The Crystal and Molecular Structure of Iso-eremolactone*

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The crystal structure of iso-eremolactone, $C_{20}H_{26}O_2$, a plant product derivative from a new biogenetic series, has been solved by the direct methods of Karle & Hauptman for non-centrosymmetric structures. The space group is $P2_12_12_1$, and $a = 12 \cdot 866$, $b = 20 \cdot 200$, $c = 6 \cdot 685$ Å. The final R value is $0 \cdot 063$. Long sp^3–sp^3 carbon–carbon bonds in the structure are associated with a high degree of substitution at the carbon atoms, and also with bond angles which differ considerably from the ideal tetrahedral values. The thermal motion in the structure has a substantial internal component, which results from the lability of bond angles with non-ideal values.

Introduction

Eremolactone, $C_{20}H_{26}O_2$, is a novel diterpene of a new biogenetic series. Jefferies, Knox & Middleton (1962) first isolated this compound from *Eremophila fraseri* F. Muel., which is a common viscid shrub in the central Murchison district of Western Australia. Several attempts have been made to characterize this structure by spectroscopic and chemical means without success, the main problem being the small quantity of material available for chemical analysis. Birch, Grimshaw & Turnbull (1963) proposed on limited spectroscopic and chemical evidence that the nucleus of the diterpene is tricyclic and suggested (I) (Fig. 1) as the possible structure. Jefferies & Middleton (1964) on the other hand considered that the spectroscopic and chemical evidence available was inadequate for a useful speculation

on the stereochemistry of this compound and an X-ray analysis was suggested. Both groups of workers agreed, however, that the molecule contained a conjugated γ-lactone side chain and a gem-dimethyl group.

An X-ray analysis was commenced on eremolactone itself, but it was found that although the cell dimensions remained constant some of the intensities varied from crystal to crystal. A check on the melting point revealed that the sample was impure. Partial isomerization had apparently occurred during recrystallization. It proved difficult to obtain a pure sample, and the completely isomerized compound was preferred. The structure proposed for iso-eremolactone by Birch, Grimshaw & Turnbull (1963) is shown as (II) in Fig. 1.

Crystal data

Iso-eremolactone. $C_{20}H_{26}O_2$ M.W. 298·4
m.p. 159–160 °C. Prismatic c, $\{110\}$ well developed.

$a = 12 \cdot 8660$ ($\sigma = 0 \cdot 0032$) Å ($\sim 20 °C$)
$b = 20 \cdot 2001$ ($\sigma = 0 \cdot 0016$)
$c = 6 \cdot 6846$ ($\sigma = 0 \cdot 0007$)

Thoria calibration ($a_0 = 5 \cdot 5969$ (5) Å at 20 °C; Kempter & Elliott, 1959).

$V = 1737 \cdot 3$ ($\sigma = 0 \cdot 5$) Å^3
$Z = 4$, $D_x = 1 \cdot 139$ g.cm^{-3}
$D_m = 1 \cdot 143$ ($\sigma = 0 \cdot 003$) g.cm^{-3} ($\sim 20 °C$)

Space group $P2_12_12_1$ from absences and structure analysis.

$\mu = 5 \cdot 67$ cm^{-1} for Cu $K\alpha$ ($\lambda = 1 \cdot 5418$ Å).

Appreciable intensities were recorded for the space group forbidden reflexions 300, 500 and 700, but it was suspected from their spot shape that these were Renninger reflexions. This was supported by the reflexions having the relationship

$$H_R = H_1 + H_2,$$

where H_i are Miller triples, and both H_1 and H_2 are strong reflexions (Lipson & Cochran, 1966). Nevertheless the alternative space group $P22_12_1$ was treated
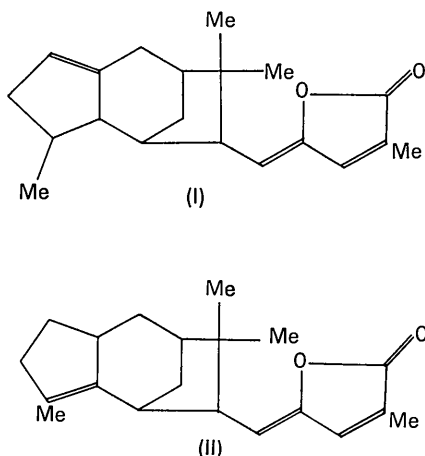
Fig. 1. Structures proposed by Birch, Grimshaw & Turnbull (1963) for (I) eremolactone and (II) iso-eremolactone.

as equally probable in attempting the solution of the structure. The successful analysis in only one space group confirmed that the original assignment was correct.

Intensity data were recorded photographically with Cu $K\alpha$ radiation. The region of reciprocal space scanned covered 94·6% of the unique reflexions within the Cu $K\alpha$ sphere. Errors due to absorption were estimated, found to be small compared with those expected in the intensity measurements, and were neglected. The intensity data were scaled by the method of Hamilton, Rollett & Sparks (1965) and standard deviations were calculated using the scaling algorithm given by these authors.

Structure analysis

The structure was solved by direct methods, using the procedure suggested by Karle & Hauptman (1956) with some modifications. Normalized structure factors, E_H, were calculated by evaluating a scale factor and mean isotropic temperature factor coefficient from a Wilson plot. The structure factors were sorted in descending order of magnitude of E_H, and the Σ_1 formula (Karle & Hauptman, 1956) was used to calculate $P_+(E_{2H})$ for all even zero layer reflexions with $E_{2H} \geq 1\cdot5$. The results are given, together with the signs from the refined structure, in Table 1. Where $P_+(E_{2H})$ gives a firm indication of sign it agrees with the true value. Nevertheless the present analysis was conducted successfully without utilizing any of these signs.

Table 1. Σ_1 phases and probabilities ($E_{2H} \geq 1\cdot5$)

h	k	l	E_{2H}	$P_+(E_{2H})$	$\varphi\Sigma_1$	φ true
2	0	8	3·09	0·15	−	−
0	8	2	2·68	0·13	−	−
16	0	0	2·16	0·01	−	−
14	10	0	2·15	0·87	+	+
12	4	0	2·02	0·50	?	−
2	2	0	1·95	0·63	+ (?)	+
8	18	0	1·81	0·52	?	+
4	10	0	1·78	0·50	?	−
0	2	6	1·76	0·50	?	+
4	16	0	1·75	0·48	?	+
0	2	8	1·70	0·21	−	−
2	4	0	1·65	0·50	?	+
0	14	4	1·61	0·39	− (?)	+
0	16	0	1·59	0·73	+	+
6	10	0	1·54	0·32	− (?)	−
10	0	2	1·54	0·50	?	+
0	14	2	1·52	0·50	?	+

The Σ_2 interaction pairs were then determined for each $E_H \geq E_{min}$, where E_{min} is an arbitrary minimum. These results were then used to aid the choice of origin and enantiomorph defining phases, and to calculate the approximate phases for other reflexions from these four. The three linearly independent reflexions formed a combination occupying the cardinal points, as suggested by Karle & Hauptman (1956), and are of the type $u,g,0$; $g,0,u$; $0,u,g$. The fourth arbitrary phase, which is linearly dependent on these three and dif-

ferentiates between the two possible enantiomorphs is then a $u,0,u$ reflexion. The reflexions were selected within these groups on the basis of their own E_H values and the number of Σ_2 relationships by which they were related to other reflexions of high E_H value. The latter factor was given the higher weight in making the selection. The phases thus defined are listed at the head of Table 2. The Σ_2 formula was then applied, and with the use of some of the high E_H value general reflexions with undefined phases as intermediates approximate phases were calculated for the twenty reflexions which are listed in the latter part of Table 2. It is interesting to note (i) that some of these phases could have been obtained more directly by including the reliable phase indications from the Σ_1 formula in the phase determining process, and (ii) that although there were more equations than unknowns, so that the problem is overdetermined, four of the twenty phases are grossly in error.

Table 2. Starting phases for tangent formula

	h	k	l	E_H	φ initial	φ true	$\Delta\varphi$
Origin	11	6	0	3·6	90·0	90·0	−
and	6	0	1	2·3	90·0	90·0	−
enantio-	0	1	4	2·1	90·0	90·0	−
morph	13	0	5	2·4	90·0	90·0	−
	3	18	0	3·4	90·0	−90·0	180·0
	8	11	0	2·9	0·0	0·0	0·0
	8	13	0	3·6	0·0	0·0	0·0
	3	6	0	1·7	90·0	−90·0	180·0
	0	23	3	2·0	−90·0	−90·0	0·0
	0	24	1	2·8	0·0	0·0	0·0
	5	6	4	2·1	0·0	148·6	148·6
	14	13	0	1·6	180·0	180·0	0·0
	16	0	0	2·2	180·0	180·0	0·0
	10	11	0	1·9	0·0	0·0	0·0
	5	7	0	2·7	90·0	90·0	0·0
	5	5	0	2·4	90·0	90·0	0·0
	6	11	0	2·3	0·0	0·0	0·0
	5	17	0	2·1	90·0	−90·0	180·0
	3	18	1	2·0	45·0	34·1	10·9
	8	11	1	2·0	180·0	−156·6	33·5
	2	2	0	2·0	0·0	0·0	0·0
	3	5	0	2·0	90·0	90·0	0·0
	8	12	4	1·9	90·0	95·3	5·3
	3	4	0	2·2	−90·0	−90·0	0·0

The phase set was extended and the phases originally determined, apart from the four arbitrary phases, were refined using the tangent formula (Karle & Hauptman, 1956). It was found that the tangent iteration converged rapidly if the majority of the phases were nearly correct. Thus the strategy was to introduce a limited number of new phases at a time by a gradual lowering of E_{min} which in this analysis was lowered progressively from 1·8 to 1·6, then to 1·5, 1·4 and finally to 1·3. At each step about 30–40% of new phases were introduced, and convergence was normally achieved after four rounds of iteration. The criterion for convergence was set at a maximum phase change in the last cycle of 2°. E_{calc} values were also evaluated as described by Karle & Karle (1964). Since a small value is often

indicative of an unreliable phase, reflexions with E_{calc} less than 0·6 were omitted from the refinement of other phases. Reflexions with phases which oscillated vio-
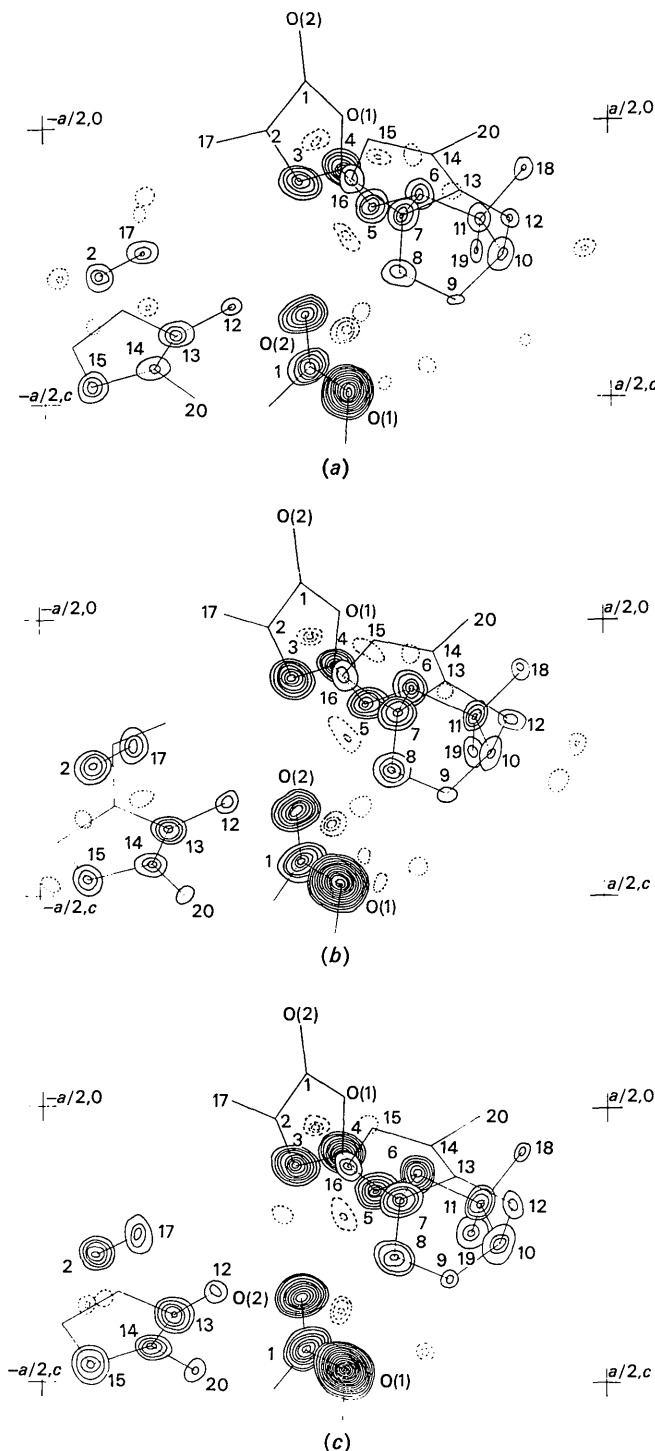

(a)

(b)

(c)

Fig. 2. Composite summary of E maps evaluated with use of (a) 200 reflexions with $E_H > 1·5$, (b) 255 reflexions with $E_H > 1·4$, (c) 330 reflexions with $E_H > 1·3$. Contours are at the same arbitrary interval in each map.

lently from cycle to cycle were also omitted, but these were few in number. There were large changes in the phases of an appreciable proportion of the reflexions during the refinement, including reversal in sign for a number of centric reflexions.

