was lowered by 0·011 to 0·094, which was encouraging in view of the relatively low contribution of the hydrogens to the total structure factors.

Least-squares refinement was continued for five rounds after the inclusion of the hydrogen atoms, anisotropic temperature factor coefficients being applied to the atoms I, O(2), C(30), C(32), C(33) and

Table 3 (*cont.*)

H	K	L	F_o	F_c	α	σ_o	σ_o'
7	9	3	477	474	254	257	252
	10		401	348	90	118	130
	12		218	209	217	197	222
	13		265	245	318	292	292
	14		224	228	355	360	14
	15		163	139	217	235	145
8	0	3	181	162	90	90	90
	1		630	641	295	296	276
	2		364	335	171	225	225
	3		539	424	88	129	113
	4		302	299	360	16	16
	5		147	169	360	71	341
	6		555	509	190	196	174
	7		404	363	247	234	234
	8		300	298	350	329	329
	9		41[illegible]	23	51	66	78
	10		140	121	222	146	111
	11		290	297	275	271	271
9	0	3	381	357	90	90	90
	1		400	395	241	191	215
	2		393	363	277	278	284
	3		285	213	12	0	10
	5		254	246	154	180	180
	6		280	218	24	75	23
	7		283	270	345	0	356
	9		175	186	265	337	247
	10		220	210	154	180	161
	11		163	152	285	350	261
10	0	3	232	223	270	270	270
	1		244	212	212	236	251
	2		214	218	130	133	107
	3		329	349	33	57	36
	5		416	433	184	176	185
	7		179	237	351	248	338
	9		163	228	149	54	125
	10		164	197	242	218	263
11	1	3	285	281	286	291	274
	3		271	270	131	154	104
	4		303	323	203	197	180
	6		145	129	351	338	360
	7		164	160	166	156	246
12	1	3	224	282	109	116	100
	3		294	226	260	305	305
	4		224	247	188	185	206
	6		252	256	345	331	351
13	0	3	324	302	270	270	270
	2		202	223	61	40	93
0	0	4	639	741	180	180	180
	1		444	496	90	270	270
	2		923	989	0	0	0
	3		595	516	270	90	90
	4		527	555	180	180	180
	5		84	73	270	270	270
	6		302	297	0	180	180
	7		98	84	90	90	90
	8		843	870	0	0	0
	9		239	197	270	270	270
	10		810	853	180	180	180
	11		125	138	270	270	270
	12		481	470	0	0	0
	13		346	319	90	90	90
1	0	4	766	735	0	0	0
	1		1022	996	267	294	308
	2		531	482	155	194	255
	3		1105	940	60	75	101
	4		794	839	121	99	85
	5		778	823	281	280	272
	6		906	928	286	288	272
	7		557	570	133	131	84
	8		395	374	84	85	99
	9		465	463	255	242	249
	13		254	243	113	129	108
	14		296	325	107	68	82
	15		257	298	252	267	275
	16		198	227	245	222	269
	17		374	371	72	75	88
2	1	4	935	984	7	8	360
	2		225	212	262	49	49
	3		672	788	183	186	180
	4		185	156	80	222	257
	5		260	170	213	320	353
	6		181	176	113	118	95
	7		228	216	25	44	0
	8		264	214	125	256	297
	9		503	525	176	183	180
	11		413	455	360	347	360
	13		528	525	180	183	180
3	1	4	596	549	282	266	244
	2		522	497	92	161	114
	3		517	517	84	106	83
	4		721	766	243	262	277
3	5	4	804	891	280	282	269
	6		590	646	85	87	87
	7		713	725	92	94	94
	8		503	508	258	255	255
	9		330	324	256	274	284
	12		202	240	83	152	130
	13		241	247	63	78	78
	14		202	205	251	283	283
	15		251	315	262	267	267
	16		231	247	92	67	91
	17		283	351	82	114	92
4	0	4	1209	1297	0	0	0
	1		265	228	60	41	14
	2		967	1019	193	187	180
	3		218	237	247	185	226
	4		185	256	36	37	355
	5		127	133	94	127	82
	8		651	651	186	200	180
	10		597	619	5	0	0
	12		468	444	180	175	180
	14		226	234	352	340	360
5	1	4	357	322	76	129	141
	2		390	374	83	39	80
	3		330	303	304	18	288
	4		573	568	283	277	267
	5		746	748	96	110	93
	6		512	502	104	100	91
	7		386	356	283	278	260
	8		505	481	279	276	276
	9		183	173	100	58	58
	10		283	279	75	145	113
	13		267	232	240	332	298
6	0	4	570	553	0	0	0
	1		593	622	171	170	180
	3		410	633	347	356	356
	6		179	173	64	286	286
	7		255	237	166	153	188
	8		296	294	259	148	148
	9		545	543	341	351	0
	10		267	314	328	339	352
	11		265	305	204	220	180
	13		247	260	20	33	360
7	0	4	175	172	180	180	180
	1		214	235	78	74	74
	2		152	167	304	354	308
	3		431	381	263	272	266
	4		428	393	89	102	102
	5		462	417	87	76	89
	6		352	382	261	265	265
	7		444	452	269	258	272
	8		332	336	45	335	65
	9		296	272	92	115	98
	13		177	240	267	227	263
	14		177	189	9	21	111
8	0	4	566	534	180	180	180
	4		333	298	176	168	168
	6		260	245	189	148	211
	10		228	274	205	196	180
	12		326	299	18	24	360
	14		251	254	166	175	175
9	4	4	243	232	97	89	89
	5		245	265	267	275	275
	6		374	358	266	274	271
	7		362	291	95	56	71
	8		199	204	104	143	93
10	1	4	421	437	4	8	360
	3		342	357	170	187	172
11	4	4	208	141	261	299	299
	5		352	383	261	265	270
	7		231	271	88	73	91
12	0	4	208	272	0	0	0
	2		299	335	231	203	176
0	1	5	936	951	270	270	270
	2		776	932	0	0	0
	3		97	71	90	90	90
	4		918	941	180	180	180
	6		272	255	0	0	0
	9		216	178	90	90	90
	11		399	451	270	270	270
	12		322	349	180	0	0
	13		592	645	90	90	90
	15		233	224	270	270	270
	18		180	194	180	180	180
	19		320	324	90	90	90
1	0	5	379	394	270	270	270
