of 1·321 Å. The torsional angles for each *trans* O and F pair are 178·5(3), 175·9(3), and 174·6(3)°.

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Crystal and Molecular Structures of Dehydroeriolanin and Dehydroeriolangin in a Co-crystalline Mix

BY R. F. BRYAN AND C. J. GILMORE

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, *U.S.A.*
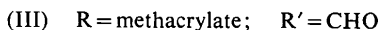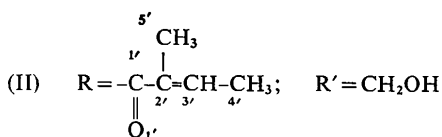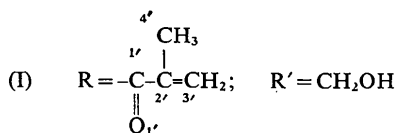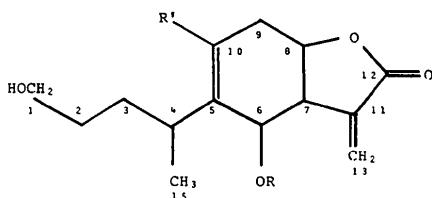
The crystal and molecular structures of dehydroeriolanin, $C_{19}H_{24}O_6$, and dehydroeriolangin, $C_{20}H_{26}O_6$, oxidation products of the antileukemic *seco*-eudesmanolides eriolanin and eriolangin are described. The two compounds cocrystallize, randomly occupying equivalent sites in an orthorhombic unit cell having $a = 8·115$ (1), $b = 10·260$ (2), and $c = 22·857$ (3) Å, with space group $P2_12_12_1$ and $Z = 4$. About 30 % of the mix in the crystal studied is dehydroeriolangin which differs from its congener only in the substitution of an angelate for a methacrylate residue at C(6). The structure was solved by direct methods of phase determination, and refined by least-squares methods to $R = 0·063$ for 1293 reflections whose intensities were measured by counter diffractometry. Hydrogen atoms were located except in the C(6) ester group. The molecules contain a cyclohexane ring in a boat conformation, 7,8-*cis* fused to an α-methylene-γ-lactone ring having a near planar half-chair conformation. The mixed C(6) ester group is roughly planar and roughly parallel to the plane of the lactone ring. Several fairly close O···H and H···H interactions are involved in the overall molecular conformation. The molecules are joined in the crystal by hydrogen bonds involving the hydroxyl and aldehyde oxygen atoms so as to form chains extended along a.

Introduction

Eriolanin (I), $C_{19}H_{26}O_6$, and eriolangin (II), $C_{20}H_{28}O_6$, are sesquiterpene lactones isolated from *Eriophyllum lanatum* Forbes (Compositae) which show activity *in*

vivo against P388-leukemia in the mouse and, *in vitro*, against cell cultures derived from human carcinoma of the nasopharynx (KB). Their isolation and structural characterization by n.m.r. and mass-spectral techniques, and by X-ray analysis of a mixed crystal of de-

hydroeriolanin (III) and dehydroeriolangin (IV) have been briefly reported (Kupchan, Baxter, Chiang, Gilmore & Bryan, 1973). We give here details of the X-ray analysis and stereochemistry of (III) and (IV), which like the parent compounds (I) and (II) belong to the rare 1,10-*seco*-eudesmanolide class of sesquiterpenes of which only one other representative, ivangulin (V), had been previously reported (Herz, Sumi, Sudarsanam & Raulais, 1967).

(I) $R = -C-C=CH_2$; $R' = CH_2OH$

(II) $R = -C-C=CH-CH_3$; $R' = CH_2OH$

(III) R = methacrylate; R' = CHO

(IV) R = angelate; R' = CHO

(V)
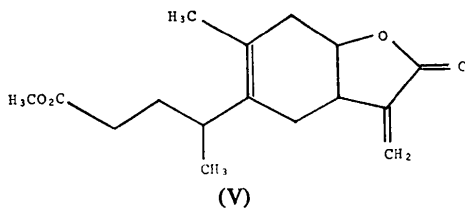
Experimental

Manganese dioxide oxidation of an apparently homogeneous crystalline fraction from a chloroform extract of plant material yielded well formed single crystals which proved to contain a mixture of (III) and (IV).