The first E maps were computed with 200 phases for $E_{min} = 1·5$, which is equivalent to nine phases per non-hydrogen atom. A cursory inspection of the E maps revealed the sites of the atoms in the γ-lactone side chain and four others, making twelve in all, the oxygen atoms being readily distinguishable from the carbon atoms by their peak heights [Fig. 2(a)]. There were sixteen other peaks with densities between 1·2 and 2·0 units on an arbitrary scale, eight of which could be rejected on stereochemical grounds. The remainder were accepted as trial atomic positions and were found to be correct. The remaining two non-hydrogen atoms were located by conventional methods using a difference synthesis.

The structure was refined by a block-diagonal least-squares method which minimizes $\Sigma \omega |F_o - F_c|^2$. Unobservably weak reflexions were assigned the value of the minimum observable threshold, but were included in the refinement and in R index $(\Sigma |F_o - F_c|)/\Sigma |F_o|$ calculation only when $|F_o| < |F_c|$. The block-diagonal matrix consisted of a 2×2 block for the scale and mean isotropic temperature factor and 3×3 and 6×6 blocks for the positional and thermal parameters respectively.

The scattering factors were those of Hanson, Herman, Lea & Skillman (1964). Hydrogen atoms were identified in a difference map computed when the R value was 0·109, and were included in the later rounds of refinement with isotropic temperature factors. The weighting scheme adopted was

$$\omega = (a + bF_o + cF_o^2)^{-1},$$

where a, b and c were derived from a quadratic curve of best fit for $\langle \sigma(F_o) \rangle$ as a function of F_o where $\langle \sigma(F_o) \rangle$ denotes the expectation value of $\sigma(F_o)$ over ranges of F_o. The numerical values of a, b and c are respectively 0·35, −0·015 and 0·083. The effects of extinction were just detectable in an agreement analysis but were serious only for the two strongest reflexions, 220 and 111, which were omitted from the refinement. Interactions between hydrogen parameters and those of the associated carbon atoms were observed to be strong. When the shifts in the hydrogen parameters were large they affected the positions of the associated carbons by amounts of up to 1σ. At the conclusion of the refinement R was 0·063, and the shifts in the positional and thermal parameters for non-hydrogen atoms were all less than $\sigma/3$ and $\sigma/2$ respectively. Those for the hydrogen atoms were approximately σ. A list of the final structure factors is given in Table 3, and the structural parameters are given in Tables 4 to 6. The numbering of the atoms in the molecule is given in Fig. 3. The r.m.s. standard deviation in an observed structure amplitude of unit weight $\{ \Sigma \omega |F_o - F_c|^2 / (m - n) \}^{\frac{1}{2}}$ is 1·1, indicating that the experimental data are relatively

Table 3. *Observed and calculated structure factors*

U=unobserved; E=exclusion from least-squares calculations

H	K	L	FO	FC	AO	BO

(Full multi-column numerical listing of observed and calculated structure factors; data omitted.)

Table 3 (*cont.*)