	1		392	387	97	77	101
	2		409	405	90	108	71
	3		382	378	341	337	308
1	4	5	656	646	220	246	220
	5		535	554	159	155	169
	6		647	661	347	356	343
	7		406	429	30	57	36
	8		399	389	136	127	120
	9		473	498	228	248	248
	10		283	261	255	256	278
	11		432	466	92	100	91
	12		271	243	66	69	80
	13		239	259	331	323	295
	14		216	216	246	250	236
	15		308	298	180	156	149
	16		126	111	69	53	10
	20		194	245	323	286	286
	22		121	190	136	153	88
2	0	5	857	877	270	270	270
	1		152	100	218	335	348
	2		513	499	54	47	83
	3		500	532	180	196	180
	4		371	293	273	271	246
	5		503	514	339	354	360
	6		222	191	166	320	320
	7		331	352	161	172	180
	8		388	401	105	118	102
	9		289	299	60	34	6
	10		541	561	280	284	273
	11		190	204	249	300	300
	12		381	347	77	73	86
	13		254	251	205	209	175
	14		192	159	125	232	257
	15		217	207	12	31	360
	16		194	185	32	294	24
3	0	5	479	450	90	90	90
	1		690	656	83	98	83
	2		390	360	297	295	299
	3		375	362	210	244	244
	4		559	521	163	169	153
	5		364	405	27	60	16
	6		343	324	17	11	11
	7		330	341	130	109	131
	8		291	258	185	138	228
	9		389	409	286	273	284
	10		394	434	81	94	78
	11		131	157	34	55	89
	12		261	267	243	254	286
	15		194	220	60	67	43
	16		194	207	360	338	360
	17		162	143	199	192	154
4	1	5	687	669	99	96	84
	2		350	331	200	188	169
	3		318	287	290	266	246
	4		351	346	337	345	356
	5		327	299	352	345	17
	6		428	438	159	172	180
	8		367	389	360	7	7
	10		223	225	304	298	208
	11		304	229	93	97	89
	13		383	333	256	215	255
	14		266	283	20	5	355
5	0	5	218	229	90	90	90
	1		585	587	279	272	288
	2		245	212	268	310	258
	3		400	448	154	154	142
	4		400	393	12	68	54
	5		454	511	8	23	354
	6		414	411	180	161	153
	7		337	357	237	238	204
	8		171	207	23	19	290
	10		267	251	98	85	95
	11		188	154	267	272	272
	12		432	481	253	259	264
	13		178	215	68	80	127
	15		194	208	342	0	340
6	0	5	638	603	90	90	90
	2		291	289	252	235	249
	3		471	479	10	9	351
	4		326	343	55	36	36
	5		551	537	168	165	180
	6		210	153	213	200	164
	7		396	360	337	360	5
	8		366	372	275	303	303
	10		438	453	75	78	99
	12		220	228	257	243	259
	14		163	161	197	84	53
7	1	5	449	508	240	254	266
	2		304	278	161	162	133
	3		367	350	15	52	74
	4		653	636	350	351	344
	5		206	227	117	117	207
	6		154	175	180	166	186
	8		138	134	95	93	32
	9		174	170	203	125	98
	10		344	307	265	277	250
	11		254	266	261	253	270
	12		303	269	22	56	116
	13		207	226	96	109	80
8	0	5	296	328	90	90	90
	1		134	139	270	305	257
	3		398	404	116	78	46
	4		395	423	184	180	173
	5		328	264	248	180	188
	6		415	412	9	4	0
	7		316	266	332	9	330
	8		147	173	171	194	194
	9		233	226	103	116	116
	11		313	335	260	244	269
	13		192	184	74	36	60
	14		159	190	180	147	168
9	0	5	236	319	270	0	270
	1		225	188	90	32	122
	5		283	259	165	191	180
	6		194	190	59	5	317
	7		295	293	24	12	12
	8		243	225	114	10	100
10	0	5	209	245	270	270	270
	1		209	223	338	309	309
	2		142	159	112	129	55
	3		256	252	185	167	162
	4		286	300	216	189	202
0	1	6	431	371	270	270	270
	2		130	94	0	180	180
	3		537	516	90	90	90
	5		508	493	270	270	270
	7		469	506	90	90	90
	9		116	112	270	270	270
	11		72	55	270	270	270
	12		150	138	180	180	180
	13		180	186	90	90	90
	17		322	303	90	90	90
	18		210	209	180	180	180
	19		236	223	270	270	270
	22		131	136	0	180	180
1	0	6	562	616	0	0	0
	1		526	574	360	3	3
	2		400	414	176	159	168
	3		415	390	186	211	198
	4		238	258	350	322	322
	5		149	114	141	81	66
	6		154	101	343	75	65
	7		218	209	321	293	331
	8		232	208	185	221	201
	9		336	338	170	157	172
	10		234	217	360	355	5
	11		357	344	48	31	0
	12		167	167	157	156	174
	13		315	313	203	211	191
	14		224	205	13	348	337
	15		105	92	294	305	35
	17		220	225	59	287	307
	20		121	123	75	37	10
2	0	6	144	140	0	0	0
	1		122	120	23	187	187
	2		364	387	95	114	93
	3		126	96	222	48	23
	4		544	580	275	277	271
	5		135	114	294	251	251
	6		652	678	100	97	90
	8		516	504	259	258	268
	9		285	266	185	348	348
	10		313	281	37	82	82
	11		208	187	306	180	180
	12		207	213	81	82	95
	13		154	136	330	14	14
	14		231	236	231	247	272
	15		239	211	103	254	223
	16		162	169	81	98	90
	18		222	234	293	266	269
3	0	6	334	532	0	0	0
	1		390	399	180	184	172
	2		446	438	180	195	188
	3		410	406	360	341	333
	4		68	78	326	0	26
	5		144	116	301	161	106
	6		266	243	9	307	307
	7		218	198	207	269	222
	8		172	155	191	146	167
	9		375	334	356	30	15
	10		169	141	14	20	360
	11		343	280	143	153	180
	12		290	252	198	193	180
	13		163	150	354	330	343
	14		333	313	348	356	15
	15		145	153	163	107	132
4	1	6	405	388	67	93	103
	3		588	568	282	296	274
	5		506	501	90	95	91
	6		104	122	144	128	102
	7		369	365	254	252	268
	9		239	244	129	126	83
	10		223	204	355	170	170