Crystal data

0·7 Dehydroeriolanin ($C_{19}H_{24}O_6$) – 0·3 dehydroeriolangin ($C_{20}H_{26}O_6$). Orthorhombic, $a = 8·115(1)$, $b = 10·260(2)$, $c = 22·857(3)$ Å ($\lambda = 1·5418$ Å). $U = 1903$ Å³, $Z = 4$ for $D_c = 1·24$ g cm⁻³. Space group $P2_12_12_1$. Systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd. $\mu = 8$ cm⁻¹ for Cu $K\alpha$ radiation.

The unit-cell dimensions were determined from the values of $\pm 2\theta$, measured on the diffractometer at room temperature, for 20 general reflections of medium

intensity. Intensity measurements were made with a crystal 0·7 × 0·7 × 0·7 mm cut from a larger needle and mounted with c* parallel to the φ axis of a Picker four-circle diffractometer operated under the control of an XDS Sigma 2 computer. Graphite monochromatized Cu $K\alpha$ radiation was used and 1616 reciprocal lattice points were surveyed within a single octant within the limits $0·03 \le \sin \theta/\lambda \le 0·56$. Scintillation counting was used with pulse-height discrimination and scattered intensity significantly above background [$I > 3\sigma(I)$] was detected at 1293 locations. The θ–2θ scan method was used with scan speed 2° min⁻¹ and scan range 3·5° in 2θ. Background measurements were made for 10 s intervals with both crystal and counter stationary at the beginning and end of each scan. Two reference reflections, measured after every 50 reflections, showed a fluctuation about their mean intensities of <1%. Structure amplitudes were derived without correction for the effects of absorption. For the crystal used transmission coefficients are estimated to be in the range 0·50 to 0·57.

Structure determination and refinement

The phase problem was solved by use of the multiple-solution weighted tangent-formula procedure (Germain, Main & Woolfson, 1971). Reflections 016, 081, and 102 were used to define the origin, 144 to define the enantiomorph. Reflections 710 and 052 were assigned initial phases of $\pm \pi/2$ and 181 phases $\pm \pi/4$ and $\pm 3\pi/4$. The solution of highest figure of merit yielded an E map containing peaks corresponding to 24 of the expected 25 non-hydrogen atoms of (III), and the remaining atom was found from a three-dimensional electron density synthesis.

Refinement was by block-diagonal least-squares methods (3 × 3, 6 × 6), and with individual anisotropic thermal parameters assumed gave $R = 0·085$ at convergence. A difference electron-density map showed 18 of the hydrogen atoms of (III) and a peak corresponding to C(4') of (IV) present with an occupancy of about 0·3, as well as some indications of slight disorder at the positions of C(2') and C(3') of (III). An examination of the apparently homogeneous starting material by chemical-ionization mass spectrometry showed that the two highest ions had m/e ratios of 365 and 351, confirming a mixture.

The refinement was continued assuming complete overlap of the atomic sites common to (III) and (IV) and an additional 0·3 carbon atom as C(4') of (IV). At convergence, with the 18 hydrogen atoms included in fixed positions and with fixed values of $B = 3·0$ Å², R was 0·063 and wR, defined as $\sum w|\Delta F|/\sum w|F_o|$, was 0·069. The standard deviation of an observation of unit weight was 0·96. No attempt was made to refine the occupancy factor for C(4').