H	K	L	FO	FC	AO	BO
8	10	1	4.28	4.36	.85	-4.20
	11		17.81	18.09	-16.28	-7.20
	12		9.65	9.74	2.99	9.17
	13		5.97	6.28	-1.34	5.82
	14		8.87	8.92	-7.11	5.30
	15		5.30	5.48	2.49	-4.67
	16		1.60	.62	1.60	.02
	17		1.92	2.14	.85	1.72
	18		2.54	2.63	-2.16	1.34
	19		3.89	3.71	-3.53	-1.61
	20		2.57	2.69	2.29	1.16
	21		1.05U	.82	-.25	-1.02
	22		3.33	3.09	-3.27	.62
9	0		1.70	1.49	0.00	-1.70
	1		5.10	4.59	-1.17	-4.97
	2		12.91	12.51	12.65	-2.54
	3		2.24	1.22	2.15	-.63
	4		13.43	14.01	-2.03	13.27
	5		8.42	8.64	5.23	-6.60
	6		13.51	13.32	5.33	-12.42
	7		10.28	10.08	-9.74	-3.26
	8		10.48	10.51	-9.04	-5.30
	9		10.61	11.01	-.15	-10.61
	10		15.23	14.88	-14.73	-3.85
	11		3.70	3.38	-.04	-3.70
	12		4.01	5.01	.99	3.88
	13		4.21	4.48	2.10	3.65
	14		9.87	10.19	-5.72	-8.04
	15		1.58U	1.50	-1.41	-.71
	16		2.01	1.41	.73	-1.87
	17		2.69	2.95	.21	2.68
	18		2.45	2.68	2.26	-.94
	19		4.59	4.52	-.14	-4.59
	20		1.88	1.84	-1.76	-.65
10	0		5.24	5.00	0.00	5.24
	1		6.18	6.15	-1.50	-5.99
	2		21.02	20.19	-5.49	20.29
	3		10.03	10.24	9.07	-4.27
	4		12.09	11.80	10.53	-5.93
	5		15.40	16.53	15.09	-3.07
	6		8.69	8.94	.62	-8.67
	7		6.64	6.46	-6.61	.68
	8		6.30	6.14	4.93	-3.91
	9		5.61	5.90	-2.14	-5.18
	10		6.46	6.87	-3.85	-5.19
	11		2.68	2.62	2.00	1.79
	12		4.55	4.53	1.61	4.25
	13		3.59	3.48	-1.65	-3.19
	14		3.95	4.15	.42	3.93
	15		1.47U	.55	.73	-1.28
	16		6.81	5.77	.09	6.81
	17		1.98	2.38	-.43	-1.93
	18		4.49	4.44	-1.39	4.27
	19		2.94	2.96	2.16	-1.99
	20		2.00	2.11	-.56	-1.92
11	0		2.85	3.06	0.00	2.85
	1		4.90	4.50	4.46	2.02
	2		14.81	14.74	-.22	14.81
	3		3.06	3.12	-1.80	2.48
	4		19.68	19.73	5.63	-18.85
	5		10.71	10.40	-5.91	-8.93
	6		6.35	6.36	-.56	6.33
	7		6.42	6.35	-3.62	-5.30
	8		3.60	3.38	-.43	-3.57
	9		4.18	4.09	-4.16	-.44
	10		4.85	5.09	-1.35	4.66
	11		1.78	1.96	-1.65	-.65
	12		8.09	8.29	-4.25	-6.88
	13		1.49U	.24	-1.46	.25
	14		1.41U	.58	.61	1.28
	15		3.18	2.83	2.92	1.24
	16		2.64	2.17	.32	-2.62
	17		1.80	1.80	-.42	-1.75
	18		3.14	3.11	.27	-3.12
	19		3.70	4.02	-1.69	-3.29
12	0		4.70	4.77	0.00	4.70
	1		7.80	7.80	7.80	.10
	2		7.72	7.51	5.84	-5.05
	3		6.72	6.47	2.56	-6.22
	4		3.88	3.81	3.68	-1.22
	5		8.82	8.79	-3.53	-8.08
	6		1.63	2.39	-1.42	-.79
	7		2.99	2.96	2.97	-.38
	8		5.05	4.95	3.39	-3.74
	9		3.20	3.74	2.68	-1.73
	10		1.52	1.56	-.70	1.35
	11		4.92	5.02	-2.90	3.97
	12		2.31	2.49	.87	2.14
	13		2.91	2.92	1.02	-2.73
	14		3.32	3.26	3.30	-.35
	15		1.13U	.29	1.10	-.27
	16		4.39	1.92	2.83	3.36
	17		4.90	4.64	4.28	-2.37
13	0		1.59U	.57	0.00	1.59
	1		2.98	3.20	2.55	1.55
	2		3.84	4.02	2.76	2.66
	3		4.58	4.62	.72	-4.53
	4		3.07	3.12	2.53	1.73
	5		1.54U	1.33	0.00	1.54
	6		2.72	3.43	2.68	.45
	7		4.49	4.90	-3.45	-2.86
	8		1.45U	.76	-.55	-1.34
	9		2.42	2.38	-1.85	-1.56
	10		1.35U	.96	-.95	-.96
	11		3.62	3.17	1.42	3.33
	12		2.69	2.90	-1.31	2.35
	13		1.88	1.75	-.38	-1.84
	14		1.40	1.06	-.67	-1.23
	15		1.85	1.80	-1.11	-1.48
14	0		1.45	1.29	0.00	-1.45
	1		3.55	3.81	3.39	-1.05
	2		2.50	2.69	2.50	0.00
	3		3.99	3.89	1.23	-3.79
	4		2.69	3.20	2.55	-.84
	5		2.51	2.68	-1.49	-2.02
	6		2.33	2.38	-1.01	-2.10
	7		2.05	2.58	1.92	-.71
	8		1.25U	.84	-.75	-1.00
	9		3.23	3.14	-3.18	.60
	10		2.03	2.06	1.49	-1.37
	11		3.42	3.55	3.30	.89
	12		5.94	5.60	5.26	-2.76
	13		1.88	2.05	1.42	1.23
15	0		1.23U	1.13	0.00	1.23
	1		6.74	6.37	6.22	-2.60
	2		1.21U	.75	.04	1.21
	3		4.40	4.30	.90	-4.30
	4		2.51	2.76	-.43	2.47
	5		1.13U	.58	.54	-.99
	6		1.34	1.55	.40	1.27
	7		3.36	3.52	-2.40	2.34
	8		1.88	1.81	.74	-1.73
	9		1.06	.75	.31	1.02
	10		4.06	4.46	.38	4.04
16	0		.90U	1.11	0.00	-.90
16	1	1	1.93	1.96	.35	-1.90
	2		2.57	2.47	-2.53	.44
	3		1.68	1.42	1.66	.25
	4		.79U	.73	-.79	0.00
	5		2.33	2.48	.47	-2.28
0	0	2	.83U	.22	-.83	0.00
	1		9.53	10.28	0.00	9.53
	2		19.34	17.35	19.34	0.00
	3		26.13	27.37	0.00	-26.13
	4		16.34	16.76	-16.34	0.00
	5		12.68	13.59	0.00	-12.68
	6		11.58	11.34	11.58	0.00
	7		13.53	13.57	0.00	-13.53
	8		62.79	63.65	-62.79	0.00
	9		5.15	4.62	0.00	-5.15
	10		5.03	5.63	5.03	0.00
	11		1.31U	.74	0.00	-1.31
	12		3.07	3.49	-3.07	0.00
	13		9.85	10.08	0.00	-9.85
	14		18.54	18.59	18.54	0.00
	15		5.92	5.91	0.00	5.92
	16		9.95	9.46	9.95	0.00
	17		6.67	5.97	0.00	-6.67
	18		6.54	5.80	6.54	0.00
	19		5.23	5.64	0.00	-5.23
	20		3.47	3.60	-3.47	0.00
	21		1.28	.37	0.00	-1.28
	22		1.40U	1.34	-1.40	0.00
	23		1.25U	.61	0.00	-1.25
	24		3.44	3.05	-3.44	0.00
	25		.96	1.36	0.00	.96
1	0		28.32	25.45	-28.32	0.00
	1		42.40	37.65	-33.63	25.82
	2		30.18	32.14	20.42	22.22
	3		37.73	40.60	27.53	-25.80
	4		6.78	8.64	6.51	1.86
	5		25.72	26.56	-13.31	-22.00
	6		25.23	26.06	-11.74	22.33
	7		28.86	26.53	-13.59	25.45
	8		30.71	30.76	24.63	18.35
	9		13.64	12.29	-6.09	12.20
	10		18.26	18.57	-11.68	14.03
	11		8.98	9.62	.06	-8.98
	12		18.07	17.27	7.62	16.38
	13		3.06	3.29	2.86	1.09
	14		7.61	7.17	-2.45	7.20
	15		11.54	10.68	8.57	7.73
	16		7.08	7.19	1.11	6.99
	17		10.89	10.60	-5.26	-9.54
	18		3.97	4.03	3.94	-.48
	19		3.79	3.51	.55	3.75
	20		3.51	3.38	-3.42	.77
	21		5.09	5.21	-4.48	2.43
	22		4.99	4.80	.23	4.98
	23		3.03	3.05	-2.06	2.22
	24		5.94	5.34	3.82	4.55
	25		1.60	1.77	-.87	-1.35
2	0		30.50	31.75	-30.50	0.00
	1		21.13	19.59	5.74	-20.33
	2		41.40	42.67	-34.45	-22.95
	3		14.85	12.49	-13.23	-6.75
	4		6.95	7.54	-3.94	-5.73
	5		32.23	31.62	-31.39	-7.32
	6		17.78	17.67	-15.71	-8.32
	7		14.90	14.89	-8.92	-11.93
	8		16.15	14.61	9.08	13.35
	9		5.44	5.29	-3.75	-3.94
	10		4.26	4.29	1.06	4.12
	11		17.55	16.91	-13.33	11.42
	12		8.51	8.32	.88	-8.46
	13		2.68	2.70	-2.08	1.70
	14		3.19	3.70	2.91	1.32
	15		6.49	6.51	-1.57	-6.30
	16		5.64	5.17	1.35	-5.48
	17		10.46	10.70	-3.88	-9.71
	18		4.06	3.99	-1.38	3.81
	19		8.36	8.69	-8.36	.05
	20		2.13	2.47	-1.56	-1.45
	21		5.03	5.34	-3.77	-3.33
	22		2.38	2.51	-2.32	-.53
	23		1.31	1.40	1.31	-.06
	24		3.24	2.89	3.23	.18
3	0		7.03	6.59	7.03	0.00
	1		17.86	17.40	17.79	-1.57
	2		30.48	32.04	13.96	-27.09
	3		11.56	10.32	-7.79	-8.54
	4		8.18	6.50	8.06	-1.40
	5		3.16	3.27	1.91	2.51
	6		8.12	8.22	6.72	-4.55
	7		23.04	23.13	6.81	-22.01
	8		9.43	8.19	-9.24	-1.85
	9		11.60	11.35	-6.71	9.46
	10		29.83	29.91	14.55	26.04
	11		10.95	11.06	-1.01	10.91
	12		11.61	11.86	7.74	8.65
	13		2.77	2.51	2.46	1.26
	14		12.52	12.53	5.86	11.06
	15		7.34	7.54	-6.30	-3.75
	16		9.46	9.65	-4.14	-8.50
	17		8.84	8.98	7.99	3.77
	18		1.95	1.78	-1.90	.43
	19		4.64	4.77	-4.49	1.19
	20		1.89	2.32	1.82	-.51
	21		4.20	4.23	-.79	4.13
	22		1.93	2.06	1.61	1.07
	23		2.76	2.78	-2.32	-1.50
	24		1.56	1.74	-.75	-1.36
4	0		.92U	1.32	.92	0.00
	1		32.81	31.13	-31.84	7.90
	2		16.34	14.52	9.63	-13.19
	3		2.35	2.15	1.89	-1.38
	4		41.22	40.68	-41.18	-1.71
	5		18.82	17.94	-1.31	-18.78
	6		10.47	8.84	-7.67	7.13
	7		36.11	35.03	-29.11	21.36
	8		13.10	12.61	-12.96	-1.89
	9		9.16	8.99	-9.10	1.08
	10		3.84	4.54	-3.84	0.00
	11		8.07	7.49	-6.26	-5.09
	12		3.23	3.48	-3.02	-1.14
	13		4.58	4.90	.41	-4.56
	14		7.80	7.67	7.62	-1.65
	15		8.95	9.30	-8.95	.25
	16		5.58	5.23	-3.70	-4.18
	17		11.60	11.16	-11.60	.39
	18		3.09	3.25	-2.65	-1.58
	19		4.05	4.57	-2.23	-3.38
	20		1.52U	.68	1.48	-.35
	21		2.83	2.72	-2.13	-1.87
	22		1.42	1.30	.99	1.02
	23		2.35	2.20	-2.22	.74
	24		1.94	1.98	-1.28	-1.46
5	0		4.63	4.59	4.63	0.00
	1		42.65	43.86	-27.20	-32.84