C(34). Shifts calculated from these rounds were not applied directly but were made only after considering the shifts from previous rounds. It was found that the shifts calculated by least squares were generally overestimated and had to be reduced to damp the oscillations of the atomic sites about their mean positions. This individual examination of shifts, although tedious and therefore perhaps not possible with larger structures, accelerated the refinement considerably.

After the ninth round of least squares the only calculated shifts greater than 0·25 of the atomic standard deviation were those on the oxygen O(2) coordinates. A round of least squares was carried out on this atom alone and the shifts, corrected by the appropriate relaxation factor, were applied to its

Table 3 (*cont.*)

H	K	L	F_o	F_c	α	α_o	α_o
4	11	6	264	207	251	152	152
	13		163	202	295	288	276
	15		152	174	96	73	91
	17		171	165	251	245	269
5	0	6	133	40	180	180	180
	1		4?3	428	142	154	180
	2		26	258	317	303	340
	3		581	647	340	11	11
	4		445	396	159	115	128
	5		268	229	237	276	233
	6		325	274	95	231	254
	7		276	229	152	133	161
	8		316	302	316	11	31
	9		409	415	354	356	356
	10		340	333	180	188	188
	11		217	196	197	192	180
	12		252	251	38	34	349
	13		243	234	32	18	5
	14		115	137	269	235	144
6	0	6	299	282	0	180	180
	1		278	280	150	354	18
	2		346	331	254	265	280
	4		363	397	142	146	93
	5		334	311	352	77	84
	6		457	431	289	296	269
	7		207	165	232	274	293
	8		510	464	61	67	84
	9		235	237	132	190	146
	10		268	258	217	157	247
	11		172	158	40	314	0
	12		239	221	255	274	288
	14		258	266	80	76	95
	16		168	192	250	246	271
7	0	6	163	114	180	180	180
	1		535	546	354	8	348
	2		493	486	45	21	3
	3		256	222	81	48	138
	4		311	268	198	189	196
	5		218	152	163	294	280
	6		119	135	247	187	143
	7		113	106	257	327	57
	8		237	224	360	360	353
	9		181	131	167	188	203
	10		145	156	180	189	180
	14		181	167	136	151	188
	15		153	121	344	270	298
8	1	6	281	238	308	349	297
	2		103	101	271	153	226
	3		337	329	91	93	97
	5		356	373	257	287	271
	7		200	171	53	41	86
	9		190	182	330	330	256
	11		155	127	122	258	348
	15		130	135	318	285	273

H	K	L	F_o	F_c	α	α_o	α_o
9	0	6	262	288	0	0	0
	1		298	275	355	345	0
	2		145	132	160	118	144
	3		189	181	180	186	186
	6		93	128	286	37	82
	9		235	227	193	173	180
	10		175	153	343	285	15
	11		147	132	325	341	0
	12		146	143	200	159	159
	13		142	183	161	180	180
10	1	6	110	115	254	211	211
	2		133	146	94	107	107
	4		277	250	268	275	275
	6		304	332	83	59	88
	8		139	137	282	275	260
11	0	6	303	277	0	0	0
	1		119	146	212	241	151
	2		238	246	154	154	180
12	5	6	185	210	85	91	91
	7		173	179	280	253	263
13	1	6	133	152	180	180	180
	3		114	114	15	0	0
0	1	7	360	363	90	90	90
	2		221	231	0	0	0
	3		233	239	270	270	270
	4		397	439	180	180	180
	5		168	170	90	90	90
	6		240	220	0	0	0
	7		97	115	90	90	90
	8		381	381	180	180	180
	9		386	392	270	270	270
	10		99	112	0	0	0
	11		208	180	90	90	90
	14		128	157	180	180	180
1	0	7	329	311	270	270	270
	1		239	247	75	34	54
	2		250	281	118	131	141
	3		173	177	208	180	199
	4		302	296	288	308	348
	5		241	254	353	346	0
	6		261	257	189	180	180
	7		181	179	103	149	170
	8		359	366	66	41	25
	9		89	85	360	0	326
	10		185	148	252	251	244
	11		119	130	173	173	85
	12		90	81	92	159	123
	13		176	171	258	224	210
	14		166	178	340	310	338
	15		212	210	45	13	9
	16		191	222	157	180	180