The ratio of observations to parameters in the final cycle was 5·7:1. Weights were assigned following Grant, Killean & Lawrence (1969). Scattering functions were taken for C and O from Hanson, Herman,

Lea & Skillman (1964) and for H from Stewart, Davidson & Simpson (1965). No allowance was made for anomalous dispersion, and because of the uncertainties in the model introduced by the disorder no attempt was made to derive the absolute configuration of the molecules. A final difference map was structurally featureless with peak heights ranging from -0.25 to 0.20 $e\text{Å}^{-3}$.
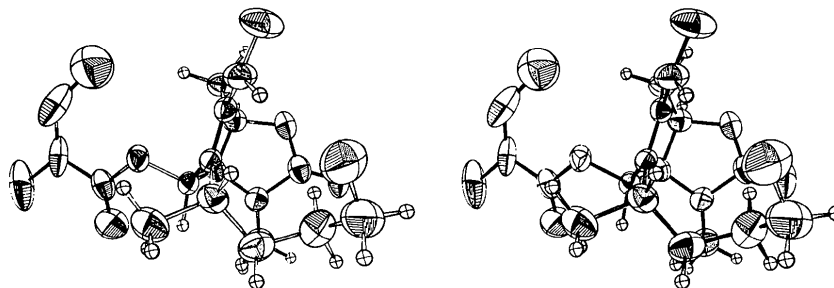

Fig. 1. Perspective stereoscopic view (*ORTEP*) of the averaged molecule of dehydroeriolanin–dehydroeriolangin as found in the crystal. Thermal ellipsoids for the C and O atoms are drawn with the 50 % probability level as boundary surface. H atoms, where located, have been included with arbitrary radius.
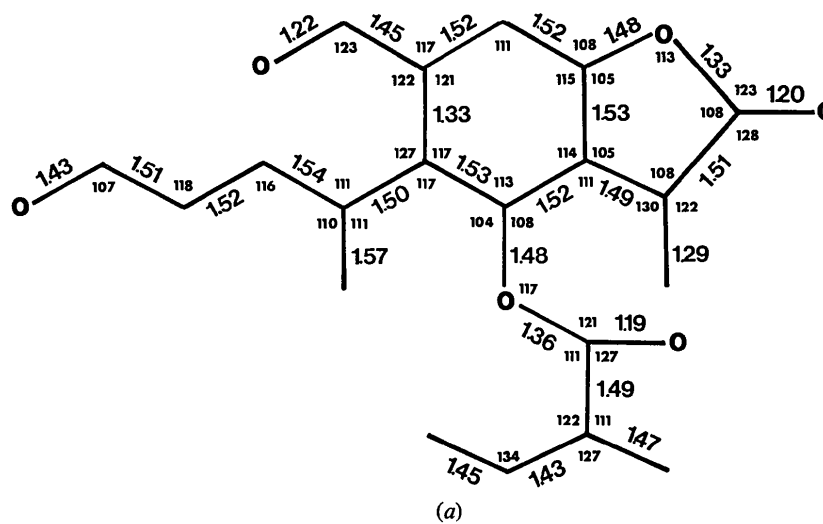

(a)

(b)
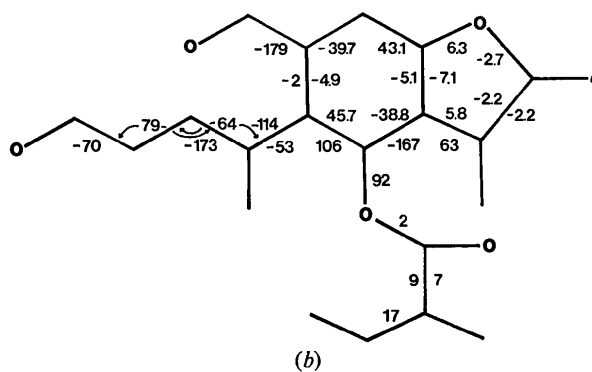
Fig. 2. (a) Bond lengths (Å) and bond angles (°) for the non-hydrogen atoms in the molecular unit. Except for the atoms involved in the molecular disorder, where the errors are uncertain, e.s.d.'s are <0.01 Å, $0.7°$. (b) Torsion angles in the molecular unit. Unless otherwise indicated these apply to *cisoid* groups of atoms about the labeled bonds. Clockwise rotations are positive, counter-clockwise rotations negative. Except for bonds involving atoms in the disordered region, e.s.d.'s are about 2°.

