is at a similar distance from atom O_3'' of the molecule at $(x-a, y, z-c)$. The molecules are thus linked by the H bonding into long chains, the shortness of the O–H–O distance showing that the bonding is very strong as has already been indicated by the infra-red spectral data. The binding between chains is much weaker since no H-bonding is then involved. A diagrammatic picture of the bonding is shown in Fig. 4.

We wish to express our thanks to Prof. L. J. Haynes of the Department of Chemistry for suggesting this investigation of the tetronic acids to us, and to Dr J. R. Plimmer of the Natural Products Unit for supplying the crystals. To both of them we are also indebted for most helpful discussions.

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The Direct Determination of Molecular Structure: The Crystal Structure of the Bromodilactone from Jacobine at −150 °C

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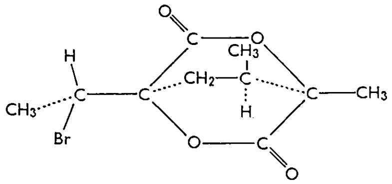
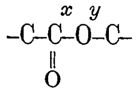
The bromodilactone from jacobine, $C_{10}H_{13}O_4Br$, crystallizes in the monoclinic space group $P2_1$ with cell dimensions, $a = 8{\cdot}70$, $b = 6{\cdot}34$, $c = 10{\cdot}44$ Å, $\beta = 98{\cdot}2°$ at −150 °C. The structure was determined by use of the heavy atom to obtain the projected distributions ${}_1\varrho_0(x, z)$ and the generalized projection ${}_1C_1(x, z)$. With the available range of data, up to $k = 4$, least-squares refinement, with two different weighting schemes, one a function of $|F|$ and the other of sin θ, has reduced the overall reliability index, R, to 0·12.



Bond lengths and angles in the absolute structure (above) are normal, the lactone group containing certain features of interest. Both groups



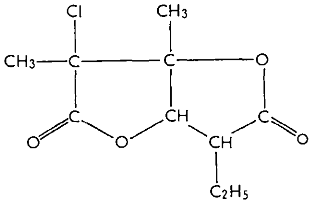
$$\begin{array}{c} x\ \ y \\ -C-C-O-C- \\ \| \\ O \end{array}$$

are planar within experimental error, the bond y being longer than bond x by approximately 0·1 Å.

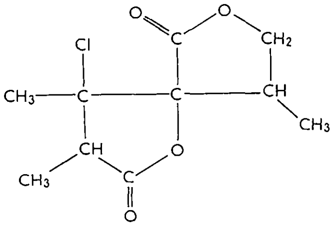
The analysis, together with that of jacobine bromhydrin, provides clarification of the structural and configurational aspects of the pyrrolizidine alkaloids of the jacobine group.

Introduction

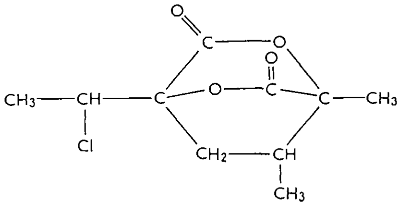
From *Senecio jacobaea L.*, several alkaloids have been isolated and studied (for earlier work, see Bradbury & Culvenor (1954) and Adams, Gianturco & van Duuren (1956)). Three of these, jacobine, jaconine and jacoline, are closely related as epoxide–chlorhydrin–glycol. The alkaloids can all be hydrolysed into a pyrrolizidine base, retronecine, and a dibasic acid, indicating a di-ester structure. In 1958, the dibasic acid represented the principal structural problem of the alkaloids, and this problem was critically dependent on the interpretation of the structure of the dilactone obtained by HCl hydrolysis of jacobine. Both Adam *et al.* (1956) and Bradbury & Willis (1956) formulated the dilactone as a γ-lactone, I and II respectively, being guided mainly by the interpretation of the infra-red data. However, Geissman (1959) pointed out serious objections to I and II which would disappear if the compound were formulated as a di-δ-lactone, III.



(I)



(II)



(III)

At this stage, the structure of the dilactone constituted a major clue to the elucidation of the structures of the group of alkaloids and warranted structure analysis. For X-ray studies, the bromodilactone was considered more suitable and we are indebted to Dr C. C. J. Culvenor of the Organic Chemistry Division, C.S.I.R.O., for the supply of excellent crystals of this derivative.

A brief note on the preliminary structure analysis was presented at the First I.U.P.A.C. Symposium on the Chemistry of Natural Products, Australia (Taylor, 1960): comments on the conformation of the lactone group were also given subsequently (Mathieson & Taylor, 1961). In conjunction with the analysis of the bromhydrin of jacobine (Fridrichsons, Mathieson & Sutor, 1960), this analysis provides clarification of the structural aspects—configurational and conformational—of the pyrrolizidine alkaloids of the jacobine group. Chemical evidence has been presented in parallel by Geissman (1959) and by Bradbury & Masamune (1959) regarding structure and by Masamune (1960) regarding configurational details.

Experimental

The compound, $C_{10}H_{13}O_4Br$, crystallized from ethyl alcohol in the form of needles elongated along *b* belongs to the monoclinic system, the cell dimensions, determined against a standard (Si, $a = 5{\cdot}43054$ Å at 20 °C), being

$$a = 8{\cdot}70,\ b = 6{\cdot}34,\ c = 10{\cdot}44\ \text{Å};$$
$$\beta = 98{\cdot}2^\circ\ \text{at}\ -150\ ^\circ\text{C}.$$

The space group is $P2_1$; the density, as measured by flotation in $MgBr_2$ solution, is $1{\cdot}55$ g.cm^{-3}, which accords with $1{\cdot}95$ (*i.e.*, 2) molecules in the unit cell.

Intensity data were collected at -150 °C (for details, see Fridrichsons & Mathieson, 1962*a*) for the 0–4 layers about the *b* axis, two packs of four films being exposed for 6hr. and 10 min. respectively for each layer (Cu $K\alpha$, 200 mA, 35 kV). The amount of data collected was 85% of theoretical (Table 1).

Table 1. *Observed, n, and total, N, number of terms in each layer with the final values for the reliability index, R, which was determined only for the observed reflections*

k	*n*	*N*	*R*
0	214	256	0·094
1	212	251	0·111
2	194	225	0·125
3	171	210	0·130
4	156	183	0·214
0–4	947	1125	0·122

Two-dimensional structure factors and Fourier syntheses were computed on SILLIAC (Freeman, 1957) while corresponding three-dimensional calculations and least-squares refinements were carried out on UTECOM ($\equiv$ DEUCE) using coordinated programs devised by Rollett (1961).