H	K	L	F_o	F_c	α	α_o	α_o
2	0	7	244	197	90	90	90
	1		140	155	334	343	40
	2		367	394	274	282	272
	3		344	348	180	213	191
	4		171	168	149	150	96
	5		386	388	352	15	0
	6		114	111	135	109	72
	7		313	284	185	184	174
	8		243	221	313	298	267
	9		307	275	7	338	339
	10		240	253	83	89	89
	11		88	79	15	172	82
	12		182	201	240	257	271
	13		130	105	197	198	198
	15		214	215	23	14	0
3	0	7	216	223	90	90	90
	1		244	217	105	105	114
	2		241	233	256	222	207
	3		276	270	316	350	331
	4		228	175	26	14	7
	5		324	333	161	180	180
	6		356	356	170	180	180
	7		100	115	57	74	17
	8		273	289	355	10	343
	9		122	128	187	187	228
	11		138	158	92	115	93
	12		275	291	240	212	223
	13		167	163	282	281	318
4	0	7	182	160	90	90	90
	1		369	361	281	293	272
	2		182	159	186	217	217
	3		123	94	109	97	97
	4		268	279	11	18	12
	5		174	149	211	235	311
	6		224	218	171	146	180
	7		147	124	203	244	258
	8		314	305	355	336	336
	9		315	336	72	82	86
	10		101	107	342	207	117
	11		211	235	277	270	271
	13		138	127	95	107	94
5	0	7	314	333	90	90	90
	1		331	338	270	213	220
	2		299	336	326	338	308
	3		128	137	310	282	12
	4		289	247	137	172	160
	5		237	223	180	175	180
	6		148	170	48	50	6
	7		164	189	26	38	354
	8		207	202	260	269	218
	10		157	155	92	91	73
	11		149	150	296	354	263
	12		156	169	247	272	292
	13		136	139	58	37	18
6	0	7	493	494	270	270	270
	1		191	220	266	262	249

H	K	L	F_o	F_c	α	α_o	α_o
6	2	7	323	314	100	110	96
	3		224	223	360	11	32
	4		97	107	81	352	280
	5		317	347	158	150	180
	6		195	190	309	226	226
	7		239	205	11	16	341
	9		231	182	185	113	128
7	0	7	147	111	270	270	270
	1		214	208	257	274	285
	2		119	132	104	105	16
	3		189	157	50	46	136
	4		218	161	202	171	180
	5		101	120	327	360	327
	6		217	221	338	355	360
	7		240	220	209	214	207
	8		174	196	127	137	170
	9		147	138	26	15	62
	11		155	170	310	292	272
	13		139	167	139	122	122
8	0	7	148	144	270	270	270
	1		160	175	75	71	94
	2		166	164	341	58	58
	3		201	162	270	300	285
	4		218	218	166	190	204
	7		182	166	36	30	65
	8		156	164	180	156	136
	9		136	128	275	276	263
	11		131	141	133	102	90
9	0	7	285	294	270	270	270
	1		90	80	59	322	23
	2		150	141	111	111	111
	4		147	158	288	244	325
	5		138	141	47	11	0
	6		88	110	208	123	194
	7		162	174	169	180	180
10	0	7	126	143	90	90	90
	2		88	91	263	258	281
	3		134	174	209	252	229
0	0	8	324	373	0	0	0
	2		220	250	180	180	180
	4		126	162	0	0	0
	10		355	403	0	0	0
	12		318	392	180	180	180
1	2	8	210	199	111	96	60
	3		229	164	282	292	292
	4		209	215	278	286	261
	5		297	278	90	93	93
	6		246	246	98	113	93
	7		290	279	245	257	257
	8		193	206	286	19	289
2	1	8	409	443	180	180	180
	3		275	272	348	345	360

Table 4. *Coordinates of hydrogen atoms*

	x/a	y/b	z/c		x/a	y/b	z/c
H(1)*	0·195	0·133	0·900	H(27)*	0·601	0·215	0·555
H(2)*	0·142	0·187	0·900	H(28)*	0·525	0·094	0·595
H(3)*	0·935	0·097	0·760	H(29)*	0·496	0·165	0·568
H(4)*	0·874	0·212	0·814	H(30)*	0·516	0·163	0·300
H(5)*	0·897	0·155	0·926	H(31)	0·700	−0·028	0·485
H(6)*	0·786	0·116	0·700	H(32)	0·632	−0·028	0·640
H(7)*	0·745	0·190	0·800	H(33)	0·585	−0·054	0·490
H(8)	0·826	0·245	0·654	H(34)*	0·640	0·087	0·058
H(9)	0·808	0·240	0·436	H(35)*	0·584	0·142	0·066
H(10)	0·723	0·252	0·563	H(36)*	0·505	0·027	0·085
H(11)*	0·848	0·100	0·489	H(37)*	0·520	0·075	−0·075
H(12)*	0·985	0·066	0·486	H(38)	0·444	0·229	−0·128
H(13)*	0·067	0·117	0·532	H(39)	0·360	0·200	−0·250
H(14)*	0·008	0·117	0·350	H(40)	0·335	0·217	−0·070
H(15)*	0·943	0·235	0·569	H(41)*	0·450	0·047	0·365
H(16)*	0·984	0·207	0·390	H(42)*	0·350	0·135	0·450
H(17)*	0·050	0·205	0·568	H(43)*	0·276	0·033	0·300
H(18)*	0·890	0·113	0·270	H(44)*	0·237	0·083	0·230
H(19)*	0·865	0·183	0·256	H(45)*	0·312	0·067	0·050
H(20)*	0·755	0·075	0·244	H(46)*	0·367	0·013	0·134
H(21)*	0·755	0·136	0·136	H(47)	0·373	0·016	0·738
H(22)	0·710	0·205	0·150	H(48)	0·453	0·033	0·601
H(23)	0·601	0·205	0·246	H(49)	0·350	−0·003	0·545
H(24)	0·685	0·226	0·345	H(50)	0·275	0·130	0·690
H(25)*	0·675	0·100	0·534	H(51)	0·218	0·070	0·630
H(26)*	0·603	0·170	0·710				