	2		38.35	36.52	38.15	3.85
5	3	2	19.94	20.08	-1.04	-19.91
	4		23.99	23.41	-23.64	-4.06
	5		5.26	5.25	-4.09	-3.31
	6		6.08	6.16	4.47	4.12
	7		8.02	6.84	2.38	7.66
	8		10.26	10.32	5.72	8.51
	9		6.09	5.37	4.27	4.34
	10		8.97	8.86	5.83	-6.81
	11		4.12	3.94	.10	4.12
	12		4.72	4.57	1.49	-4.47
	13		7.74	7.93	1.69	-7.55
	14		10.71	10.57	2.95	-10.29
	15		8.23	9.10	6.86	-4.54
	16		4.34	4.61	2.64	-3.43
	17		5.38	4.81	-4.76	-2.50
	18		3.42	3.61	3.42	.08
	19		1.46	1.68	.80	1.22
	20		1.77	1.98	-1.77	.05
	21		3.23	3.13	-2.49	2.05
	22		1.28	1.80	1.14	-.59
	23		3.49	2.99	-1.30	3.24
6	0		13.42	11.83	-13.42	0.00
	1		19.04	17.95	18.37	-5.00
	2		15.32	13.95	7.72	13.23
	3		25.23	23.29	-23.66	8.76
	4		1.60	1.46	-.95	-1.29
	5		19.49	19.64	-3.90	19.09
	6		17.00	15.86	-16.19	-5.19
	7		16.35	14.04	-15.86	-3.99
	8		11.33	10.81	-11.15	-1.99
	9		3.17	3.10	2.11	-2.36
	10		9.66	9.78	4.28	8.66
	11		9.44	9.26	-8.80	3.41
	12		8.73	9.23	6.67	-5.64
	13		3.24	3.48	2.96	1.31
	14		10.48	10.56	-10.07	-2.91
	15		7.92	8.27	-7.88	-.83
	16		4.18	4.48	-.63	-4.13
	17		1.54	.63	.80	-1.31
	18		1.48	1.34	1.11	.98
	19		3.55	3.43	-3.28	-1.36
	20		2.32	2.96	-2.32	-.09
	21		1.20U	.36	.59	-1.04
	22		2.01	2.19	.07	-2.01
	23		2.73	2.62	2.39	-1.31
7	0		7.49	6.62	-7.49	0.00
	1		28.12	27.28	21.84	-17.71
	2		7.85	7.08	-2.89	-7.30
	3		11.95	11.25	-5.04	-10.84
	4		10.02	9.77	4.67	-8.86
	5		10.00	8.60	-3.51	-9.36
	6		7.92	8.38	.58	-7.90
	7		7.40	7.42	4.30	-6.02
	8		3.99	3.68	3.67	1.56
	9		4.50	4.82	.27	-4.49
	10		3.11	2.67	.94	2.96
	11		20.02	20.30	12.41	-15.71
	12		16.77	16.00	7.77	-14.86
	13		3.58	3.70	-3.44	.95
	14		2.62	2.55	1.68	-2.01
	15		4.57	4.41	-2.94	-3.49
	16		1.84	2.19	1.34	-1.26
	17		4.23	4.23	3.32	2.62
	18		1.45U	1.27	-.93	-1.11
	19		1.35U	1.32	-.27	1.32
	20		1.23U	1.67	.31	-1.19
	21		2.54	2.44	.80	2.41
	22		1.10	1.25	-.37	-1.03
8	0		4.03	4.25	4.03	0.00
	1		7.01	5.57	-6.69	-2.11
	2		11.16	10.72	7.98	-7.81
	3		16.98	15.67	-13.95	9.69
	4		2.61	2.88	.52	-2.56
	5		17.08	16.21	-17.08	0.00
	6		9.08	9.69	3.61	8.32
	7		10.74	11.41	4.82	9.60
	8		12.64	12.29	12.64	.94
	9		7.29	7.15	5.59	4.68
	10		4.22	3.50	-3.31	-2.62
	11		11.36	11.55	10.63	-4.01
	12		2.88	2.98	2.38	1.61
	13		7.47	7.89	-6.27	4.06
	14		4.39	4.60	1.96	3.93
	15		2.85	3.48	2.07	-1.96
	16		3.96	4.15	-3.06	-2.51
	17		2.22	2.70	-2.19	.35
	18		3.20	3.12	-2.35	-2.17
	19		1.24U	.15	-1.22	-.22
	20		4.30	3.67	1.31	-4.09
	21		1.86	1.49	.28	-1.84
9	0		6.87	6.36	-6.87	0.00
	1		11.69	11.26	1.81	-11.55
	2		10.03	10.05	-6.29	-7.81
	3		17.58	16.38	-10.66	-13.98
	4		4.38	4.82	.20	4.37
	5		6.96	6.32	6.86	1.18
	6		7.82	8.13	7.64	1.68
	7		2.10	1.78	1.80	1.07
	8		9.15	10.26	-7.98	-4.47
	9		3.45	3.60	3.45	.05
	10		13.36	13.61	7.61	-10.98
	11		6.56	6.36	-3.13	-5.77
	12		6.41	5.46	-5.31	3.59
	13		6.44	6.52	5.70	-3.00
	14		5.43	5.71	4.33	-3.27
	15		2.66	2.39	1.68	-2.05
	16		1.39	1.43	.98	-.98
	17		1.63	1.70	1.23	1.06
	18		1.22U	.73	-.79	-.92
	19		2.02	2.01	-1.94	-.54
	20		2.77	2.74	.65	2.69
10	0		14.24	15.44	14.24	0.00
	1		5.71	5.63	3.90	4.16
	2		8.88	8.97	-1.64	8.73
	3		11.09	12.07	-10.89	-2.11
	4		12.03	11.91	11.37	3.93
	5		12.30	13.00	12.14	2.00
	6		11.63	10.46	11.17	3.26
	7		2.37	2.51	2.19	.90
	8		7.65	7.51	7.51	1.43
	9		4.74	4.99	3.29	3.41
	10		5.37	6.02	4.44	3.01
	11		4.17	4.60	-3.23	2.64
	12		1.56U	.97	-.65	1.42
	13		1.62	1.84	0.00	-1.62
	14		4.52	4.39	-1.27	-4.33
	15		3.06	2.80	-3.06	.07
	16		1.29U	.85	1.06	.74
	17		1.15	1.26	.98	.59
	18		1.04U	.42	.99	.31
	19		1.45	1.56	1.44	-.18
11	0		3.81	3.68	-3.81	0.00
	1		7.35	6.78	-4.01	-6.16
	2		9.87	10.29	-1.44	9.76
	3		8.56	8.57	3.62	7.75
11	4	2	5.33	5.64	-5.23	.99
	5		2.44	2.93	-.67	2.35
	6		4.59	4.84	-1.83	-4.20
	7		4.61	4.66	-3.98	2.32
	8		2.57	2.40	1.63	-1.98
	9		4.36	3.95	4.31	-.63
	10		1.74	1.80	.27	-1.72
	11		1.51U	.71	.43	1.45
	12		1.46U	.74	.22	-1.44
	13		2.92	3.04	.72	-2.83
	14		2.18	2.38	2.16	-.34
	15		1.22U	1.07	1.01	-.69
	16		1.11U	.82	.15	1.10
	17		1.63	1.99	-.68	1.49
	18		2.10	2.33	.41	2.06
12	0		3.30	3.20	3.30	0.00
	1		2.81	2.53	-2.70	-.34
	2		1.60U	.64	.85	1.36
	3		3.80	3.82	3.69	-.92
	4		11.67	11.57	11.34	2.74
	5		4.55	4.81	-4.44	.96
	6		5.08	5.06	3.23	3.92
	7		1.79	1.33	1.43	-1.08
	8		4.01	4.18	3.99	.40
	9		1.47U	1.49	-.56	1.36
	10		2.67	2.52	2.32	1.33
	11		3.24	3.51	3.06	1.06
	12		1.62	1.50	-1.52	.55
	13		1.75	2.04	1.21	1.27
	14		2.58	2.63	-.59	2.51
	15		1.72	2.02	-1.02	-1.38
	16		1.79	1.83	1.71	-.54
13	0		1.48	1.89	-1.48	0.00
	1		7.20	7.53	2.60	6.71
	2		5.09	5.03	-4.67	2.04
	3		4.53	4.51	-3.28	3.12
	4		3.85	4.23	-.67	3.79
	5		2.38	2.48	.71	2.27
	6		1.66	1.79	-1.62	-.32
	7		3.63	3.91	-2.04	2.99
	8		1.91	2.37	1.44	-1.26
	9		1.31U	1.12	-1.15	-.62
	10		3.75	3.69	.34	-3.73
	11		1.17U	1.07	-1.17	-.09
	12		4.80	3.72	4.58	-1.46
	13		5.13	4.63	2.75	4.33
	14		3.05	3.00	-3.04	.14
14	0		3.99	4.27	-3.99	0.00
	1		1.35U	1.19	.25	-1.32
	2		2.46	2.51	.04	2.46
	3		5.01	4.57	4.75	-1.58
	4		1.30U	.89	1.04	-.78
	5		1.27U	.32	-.02	1.27
	6		3.92	3.90	3.26	2.17
	7		1.16	1.50	-.63	-.98
	8		2.13	2.19	1.11	1.82
	9		3.59	3.28	2.90	2.10
	10		3.60	3.09	-2.36	2.72
	11		2.72	2.90	-2.27	-1.50
15	0		1.08	1.36	-1.08	0.00
	1		5.96	5.58	2.65	5.33
	2		1.09U	1.12	-.86	-.67
	3		1.61	1.89	-1.32	.92
	4		1.87	1.94	-1.12	-1.50
	5		1.10	.97	.31	1.05
	6		3.45	2.51	-.86	3.34
	7		3.42	3.53	-3.34	.72
	8		2.74	2.92	.72	-2.64
0	1	3	1.54	.66	0.00	-1.54
	2		42.00	39.78	-42.00	0.00
	3		1.89	1.18	0.00	1.89
	4		14.87	15.94	14.87	0.00
	5		18.16	18.63	0.00	-18.16
	6		11.74	11.86	-11.74	0.00
	7		19.69	19.36	0.00	-19.69
	8		12.09	11.42	12.09	0.00
	9		2.37	1.70	0.00	2.37
	10		2.68	2.14	-2.68	0.00
	11		1.50	2.10	0.00	1.50
	12		5.15	4.97	-5.15	0.00
	13		2.79	3.35	0.00	-2.79
	14		1.54U	1.60	1.54	0.00
	15		5.19	4.61	0.00	5.19
	16		17.23	18.14	-17.23	0.00
	17		2.31	3.12	0.00	-2.31
	18		4.07	4.15	4.07	0.00
	19		8.19	8.20	0.00	-8.19
	20		1.46U	.97	-1.46	0.00
	21		5.65	5.39	0.00	-5.65
	22		1.22U	1.43	-1.22	0.00
	23		6.50	5.97	0.00	-6.50
	24		1.03	.89	-1.03	0.00
1	0		35.15	33.42	0.00	-35.15
	1		27.37	26.97	-23.54	13.95
	2		6.27	7.49	3.63	-5.11
	3		4.10	3.82	.06	-4.10
	4		1.83	1.93	-1.80	-.32
	5		16.30	16.01	6.33	15.02
	6		17.39	17.76	7.24	15.81
	7		16.32	15.63	3.66	-15.90
	8		7.85	8.25	-7.85	0.00
	9		4.27	3.32	1.92	3.81
	10		9.83	9.22	5.23	8.32
	11		14.27	15.02	-12.35	-7.14
	12		8.55	8.01	5.87	-6.21
	13		2.22	2.05	1.11	-1.92
	14		6.89	6.81	-1.33	-6.76
	15		4.88	5.63	-2.05	4.43
	16		4.34	3.85	4.32	.41
	17		5.40	5.93	3.98	-3.64
	18		1.70	1.81	1.66	.36
	19		1.54U	.40	1.22	-.93
	20		2.53	2.48	1.63	1.93
	21		1.50	.97	1.18	-.93
	22		1.21U	.67	-1.12	.44
	23		1.41	1.27	-1.15	-.81
2	0		1.89	1.65	0.00	-1.89
	1		20.07	19.73	-17.13	-10.45
	2		8.41	7.96	-7.99	-2.63
	3		25.70	28.47	21.83	13.56
	4		28.91	31.51	-19.93	-20.94
	5		15.71	15.88	-13.58	7.89
	6		11.17	11.85	-11.06	-1.57
	7		15.78	15.27	11.26	11.05
	8		12.00	12.00	3.36	-11.52
	9		23.50	24.23	-2.08	-23.41
	10		13.79	14.44	3.22	13.41
	11		4.82	4.85	-2.19	-4.29
	12		3.68	3.57	3.57	-.89
	13		2.50	2.85	2.09	1.38
	14		5.11	4.72	-5.11	.09
	15		8.31	8.46	-8.25	-1.00
	16		6.48	6.33	3.96	-5.13
	17		6.92	6.88	6.68	-1.80
	18		6.03	6.38	-6.02	-.33