All calculations, other than *MULTAN*, were carried out with programs written in this laboratory for the Sigma 2 computer.*

Description and discussion of the structure

Positional and thermal parameters for the atoms in the asymmetric unit are given in Tables 1 and 2, and Fig. 1 shows a stereoscopic view of the averaged molecular structure of (III) and (IV) as found in the crystal. Bond lengths, valence angles, and torsion angles involving the non-hydrogen atoms are given in Fig. 2.

* A list of structure amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31012 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates for eriolangin*

Coordinates for C and O, and e.s.d.'s in parentheses, are multiplied by 10^4 and for H by 10^3. Oxygen and hydrogen atoms are numbered according to the carbon to which they are attached. C(4') of eriolanin corresponds to C(5') of eriolangin.

	x	y	z
C(1)	191 (9)	3031 (7)	4330 (4)
O(1)	1613 (7)	3089 (5)	4701 (2)
C(2)	349 (9)	4109 (7)	3887 (3)
C(3)	163 (8)	5505 (7)	4098 (3)
C(4)	1682 (8)	6104 (6)	4402 (3)
C(5)	3103 (7)	6213 (5)	3988 (2)
C(6)	2942 (7)	7221 (6)	3499 (2)
O(6)	4045 (5)	8293 (4)	3681 (2)
C(7)	3551 (8)	6718 (6)	2911 (2)
C(8)	5097 (7)	5871 (6)	2951 (3)
O(8)	4566 (6)	4552 (4)	2770 (2)
C(9)	5858 (7)	5765 (6)	3558 (3)
C(10)	4529 (7)	5572 (5)	4019 (2)
C(11)	2290 (8)	5859 (6)	2635 (3)
C(12)	3022 (9)	4516 (6)	2577 (3)
O(12)	2389 (7)	3551 (4)	2388 (2)
C(13)	822 (9)	6121 (8)	2460 (3)
C(14)	4913 (7)	4861 (6)	4494 (3)
O(14)	6222 (6)	4107 (5)	4535 (2)
C(15)	1233 (9)	7477 (7)	4662 (3)
C(1')	3591 (9)	9522 (6)	3532 (3)
O(1')	2341 (7)	9718 (5)	3266 (2)
C(2')	4849 (10)	10503 (6)	3707 (3)
C(3')	6424 (11)	10124 (8)	3931 (3)
C(4')	7363 (35)	8919 (23)	3918 (11)
C(5')	4271 (15)	11842 (7)	3598 (4)
H(1)	−88	318	459
H(1)'	18	212	411
H(2)	−64	394	356
H(2)'	151	403	367
H(3)	−86	552	440
H(3)'	−14	611	373
H(4)	200	540	479
H(6)	156	754	352
H(7)	379	738	258
H(8)	592	592	263
H(9)	653	664	365
H(9)'	670	494	357
H(13)	8	542	225
H(13)'	3	677	243
H(14)	388	442	481
H(15)	38	729	496
H(15)'	75	792	431
H(15)''	225	767	496

Table 2. *Thermal parameters and e.s.d.'s* ($\times 10^4$)

in the form $exp\,[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$

The numbering scheme for eriolangin is adopted. Thermal parameters for hydrogen atoms were held fixed at $B = 3\cdot0$ Å².