* Group I hydrogen atoms

coordinates. All atoms were included in a final round of least-squares refinement. Although the shifts on all atoms were less than 0·25 of the estimated standard deviations, they were applied to the coordinates and a final round of structure factors was calculated.

Since the calculated shifts had become insignificant with respect to the estimated standard deviations and the value of $\Sigma w(F_o-F_c)^2$, which is listed in Table 1, had reached a satisfactory minimum of 40×10^2 e^2 it was considered that the structure had been refined to the limit of the data. The final R value was 0·079.

Discussion

General

As reported earlier (Chopra *et al.*, 1963) the structure of methyl melaleucate iodoacetate has confirmed the constitution of melaleucic acid as 3β-hydroxylup-20(29)-ene-27,28-dioic acid.

The final reliability index of the structure is 0·079 for 1342 observed reflexions, which is consistent with the accuracy of 0·07 estimated during correlation of common row lines of two separate sets of data. The general accuracy of the structure was enhanced by the use of both hkl and $\bar{h}\bar{k}\bar{l}$ reflexions in estimating the observed structure factors.

Bond lengths and angles

The bond lengths and angles, calculated from the atomic coordinates given in Table 2, together with the appropriate standard deviations, are listed in Tables 5 and 6. The standard deviations are estimated by the use of Cruickshank & Robertson's (1953) formulae.

Several carbon–carbon bonds and C–C–C angles deviate by more than 3σ from the accepted values of 1·54 ± 3 Å and 109·3°, particularly the C(4)–C(5) and C(8)–C(14) bonds of 1·64 and 1·66 Å and the angles C(4)–C(3)–O(1); C(2)–C(3)–C(4) and C(4)–C(5)–C(10) of 100·5°, 119·8° and 120·2° respectively.

Two factors appear to be responsible for these deviations. They are the degree of substitution at the carbon atoms in the bonds and the presence of long range steric strain in the structure. Each of these points will be considered in turn.

It seems significant that all the long C–C bonds are attached to at least one of the five fully substituted carbon atoms C(4), C(10), C(8), C(14) and

Table 5. *Bond lengths of covalent bonds between non-hydrogen atoms*

Bond	Length (Å)	e.s.d. (Å)	Bond	Length (Å)	e.s.d. (Å)
I–C(32)	2·058	0·027	C (7)–C (8)	1·534	0·023
O (2)–C(31)	1·189	0·039	C (8)–C (9)	1·532	0·020
C(30)–C(20)	1·435	0·034	C (8)–C(14)	1·660	0·022
C(29)–C(20)	1·301	0·043	C (8)–C(26)	1·565	0·025
C(32)–C(31)	1·491	0·039	C (9)–C(10)	1·503	0·022
C(33)–O (6)	1·469	0·027	C (9)–C(11)	1·548	0·024
C(34)–O (3)	1·490	0·026	C(10)–C(25)	1·593	0·023
O (1)–C (3)	1·560	0·027	C(11)–C(12)	1·534	0·025
O (1)–C(31)	1·285	0·032	C(12)–C(13)	1·529	0·024
O (3)–C(27)	1·254	0·025	C(13)–C(14)	1·539	0·023
O (4)–C(27)	1·244	0·026	C(13)–C(18)	1·528	0·024
O (5)–C(28)	1·237	0·026	C(14)–C(15)	1·564	0·023
O (6)–C(28)	1·295	0·026	C(14)–C(27)	1·565	0·027
C (1)–C (2)	1·528	0·026	C(15)–C(16)	1·506	0·029
C (1)–C(10)	1·571	0·026	C(16)–C(17)	1·578	0·030
C (3)–C (4)	1·516	0·029	C(17)–C(18)	1·544	0·023
C (3)–C (2)	1·461	0·027	C(17)–C(22)	1·487	0·026
C (4)–C (5)	1·646	0·025	C(17)–C(28)	1·535	0·028
C (4)–C(23)	1·479	0·029	C(18)–C(19)	1·544	0·026
C (4)–C(24)	1·553	0·029	C(19)–C(20)	1·507	0·031
C (5)–C (6)	1·542	0·026	C(19)–C(21)	1·552	0·033
C (5)–C(10)	1·585	0·023	C(21)–C(22)	1·463	0·034
C (6)–C (7)	1·467	0·026			