Structure analysis

The bromine atom of the asymmetric unit was located from the Patterson projection for which $F_o^2(h0l)$ terms were sharpened to correspond approximately to point atoms. Attention was first concentrated on the centrosymmetric *b* axis projection. The first distributions were (*a*) ${}_1\varrho_0(x,z)$ (Fig. 1(*a*)) using terms for which the geometrical structure factor, $S_{\rm Br} > 0{\cdot}1$ and (*b*) an image-seeking function, $\Sigma(x,z)$, using terms $F_o^2.\varphi_{\rm Br}$ (Fridrichsons & Mathieson, 1962*b*), Fig. 1(*b*). Most of the peaks were common to the two functions but, in the image-seeking distribution, a high peak in the region of $x=\frac{1}{2}$, $z=\frac{1}{2}$ was obviously spurious, due to failure to remove the Br–Br vector from the calculations by the alternative use of $(F_o^2-\varphi_{\rm Br}^2).\varphi_{\rm Br}$. The peaks common to the two distri-

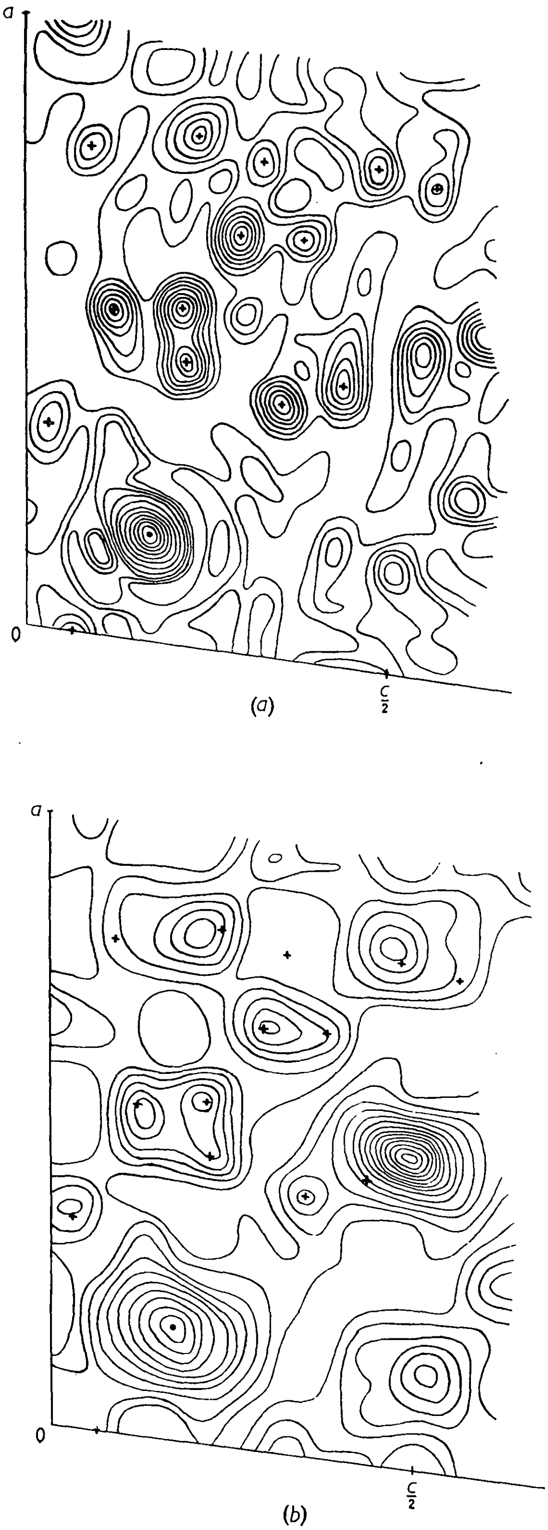


Fig. 1. Distribution corresponding to (a) the electron-density function ${}_1\varrho_0(x, z)$ and (b) the image-seeking function $\Sigma(x, z)$. The atom sites shown are those selected at this stage of the analysis. Contour intervals are arbitrary as also in Fig. 2.

butions were selected, without reference to a chemical model (see Figs. 1(*a*) and (*b*)) and the structure factors for the atoms selected (Br+14 atoms weighted as C) gave an R of 0·30. The analysis was continued with ϱ and $\Delta\varrho$ distributions; ${}_2\varrho_0$ and ${}_2\Delta\varrho$ showed that four of the sites were incorrect (*cf.* Figs. 1 and 2) and indicated three alternative locations. The resultant structure factors improved to $R=0·235$. After ${}_3\varrho_0$ and ${}_3\Delta\varrho$, the distribution in projection could be correlated with a chemically sensible skeleton, essentially based on the structure proposed by Geissman (1959), Fig. 2. With the lighter atoms differentiated into C and O by the difference maps, R was reduced to 0·18.

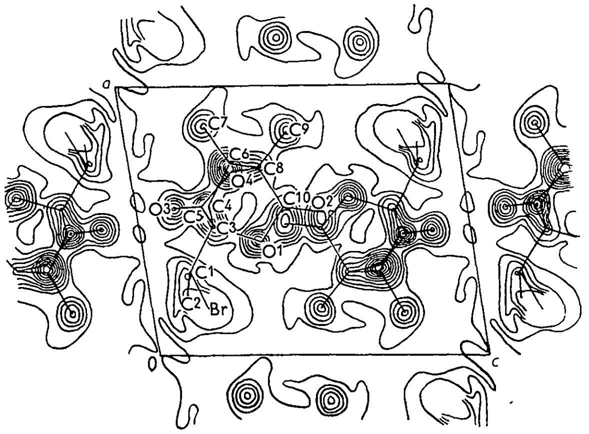


Fig. 2. Electron-density distribution ${}_3\varrho_0(x, z)$ with the molecular model superimposed.

To locate the y parameters of the light atoms, the cosine generalized projection for the hll data was calculated with signs based on the Br contribution ($y_{\mathrm{Br}}=0$). From this symmetrical distribution, approximate values for y parameters were derived and rendered a little more precise relative to one another by reference to reasonable bond lengths. For (C_4, C_5) and (C_6, O_4), y parameters were not deducible directly from ${}_1C_1(x, z)$, but satisfactory assessment was possible by reference to the probable stereochemistry. Two cycles of sine and cosine generalized projections were used to refine the y parameters and improved x, z coordinates were obtained from a modulus projection $|\varrho_1|$ (Fridrichsons & Mathieson, 1955).

Further refinement was carried out by the least-squares program of Rollett (1961) which utilizes a block diagonal. The weighting scheme used, a standard one in Rollett's program, was as follows, the optimum value, $|F^*|$, being taken as 20 (see Table 5):

$$\sqrt{w_2}=|F_o|/|F^*| \quad \text{for} \quad |F_o|\le|F^*|$$

or

$$\sqrt{w_2}=|F^*|/|F_o| \quad \text{for} \quad |F_o|>|F^*| .$$

With the hll data, three cycles using quarter shifts reduced the corresponding R to 0·15. The other layers were then scaled against F_c values and included in