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	213 (16)	149 (11)	47 (3)	1 (13)	9 (6)	38 (5)
O(1)	271 (12)	181 (7)	42 (2)	−46 (9)	−13 (4)	36 (3)
C(2)	219 (15)	145 (10)	27 (2)	−28 (12)	−1 (5)	−5 (4)
C(3)	137 (12)	136 (9)	27 (2)	−14 (10)	6 (4)	8 (4)
C(4)	136 (11)	94 (7)	19 (1)	8 (9)	12 (4)	−1 (3)
C(5)	104 (10)	59 (6)	14 (1)	−8 (7)	−5 (3)	1 (2)
C(6)	125 (11)	71 (6)	16 (1)	−2 (8)	−8 (3)	−4 (3)
O(6)	192 (8)	64 (4)	19 (1)	2 (6)	−19 (3)	1 (2)
C(7)	164 (12)	64 (6)	14 (1)	10 (9)	1 (4)	3 (3)
C(8)	137 (11)	94 (7)	19 (1)	1 (9)	1 (4)	6 (3)
O(8)	209 (9)	71 (4)	21 (1)	9 (6)	2 (3)	−4 (2)
C(9)	102 (10)	97 (8)	19 (1)	−1 (8)	5 (4)	7 (3)
C(10)	121 (10)	62 (6)	14 (1)	−9 (7)	−4 (3)	1 (3)
C(11)	170 (13)	85 (7)	16 (1)	−8 (9)	−15 (4)	6 (3)
C(12)	223 (15)	82 (7)	17 (1)	6 (9)	−2 (4)	2 (3)
O(12)	345 (13)	86 (5)	31 (1)	−38 (8)	−16 (4)	−13 (2)
C(13)	229 (17)	142 (10)	33 (2)	20 (12)	−41 (6)	−3 (4)
C(14)	126 (12)	104 (8)	23 (2)	36 (11)	13 (5)	−6 (4)
O(14)	182 (9)	158 (7)	34 (1)	33 (8)	−7 (3)	39 (3)
C(15)	198 (15)	141 (9)	23 (2)	36 (11)	13 (5)	−6 (4)
C(1')	252 (15)	61 (6)	20 (1)	16 (10)	3 (4)	5 (3)
C(2')	394 (20)	77 (7)	15 (1)	−55 (12)	2 (5)	−9 (3)
C(3')	381 (22)	210 (13)	24 (2)	−136 (17)	−28 (6)	0 (4)
C(4')	Refined isotropically, $B = 11$ Å²					
C(5')	715 (34)	59 (7)	41 (3)	−12 (16)	−7 (9)	−8 (4)
O(1')	289 (12)	116 (6)	53 (2)	47 (9)	−46 (4)	20 (3)

The structure analysis shows that (III) and (IV), and hence (I) and (II), are oxygenated sesquiterpene lactones of the 1,10-*seco*-eudesmanolide class, of which only one other example, ivangulin (V), has been reported.

The observed molecular geometry supports an exact overlap of atomic sites in the crystal for IIII) and (IV), except for the terminal atoms C(3'), C(4'), and C(5') of the C(6) ester residue where disorder is apparent.* Chemical evidence, and subsequent isolation of (I) and (II) by column chromatography (Kupchan, Baxter, Chiang, Gilmore & Bryan, 1973), confirm the identification of the C(6) ester residue in (I) and (III) as methacrylate, and in (II) and (IV) as angelate. Substitution of an angelate residue for methacrylate involves only replacement of a terminal C(3') hydrogen atom by a methyl group, but the geometric anomalies in the ester group suggest that the methacrylate residue may itself be disordered by random interchange in the crystal of the C(3') methylene and C(4') methyl groups. Presumably because of the disorder, none of the hydrogen atoms of the ester group was found in the difference maps.

Within the angelate residue, atoms O(6), O(1'), C(1'), and C(2') are rigorously planar, $\sum|d_4|$, the sum of the absolute values of the displacements of the four atoms

* The reader should note the difference in numbering scheme for the atoms of the methacrylate and angelate residues. C(4') of the methacrylate corresponds to C(5') of the angelate.

from their least-squares mean plane, being only 0·007 Å. By contrast, $\sum|d_5|$ for the expected coplanar atoms C(1'), C(2'), C(3'), C(4'), and C(5') is 0·37 Å, and this plane makes an angle of 13° with the first. In the crystal the conformation adopted by the angelate residue has the carbonyl oxygen O(1') cis to the C(5') methyl group with O(1')···C(5') 2·79 Å. This conformation is opposite to that observed in euparotin bromoacetate (McPhail & Sim, 1973) and in the o-bromobenzoate of a reduction product of liatrin (Kupchan, Davies, Fujita, Cox, Restivo & Bryan, 1973) but is the same as is found in crystalline angelic acid (Porte & Robertson, 1959). However, in berlandin (Cox, 1972) the torsion angle O=C–C–CH₃ is 137° confirming that there is little hindrance to rotation about C(1')–C(2').