Table 6. *Bond angles for covalent bonds between non-hydrogen atoms*

Angle		e.s.d.	Angle		e.s.d.	Angle		e.s.d.
I–C(32)–C(31)	114·6°	1·8°	C(4)–C(8)–C(26)	107·1°	1·2°	C(16)–C(17)–C(28)	106·1°	1·5°
C(3)–O(1)–C(31)	115·9	1·7	C(8)–C(9)–C(10)	118·7	1·2	C(18)–C(17)–C(22)	100·3	1·4
C(33)–O(6)–C(28)	117·7	1·9	C(8)–C(9)–C(11)	110·1	1·2	C(18)–C(17)–C(28)	114·7	1·5
C(34)–O(3)–C(27)	117·5	1·7	C(10)–C(9)–C(11)	113·8	1·2	C(22)–C(17)–C(28)	108·1	1·5
C(2)–C(1)–C(10)	112·9	1·5	C(1)–C(10)–C(5)	107·3	1·3	C(13)–C(18)–C(17)	110·0	1·4
O(1)–C(3)–C(4)	100·5	1·5	C(1)–C(10)–C(9)	112·7	1·3	C(13)–C(18)–C(19)	119·7	1·4
O(1)–C(3)–C(2)	108·2	1·5	C(1)–C(10)–C(25)	106·1	1·3	C(17)–C(18)–C(19)	103·5	1·4
C(4)–C(3)–C(2)	119·8	1·7	C(5)–C(10)–C(9)	107·1	1·2	C(18)–C(19)–C(20)	120·5	1·6
C(3)–C(4)–C(5)	102·0	1·5	C(5)–C(10)–C(25)	107·2	1·3	C(18)–C(19)–C(21)	101·3	1·6
C(3)–C(4)–C(23)	112·2	1·7	C(9)–C(10)–C(25)	115·8	1·3	C(20)–C(19)–C(21)	109·8	1·7
C(3)–C(4)–C(24)	115·3	1·6	C(9)–C(11)–C(12)	111·7	1·3	C(29)–C(20)–C(30)	123·4	2·5
C(5)–C(4)–C(23)	109·4	1·5	C(11)–C(12)–C(13)	111·1	1·3	C(30)–C(20)–C(19)	119·4	2·0
C(5)–C(4)–C(24)	109·0	1·5	C(12)–C(13)–C(14)	113·6	1·3	C(29)–C(20)–C(19)	116·9	2·3
C(3)–C(4)–C(24)	108·4	1·6	C(12)–C(13)–C(18)	112·8	1·4	C(19)–C(21)–C(22)	108·5	1·9
C(1)–C(2)–C(3)	111·2	1·5	C(14)–C(13)–C(18)	108·3	1·3	C(17)–C(22)–C(21)	105·7	1·7
C(4)–C(5)–C(6)	114·6	1·4	C(8)–C(14)–C(13)	109·8	1·2	O(3)–C(27)–O(4)	124·4	1·9
C(4)–C(5)–C(10)	120·2	1·3	C(8)–C(14)–C(15)	112·1	1·2	O(3)–C(27)–C(14)	113·6	1·7
C(6)–C(5)–C(10)	111·8	1·3	C(8)–C(14)–C(27)	108·1	1·3	O(4)–C(27)–C(14)	121·5	1·8
C(5)–C(6)–C(7)	110·9	1·5	C(13)–C(14)–C(15)	109·3	1·3	O(5)–C(28)–O(6)	121·9	1·8
C(6)–C(7)–C(8)	112·5	1·4	C(13)–C(14)–C(27)	112·8	1·4	O(5)–C(28)–C(17)	123·8	1·8
C(7)–C(8)–C(9)	110·6	1·2	C(15)–C(14)–C(27)	104·4	1·3	O(6)–C(28)–C(17)	114·0	1·8
C(7)–C(8)–C(14)	109·1	1·2	C(14)–C(15)–C(16)	116·2	1·5	O(2)–C(31)–C(32)	118·9	2·8
C(7)–C(8)–C(26)	106·9	1·3	C(15)–C(16)–C(17)	109·1	1·7	O(2)–C(31)–O(1)	129·6	2·7
C(9)–C(8)–C(14)	108·9	1·2	C(16)–C(17)–C(18)	110·4	1·5	C(32)–C(31)–O(1)	109·3	2·2
C(9)–C(8)–C(26)	113·8	1·3	C(16)–C(17)–C(22)	117·2	1·6			

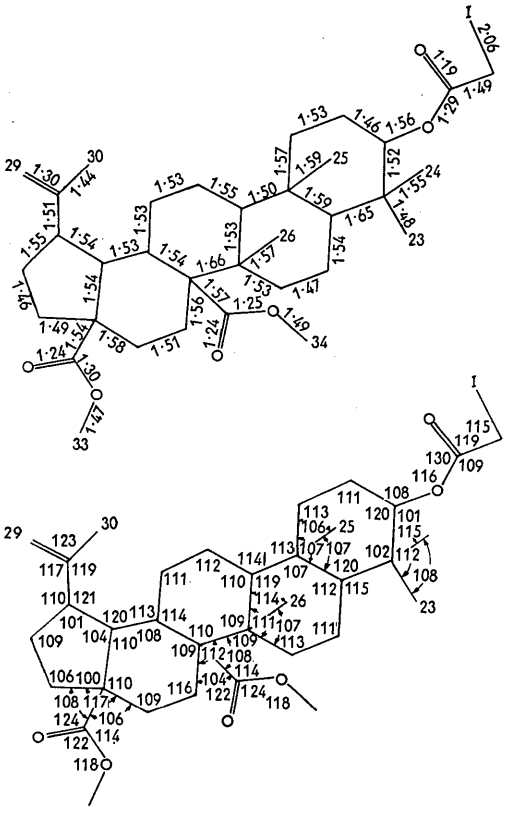

Fig. 7. The structure showing bond lengths (Å) and bond angles (°) between non-hydrogen atoms.