Table 2(*a*). *Positional parameters derived from w_2 and w_3 weighting schemes and their mean; for one molecule in the unit cell defined by a right-handed set of axes*

	x		*y*		*z*	
Atom	w_2	w_3	w_2	w_3	w_2	w_3
Br	$0{\cdot}169_9$	$0{\cdot}169_9$	$1{\cdot}015_0$	$1{\cdot}015_0$	$0{\cdot}165_5$	$0{\cdot}165_5$
C_1	$0{\cdot}299_5$	$0{\cdot}304_5$	$0{\cdot}771_4$	$0{\cdot}769_4$	$0{\cdot}125_7$	$0{\cdot}126_5$
C_2	$0{\cdot}217_2$	$0{\cdot}213_6$	$0{\cdot}560_2$	$0{\cdot}562_0$	$0{\cdot}108_2$	$0{\cdot}109_6$
C_3	$0{\cdot}456_8$	$0{\cdot}456_9$	$0{\cdot}788_8$	$0{\cdot}782_2$	$0{\cdot}219_9$	$0{\cdot}220_2$
C_4	$0{\cdot}550_3$	$0{\cdot}553_4$	$0{\cdot}586_6$	$0{\cdot}591_0$	$0{\cdot}207_6$	$0{\cdot}206_8$
C_5	$0{\cdot}556_2$	$0{\cdot}553_0$	$0{\cdot}978_9$	$0{\cdot}981_5$	$0{\cdot}203_1$	$0{\cdot}204_3$
C_6	$0{\cdot}702_2$	$0{\cdot}702_6$	$0{\cdot}613_4$	$0{\cdot}606_1$	$0{\cdot}305_2$	$0{\cdot}305_6$
C_7	$0{\cdot}850_4$	$0{\cdot}850_1$	$0{\cdot}601_8$	$0{\cdot}595_6$	$0{\cdot}243_1$	$0{\cdot}241_8$
C_8	$0{\cdot}693_3$	$0{\cdot}694_4$	$0{\cdot}816_2$	$0{\cdot}809_3$	$0{\cdot}385_9$	$0{\cdot}388_1$
C_9	$0{\cdot}830_4$	$0{\cdot}828_3$	$0{\cdot}880_4$	$0{\cdot}864_8$	$0{\cdot}491_6$	$0{\cdot}491_4$
C_{10}	$0{\cdot}546_0$	$0{\cdot}544_6$	$0{\cdot}791_2$	$0{\cdot}794_5$	$0{\cdot}445_8$	$0{\cdot}446_0$
O_1	$0{\cdot}413_9$	$0{\cdot}414_0$	$0{\cdot}792_4$	$0{\cdot}788_9$	$0{\cdot}352_7$	$0{\cdot}352_1$
O_2	$0{\cdot}525_1$	$0{\cdot}525_5$	$0{\cdot}779_9$	$0{\cdot}781_7$	$0{\cdot}557_1$	$0{\cdot}557_0$
O_3	$0{\cdot}543_0$	$0{\cdot}539_9$	$1{\cdot}102_1$	$1{\cdot}103_9$	$0{\cdot}116_7$	$0{\cdot}116_3$
O_4	$0{\cdot}680_0$	$0{\cdot}679_4$	$0{\cdot}985_6$	$0{\cdot}987_8$	$0{\cdot}298_5$	$0{\cdot}298_1$

Table 2(*b*). *The corresponding e.s.d. of the carbon and oxygen atoms*

	x(C)	*y*(C)	*z*(C)	*x*(O)	*y*(O)	*z*(O)
w_2	0·022 Å	0·040 Å	0·021 Å	0·015 Å	0·021 Å	0·012 Å
w_3	0·020	0·039	0·020	0·015	0·025	0·012

the refinement, half-shifts being used at this stage. From an overall value of 0·27, *R* reduced steadily to 0·134. During the later stages, the Br atom parameters were not varied.

It was considered advisable to reduce the influence of low-angle terms since these are more specifically affected by such factors as spot-shape, absorption and extinction, and to accentuate the contributions of high-angle terms. To this end, a different weighting scheme was adopted in which terms are weighted according to their sin θ value *i.e.* $w_3 = \sin\theta$. It may be noted that this weighting scheme bears a close relationship to $w = 1/f$, which Cochran (1951) has shown is equivalent to refinement by difference syntheses. For completeness, the refinement was carried through by both w_2 and w_3 weighting schemes to determine whether any significant difference occur-

Table 3(*a*). *Bond lengths within the molecule for the different weighting schemes and from the mean parameters*

	Bond lengths			
Bond	w_2	w_3	Mean	(σl)
Br–C_1	$1{\cdot}99_7$ Å	$2{\cdot}02_4$ Å	$2{\cdot}00_7$	0·03
C_1–C_2	$1{\cdot}51_7$	$1{\cdot}53_2$	$1{\cdot}52_4$	0·06
C_1–C_3	$1{\cdot}57_2$	$1{\cdot}53_4$	$1{\cdot}55_2$	0·03
C_3–C_4	$1{\cdot}53_3$	$1{\cdot}49_2$	$1{\cdot}51_2$	0·05
C_4–C_6	$1{\cdot}55_9$	$1{\cdot}54_2$	$1{\cdot}55_0$	0·03
C_6–C_7	$1{\cdot}52_6$	$1{\cdot}52_9$	$1{\cdot}52_7$	0·03
C_6–C_8	$1{\cdot}54_4$	$1{\cdot}55_8$	$1{\cdot}55_1$	0·05
C_8–C_9	$1{\cdot}55_9$	$1{\cdot}51_2$	$1{\cdot}53_5$	0·03
C_3–C_5	$1{\cdot}50_8$	$1{\cdot}53_7$	$1{\cdot}52_2$	0·05
C_8–C_{10}	$1{\cdot}51_2$	$1{\cdot}51_4$	$1{\cdot}51_3$	0·03
C_5–O_3	$1{\cdot}18_6$	$1{\cdot}19_5$	$1{\cdot}19_0$	0·04
C_{10}–O_2	$1{\cdot}20_5$	$1{\cdot}19_7$	$1{\cdot}20_0$	0·02
C_5–O_4	$1{\cdot}36_0$	$1{\cdot}36_5$	$1{\cdot}36_2$	0·02
C_{10}–O_1	$1{\cdot}39_6$	$1{\cdot}39_1$	$1{\cdot}39_3$	0·02
O_4–C_8	$1{\cdot}40_3$	$1{\cdot}47_0$	$1{\cdot}43_7$	0·04
O_1–C_3	$1{\cdot}48_6$	$1{\cdot}47_8$	$1{\cdot}48_2$	0·02

Table 3(*b*). *Approach distances in the crystal. The number inside the bracket denotes the molecule* (*see Fig.* 5)

Atoms	Approach distance
C_5(1)–O_2(2)	3·29 Å
C_8(1)–O_2(2)	3·62
C_{10}(1)–C_{10}(2)	3·49
C_{10}(1)–O_2(2)	3·15
O_1(1)–O_2(2)	3·27
O_2(1)–C_4(2)	3·29
O_2(1)–C_6(2)	3·34
O_2(1)–C_{10}(2)	3·30
O_2(1)–O_1(2)	3·39
O_2(1)–O_2(2)	3·39
O_4(1)–O_2(2)	3·11
C_1(1)–O_3(3)	3·22
C_2(1)–O_3(3)	3·39
C_3(1)–O_3(3)	3·70
C_4(1)–O_3(3)	3·36
O_3(1)–O_3(3)	4·00
C_9(1)–C_7(4)	3·92