Table 3 (*cont.*)

H	K	L	FO	FC	AO	BO
2	19	3	1.50	1.90	-1.03	-1.08
	20		2.69	2.67	-2.38	-1.26
	21		1.83	1.90	-1.28	-1.31
	22		1.39	1.22	-1.33	.40
3	0		16.07	15.49	0.00	16.07
	1		23.02	21.95	21.21	8.94
	2		16.99	15.99	4.55	-16.37
	3		23.67	22.43	-8.20	22.21
	4		16.07	16.57	15.31	-4.87
	5		15.30	12.48	15.29	.55
	6		2.61	2.40	-1.64	2.03
	7		12.59	12.99	-11.46	-5.21
	8		7.58	7.29	4.66	5.98
	9		7.30	6.99	-4.22	-5.95
	10		13.68	12.74	-10.39	-8.89
	11		6.47	6.55	4.20	-4.85
	12		6.51	6.30	2.20	-6.13
	13		7.71	7.75	-3.60	-6.82
	14		11.66	11.85	10.73	4.55
	15		4.66	4.97	4.66	.05
	16		8.54	8.53	8.23	-2.28
	17		4.04	3.80	2.86	-2.85
	18		1.59	1.43	1.57	-.25
	19		2.92	2.68	2.92	-.09
	20		2.95	3.04	2.41	1.70
	21		2.84	2.64	1.69	-2.27
	22		3.42	3.45	2.63	2.17
	23		2.28	2.04	-2.13	.82
	0		.95U	2.30	0.00	-.95
	1		6.83	6.71	-4.04	5.51
	2		6.20	7.07	3.07	5.38
	3		15.77	14.53	-10.45	11.81
	4		17.10	14.99	-11.72	-12.45
	5		19.22	19.50	9.56	-16.67
	6		10.44	10.40	1.87	-10.27
	7		14.71	15.80	13.82	-5.02
	8		6.13	5.84	-5.64	2.39
	9		8.14	7.65	1.14	8.06
	10		10.56	10.06	10.56	-.16
	11		7.34	6.79	-.06	7.34
	12		2.62	2.60	-1.70	1.99
	13		6.06	5.70	-5.88	-1.46
	14		3.44	3.89	2.04	2.77
	15		4.57	4.61	3.43	3.01
	16		1.68	2.17	-1.53	.69
	17		4.19	4.19	-2.60	3.28
	18		4.22	4.42	-2.32	-3.52
	19		2.37	2.18	-1.00	2.14
	20		1.52	1.20	-.69	1.35
	21		2.15	2.32	.64	-2.05
	22		1.77	1.79	1.20	-1.30
	23		1.28	1.04	1.28	.01
5	0		21.12	20.37	0.00	-21.12
	1		8.64	6.85	7.16	-4.84
	2		5.90	5.41	5.89	-.34
	3		16.13	15.81	15.93	-2.51
	4		6.28	4.61	1.99	-5.95
	5		17.45	15.90	-13.75	10.73
	6		12.57	13.94	-12.35	2.31
	7		13.77	13.90	13.08	-4.29
	8		5.99	6.45	-2.99	-5.19
	9		14.33	14.52	10.94	-9.25
	10		12.47	12.57	1.58	12.37
	11		8.93	9.37	-3.25	-8.32
	12		12.46	12.82	12.23	-2.39
	13		8.93	8.76	4.20	7.88
	14		2.69	2.36	2.65	-.50
	15		7.49	7.59	-3.70	-6.51
	16		7.50	7.68	2.86	-6.93
	17		1.74	1.80	1.53	.82
	18		3.09	3.70	2.44	1.90
	19		1.35U	1.23	1.33	.23
	20		1.24U	.82	.82	-.93
	21		1.10U	.83	-1.06	-.30
	22		1.72	2.04	-1.52	.80
	23		2.78	2.78	2.19	-1.71
6	0		7.03	7.17	0.00	-7.03
	1		12.76	13.37	-6.80	-10.80
	2		10.51	10.31	3.33	9.96
	3		17.75	18.65	3.57	-17.38
	4		4.02	3.53	1.77	3.60
	5		13.30	12.77	9.91	8.87
	6		8.82	8.97	5.52	6.87
	7		8.48	8.13	8.46	.57
	8		10.02	9.79	-4.95	-8.71
	9		12.98	12.99	10.45	7.70
	10		8.88	9.10	-5.51	6.97
	11		4.75	4.67	-4.45	-1.66
	12		12.32	13.27	8.29	9.11
	13		8.09	8.01	4.61	6.64
	14		3.65	3.71	-.52	3.62
	15		7.52	7.17	-6.44	3.88
	16		1.51U	1.52	1.51	-.02
	17		1.95	2.34	-1.48	1.26
	18		1.38U	.69	-1.38	-.08
	19		3.12	3.13	.65	3.05
	20		3.92	3.58	2.78	-2.77
	21		2.51	2.42	.43	2.47
7	0		2.89	1.54	0.00	2.89
	1		7.35	6.96	6.56	-3.31
	2		4.36	3.84	2.04	3.85
	3		14.67	14.75	2.86	14.39
	4		1.91	1.93	1.30	1.39
	5		7.08	6.61	6.97	-1.27
	6		9.79	10.10	2.66	-9.42
	7		7.04	6.59	-7.02	-.51
	8		8.90	8.31	.79	8.87
	9		10.61	11.66	-9.31	5.08
	10		6.91	7.14	-3.89	-5.71
	11		9.75	9.63	5.24	-8.22
	12		7.88	7.82	-4.23	6.65
	13		7.94	7.91	.91	-7.89
	14		5.72	5.98	-1.73	-5.45
	15		1.51U	.59	-.87	1.23
	16		4.21	4.35	3.43	2.44
	17		1.76	1.95	-.49	1.69
	18		1.29U	.80	-.88	.95
	19		1.18U	1.33	-.70	.94
	20		1.03U	.56	.34	.97
	21		4.19	3.63	4.17	.35
8	0		1.40U	.95	0.00	1.40
	1		6.46	6.39	3.32	5.53
	2		7.93	7.58	2.46	7.53
	3		8.62	8.23	5.75	-6.42
	4		3.39	3.65	.34	-3.38
	5		6.40	6.30	3.22	-5.53
	6		10.21	10.88	-1.58	10.08
	7		6.40	6.73	-1.29	6.26
	8		11.00	11.44	2.02	10.81
	9		2.67	3.18	2.43	-1.09
	10		6.74	6.72	-.21	6.74
	11		9.30	9.44	7.56	5.41
	12		4.62	4.73	2.50	-3.88
	13		5.99	6.67	-5.90	-1.05
	14		3.55	3.67	-.44	3.52
8	15	3	1.68	1.72	.58	1.57
	16		2.89	2.88	2.68	-1.10
	17		3.13	3.29	-1.17	2.90
	18		1.37	1.18	.95	.97
	19		2.59	2.43	2.58	.21
	20		3.29	3.06	-1.42	-2.97
9	0		2.57	2.55	0.00	2.57
	1		11.47	11.30	1.77	11.33
	2		9.22	10.50	-5.30	7.55
	3		6.99	7.18	-3.45	-6.08
	4		8.57	9.11	-6.73	-5.29
	5		9.61	10.23	-8.51	4.47
	6		7.77	7.17	2.73	7.28
	7		4.44	4.41	-3.19	3.09
	8		1.80	1.91	-1.53	-.95
	9		7.10	7.01	-2.67	-6.58
	10		1.97	1.99	-1.96	.25
	11		3.74	3.44	-3.73	-.29
	12		1.51U	1.46	.25	1.49
	13		5.55	5.75	-4.85	-2.70
	14		2.74	2.60	-.46	2.70
	15		1.56	1.11	1.52	-.37
	16		1.46	1.76	1.14	.91
	17		4.14	3.78	.28	4.13
10	0		1.79	1.59	0.00	1.79
	1		2.25	2.39	2.03	-.96
	2		3.61	2.67	3.41	1.19
	3		5.93	6.61	-5.77	1.35
	4		6.21	6.96	1.64	5.99
	5		2.56	2.13	2.47	.64
	6		1.56U	.08	1.20	-.99
	7		8.99	9.28	5.44	-7.15
	8		3.99	3.99	1.69	-3.62
	9		4.26	4.22	2.74	3.27
	10		2.72	2.56	2.72	.13
	11		1.71	2.01	1.47	-.87
	12		4.30	4.78	-4.10	1.27
	13		3.15	3.43	-1.14	2.94
	14		1.69	1.75	1.32	1.04
	15		2.11	2.34	-2.03	-.57
	16		1.11U	.22	0.00	1.11
	17		2.57	2.38	-2.37	-.99
	18		1.12	1.57	.56	-.96
11	0		8.17	8.26	0.00	8.17
	1		4.36	4.69	-4.34	-.46
	2		1.55U	1.89	-.30	-1.52
	3		5.22	5.03	-3.95	-3.41
	4		7.99	8.60	-.54	7.97
	5		3.37	3.97	-2.20	2.55
	6		4.24	3.80	-4.22	-.40
	7		6.77	6.54	-6.76	-.41
	8		1.49U	1.52	1.49	0.00
	9		3.52	3.94	-3.17	-1.52
	10		1.41U	1.90	1.40	.22
	11		4.28	3.45	-4.20	.83
	12		1.69	1.63	1.43	-.90
	13		1.23U	.37	.98	.74
	14		2.92	2.82	-1.44	2.54
	15		1.03U	.57	1.03	-.02
	16		3.45	2.71	1.60	3.06
	17		2.47	2.36	-2.44	.38
12	0		5.37	5.68	0.00	-5.37
	1		4.10	4.52	-1.75	3.71
	2		2.58	2.73	-1.14	-2.31
	3		4.48	4.22	.98	-4.37
	4		5.33	5.49	1.66	-5.07
	5		1.68	1.73	-1.19	1.19
	6		4.98	5.53	4.66	1.75
	7		2.87	2.75	.53	-2.82
	8		1.37U	1.07	-.94	.99
	9		1.53	1.62	-.86	1.26
	10		2.38	2.04	-1.80	-1.55
	11		2.74	2.65	-2.61	-.82
	12		1.12U	.75	.97	-.56
	13		5.12	4.33	-2.78	4.30
	14		3.42	3.08	-1.81	-2.90
	15		2.15	1.94	-.46	-2.10
13	0		1.37U	.31	0.00	1.37
	1		2.75	2.88	-2.15	-1.71
	2		1.58	1.73	-.38	1.53
	3		6.12	6.12	-3.41	5.08
	4		4.99	4.81	2.63	4.24
	5		1.51	2.14	.24	-1.49
	6		1.48	1.74	-1.46	-.20
	7		1.23U	.45	1.12	.52
	8		1.50	1.87	.35	-1.46
	9		2.74	2.68	-2.60	.84
	10		1.41	1.14	-1.33	.47
	11		2.35	1.89	.63	-2.26
	12		1.21	1.35	1.17	.28
	13		2.87	3.10	-2.30	-1.71
14	0		4.74	4.39	0.00	-4.74
	1		4.19	3.56	-3.53	2.25
	2		2.02	2.23	.66	-1.91
	3		1.33	1.37	-.41	-1.26
	4		2.93	3.04	2.38	-1.70
	5		2.30	2.46	1.78	1.45
	6		3.60	3.31	-.39	-3.58
	7		4.38	4.12	-4.18	1.29
	8		2.21	2.70	1.34	-1.76
15	0		6.20	5.33	0.00	6.20
	1		2.14	2.72	-.63	2.04
	2		.86U	.09	.62	.60
	3		4.43	4.35	4.08	-1.72
	4		2.84	2.41	-1.75	-2.23
	5		2.66	2.57	-2.25	1.42
0	0	4	15.97	16.92	15.97	0.00
	1		36.44	35.13	0.00	36.44
	2		4.50	4.19	4.50	0.00
	3		17.65	18.00	0.00	17.65
	4		2.85	1.24	2.85	0.00
	5		4.34	3.25	0.00	4.34
	6		7.68	8.94	-7.68	0.00
	7		5.25	3.94	0.00	-5.25
	8		6.60	7.98	6.60	0.00
	9		19.71	19.65	0.00	-19.71
	10		7.68	7.73	-7.68	0.00
	11		1.89	1.31	0.00	-1.89
	12		12.94	14.08	12.94	0.00
	13		1.46U	0.00	0.00	1.46
	14		11.80	11.18	11.80	0.00
	15		9.30	9.61	0.00	9.30
	16		1.51U	.55	-1.51	0.00
	17		6.92	7.27	0.00	6.92
	18		2.42	2.41	2.42	0.00
	19		1.91	2.09	0.00	-1.91
	20		1.10	.83	1.10	0.00
	21		1.93	1.60	0.00	1.93
	22		3.10	2.87	3.10	0.00
	23		4.53	5.54	0.00	-4.53
1	0		19.67	18.01	-19.67	0.00
	1		3.65	3.94	-3.59	.62
	2		8.82	8.17	6.32	-6.14
	3		20.13	19.35	18.51	7.91
	4		8.58	9.05	-.45	8.57
1	5	4	22.44	21.19	22.02	-4.34
	6		8.85	8.69	1.18	8.77
	7		12.34	12.73	10.86	5.84
	8		11.91	11.40	-4.51	11.03
	9		17.23	17.77	15.95	6.51
	10		5.75	5.62	-4.49	3.58
	11		11.43	11.52	-10.20	-5.14
	12		7.80	7.64	6.22	4.69
	13		4.87	4.73	3.81	3.03
	14		5.28	5.23	-4.98	1.74
	15		1.73	1.67	-.57	-1.63
	16		4.54	4.76	3.92	-2.29
	17		9.27	9.88	8.10	4.49
	18		3.35	3.43	1.70	2.89
	19		6.85	6.51	6.84	.14
	20		1.74	1.74	.35	1.71
	21		3.60	3.31	3.58	-.36
	22		1.30	.91	-.15	1.29
2	0		4.90	5.01	-4.90	0.00
	1		19.49	20.92	-7.28	18.07
	2		7.20	6.54	-4.39	5.70
	3		19.18	18.11	-10.70	15.92
	4		5.76	4.78	-4.86	-3.10
	5		8.71	8.64	-6.78	5.46
	6		2.51	2.30	.70	2.41
	7		10.62	10.28	8.12	-6.85
	8		2.47	2.26	.25	-2.46
	9		12.60	13.20	-12.58	.70
	10		20.37	20.05	16.22	12.31
	11		4.45	4.23	2.30	-3.81
	12		9.75	9.68	-.38	9.71
	13		5.31	5.05	1.15	5.18
	14		8.46	8.19	1.12	8.38
	15		7.93	9.41	-6.71	4.23
	16		3.60	3.86	1.87	3.07
	17		4.08	4.25	-.47	4.05
	18		3.36	3.61	.13	-3.36
	19		1.93	1.61	-1.54	-1.17
	20		2.32	2.14	.17	2.31
	21		4.14	3.65	.09	-4.14
	22		1.24	1.36	-.18	-1.22
3	0		9.74	11.26	-9.74	0.00
	1		21.63	18.91	20.93	-5.42
	2		6.94	6.87	1.97	6.65
	3		17.65	18.53	13.41	11.47
	4		15.72	15.00	-14.96	-4.83
	5		23.88	23.36	22.96	6.55
	6		7.94	7.59	-7.11	-3.53
	7		10.31	9.63	8.55	5.75
	8		7.85	7.48	4.30	6.56
	9		7.53	8.10	-6.22	-4.24
	10		18.11	17.35	-13.65	11.90
	11		8.55	9.29	-1.45	8.43
	12		1.97	1.84	1.88	-.60
	13		6.28	5.83	-6.26	-.44
	14		2.60	2.72	1.59	-2.05
	15		4.34	4.32	2.04	3.83
	16		7.96	8.58	7.33	3.10
	17		3.77	4.01	1.40	3.50
	18		3.06	3.50	.81	-2.95
	19		6.41	6.05	5.77	2.81
	20		3.37	2.94	-2.94	-1.64
	21		3.05	2.67	3.01	.52
4	0		15.53	14.48	-15.53	0.00
	1		17.81	17.05	.05	17.81
	2		7.64	4.45	-7.09	-2.84
	3		7.09	6.77	-1.19	6.98
	4		6.40	6.64	-3.05	5.63
	5		9.04	8.75	-2.97	8.54
	6		7.09	7.08	-6.39	-3.07
	7		19.08	18.28	-15.15	-11.60
	8		8.39	8.27	-.12	8.39
	9		14.11	14.85	14.11	.10
	10		12.29	12.08	-6.97	10.12
	11		10.19	10.01	-9.67	-3.18
	12		14.18	14.15	7.41	12.09
	13		10.94	10.86	-6.18	9.03
	14		8.54	8.95	-3.48	7.80
	15		4.01	4.22	-2.70	2.97
	16		2.93	2.92	2.51	1.52
	17		1.81	1.84	-1.76	-.43
	18		1.37	.62	-1.33	.32
	19		2.77	2.86	-.47	2.73
	20		1.48	1.24	1.09	-1.00
	21		.90U	.60	.31	-.84
	22		.64	.42	-.52	.37
5	0		2.44	2.34	2.44	0.00
	1		16.49	15.18	16.41	-1.56
	2		10.51	10.20	-10.29	2.12
	3		15.56	13.89	3.48	-15.16
	4		7.28	7.92	6.76	2.69
	5		7.11	6.84	3.97	5.90
	6		21.87	23.19	-18.96	10.91
	7		10.48	10.43	-6.78	8.00
	8		14.43	15.42	-13.64	-4.69
	9		9.73	9.36	-6.81	6.94
	10		12.86	13.31	-12.30	-3.77
	11		7.43	6.99	.65	-7.40
	12		2.90	3.09	1.44	-2.51
	13		4.66	5.15	-4.01	2.37
	14		5.58	6.28	5.36	1.56
	15		3.32	3.58	2.40	2.29
	16		6.50	5.90	3.01	-5.76
	17		1.32U	.33	.54	1.20
	18		3.89	3.70	3.89	.07
	19		1.12U	.94	-1.11	.17
	20		.98U	.25	-.97	.12
	21		4.61	3.82	-.33	4.60
6	0		7.06	6.84	-7.06	0.00
	1		11.25	11.80	5.67	9.72
	2		11.70	12.68	-5.26	-10.45
	3		7.44	7.34	-7.39	.85
	4		11.23	9.70	-11.23	-.07
	5		12.54	12.92	-6.30	-10.84
	6		5.20	5.09	2.27	-4.68
	7		9.93	10.45	9.17	-3.83
	8		13.69	14.64	-2.12	13.53
	9		13.61	13.79	-13.49	-1.78
	10		3.67	3.43	-2.96	2.18
	11		6.48	7.40	3.77	5.27
	12		9.87	10.36	-4.69	8.67
	13		4.41	4.46	-4.11	1.60
	14		5.12	5.49	2.07	4.68
	15		1.39U	1.23	1.30	.48
	16		1.33U	1.23	-.68	1.14
	17		2.51	2.96	-.25	2.49
	18		1.15U	1.15	-.97	-.62
	19		1.03U	.67	.12	-1.02
	20		2.61	2.82	-1.31	-2.26
	21		1.50	1.89	1.50	-.04
7	0		12.26	11.58	12.26	0.00
	1		10.92	10.24	-5.22	-9.60
	2		10.18	9.85	-10.17	.43
	3		5.32	5.68	1.32	5.15
	4		10.81	10.19	-9.19	5.69
7	5	4	6.98	6.83	.35	-6.97
	6		12.91	13.34	-12.35	-3.77
	7		8.47	8.95	-.85	-8.43
	8		11.02	11.15	-11.01	-.35
	9		7.16	7.70	-6.96	-1.71
	10		2.73	2.77	-1.35	-2.37
	11		7.53	7.37	-7.46	-.99
	12		2.35	2.53	-1.42	1.87
	13		2.23	2.12	1.13	1.92
	14		4.90	4.91	3.30	-3.62
	15		4.18	4.06	-3.02	-2.89
	16		1.44	1.70	1.21	.77
	17		5.12	4.28	-.92	5.04
	18		1.80	1.60	-.70	-1.65
	19		6.60	5.69	-4.10	5.18
	20		1.89	1.99	-1.82	.53
8	0		1.43	.94	1.43	0.00
	1		7.23	7.25	-2.64	-6.73
	2		10.16	10.20	-8.76	-5.14
	3		4.77	4.96	-4.74	-.52
	4		14.61	15.68	5.70	-13.45
	5		14.05	14.78	3.64	-13.57
	6		3.34	4.15	-.77	-3.25
	7		8.61	9.30	-7.46	4.30
	8		1.88	1.93	.62	1.77
	9		4.32	4.36	3.45	-2.60
	10		8.53	8.46	1.24	8.43
	11		1.44U	1.17	.68	1.31
	12		9.30	9.75	-.72	9.27
	13		1.84	2.49	1.83	.18
	14		2.71	2.28	-1.58	-2.19
	15		2.86	3.05	-2.00	-2.05
	16		1.15U	.94	-1.13	.18
	17		1.51	1.37	-1.50	-.15
	18		2.57	2.58	-1.39	-2.16
	19		1.92	2.41	1.73	-.83
9	0		6.62	7.33	6.62	0.00
	1		2.70	2.66	-1.62	-2.15
	2		6.43	5.92	4.40	4.68
	3		8.97	10.91	2.00	-8.74
	4		6.16	5.97	-5.99	-1.46
	5		8.59	9.51	-8.47	-1.45
	6		9.89	11.28	-9.83	1.00
	7		3.07	3.05	-1.53	-2.66
	8		4.78	5.08	-4.78	-.08
	9		3.70	3.71	-3.38	-1.51
	10		3.78	4.02	-3.41	-1.63
	11		2.12	2.41	.38	2.09
	12		2.37	2.53	1.79	-1.56
	13		3.83	3.76	-1.91	-3.32
	14		1.82	1.84	-1.67	.74
	15		3.90	3.21	-2.75	2.77
	16		3.05	2.64	2.44	1.84
	17		1.08	.40	-.81	.72
10	0		1.46U	.84	1.46	0.00
	1		9.79	10.49	-1.00	-9.74
	2		4.51	4.79	1.48	-4.25
	3		8.90	9.41	5.79	-6.76
	4		8.85	8.72	3.97	-7.91
	5		2.59	2.60	-1.78	1.88
	6		2.41	2.99	1.58	1.82
	7		3.73	3.19	.78	-3.64
	8		2.03	2.38	1.74	-1.03
	9		1.98	2.56	-.93	-1.75
	10		4.87	5.35	2.63	4.09
	11		3.92	4.20	-3.68	-1.36
	12		1.77	1.64	.17	-1.76
	13		4.34	3.67	-2.68	-3.41
	14		3.16	2.93	-2.82	-1.42
	15		1.53	1.56	1.32	-.78
	16		1.18	1.28	-1.15	.26
11	0		8.21	8.06	8.21	0.00
	1		4.14	4.73	-4.10	-.54
	2		3.90	4.02	3.90	.05
	3		4.19	4.80	-4.18	-.16
	4		2.36	2.31	1.85	1.46
	5		3.96	4.23	-2.18	-3.31
	6		4.27	4.34	-4.08	-1.25
	7		2.48	2.43	-1.84	1.66
	8		3.13	3.35	-2.91	1.17
	9		1.28	.92	.14	-1.27
	10		2.09	2.15	-1.98	-.67
	11		3.38	3.57	1.99	-2.74
	12		2.56	2.23	2.55	.21
	13		3.27	2.81	-2.29	2.32
	14		2.27	2.30	1.62	-1.58
	15		1.63	1.89	1.57	.44
12	0		3.80	3.52	3.80	0.00
	1		5.66	6.32	2.05	-5.28
	2		5.43	5.17	4.40	-3.17
	3		5.53	5.99	-.31	-5.52
	4		4.46	4.49	-1.86	-4.05
	5		3.82	3.60	-2.52	2.87
	6		5.61	5.45	4.08	-3.85
	7		1.21	1.33	-.96	-.73
	8		1.97	2.26	1.95	.26
	9		1.11	1.25	-1.10	.14
	10		1.04	1.07	-.52	-.89
	11		2.28	1.95	-.07	-2.28
	12		2.53	2.51	-1.83	1.75
	13		3.68	3.66	-.84	-3.58
13	0		5.08	4.28	5.08	0.00
	1		2.25	2.13	-2.01	1.02
	2		3.74	3.28	2.13	-3.07
	3		4.62	4.21	-4.05	2.22
	4		3.49	3.50	3.49	-.06
	5		4.54	4.82	-4.28	1.50
	6		4.58	4.22	3.47	2.99
	7		3.18	2.81	.89	-3.05
	8		3.56	3.14	-.47	-3.52
	9		2.83	2.77	2.67	-.93
	10		2.79	2.71	2.18	-1.74
14	0		.89U	.67	.89	0.00
	1		5.76	5.25	-4.70	-3.32
	2		2.00	1.86	-.87	-1.79
	3		.85U	.40	.45	.72
	4		3.60	3.99	3.51	.82
	5		2.72	2.59	2.63	-.68
	6		2.97	3.15	-1.56	-2.53
0	1	5	12.09	13.01	0.00	-12.09
	2		4.57	4.80	-4.57	0.00
	3		1.91	1.69	0.00	-1.91
	4		5.30	6.14	-5.30	0.00
	5		6.22	6.93	0.00	-6.22
	6		1.37	1.42	1.37	0.00
	7		10.85	10.53	0.00	-10.85
	8		12.09	12.67	12.09	0.00
	9		4.82	5.09	0.00	4.82
	10		1.27U	.74	-1.27	0.00
	11		11.40	10.96	0.00	-11.40
	12		11.49	11.52	11.49	0.00
	13		2.53	2.69	0.00	-2.53
	14		1.36U	1.26	1.36	0.00
	15		2.57	3.12	0.00	-2.57
	16		1.36	1.60	1.36	0.00

Table 3 (cont.)