The axial orientation of the ester group and the 2° torsion angle C(6)–O(6)–C(1')–O(1') give O(1')···C(6) 2·66 Å and O(1')···H(6) 2·39 Å, both fairly close contacts but presumably leading to little increase in molecular energy since rotation of the ester group about C(6)–O(6) is not initially prevented by intramolecular steric factors.

The cyclohexene ring has a 1,4-diplanar (boat) conformation. The minimum energy conformations for cyclohexenes are the monoplanar (half-chair) and 1,2-diplanar (sofa) forms, with an energy difference of 7 kcal mole⁻¹ calculated by Bucourt & Hainaut (1965) between the monoplanar and 1,4-diplanar forms. A
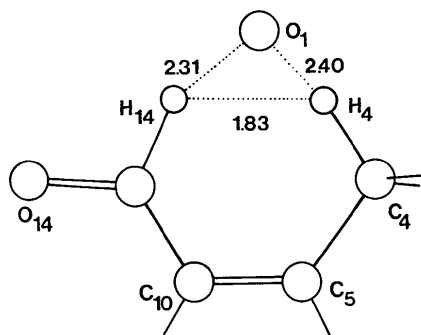
somewhat lower energy difference between these two conformations has been suggested by variable-temperature n.m.r. studies of 4-halocyclohexenes (Jensen & Bushweller, 1969), and it is difficult to identify steric features which would account for a preference for the observed conformation if the energy differences are indeed so high. However, there are some interesting steric consequences of the conformation adopted. The 1,6-diaxial contact O(6)···H(9) is 2·64 Å, corresponding to a normal van der Waals separation and not obviously energetically unfavorable. As may be seen from Fig. 3, however, H(6) is involved in two close contacts with hydrogen atoms attached to C(3) and the C(15) methyl group. This triangle of interactions acts as a steric lock constraining H(4) to lie in the plane of the olefenic bond and the conjugated aldehyde group only 1·82 Å from H(14).* As may be seen from Fig. 4, O(1) is very close to these same two hydrogen atoms, also with O···H contact distances less than the accepted sum of the van der Waals radii. Since the H(4)···H(14) interaction must be repulsive, and since the C(15) methyl group might by a small rotation readily loose the steric lock constraining H(4) in its unfavorable location, it seems clear that the O···H approaches reflect strongly attractive dipolar interactions. It is not clear whether they are strong enough to dictate the 1,4-diplanar conformation of the cyclohexene ring, but the observed conformation is dependent on the locking of H(6) by the side-chain hydrogens.

Two rigorously planar contiguous four-atom groupings may be recognized in the α-methylene-γ-lactone ring which is 7,8-cis fused to the cyclohexene ring. For C(7), C(11), C(12), and C(13), $\sum|d_4|$ is 0·006 Å, and for O(8), O(12), C(11), and C(12) is 0·005 Å These two planes are inclined to one another, the torsion angle O(8)–C(12)–C(11)–C(7) being −2·2° The description of conformation in lactone rings presents difficulties, but the notation of Altona, Geise & Romers (1968), developed for the general cyclopentane ring, may be usefully modified for the purpose by evaluating Δ for each of the five choices of φ_0 and by accepting $\bar{\Delta}$, the mean of these values, as approximating the phase angle of pseudorotation. The deviation of individual values from the mean is usually less than 3°. McPhail & Sim (1972, 1973) have used a parameter $\sum|\omega|$, the sum of the endocyclic torsion angles, to usefully describe the extent of ring pucker, and this parameter is obviously related to φ_m. However, the numerous substantial deviations from ideal forms found in these ring systems have made the use of conventional descriptions such as envelope and half-chair somewhat subjective.
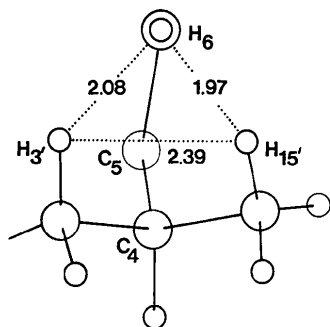

Fig. 3. View of the close interactions between hydrogen atoms involving H(6).