Table 4. *Planes through the lactone groups and the deviation of each atom. Equations refer to orthogonal axes X, Y, Z, Y and Z being coincident with y and z, while X is perpendicular to z.*

Lactone group 1

Plane: $-0{\cdot}0996X - 0{\cdot}9949Y - 0{\cdot}0155Z - 1{\cdot}6445 = 0$

Atom	In Å
C_3	+0·04
C_8	+0·02
C_{10}	−0·00
O_1	−0·07
O_2	+0·02

Lactone group 2

Plane: $-0{\cdot}6181X - 0{\cdot}5461Y - 0{\cdot}5654Z - 1{\cdot}7193 = 0$

Atom	In Å
C_3	−0·01
C_5	−0·04
C_8	+0·04
O_3	+0·05
O_4	−0·04

Table 5. *Comparison of measured structure factors with values calculated from w_3 parameters.*

	F_c	F_o
00ℓ		
1	8.4	9.1
2	57.5	58.2
3	78.1	74.4
4	34.6	32.4
5	8.8	11.7
6	33.6	29.2
7	16.3	14.8
8	9.6	10.3
10ℓ		
-13	10.4	8.7
-12	22.2	21.3
-11	15.8	15.5
-10	15.0	12.4
-9	19.5	16.9
-8	16.1	15.3
-7	27.3	25.7
-6	20.8	21.2
-5	43.2	38.4
-4	39.2	34.4
-3	10.5	12.6
-2	75.9	68.7
-1	53.7	50.4
0	57.3	46.0
2	73.6	71.7
3	38.8	45.1
4	39.8	38.5
5	47.0	40.0
6	21.0	20.0
7	9.7	9.8
8	13.7	12.5
9	35.3	31.2
11	17.9	15.9
12	10.6	10.6
20ℓ		
-12	11.7	13.4
-10	15.1	13.6
-9	16.1	17.0
-8	24.4	21.7
-7	7.4	4.0
-6	34.9	33.3
-5	18.1	17.4
-4	11.6	10.6
-3	4.0	6.0
-2	63.6	67.3
-1	31.3	27.3
0	17.2	19.1
1	71.9	72.2
2	27.4	28.7
3	4.6	5.2
4	45.1	42.7
5	40.0	38.9
6	15.4	16.9
7	38.1	32.9
8	27.7	24.1
9	35.4	30.4
10	12.1	9.5
12	7.9	4.0
30ℓ		
-12	13.0	12.2
-11	11.5	12.1
-10	11.2	11.3
-9	7.5	4.9
-8	9.5	9.6
-6	15.6	13.8
-5	28.8	31.8
-4	22.3	21.8
-3	80.3	87.3
-2	31.0	30.8
-1	27.2	26.7
0	76.3	83.5
1	19.7	14.5
2	48.4	50.7
3	82.0	82.8
4	2.8	8.6
5	22.0	23.7
6	32.0	28.6
7	11.9	10.1
8	9.0	9.0
9	7.4	4.9
10	15.3	12.5
12	9.7	7.6
40ℓ		
-13	6.2	6.7
-12	6.4	4.8
-11	8.8	9.0
-10	19.3	19.1
-9	16.5	17.7
-8	22.3	23.4
-7	20.4	21.5
-6	17.3	15.8
-5	24.8	24.5
-4	12.2	10.5
-3	3.2	3.2
-2	16.5	18.9
-1	50.0	50.2
0	6.2	7.9
1	35.9	37.0
2	18.1	12.3
3	5.2	3.6
4	8.2	10.2
5	37.0	30.6
6	18.1	15.4
7	21.3	18.0
8	21.4	18.7
9	12.9	10.9
10	7.7	6.7
11	14.4	11.7

	$\lvert F_c\rvert$	$\lvert F_o\rvert$
50ℓ		
-12	7.5	7.7
-11	8.3	7.5
-8	12.1	11.2
-7	21.4	21.0
-6	20.4	19.8
-5	34.8	29.7
-4	16.7	15.8
-3	26.5	23.2
-2	44.5	38.9
-1	6.5	7.6
0	8.4	8.8
1	35.0	35.9
2	31.1	28.2
3	15.8	16.0
4	35.5	29.4
5	14.0	9.6
6	18.4	15.8
7	12.0	10.8
8	13.3	9.4
9	11.7	11.9
10	16.0	13.9
60ℓ		
-12	7.0	8.7
-11	6.3	6.1
-9	19.2	18.9
-8	4.8	3.4
-7	17.4	16.6
-6	14.8	13.1
-5	1.2	3.2
-4	5.3	4.3
-3	30.0	26.9
-2	10.0	7.1
-1	27.5	26.7
0	37.7	40.2
1	5.9	6.7
2	13.6	15.0
3	31.3	29.2
4	7.4	4.8
5	8.6	9.0
6	20.0	18.0
7	14.9	12.9
8	6.9	7.6
9	13.6	13.7
70ℓ		
-11	11.5	13.1
-10	4.4	4.0
-8	9.6	10.6
-7	7.3	4.9
-6	7.3	8.3
-5	5.1	4.8
-4	23.0	21.7
-2	11.4	10.1
-1	9.4	10.6
0	24.4	25.6
1	8.0	8.7
2	36.6	37.2
3	7.2	7.6
4	15.9	17.3
5	20.1	19.4
6	9.3	8.7
7	11.2	12.8
8	13.4	14.4
9	5.8	5.5
80ℓ		
-10	9.2	10.6
-8	10.1	10.2
-7	7.9	6.6
-6	9.9	11.1
-5	20.6	19.6
-3	14.9	14.5
-2	22.5	22.6
-1	9.6	9.6
0	29.0	29.9
1	15.7	16.0
3	9.8	12.2
4	16.6	17.0
5	11.8	11.2
6	10.8	11.8
7	13.0	12.1
8	4.9	3.2
90ℓ		
-9	5.9	5.6
-6	11.8	12.0
-4	8.4	7.0
-3	8.5	7.8
-2	3.2	4.0
-1	7.3	7.5
0	8.9	8.8
2	9.9	10.6
3	13.1	15.0
5	7.1	8.9
6	14.5	15.0
100ℓ		
-7	3.6	5.5
-4	3.5	4.0
-3	12.7	13.1
-1	12.9	12.6
0	5.6	4.2
1	7.3	8.4
2	11.6	12.5
3	8.0	6.4
4	14.5	15.6
110ℓ		
-3	13.1	12.9
0	6.9	7.5
1	7.2	7.7