H	K	L	FO	FC	AO	BO		H	K	L	FO	FC	AO	BO		H	K	L	FO	FC	AO	BO		H	K	L	FO	FC	AO	BO		H	K	L	FO	FC	AO	BO
0	17	5	1.23U	.81	0.00	1.23		5	18	5	3.12	2.48	-1.34	-2.82		12	6	5	1.87	1.65	-1.49	1.12		0	9	7	1.15	.68	0.00	-1.15

free from systematic errors and that the weighting is correct. m and n are the number of observations and the number of parameters respectively.

Table 4. *Coordinates of the non-hydrogen atoms* $\times 10^5$

(e.s.d.'s in parenthesis)

	x/a	y/b	z/c
C(1)	−3569 (25)	47274 (15)	−13437 (50)
C(2)	−9066 (24)	51035 (14)	2017 (49)
C(3)	−5391 (23)	49002 (15)	19701 (45)
C(4)	−2525 (22)	43988 (13)	16335 (43)
C(5)	8316 (23)	40729 (14)	29425 (44)
C(6)	16739 (21)	35819 (13)	24839 (44)
C(7)	13405 (22)	28652 (13)	30472 (53)
C(8)	12000 (35)	28276 (18)	53165 (67)
C(9)	22197 (55)	30152 (28)	63262 (75)
C(10)	30742 (30)	31530 (17)	47861 (72)
C(11)	27519 (23)	37466 (14)	34751 (56)
C(12)	32428 (28)	25374 (17)	34587 (104)
C(13)	22178 (22)	24042 (14)	24646 (55)
C(14)	19404 (27)	19436 (14)	12026 (53)
C(15)	8064 (33)	19995 (19)	7028 (69)
C(16)	4112 (25)	26061 (21)	18324 (79)
C(17)	−17185 (37)	56122 (21)	−3198 (67)
C(18)	35524 (29)	38749 (29)	17944 (95)
C(19)	27425 (36)	43803 (19)	47258 (90)
C(20)	26294 (41)	14177 (18)	3127 (79)
O(1)	3512 (16)	43120 (10)	−4352 (30)
O(2)	−4511 (24)	47362 (14)	−31248 (36)

Discussion

Method of solution

The success of the present analysis depended heavily on the power of the tangent formula. It is readily seen from Fig. 4 that the agreement between the tangent refined and true phases is excellent. The frequency distributions for all four values of E_{min} are closely similar.

The number of reflexions falls almost exponentially with increasing φ error, and in all cases more than 40% of the phases are accurate to within 5°. Such errors are very much less than would be expected from Cochran's (1955) assessment of phase errors in applying direct methods to non-centrosymmetric structures, which is based on the use of the Σ_2 formula. The Σ_2 phases were actually computed after each series of tangent refinement cycles. These are given in histogram form in Fig. 5. It should be noted that these are new phases only and should be compared with differences between neighbouring histograms in Fig. 4. Nevertheless the difference between the two is striking. The even distribution of errors in Fig. 5 indicates that the Σ_2 phases are virtually random, which is in agreement with Cochran's (1955) calculations. Thus the Σ_2 formula is extremely restrictive, and is inaccurate even for moderately large E_H. Because of the rapid propagation of error which occurs when a phase set is extended this is a serious disadvantage. For this reason extensive application of the symbolic addition method
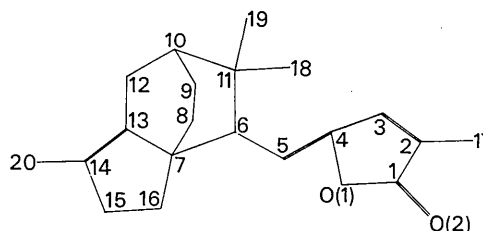
Fig. 3. The molecular structure of iso-eremolactone, showing the numbering of the non-hydrogen atoms. The hydrogens are numbered using a three-digit code in which the first two digits identify the carbon atom to which the hydrogen is bonded.

Table 5. *Anisotropic temperature factor coefficients* $\times 10^6$

(e.s.d.'s in parenthesis)

$$T = \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\right]$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	6135 (178)	2631 (71)	19271 (657)	−71 (197)	−136 (680)	−339 (371)
C(2)	6124 (170)	2535 (68)	19234 (681)	814 (192)	418 (658)	−160 (376)
C(3)	5587 (157)	2682 (69)	17494 (635)	1586 (185)	1002 (619)	−1368 (372)
C(4)	5687 (155)	2228 (61)	16196 (573)	1277 (170)	4019 (613)	−462 (330)
C(5)	5579 (161)	2710 (72)	17064 (609)	1779 (186)	2506 (622)	−204 (373)
C(6)	4693 (140)	2266 (62)	18790 (614)	1152 (159)	1835 (587)	−521 (345)
C(7)	4624 (141)	2266 (63)	26910 (804)	−60 (173)	−276 (668)	−311 (394)
C(8)	10925 (332)	3318 (97)	29164 (986)	−333 (322)	5579 (1146)	3293 (577)
C(9)	17276 (555)	5506 (161)	28432 (1095)	−5352 (560)	−12412 (1581)	6845 (800)
C(10)	8486 (262)	3011 (87)	37294 (1199)	71 (259)	−20958 (1006)	−712 (574)
C(11)	5378 (164)	2340 (65)	28540 (852)	−159 (185)	−908 (732)	−2346 (428)
C(12)	6569 (214)	2530 (79)	81647 (2262)	2049 (236)	−23008 (1328)	−6645 (818)
C(13)	4580 (146)	2198 (63)	31348 (900)	106 (164)	−3113 (684)	−352 (419)
C(14)	7358 (218)	2217 (64)	23911 (777)	228 (203)	794 (738)	982 (390)
C(15)	8687 (265)	3097 (89)	36741 (1173)	−1656 (269)	−11984 (1070)	−1795 (608)
C(16)	4652 (167)	4034 (110)	44533 (1351)	−549 (233)	5209 (900)	−3628 (729)
C(17)	10220 (296)	4287 (122)	27789 (1005)	5515 (338)	−5372 (1076)	891 (645)
C(18)	5598 (217)	6470 (173)	47820 (1577)	−1137 (343)	7672 (1093)	4679 (1015)
C(19)	9518 (298)	3177 (99)	54183 (1781)	−1758 (302)	−9210 (1378)	−9936 (770)
C(20)	12691 (385)	2725 (86)	40955 (1357)	1665 (325)	7668 (1404)	−3385 (639)
O(1)	6301 (122)	2603 (49)	17460 (429)	1114 (138)	2523 (463)	−1278 (261)
O(2)	10818 (213)	4838 (91)	16915 (502)	2498 (254)	−886 (659)	−559 (377)

Table 6. *Hydrogen coordinates* × 10³
and temperature factor coefficients

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

	x/a	y/b	z/c	B
H(031)	−80	506	315	3·0 Å²
H(051)	54	415	419	3·1
H(061)	176	357	107	2·3
H(081)	74	310	582	3·3
H(082)	91	226	559	3·3
H(091)	245	270	721	7·1
H(092)	205	346	704	9·6
H(101)	362	326	547	4·2
H(121)	370	252	264	7·6
H(122)	352	221	481	8·7
H(151)	51	161	135	6·2
H(152)	79	206	−95	6·1
H(161)	14	286	79	8·6
H(162)	−22	253	262	3·2
H(171)	−214	544	−141	9·9
H(172)	−228	555	63	10·9
H(173)	−145	603	−85	11·7
H(181)	318	419	98	9·5
H(182)	430	394	268	8·0
H(183)	352	342	85	5·1
H(191)	237	422	598	4·3
H(192)	348	439	554	6·6
H(193)	246	481	466	8·8
H(201)	223	102	52	5·2
H(202)	335	148	118	6·3
H(203)	295	150	−103	6·4

using the Σ_2 formula is undesirable in using direct methods for non-centrosymmetric structures. The advantage of the tangent formula is that it is valid for all E_H values, and when applied iteratively it minimizes the errors in the known phases, and this in turn reduces the propagation of error in the next extension of the phase set. If the experience with the present structure is typical the tangent refinement can function correctly in spite of a few large errors in the initial phase set; so the direct approach seems preferable to the symbolic addition method as soon as trial phases for the very large E_H values have been determined.

An examination was also made of the effect of increasing the number of tangent refined phases in the E map with a view to ascertaining the optimum number of phases per non-hydrogen atom. Composite summaries made for the E maps used for the original solution, for 255 phases with $E_{min} = 1·4$ and for 330 phases with $E_{min} = 1·3$, are shown in Fig.2(a) to (c). It is evident that the quality of the E maps improves steadily with the increasing number of phases used. Thus in Fig.2(c) the two carbon atoms which were not located in the original E map are almost distinguishable. These two carbon atoms have temperature coefficients which are much higher than the average,
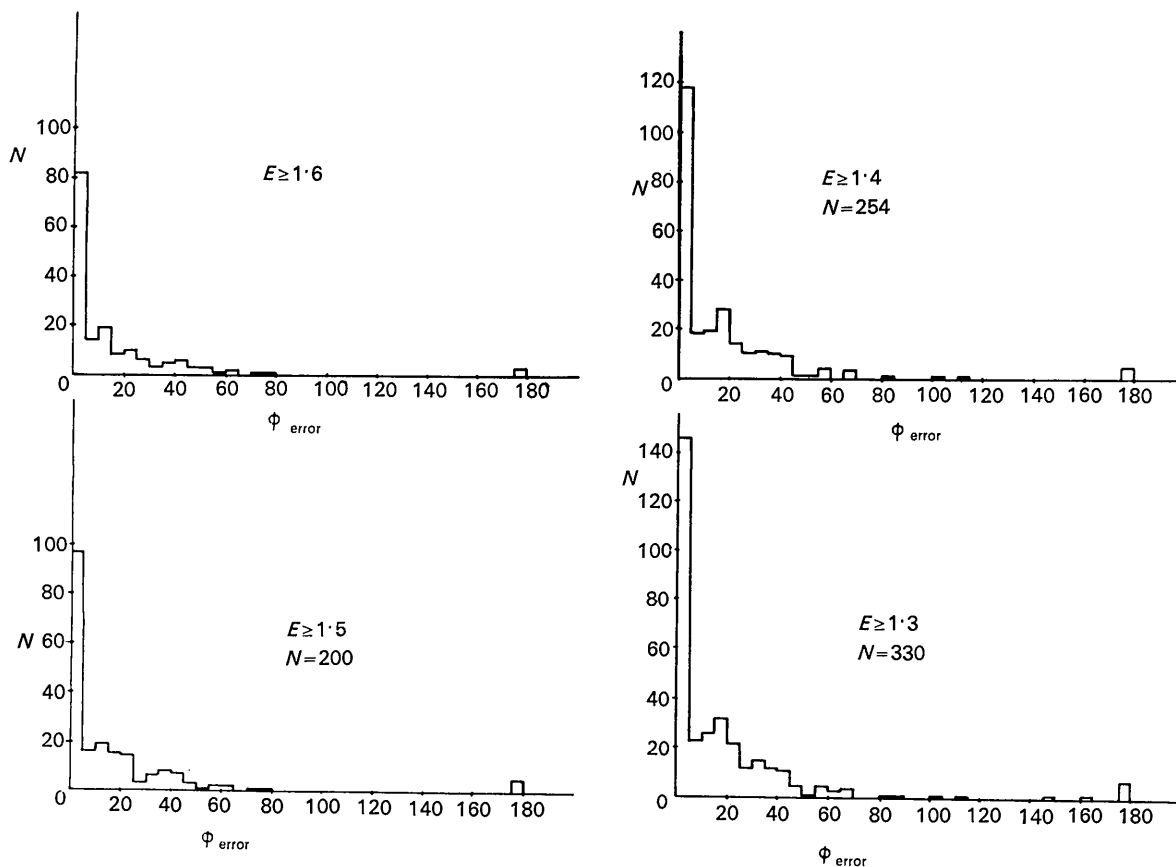
Fig.4. Error distribution of tangent refined phases.

which accounts for their low peak heights in the E maps. However, the computing time in applying the tangent refinement method rises rapidly with the number of phases, and atoms with higher than average B values are located more efficiently by difference Fourier methods. Thus the nine phases per non-hydrogen atom used for the original analysis appears to be adequate.

Description of the structure

The structure shown in Fig. 3 is similar, but not identical with the stereochemical model of Birch, Grimshaw & Turnbull (1963) and the differences have already been reported (Oh & Maslen, 1966b). The nucleus of iso-eremolactone consists of a novel cyclo-octane ring of the atisine type, to which is attached a five-membered ring containing a nuclear double bond. The conjugated γ-lactone group is linked to the nuclear skeleton at C(6) and the gem-dimethyl group occurs at the quaternary carbon C(11).

The bridging of the three six-membered rings in the boat configuration at two pivoting points, viz. C(7) and C(10), gives rise to a highly symmetrical system but, the axial symmetry is strained by the fusion of the five membered ring system at atoms C(7) and C(13). This strain is manifested in the distortion of various bond angles from the ideal tetrahedral configuration (Table 8). The principal source of strain arises from the nuclear double bond C(13) = C(14) which constrains atoms C(7), C(12), C(13), C(14), C(15) and C(20) to lie on a plane, for which the least-squares equation is

$$-0.235X - 0.608Y + 0.758Z + 2.366 = 0$$

where X, Y and Z are in Å. The planarity of the group is only approximate since the out of plane distortions for C(12) and C(15) are 0.02 Å, which exceeds 3σ.