C(17), that the longest bond C(8)–C(14), is the only one which joins two such atoms. The degree of substitution at the bonding carbon atoms appears therefore to bear some relationship to the length of the C–C bond. The exact influence of substitution on bonding is not clear but it would appear that the increase in the number of sp^3–sp^3 bonds in the environment of the C–C bond is associated with the weakening. The usual explanation of this lengthening which has also been observed in hexamethylethane (Bauer & Beach, 1942) is steric repulsion rather than any direct effect on the state of hybridization of the substituent atom.

The second possible factor which may account for the bond and angle deviations is the presence of long range steric strain in the molecule. This type of strain is evident in both the general 'bowing' of the basic plane of the ring system which is illustrated in Fig. 4(*b*), and the obvious distortion of the *A* ring (Fig. 4(*a*)). There appear to be three sources of long range strain in the structure.

The first is a strain on the ring system due to the steric interaction between the three methyl groups at C(24), C(25) and C(26) which are attached to atoms C(4), C(10) and C(8). As the van der Waals radius for a methyl group is about 2·0 Å and the C(24)···C(25) and C(25)···C(26) distances are 3·17 and 3·30 Å respectively, it is evident that, even with the hydrogen atoms in the least hindered positions, there will be considerable interaction in this region. The degree of interaction may be gauged by comparing the inter-methyl carbon distances with the C(10)···C(8) contact of 2·59 Å which at first sight appears as if it would be equivalent. The separation of C(24) and C(25) as a result of steric repulsion would tend to flatten the *A* ring at C(4) and C(10), accounting for the large angles C(2)–C(3)–C(4), C(4)–C(5)–C(10) and C(10)–C(1)–C(2) of 119·8°, 120·2° and 112·9° respectively. The hindrance of C(26) would also explain the large angles C(10)–C(9)–C(8) and C(8)–C(7)–C(6) of 118·7° and 112·5°, though as discussed later, these deviations are probably due to another source of strain. With the presence of tensile strain between C(4) and C(10) a slight lengthening of the bonds would be expected, but this alone is unlikely to account for the deviations of 0·1 Å. It is more probable that the distortion from the ideal tetrahedral configuration has resulted in a general weakening of the adjacent bonds similar to that described by Pauling (1960). The decrease in bond strength presumably accounts for the additional lengthening of the bonds C(4)–C(5) and C(5)–C(10) and the subsequent reduction of the angles C(3)–C(4)–C(5) and C(5)–C(10)–C(1). It is interesting to note that the shorter bonds C(2)–C(3) and C(6)–C(7) are consistent with the strain in the *A* and *B* rings resulting in a compressional force on these bonds. Also in agreement with the concept that distorted bond angles result in weaker bonds, the bonds of the three hindered methyl groups to the ring system, C(4)–C(24), C(10)–C(25) and C(8)–C(26) are all longer than normal.

The second source of strain arises from the attachment of the five-membered *E* ring to the six-membered *D* ring. The degree and direction of steric strain resulting from this junction is difficult to assess but from a Drieding model of the structure it seems likely that this could account for the short C(17)–C(22) and C(22)–C(21) bonds of 1·49 and 1·46 Å. This may also cause the *D* ring to be distorted, the puckering being centred at the carbon C(14) on the junction with the *C* ring. The strain and distortion at this point may well contribute to the lengthening of the C(8)–C(14) bond to 1·66 Å and this together with the degree of substitution in the environment of the bond may account for this large deviation. This source of strain, rather than the methyl interaction, appears therefore to be responsible for the large angles of C(10)–C(9)–C(8) and C(14)–C(15)–C(16).

The third source of strain is due to the attachment of the iodoacetate group to the carbon C(3) in the basic ring system. The presence of this strain, which appears to be due to inter- rather than intra-molecular forces, is evident from the low C(4)–C(3)–O(1) angle of 100·5°. The distortion of C(3)–O(1) from the ideal tetrahedron may well explain the elongation of this bond to 1·56 Å. It is interesting to note that a similar

attachment in the structure of epiliminol iodoacetate (Arnott, Davie, Robertson, Sim & Watson, 1961) has comparable C–O and C–C–O values of 1·59 Å and 102° respectively. It is unlikely in methyl melaleucate iodoacetate that the flattening of the *A* ring will significantly affect the value of the C(4)–C(3)–O(1) angle so the distortion can only be explained in terms of packing forces.

It generally appears then that the longer C–C bonds are dependent on both the degree of substitution in the bonded carbons and the effect of long range steric strain on the bond, whereas the shorter C–C bonds and the abnormal C–C–C angles are only due to the strain.

In the isopropenyl side chain the C(20)–C(29) double bond of 1·30 Å and the C(20)–C(30) single bond of 1·44 Å compare reasonably with the values of 1·33 and 1·50 Å in propylene (Lide & Christensen, 1962). The bond lengths and angles in the two methoxycarbonyl groups are generally consistent with one another and do not differ significantly from values in methyl acetate and methyl chloroformate (O'Gorman, Shand & Schomaker, 1950) and dimethyl oxalate (Dougill & Jeffrey, 1953).

The shorter intermolecular distances shown in Fig. 4(*b*) are consistent with van der Waals contacts.