	$\lvert F_c\rvert$	$\lvert F_o\rvert$
01ℓ		
1	74.4	65.1
2	51.4	45.1
3	14.0	12.7
4	35.7	40.0
5	43.9	47.1
6	15.2	19.4
7	27.6	29.1
8	25.4	26.2
10	16.6	17.0
11	11.0	8.7
13	5.8	4.9
11ℓ		
-13	7.5	7.8
-12	15.2	15.7
-11	13.6	14.1
-10	4.9	3.9
-9	18.9	19.3
-8	25.4	24.6
-7	7.4	9.2
-6	30.9	34.9
-5	44.4	44.8
-4	16.0	16.5
-3	38.9	39.3
-2	48.7	49.8
-1	51.3	51.8
0	42.4	26.6
1	34.1	31.4
2	18.3	22.5
3	44.3	44.1
4	41.3	48.0
5	12.6	17.2
6	36.8	37.5
7	31.0	29.2
8	9.3	11.5
9	20.3	19.0
10	24.5	23.7
11	5.3	2.8
12	10.8	8.6
13	11.8	6.6
21ℓ		
-13	9.4	9.4
-12	5.6	4.6
-11	6.1	6.5
-10	20.7	22.0
-9	17.5	18.6
-8	8.5	10.5
-7	37.6	38.2
-6	36.5	37.6
-5	7.2	7.5
-4	38.1	36.3
-3	50.3	44.6
-2	28.7	31.4
-1	38.8	34.3
0	58.8	46.2
1	16.8	15.1
2	40.5	41.8
3	36.1	34.8
4	1.6	6.3
5	30.0	31.1
6	22.6	22.1
7	13.3	15.0
8	30.3	27.6
9	17.7	16.9
11	15.0	12.4
12	11.3	7.3
31ℓ		
-13	7.0	6.2
-11	11.2	11.6
-10	11.9	10.8
-8	20.5	19.0
-7	20.5	20.6
-6	17.8	18.8
-5	34.1	33.2
-4	35.9	30.7
-3	14.4	15.1
-2	45.3	38.6
-1	29.6	23.9
0	7.1	6.5
1	34.2	26.3
2	48.0	48.3
3	32.1	31.7
4	39.6	36.4
5	33.8	36.0
7	29.8	27.6
8	18.2	17.0
10	12.5	11.0
11	12.3	8.8
41ℓ		
-13	5.3	4.3
-12	9.5	8.1
-11	7.8	7.2
-10	5.3	5.0
-9	17.1	16.8
-8	19.7	17.1
-7	9.2	9.2
-6	26.6	24.6
-5	32.6	28.1
-4	9.7	11.1
-3	27.7	27.2
-2	40.0	29.7
-1	1.7	2.7
0	33.3	31.6
1	27.8	30.9
2	25.3	22.4
3	30.8	28.6
4	22.3	21.5
5	5.4	2.7
6	22.1	19.0
7	23.5	21.5
9	21.7	15.0
10	18.1	30.7
11	3.8	2.6

	$\lvert F_c\rvert$	$\lvert F_o\rvert$
51ℓ		
-12	7.3	5.0
-11	3.8	3.2
-10	14.0	12.7
-9	7.4	4.2
-8	17.0	17.5
-7	25.6	24.9
-6	15.4	15.1
-5	5.8	2.5
-4	32.4	26.4
-3	32.9	27.7
-2	2.5	2.1
-1	34.3	33.5
0	31.9	31.3
1	8.8	10.2
2	29.1	26.2
3	30.1	27.7
5	24.4	21.0
6	13.4	10.4
7	5.9	4.2
8	15.2	10.2
9	8.9	8.4
61ℓ		
-12	3.4	3.3
-11	6.3	4.2
-10	7.8	5.6
-8	17.9	16.1
-7	13.9	10.8
-6	6.9	5.1
-5	20.7	16.2
-4	12.1	9.1
-3	8.7	8.4
-2	21.0	22.0
-1	26.6	27.1
0	7.9	7.3
1	31.0	32.5
2	24.1	25.6
3	3.2	3.2
4	21.9	20.3
5	17.8	18.1
6	4.3	4.2
7	17.4	15.6
8	13.5	11.7
9	2.7	1.9
10	11.8	8.3
71ℓ		
-11	5.3	3.0
-10	2.6	3.1
-9	9.1	8.3
-8	10.7	8.6
-6	14.3	13.1
-5	19.9	17.9
-3	24.8	22.4
-2	19.8	21.4
-1	7.5	8.1
0	17.2	18.0
1	28.7	31.9
2	9.7	9.3
3	14.4	16.7
4	16.1	17.9
5	3.5	2.9
6	14.0	13.2
7	10.9	9.2
9	10.5	7.2
81ℓ		
-10	8.0	6.9
-9	3.4	2.0
-8	7.0	7.8
-7	11.7	11.9
-6	6.7	6.2
-5	5.8	5.7
-4	15.7	17.1
-3	11.4	12.5
-1	20.2	22.7
0	20.4	24.0
1	11.1	12.9
2	19.5	20.6
3	12.4	14.3
5	11.2	11.4
6	8.9	10.4
91ℓ		
-9	2.8	4.1
-8	7.9	8.0
-7	5.3	3.2
-5	9.7	10.1
-4	9.5	8.5
-3	3.9	4.0
-2	12.9	13.3
-1	7.3	5.5
1	10.7	12.3
2	13.2	13.3
4	13.9	13.9
5	11.1	10.6
101ℓ		
-7	2.9	3.3
-6	9.4	10.3
-5	7.4	7.3
-4	6.6	6.7
-3	9.2	10.3
-2	11.3	12.3
-1	3.8	4.0
0	11.6	12.4
1	9.4	10.0
3	7.4	6.9
4	8.5	7.1

	$\lvert F_c\rvert$	$\lvert F_o\rvert$
111ℓ		
-4	9.2	8.2
-3	5.8	5.7
-2	3.8	5.3
-1	8.4	8.5
0	5.7	7.6
02ℓ		
1	57.2	67.0
2	52.7	62.1
3	40.6	45.9
4	10.7	13.6
5	8.7	12.5
6	33.0	33.2
7	16.4	18.7
8	12.2	14.0
9	22.6	25.9
10	3.7	2.7
12	10.2	7.6
12ℓ		
-12	5.0	2.9
-11	5.9	7.9
-10	29.1	30.9
-8	13.0	12.8
-7	20.7	23.1
-6	12.7	14.5
-5	11.2	13.1
-4	48.0	51.0
-3	17.4	21.8
-2	39.3	39.9
-1	17.8	17.6
0	37.4	25.6
1	23.7	25.3
2	31.1	38.8
3	28.1	29.7
4	23.9	28.0
5	37.7	41.8
6	7.4	7.4
7	8.4	8.7
8	24.8	25.4
9	4.0	4.1
11	14.6	14.4
22ℓ		
-13	4.5	3.9
-12	3.3	3.6
-11	11.7	10.6
-10	6.9	9.4
-8	22.4	22.3
-7	9.3	8.9
-6	16.8	15.7
-5	34.6	37.4
-4	15.9	17.0
-3	12.9	13.7
-2	41.3	43.7
-1	62.7	58.0
0	37.4	33.0
1	46.9	44.5
2	21.3	26.0
3	19.9	21.5
4	24.0	27.1
5	26.1	29.4
6	10.5	12.4
7	31.6	35.1
8	9.3	10.1
9	3.8	3.9
10	17.1	15.4
12	8.3	3.8
32ℓ		
-12	11.5	9.1
-11	4.4	3.4
-10	3.7	3.8
-9	16.9	14.1
-8	5.7	4.8
-7	6.1	3.7
-6	34.3	32.1
-5	13.3	16.3
-4	38.3	36.8
-3	39.9	37.9
-2	19.5	19.2
-1	62.7	47.0
0	36.4	33.3
1	19.7	15.2
2	24.8	25.0
3	41.6	38.8
4	23.0	23.0
5	23.2	26.0
6	17.2	18.2
7	9.5	10.0
8	9.9	11.4
9	18.0	16.5
10	6.9	4.9
42ℓ		
-11	6.2	4.1
-10	15.7	12.2
-9	4.7	4.1
-8	13.9	16.0
-7	26.3	24.3
-6	16.0	18.2
-5	13.4	15.3
-4	12.1	13.4
-3	15.4	14.9
-2	25.0	18.3
-1	23.7	20.2
0	19.0	18.1
1	19.8	17.3
2	34.2	27.7
3	19.1	14.5
4	12.2	12.3
5	28.7	26.3
6	21.2	19.2
7	9.8	9.3
8	27.5	23.9
11	8.5	9.0