The nine atoms in the γ-lactone group C(1), C(2), C(3), C(4), C(5), C(6), C(17), O(1) and O(2) are also expected to be coplanar because of the double bonds C(2) = C(3), C(4) = C(5) and C(1) = O(2). The least-squares equation for this plane is

$$0.695X + 0.717Y - 0.047Z - 6.571 = 0$$

and the only significant distortions from the plane are shown by the substituent atoms C(6) and C(17), amounting to 0.03 and 0.04 Å respectively.

Bond lengths and angles

The bond lengths and the bond angles involving non-hydrogen atoms are listed in Tables 7 and 8 respectively, together with their associated standard deviations. The mean standard deviation for the C–H bonds evaluated from the least-squares matrix e.s.d.'s is 0.06 Å, but from the differences in the lengths of bonds in similar environments it appears that this is underestimated. It is clear that the neglect of the effect of interaction between the parameters of different atoms has resulted in e.s.d.'s for the hydrogen coor-

dinates which are too low. This is supported by the fact that at the conclusion of the refinement the shifts in the hydrogen coordinates are nearly 1σ compared with about 0.3σ for the carbon atoms. It appears probable that the true standard deviations on the C–H bonds are at least doubled, i.e. have an average value of 0.12 Å.

Table 7. Bond lengths

(e.s.d.'s parenthesis)

C–C bonds
sp^3–sp^3

C(6)—C(7)	1·554 (4) Å
C(6)—C(11)	1·574 (4)
C(7)—C(8)	1·531 (6)
C(7)—C(16)	1·539 (5)
C(8)—C(9)	1·523 (8)
C(9)—C(10)	1·534 (8)
C(10)–C(11)	1·541 (5)
C(10)–C(12)	1·542 (6)
C(11)–C(18)	1·549 (6)
C(11)–C(19)	1·530 (6)
C(15)–C(16)	1·527 (6)
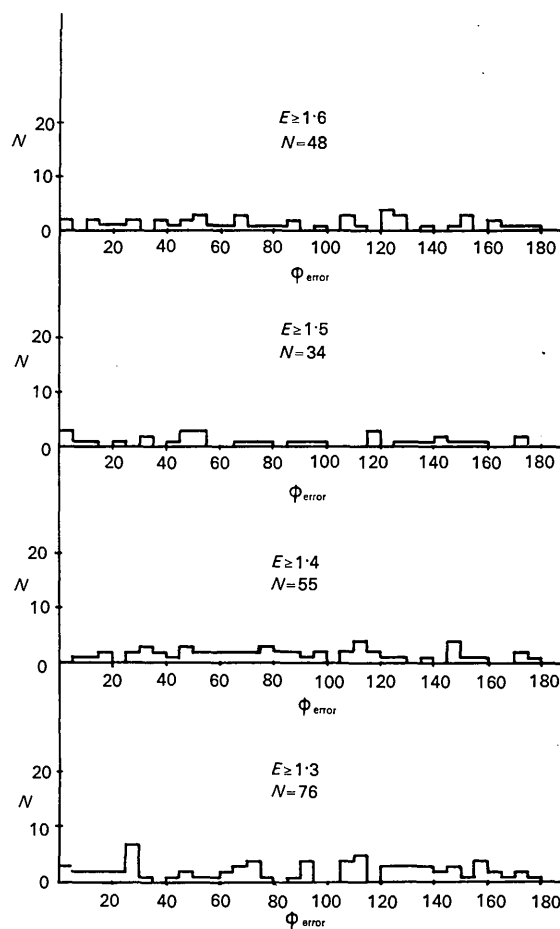
Fig. 5. Error distribution of new phases generated using the Σ_1 formula.

Table 7 (cont.)

sp²–sp³

C(2)—C(17)	1·506 (5)
C(5)—C(6)	1·502 (4)
C(13)–C(7)	1·514 (4)
C(13)–C(12)	1·502 (5)
C(14)–C(15)	1·503 (5)
C(14)–C(20)	1·506 (5)

sp²–sp²

C(1)–C(2)	1·466 (4)
C(3)–C(4)	1·454 (4)

C=C bonds

C(2)—C(3)	1·339 (4)
C(4)—C(5)	1·324 (4)
C(13)–C(14)	1·306 (5)

C–O bonds

C(1)–O(1)	1·379 (4)
C(4)–O(1)	1·400 (4)

C=O bonds

C(1)–O(2)	1·197 (4)

C–H bonds*

C(3)—H(031)	0·91 (4)
C(5)—H(051)	0·93 (4)
C(6)—H(061)	0·95 (4)
C(8)—H(081)	0·88 (4)
C(8)—H(082)	1·23 (4)
C(9)—H(091)	0·92 (5)
C(9)—H(092)	0·99 (7)
C(10)–H(101)	0·87 (5)
C(12)–H(121)	0·80 (5)
C(12)–H(122)	1·21 (7)
C(15)–H(151)	0·95 (5)
C(15)–H(152)	1·09 (5)
C(16)–H(161)	0·80 (7)
C(16)–H(162)	0·97 (4)
C(17)–H(171)	0·95 (8)
C(17)–H(172)	0·96 (10)
C(17)–H(173)	0·98 (8)
C(18)–H(181)	0·97 (7)
C(18)–H(182)	1·15 (6)
C(18)–H(183)	1·12 (4)
C(19)–H(191)	1·02 (5)
C(19)–H(192)	1·10 (6)
C(19)–H(193)	0·92 (5)
C(20)–H(201)	0·98 (4)
C(20)–H(202)	1·11 (6)
C(20)–H(203)	1·02 (6)

* The standard deviations for C–H bonds are probably underestimated by a factor of two (see text).

The two =C–O bonds of the ether oxygen in the γ-lactone ring are significantly longer than the normal value of 1·334 Å (Wilson, 1962). The extension in bond lengths appears to be associated with the small interior angles at C(1), C(4) and O(1) (108°, 108° and 107°), small angles tending to induce a greater p-character in the bonds (Dewar, 1962). The values for the two bonds C(1)–O(1) and C(4)–O(1) differ significantly from one another, which probably arises from the difference between the electronegativities of the next nearest neighbours O(2) and C(5).

The asymmetry of the carbonyl bond angles C(2)–C(1)–O(2) and O(1)–C(1)–O(2) seems to arise from the close intermolecular approaches of C(3), C(4) and C(5) to the carbonyl oxygen O(2). Such angular asymmetry is not uncommon in lactones, e.g. α_1-bromopicrotoxinin (Craven, 1962) and α-methyltetronic acid (MacDonald & Alleyne, 1963).

The exterior angles at C(2) and C(4) are also asymmetric. Intramolecular proton repulsion and intermolecular van der Waals interactions appear to be jointly responsible. Interaction between H(031) and the methyl protons at C(17) is indicated by the multiple splitting of the peak at $\tau = 3\cdot00$ in the nuclear magnetic resonance (n.m.r.) spectrum (Jefferies & Middleton, 1964).

There are two =C–C= bonds in the structure and the mean value of 1·460 Å agrees well with similar bonds in other structures e.g. 1·462 Å in cyclo-octatetraene (Bastiansen, Hedberg & Hedberg, 1957) and 1·464 Å in buta-1,3-diene (Cole, Mohay & Osborne, 1966).

Table 8. Bond angles

(e.s.d.'s in parenthesis)

	θ (degrees)
C(2)—C(1)—O(1)	108·9 (3)
C(2)—C(1)—O(2)	130·2 (3)
O(1)—C(1)—O(2)	120·9 (3)
C(1)—C(2)—C(3)	107·1 (3)
C(1)—C(2)—C(17)	121·7 (3)
C(3)—C(2)—C(17)	131·2 (3)
C(2)—C(3)—C(4)	109·0 (3)
C(3)—C(4)—C(5)	129·7 (3)
C(3)—C(4)—O(1)	107·7 (2)
C(5)—C(4)—O(1)	122·6 (3)
C(4)—C(5)—C(6)	126·9 (3)
C(5)—C(6)—C(7)	111·5 (2)
C(5)—C(6)—C(11)	114·3 (2)
C(7)—C(6)—C(11)	109·8 (2)
C(6)—C(7)—C(8)	108·6 (2)
C(6)—C(7)—C(13)	107·7 (2)
C(6)—C(7)—C(16)	113·8 (3)
C(8)—C(7)—C(13)	108·2 (3)
C(8)—C(7)—C(16)	114·5 (3)
C(13)–C(7)—C(16)	103·6 (3)
C(7)—C(8)—C(9)	109·0 (4)
C(8)—C(9)—C(10)	111·5 (4)
C(9)—C(10)-C(11)	109·3 (3)
C(9)—C(10)-C(12)	110·0 (4)
C(11)-C(10)-C(12)	109·7 (4)
C(6)—C(11)-C(10)	108·2 (3)
C(6)—C(11)-C(18)	108·5 (3)
C(6)—C(11)-C(19)	113·6 (3)
C(10)-C(11)-C(18)	111·4 (3)
C(10)-C(11)-C(19)	110·0 (3)
C(18)-C(11)-C(19)	105·2 (3)
C(10)-C(12)-C(13)	106·0 (3)
C(7)—C(13)-C(12)	115·5 (3)
C(7)—C(13)-C(14)	113·6 (3)
C(12)-C(13)-C(14)	130·8 (3)
C(13)-C(14)-C(15)	110·9 (3)
C(13)-C(14)-C(20)	126·7 (3)
C(15)-C(14)-C(20)	122·5 (3)
C(14)-C(15)-C(16)	105·9 (3)
C(17)-C(16)-C(15)	106·0 (3)
C(1)—O(1)—C(4)	107·4 (2)

There are six sp^3–sp^2 bonds in the structure and the only one which differs from the normal value of 1·501 Å (Lide, 1962) is the long bond C(7)–C(13) associated with a fully substituted carbon atom C(7).

Long sp^3–sp^3 C–C bonds are also observed associated with the degree of substitution at the ca... atoms. For example C(6)–C(11), C(6)–C(7) and C(1... C(18) are all significantly longer than the value
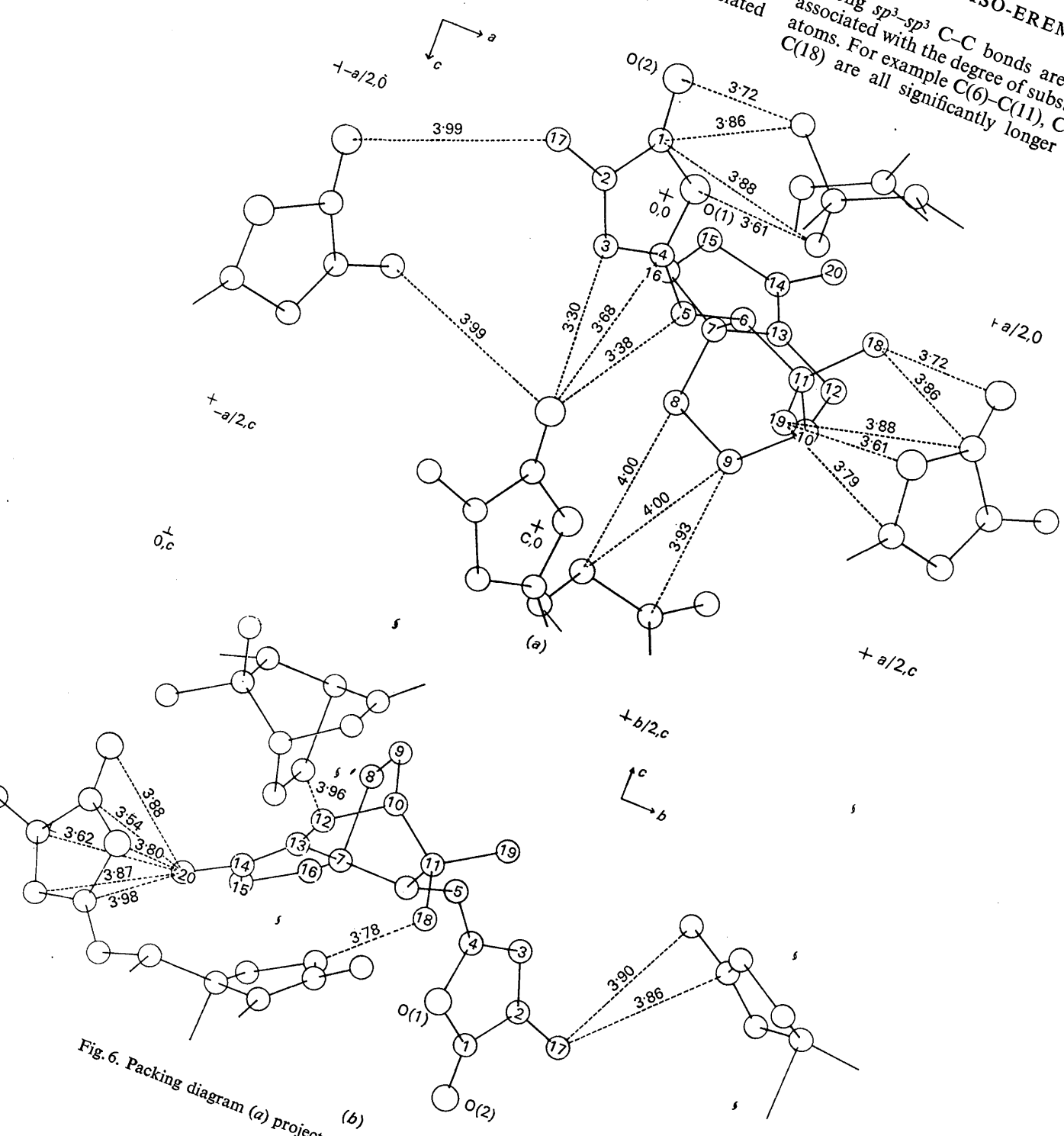

Fig. 6. Packing diagram (a) projected down [010], (b) projected down [100].