Hydrogen atom positions

The atomic coordinates of the hydrogen atoms are listed in Table 3, and Fig. 6 shows diagrammatically the positions of these atoms in the unit cell, viewed down the *b* axis.

All group I hydrogen atoms except H(16) and H(30) are close to their expected atomic sites. The group II hydrogen atoms are of more interest since their positions are governed by the intramolecular packing. Fig. 8 shows the positions of the methyl hydrogen atoms attached to C(24), C(25) and C(26) with the van der Waals radius of 1·0 Å. The staggered configuration of these hydrogens appears to be determined by the condition of minimum hindrance to one another, though the orientation of the hydrogen atoms attached to the axial *gem*-dimethyl carbon atom C(24) is also affected by the adjacent equatorial methyl group. It is interesting to note that the positions of the methyl hydrogen atoms attached to C(25) and C(26) are independent of packing with the adjacent ring system, and this contrasts with arrangements often found in unhindered methyl groups.

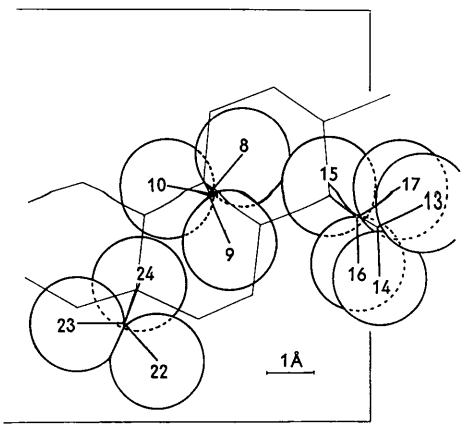

Fig. 8. Part of the structure showing the hydrogen atoms attached to C(23), C(24), C(25) and C(26) with a van der Waals radius of 1·0 Å.

Hydrogen atoms in the methoxycarbonyl groups at C(33) and C(34) are oriented for minimum hindrance with the adjacent oxygen atoms O(5) and O(4). As the methyl and oxygen van der Waals radii are 2·0 and 1·4 Å and the C(34) · · · O(4) and C(33) · · · O(5) distances are 2·66 and 2·65 Å, it would be expected that the close-packing between these atoms is the controlling factor in the orientation of the methoxyl hydrogen atoms. The hydrogen atom sites are consistent with this idea.

The orientation of the isopropenyl side chain with respect to C(20) appears to depend on the hydrogen atom packing with the surrounding atoms. Moreover positions of the hydrogen atoms attached to the C(30) methyl and the C(29) vinylidene carbon atoms within the group are also determined by this packing.

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Interferometric Studies on Very Pure Silicon Carbide Crystals

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Optical multiple-beam interferometric studies are reported for over one hundred extremely pure, clear, colourless, transparent silicon carbide crystals. With one exception they are thin, effectively parallel-sided plates, having surfaces of very high interferometric quality. Most surfaces show regular steps or curvature and these may be due to slip and to buckling after cooling.

The spiral growths so common on the less pure common quality commercial silicon carbide crystals appear here on one crystal only. A defect goes right through the crystal plate and a pair of spirals develops simultaneously, one on the back and one on the front of the plate, from this common defect. Spiral steps measured interferometrically exhibit unusual anomalies which are discussed.

It is well known that a large proportion of even the best-formed silicon carbide crystals hitherto examined exhibit notable growth spirals on the basal pinacoid. These have been studied by many investigators, notably Verma (1951), Amelinckx (1951) and others. Not only have spiral growths been established, but in addition a variety of step heights have been evaluated by using the precision techniques of multiple-beam interferometry. It is now well known that these spiral growths afford a most comprehensive confirmation of the dislocation theory of growth put forward by Burton, Cabrera & Frank (1949) and later more extensively developed especially by Frank (1951).

Most silicon carbide crystals exhibit some colour, varying from a light shade of green, through to a brilliant black. Through the courtesy of Dr Knippenberg of Phillips, Eindhoven, we have available a collection of extremely pure crystals of silicon carbide. These were received as an incrustation of transparent colourless thin crystal plates (some hundreds), growing out towards the centre from an annular ring of friable graphite. The crystals (many of them several millimetres across) were all beautifully formed and each was clearly a single crystal, all being notable for their transparency and complete absence of any colour. They were clearly of much higher purity than the usual commercial silicon carbide crystals.

Since spiral growth formation is certainly linked to the presence of severe dislocation, and as included impurities must clearly encourage development of such screw dislocations, it was suggested to us by S. Tolansky that there was a considerable likelihood that these very pure silicon carbide crystals might indeed not exhibit any spiral growths at all, in contradistinction to the usual run of silicon carbide crystals. We have therefore carried through a multiple-beam interferometric study of the surface microtopographies of over a hundred of these pure crystals and this report summarizes the findings. The crystals studied were mostly of similar thickness, transparent plates of the order of a quarter of a millimetre thick, all plane, and exhibiting well developed pinacoid (0001) faces. In accordance with standard practice in this laboratory (Tolansky, 1948) the crystals were silvered (reflectivity $>95\%$) and examined, first by phase contrast, then with multiple-beam Fizeau fringes (green mercury source) and in selected cases with white-light fringes of equal chromatic order. In specific instances information was obtained without silvering, and at times by the use of polarized light.

Observations

With one single and obviously an unusual exception, our examination of over 100 crystals failed to reveal any spiral growths at all. Now evidence has long since accumulated that the familiar spirals on silicon carbide have step heights normally several integral multiples