	$\lvert F_c\rvert$	$\lvert F_o\rvert$
52ℓ		
-11	6.1	3.7
-9	4.4	3.9
-8	7.0	4.1
-7	4.3	4.1
-6	3.1	3.8
-5	27.8	23.2
-4	14.1	11.9
-3	27.9	20.5
-2	22.7	19.3
-1	14.3	15.9
0	19.0	20.8
1	37.6	35.6
2	22.1	22.0
3	26.3	24.6
4	34.7	29.4
5	8.1	5.5
6	11.7	12.0
7	22.1	18.3
9	5.1	3.2
10	7.9	8.5
62ℓ		
-11	6.2	6.4
-9	12.8	9.3
-8	8.6	7.3
-7	7.8	6.9
-6	17.2	12.9
-4	14.7	13.7
-3	16.4	14.2
-2	7.4	10.7
-1	25.9	23.1
0	27.1	27.6
1	6.2	9.8
2	29.7	29.6
3	11.0	11.1
4	8.1	4.1
5	8.6	8.5
6	22.4	21.1
7	7.2	3.6
8	3.0	3.2
9	10.0	8.4
72ℓ		
-11	7.9	7.1
-10	10.4	8.3
-8	4.6	3.6
-7	11.1	9.7
-6	5.9	4.9
-5	10.9	10.2
-4	9.3	10.2
-3	3.9	3.9
-2	8.8	8.8
-1	13.0	14.4
0	3.9	3.9
1	4.0	4.1
2	16.3	17.4
3	13.8	14.6
4	15.9	17.5
5	19.7	18.6
6	5.0	2.4
7	6.7	6.1
8	17.0	13.2
82ℓ		
-10	3.3	4.2
-8	12.1	12.5
-6	7.4	7.8
-5	6.6	6.6
-4	10.6	9.5
-3	7.2	8.4
-2	19.4	16.6
-1	7.1	9.3
0	9.5	9.3
1	17.3	15.5
3	10.6	10.2
4	14.0	13.2
6	9.9	7.8
7	11.4	8.3
92ℓ		
-6	8.6	7.6
-5	7.1	7.4
-4	10.1	9.5
-3	10.9	10.2
-1	6.1	5.2
0	9.7	10.8
1	4.8	7.0
2	8.2	7.8
3	11.7	10.5
4	2.7	1.8
5	4.5	3.6
102ℓ		
-6	2.7	2.2
-5	4.5	5.1
-4	7.6	7.0
-3	3.0	2.9
-2	2.6	2.9
-1	11.4	11.7
0	4.4	3.9
1	6.5	6.1
2	9.1	6.9
03ℓ		
1	29.4	33.3
2	28.5	35.9
3	19.3	23.3
4	21.2	23.3
5	24.2	28.2
6	4.3	8.3
7	23.4	24.1
8	18.7	21.1
9	10.0	11.6
10	10.1	10.7
11	10.0	8.6

	$\lvert F_c\rvert$	$\lvert F_o\rvert$
13ℓ		
-12	7.8	5.8
-11	8.2	7.8
-9	20.2	20.1
-8	11.0	11.6
-7	10.4	10.9
-6	19.1	18.4
-5	31.5	32.0
-4	10.9	14.2
-3	37.8	44.8
-2	17.5	21.5
-1	9.2	11.0
0	28.3	16.6
1	25.0	24.0
2	23.1	21.0
3	27.1	28.2
4	21.5	26.3
6	21.5	24.1
7	13.6	16.2
9	12.4	14.4
10	12.3	10.8
12	8.7	4.2
23ℓ		
-12	4.7	3.3
-11	5.1	3.4
-10	9.8	8.4
-9	10.8	10.7
-8	6.3	4.2
-7	19.2	18.5
-6	19.3	19.1
-5	6.4	4.2
-4	18.3	17.4
-3	26.6	26.0
-2	12.2	14.2
-1	29.3	23.2
0	37.6	29.7
1	4.7	2.2
2	29.5	31.4
3	20.1	19.8
4	15.2	16.5
5	16.4	19.5
6	25.8	29.7
7	4.5	4.2
8	14.9	16.5
9	11.6	11.6
11	9.0	6.4
33ℓ		
-11	8.2	7.0
-10	7.9	9.1
-8	12.5	12.9
-7	19.4	19.0
-5	26.3	25.3
-4	27.4	23.3
-3	3.3	4.8
-2	29.0	27.9
-1	19.8	16.3
0	2.1	2.6
1	20.8	15.6
2	22.5	20.1
3	9.2	11.0
4	25.2	26.2
5	20.5	21.3
6	7.9	10.5
7	15.2	16.5
8	14.0	15.4
9	1.9	3.8
10	10.6	4.7
11	8.1	7.2
43ℓ		
-9	10.1	9.1
-8	13.7	12.1
-7	19.1	21.0
-6	18.6	18.2
-5	16.9	17.1
-3	20.7	18.3
-2	20.0	13.7
0	24.7	25.6
1	19.7	20.2
2	15.8	16.1
3	22.0	18.3
4	14.7	14.9
5	15.3	14.6
6	14.8	15.0
7	17.7	16.3
9	11.3	8.6
10	6.6	8.6
53ℓ		
-10	8.6	5.5
-9	6.9	4.8
-8	6.0	5.2
-7	16.5	16.5
-6	17.4	15.1
-5	8.7	8.7
-4	20.0	15.0
-3	17.9	13.5
-1	17.0	18.4
0	18.8	19.2
1	4.7	4.6
2	26.3	24.2
3	20.3	20.4
4	6.0	4.2
5	18.2	16.5
6	12.2	9.8
8	8.2	6.7
9	9.3	6.6