1·536 Å for ethane. These extensions are smaller than some of those observed in methyl melaleucate iodo-acetate (Hall & Maslen, 1965), davallol iodoacetate (Oh & Maslen, 1966a) or trimethylamine–trimethylboron (Lide, Taft & Love, 1959), but since these structures are less accurately determined larger random errors will tend to accentuate the variations in bond length, i.e. the largest apparent extensions are likely to be somewhat greater than the true values. Recent studies by electron diffraction of the structures of tetra- and hexamethylethane further confirm the reality of the substitution effect on bond lengths. For hexamethyl-ethane the central C–C bond is extended by 0·035° and the outer bonds by 0·010 Å whereas 1,1,2,2-tetra-methylethane behaves as an unstrained alkane. The precise mechanism responsible for these bond exten-sions is not known with certainty, but recent studies by Bartell & Boates (1966) tend to support non-bonded steric repulsion as the principal agent.

The two C–C bonds for the gem-dimethyl group at the quaternary carbon C(11) are not equal. C(11)–C(19) is presumably shorter because C(6)–C(11)–C(19) is larger than normal. It is interesting to note that chem-ical shifts of the two methyl groups in the n.m.r. spec-trum are fairly large (Jefferies & Middleton, 1964).

Packing

All intermolecular contacts of less than 4·00 Å be-tween pairs of non-hydrogen atoms are listed in Table 9. All atoms other than C(6), C(7), C(10), C(11), C(13) and C(16) have one or more intermolecular neighbours within 4·00 Å. The packing in the structure is illus-trated in Fig. 6. Except in the region near atoms C(9), C(10) and C(12) the structure appears to be closely packed and the intermolecular forces are predominant-ly of the van der Waals type. There may be some evi-dence for static electrical interaction around the γ-lac-tone group where the adjacent molecules could be linked together by hydrogen bridges, but the bridging hydrogen atoms H(031) and H(051) deviate significant-ly from collinearity with the respective $C \cdots O$ pairs. It is therefore not clear whether these contacts arise from hydrogen bonding of the type described by Sutor (1963).

Table 10. *Thermal eigenvalues for non-hydrogen atoms*

U_i are the r.m.s. amplitudes and $D1_i$, $D2_i$, $D3_i$, are the direc-tion cosines of the principal axes of the vibration ellipsoids.

	i	U_i	$D1_i$	$D2_i$	$D3_i$
C(1)	1	0·226 Å	−0·989	−0·142	0·011
	2	0·233	−0·143	0·985	−0·086
	3	0·208	0·000	0·087	0·996
C(2)	1	0·216	−0·725	0·635	−0·263
	2	0·239	0·657	0·753	0·011
	3	0·207	−0·206	0·165	0·964
C(3)	1	0·209	−0·662	0·324	−0·675
	2	0·250	0·528	0·840	−0·115
	3	0·186	−0·530	0·433	0·728
C(4)	1	0·208	−0·297	0·759	−0·578
	2	0·237	0·786	0·538	0·302
	3	0·172	−0·541	0·365	0·757
C(5)	1	0·208	−0·547	0·473	−0·689
	2	0·253	0·575	0·811	0·100
	3	0·183	−0·607	0·341	0·717
C(6)	1	0·210	−0·313	0·274	−0·909
	2	0·227	0·537	0·840	0·068
	3	0·180	−0·782	0·467	0·411
C(7)	1	0·197	0·997	0·062	0·035
	2	0·245	−0·030	−0·075	0·996
	3	0·216	0·064	−0·995	−0·073
C(8)	1	0·311	0·918	0·080	0·388
	2	0·276	0·285	−0·813	−0·506
	3	0·229	0·274	0·576	−0·769
C(9)	1	0·228	0·175	−0·270	0·946
	2	0·423	−0·786	0·539	0·299
	3	0·302	−0·591	−0·797	−0·118
C(10)	1	0·248	0·055	−0·998	0·001
	2	0·352	−0·652	−0·035	0·756
	3	0·177	0·755	0·042	0·653
C(11)	1	0·207	0·751	0·588	0·298
	2	0·260	−0·077	−0·370	0·925
	3	0·216	0·655	−0·718	−0·232
C(12)	1	0·224	−0·317	−0·908	−0·273
	2	0·453	−0·322	−0·167	0·931
	3	0·188	0·891	−0·383	0·239

Table 9. *Intermolecular contacts less than 4·0 Å*

I	x, y, z	II	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$	III	$\frac{1}{2}+x, \frac{1}{2}-y, -z$
IV	$x, y, 1+z$	V	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	VI	$1-x, \frac{1}{2}+y, \frac{3}{2}-z$
VII	$1+x, y, 1+z$	VIII	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$	IX	$-x, -\frac{1}{2}+y, -\frac{1}{2}-z$
X	$\frac{3}{2}-x, 1-y, \frac{1}{2}+z$	XI	$-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$		

C(1)$_{II}$	$\cdots$C(18)$_I$	3·86 Å	C(8)$_V$	$\cdots$C(12)$_I$	3·96 Å
C(1)$_{II}$	$\cdots$C(19)$_I$	3·88	C(9)$_I$	$\cdots$C(14)$_{IV}$	3·93
C(1)$_{III}$	$\cdots$C(20)$_I$	3·54	C(14)$_{VI}$	$\cdots$C(17)$_{VII}$	3·86
C(2)$_{III}$	$\cdots$C(20)$_I$	3·62	C(15)$_{III}$	$\cdots$C(18)$_I$	3·78
C(3)$_I$	$\cdots$O(2)$_{IV}$	3·30	C(17)$_{II}$	$\cdots$O(2)$_{VII}$	3·99
C(3)$_{III}$	$\cdots$C(20)$_I$	3·87	C(17)$_{VIII}$	$\cdots$C(20)$_I$	3·90
C(4)$_I$	$\cdots$O(2)$_{IV}$	3·68	C(17)$_{IX}$	$\cdots$C(20)$_I$	3·89
C(4)$_{II}$	$\cdots$C(19)$_I$	3·79	C(18)$_X$	$\cdots$O(2)$_{VII}$	3·72
C(4)$_{III}$	$\cdots$C(20)$_I$	3·98	C(19)$_{II}$	$\cdots$O(1)$_{IV}$	3·61
C(5)$_I$	$\cdots$O(2)$_{IV}$	3·38	C(20)$_V$	$\cdots$O(2)$_{VII}$	3·88
C(8)$_I$	$\cdots$C(15)$_{IV}$	4·00	C(20)$_{XI}$	$\cdots$O(1)$_{IV}$	3·80

Table 10 (cont.)

	i	U_i	$D1_i$	$D2_i$	$D3_i$
C(13)	1	0·192	0·979	−0·053	0·194
	2	0·267	−0·196	−0·040	0·979
	3	0·213	−0·044	−0·997	−0·050
C(14)	1	0·249	0·957	0·139	0·251
	2	0·234	0·280	−0·269	−0·921
	3	0·210	−0·060	0·952	−0·297
C(15)	1	0·267	0·376	−0·842	0·385
	2	0·323	−0·648	0·057	0·759
	3	0·208	0·661	0·535	0·524
C(16)	1	0·188	0·973	0·130	0·188
	2	0·332	−0·115	−0·432	0·894
	3	0·280	0·198	−0·892	−0·406
C(17)	1	0·262	0·276	−0·423	−0·862
	2	0·352	0·705	0·699	−0·118
	3	0·210	0·653	−0·575	0·491
C(18)	1	0·203	0·955	0·123	−0·268
	2	0·376	−0·006	0·916	0·399
	3	0·325	−0·295	0·379	−0·876
C(19)	1	0·294	−0·868	0·495	−0·017
	2	0·375	−0·225	−0·362	0·904
	3	0·200	0·441	0·789	0·426
C(20)	1	0·344	0·841	0·046	0·537
	2	0·299	−0·468	−0·430	0·771
	3	0·220	−0·267	0·901	0·341
O(1)	1	0·224	−0·583	0·603	−0·543
	2	0·245	0·700	0·712	0·039
	3	0·187	−0·410	0·357	0·838
O(2)	1	0·279	−0·799	0·600	0·016
	2	0·335	0·600	0·798	−0·038
	3	0·195	0·036	0·021	0·999

Thermal motion

The principal axes of the vibration ellipsoids and their associated direction cosines are given in Table 10.

For the substituent atoms C(17), C(18), C(19), C(20) and O(2) the thermal motion is strongly anisotropic, and the principal axes with the larger amplitudes are near to perpendicular to the associated bonds. For atoms C(20) and O(2), both of which have a large number of near neighbours, the lengths of the two larger principal axes are approximately equal. The thermal motions of the atoms in the lactone ring are small and nearly isotropic, consistent with the close packing around this ring system. The thermal motions of the atoms C(8), C(9), C(10) and C(12) are quite strongly anisotropic, while those of C(15) and C(16) are appreciably so. The large magnitudes for the atoms in the vicinity of C(10) are not unexpected, since this part of the structure is not tightly packed, but the thermal motion of C(10) itself appears at first sight to be anomalous in that the principal axis with the largest amplitude makes an angle of only 11·5° with the C(9)–C(10) bond. However, there is a clear relation between the direction cosines for the largest amplitudes for C(8), C(9), C(10), C(12), C(15) and C(16). This is shown on a projection of the structure in Fig. 7. A model of the thermal motion was constructed, and it was found that the thermal motion of the skeleton was consistent only with a high degree of lability in the bond angles at C(6) and C(7) and to a lesser degree at C(13). A contributing factor is a certain amount of rotation about the C(5)–C(6) bond. The most important internal mode is that depicted in Fig. 7, however, which corresponds to a libration of the partial structure C(8), C(9), C(10), C(12), C(15), C(16) about an axis which passes through C(6) and is approximately parallel to the *b* axis. A
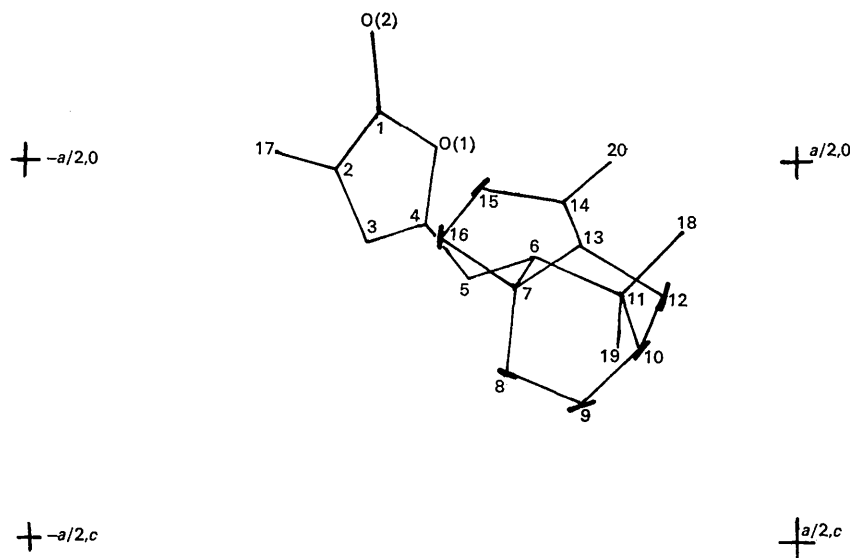

Fig. 7. R.m.s. amplitudes, drawn as heavy lines, for the major principal axis of vibration for atoms C(8), C(9), C(10), C(12), C(15) and C(16) projected down [010]. The motion corresponds to a libration with an axis which passes through C(6) and is approximately parallel to b.

feature of the internal motion is that the angles which are altered are those which are already distorted from the ideal configuration, and particularly C(5)–C(6)–C(11). This is consistent with the well known lability of the cyclopentane ring system, compared with that of cyclohexane. In the former the bond angles are considerably greater than the ideal tetrahedral value. Since in such distorted configurations steric forces must be acting in opposition to those resulting from the less than ideal orbital overlap some degree of lability is not unexpected.

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The Crystal Structure of Methyl α-D-Glucopyranoside

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The crystal structure of methyl α-D-glucopyranoside, $C_7H_{14}O_6$, has been determined by application of the sign correlation procedure to the $hk0$ projection data and by inspection of the three-dimensional E^2-1 Patterson synthesis. The space group is $P2_12_12_1$, with four molecules in a unit cell of dimensions $a=11\cdot304\pm0\cdot010$, $b=14\cdot785\pm0\cdot015$ and $c=5\cdot282\pm0\cdot005$ Å. The molecule is in the *trans* C1 chair conformation. None of the C–C or C–OH bond lengths differ significantly from their respective means. The C(1)–O(1) bond is slightly shortened and there is a significant difference between the carbon oxygen bond lengths in the pyranose ring.

Introduction

Methyl α-D-glucopyranoside, $C_7H_{14}O_6$, is the more stable of the two glycosidic anomers obtained when glucose is heated with acidic methanol. This is contrary to the expectation that the more equatorially substituted β-anomer would be the configuration of least nonbonding interaction and the 'anomeric effect' has been postulated to account for this (Lemieux & Chü, 1958; Edward, 1955).

The results of previous crystal structure determinations have suggested that the hemiacetal group (*cf.* Robertson & Sheldrick, 1965; Kim & Jeffrey, 1967), which is that part of the molecule directly involved in anomerization and mutarotation, exhibits bond length variations dependent on whether the molecule is a free pyranose sugar or a glycoside. In particular, it has been proposed that the free hydroxyl of an α anomer will have a short C(1)–O(1) bond length, whereas the corresponding bond in a glycoside will be normal, but that the differences then appear between the C–O ring links (*cf.* Berman, Chu & Jeffrey, 1967). This structure determination of the methyl glucoside was undertaken

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