	$\lvert F_c\rvert$	$\lvert F_o\rvert$
63ℓ		
-10	7.9	6.4
-8	10.5	7.9
-7	12.9	10.2
-6	5.8	4.2
-5	13.6	10.8
-4	12.3	10.2
-2	17.7	16.3
-1	14.5	13.9
1	20.1	23.1
2	17.4	16.3
4	9.1	10.4
5	12.1	13.1
7	10.2	8.7
8	8.9	7.9
73ℓ		
-10	4.7	4.7
-9	6.5	6.1
-6	11.1	9.6
-5	10.0	9.4
-3	15.9	14.1
-2	10.2	9.5
-1	6.2	7.9
0	14.7	15.7
1	9.0	8.5
2	10.3	11.6
3	15.8	15.2
4	12.2	12.1
6	10.3	8.3
7	8.5	7.2
83ℓ		
-9	9.3	8.6
-8	3.5	2.8
-7	7.5	7.8
-6	6.2	5.8
-5	5.9	7.3
-4	8.4	8.9
-3	13.9	12.9
-2	3.5	4.1
-1	13.0	12.3
0	11.2	11.3
1	3.2	4.0
2	12.7	12.1
3	7.6	5.8
5	8.2	7.8
6	7.0	7.3
93ℓ		
-7	5.3	4.3
-5	8.7	7.8
-4	7.3	7.3
-3	3.9	3.6
-2	8.6	7.2
-1	5.9	4.3
0	5.6	5.0
1	7.9	6.3
2	6.8	6.3
4	7.4	6.7
103ℓ		
-5	3.9	3.1
-3	7.1	6.2
-2	12.9	10.2
-1	3.9	3.3
0	9.1	8.1
1	5.4	3.1
04ℓ		
1	3.8	5.0
2	13.8	17.3
3	21.1	30.1
4	14.2	19.2
5	11.7	18.6
6	16.4	19.2
7	10.5	10.1
8	9.4	6.3
9	8.2	7.4
10	7.1	7.4
11	2.8	2.4
14ℓ		
-11	3.9	3.2
-9	5.2	5.9
-8	7.8	4.8
-7	11.5	15.6
-6	3.8	6.2
-5	16.6	18.4
-4	25.0	30.3
-3	8.5	10.6
-2	15.9	16.6
-1	34.0	42.2
0	9.5	5.9
1	7.2	5.6
2	26.2	38.8
3	13.5	16.4
4	7.4	11.9
5	17.4	21.7
6	10.4	13.7
7	3.6	4.0
8	5.9	4.8
9	11.9	13.7
10	3.2	3.2
24ℓ		
-11	5.2	3.2
-10	9.2	6.2
-9	3.9	4.6
-8	8.0	6.8
-6	7.8	7.4
-5	5.5	5.0
-3	8.3	5.7
-2	20.7	18.4
-1	4.2	3.7
0	12.3	5.8
1	27.4	28.6
2	6.0	8.4
3	16.6	16.8
4	25.0	30.3
5	9.2	11.1
6	6.5	9.1
7	18.0	19.3
8	14.2	17.0
9	8.3	11.3
10	8.2	6.8

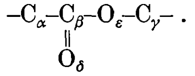
	$\lvert F_c\rvert$	$\lvert F_o\rvert$
34ℓ		
-11	5.7	3.2
-10	6.9	5.6
-9	7.9	5.2
-8	7.0	5.2
-7	6.0	4.8
-6	11.2	10.5
-5	12.5	13.1
-4	7.3	3.4
-3	18.5	18.7
-2	8.6	8.9
0	16.9	17.8
1	6.7	8.4
2	13.7	12.9
3	17.6	21.3
4	4.5	7.3
5	14.3	15.0
6	15.3	16.6
7	4.6	4.0
8	12.5	11.3
10	6.5	5.0
44ℓ		
-10	5.5	3.0
-8	4.4	3.8
-7	8.4	4.8
-6	7.4	4.8
-5	9.3	7.6
-4	15.1	14.8
-3	6.4	3.6
-1	24.2	23.2
0	6.0	10.3
1	11.7	14.3
2	15.1	16.8
4	5.5	3.8
5	10.8	10.4
6	7.3	4.8
7	6.8	4.6
8	7.5	4.8
9	4.9	4.4
54ℓ		
-8	8.4	5.2
-7	6.4	3.8
-6	7.5	7.4
-5	10.1	8.4
-4	4.9	3.8
-3	4.7	3.8
-2	15.6	18.7
-1	2.8	3.7
0	7.1	6.5
1	11.7	13.9
2	3.7	4.7
3	5.4	6.9
4	15.1	15.9
6	8.9	5.8
7	7.4	5.8
8	4.5	2.9
64ℓ		
-10	4.5	3.2
-9	6.2	4.0
-7	9.1	7.7
-6	9.2	6.6
-4	6.1	5.0
-3	11.7	11.9
-2	8.5	8.8
-1	7.9	6.2
0	12.7	13.5
1	10.2	11.3
2	6.0	4.0
3	11.8	13.9
4	4.3	3.8
5	5.3	3.7
6	5.2	4.7
7	5.7	4.0
8	6.8	3.7
74ℓ		
-8	3.8	2.8
-4	12.3	13.2
-2	9.9	8.7
-1	11.1	12.0
0	4.5	4.8
1	7.7	5.4
2	13.9	14.1
3	8.1	4.5
4	4.9	3.4
5	9.7	7.9
6	5.1	2.4
84ℓ		
-8	4.5	2.8
-7	2.4	2.4
-6	3.5	2.8
-5	7.4	8.5
-4	2.5	3.4
-3	4.4	4.3
-2	7.7	7.4
-1	3.7	4.3
0	9.2	8.7
1	10.6	9.4
3	7.0	3.1
4	8.0	3.7
5	4.1	2.0
94ℓ		
-6	4.2	2.8
-5	1.8	2.2
-4	4.4	3.2
-3	4.9	3.9
-2	1.5	2.8
-1	5.8	3.9
0	4.4	3.4
1	3.6	4.2
2	5.0	2.2
3	6.6	3.4

red.* Several cycles reduced R to 0·122. The positional parameters and standard deviations for each atom type are given in Table 2, the comparison of $|F_o|$ and $|F_c|$ in Table 5. The scattering curves used were as in Fridrichsons & Mathieson (1962*a*), the mean temperature factor being 3·0 before anisotropic vibration was allowed for.

Discussion

The experimental conditions were chosen to provide data of sufficient sin θ range and adequately populated in this range (Matheson, 1961). However, the data were recorded only to $\mu = 29°$ about b with a resultant reduction in definition in y parameters (Table 2). Consequently, the accuracy of individual bond lengths and angles depends upon the angle between the bond and the ac plane (see Table 3).

The bond lengths, grouped according to type in Table 3, are normal. One feature is of interest—the lactone groups—



$$-C_{\alpha}-\underset{\underset{O_{\delta}}{\|}}{C_{\beta}}-O_{\varepsilon}-C_{\gamma}- .$$

In both cases, the bond $\beta\varepsilon$ is shorter than bond $\varepsilon\gamma$ by approximately 0·1 Å. As a concomitant of this transference of double-bond character to the bond $\beta\varepsilon$, atom C_{γ} and bond $\varepsilon\gamma$ are constrained to lie in the same plane as C_{α}, C_{β}, O_{δ} and O_{ε}. The fit of a plane by least squares through the two lactone groups is given in Table 4. For group 1 the deviations are larger than for group 2 in accord with their relation to the projection plane. In each case, bond $\alpha\beta$ is slightly smaller than the normal value, being 1·52 Å average. Although, in this compound, the bird-cage type of ring system would tend by its nature to produce a planar conformation, the results are consistent with and supplement the observations regarding this group in himbacine hydrobromide (Fridrichsons & Mathieson, 1962*a*) and in iridomyrmecin and isoiridomyrmecin (McConnell, Mathieson & Schoenborn, 1962). The two

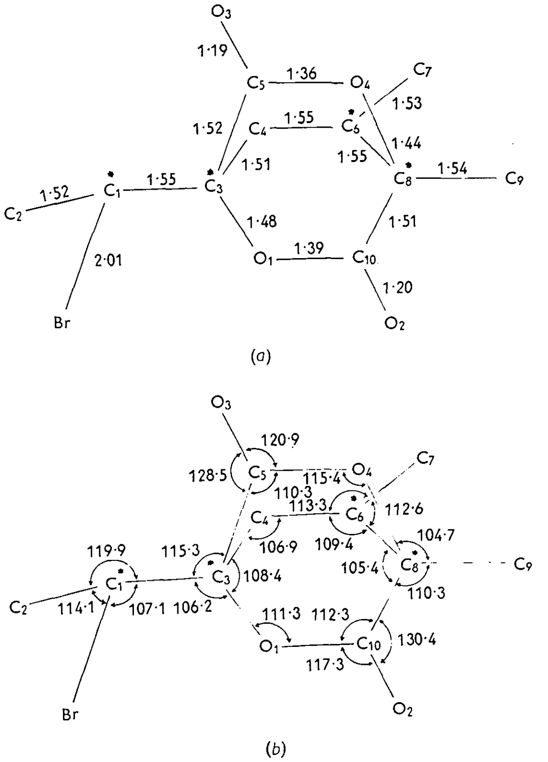


Fig. 3. (*a*) Bond lengths and (*b*) angles in the molecule calculated from the mean coordinates.

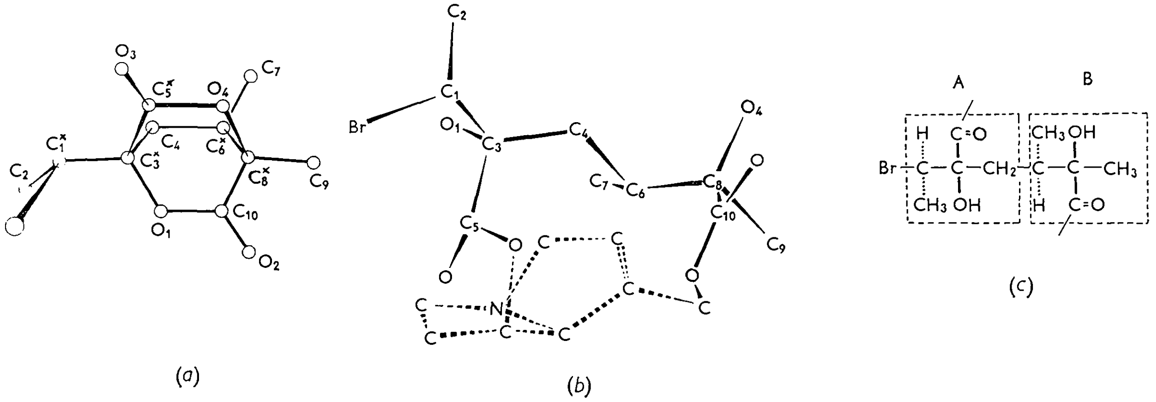


Fig. 4. The structures of (*a*) the dilactone and (*b*) jacobine bromhydrin showing their relationship by appropriate indexing of those atoms common to (*a*); (*c*) the jaconecic acid component of jacobine bromhydrin indicating the mode of linkage of the hydroxyl and carboxyl groups.

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* It appears that, although the data range was considered adequate and differences in case of certain atoms are large, no significant difference in parameter accuracy was detected. Because of the restrictive nature of the block-diagonal least-squares procedure available to us, it may be worth while to explore the effect of the weighting scheme, $w = \sin\theta$, with a full-matrix program.

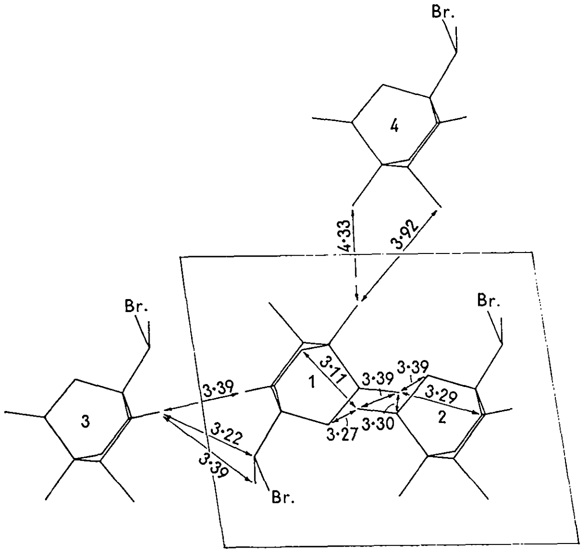

Fig. 5. Arrangement of the molecules in the crystal with approach distances derived from the mean coordinates.

factors of coplanarity and dissymmetry of nominally single C–O bonds may be considered as characteristic of lactone groups and have been proposed as a further restrictive condition in the construction of molecular models (Mathieson & Taylor, 1961).

The configurational relationships between asymmetric carbon atoms (starred in Fig. 3) are shown in Fig. 4(*a*). Comparison with the corresponding atoms in the structure of the bromhydrin of the parent alkaloid jacobine, Fig. 4(*b*), shows complete accord and thus the two analyses provide mutual support of their individual conclusions. The relative configuration of the dilactone has been placed on an absolute basis by reference to jacobine bromhydrin. That the internal configurational relationships are intimately linked with the formation of the very compact molecule is shown in Fig. 4(*c*), the internal dilactone formation following from the particular spatial dispositions of the two hydroxyl and two carboxyl groups.

The packing of the molecules is illustrated in Fig. 5. The atoms $O_1C_{10}O_2$ of the lactone group 1 (Table 4) are related by the screw axis operation to similar groups above and below, with approach distances in the range 3·15–3·39 Å (see Table 3(*b*)). O_2 is also related in the direction of $-b$ (see Table 2) to atoms C_5O_4 of the lactone group 2 by approach distances 3·29, 3·11 Å respectively, while, in the direction of $+b$, it is related to C_4 and C_6 by distances 3·29 and 3·34 Å respectively. These distances appear to indicate that the main bonding is in the direction of *b*. In the direction of *a* and *c*, bonding appears to be relatively weak, approach distances corresponding to van der Waals forces.

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