Fig. 4. Projection of atoms onto the olefin plane of the cyclohexene ring showing the close approaches.

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* The hydrogen positions, fixed on geometric considerations were not refined so that some deformation of the H–C–C angles may have taken place to relieve this very close approach. Even allowing for such adjustments the contact distance will remain significantly below the sum of the normal van der Waals radii, 2·4 Å.

In the present case Δ is 5° and φ_m 7°. These values may be compared to those found for a number of α,β'-unsaturated γ-lactones studied by X-ray methods and listed in Table 3. With the single exception of bromogaillardin, the values of Δ are closer to that

for the half-chair than for the envelope conformation. The mean value of the ratio $\sum|\omega|/\varphi_m$ is 3·4. The lactone ring in dehydroeriolanin is more nearly coplanar than the norm, and is intermediate in this respect between the conformations found in elephantol p-bromoben-

Table 3. *Conformational parameters for the α-methylene-γ-lactone rings in certain sesquiterpene lactones*

Compound	Δ	φ_m	$\sum|\omega|$	Stereochemistry of ring fusion	Reference
Berlandin	2	41	138	6,7-*trans*	(Cox, 1972)*
Elephantol p-bromobenzoate	3	3	11	7,8-*trans*	(McPhail & Sim, 1972)
Vernolepin	4	41	133	6,7-*trans*	(McPhail & Sim, 1971)
Dehydroeriolanin	5	7	24	7,8-*cis*	
Bromohelenalin	−9	38	126	7,8-*cis*	(Mazhar-ul-Haque & Caughlan, 1969)
Euparotin bromoacetate	−10	11	38	6,7-*trans*	(McPhail & Sim, 1973)
Bromomexicanin	13	28	94	7,8-*cis*	(Mazhar-ul-Haque & Caughlan, 1967)
Miscandenin	−4	32	109	5,6-*cis*	(Cox & Sim, 1974)
	−16	40	132	7,8-*trans*	
Bromogaillardin	21	25	86	7,8-*trans*	(Dullforce, Sim & White, 1967)

* We are indebted to Professor Sim for making available the data from which the calculation for berlandin was made.

Table 4. *Least-squares mean planes through selected atomic groupings*

Deviations of individual atoms from the planes are given in Å. Coefficients are given, in sequence, for the equation in the form $aX + bY + cZ = d$, where X, Y, and Z are in Å with respect to a Cartesian axial system coincident with the cell axes. All atoms were given equal weight in determining the equations of the planes.

Plane 1

Atom	C(1')	C(2')	O(1')	O(6)	
Devn.	0·00	0·00	0·00	0·00	$\sum|d_4| = 0·007$ Å
Coeffs.	−0·4767	0·1144	0·8716	6·7423	

Plane 2

Atom	C(1')	C(2')	C(3')	C(4')	C(5')	
Devn.	−0·01	−0·05	−0·13	0·10	0·08	$\sum|d_5| = 0·37$ Å
Coeffs.	−0·3215	−0·0306	0·9464	6·3769		

Plane 3

Atom	C(1')	C(2')	C(3')	C(5')	
Devn.	0·01	−0·02	0·01	0·01	$\sum|d_4| = 0·032$ Å
Coeffs.	−0·3813	0·0216	0·9242	6·5457	

Plane 4

Atom	O(6)	C(1')	C(2')	O(1')	C(3')	C(5')	
Devn.	−0·09	0·00	−0·01	0·09	0·09	−0·07	$\sum|d_6| = 0·35$ Å
Coeffs.	−0·4207	0·0634	0·9050	6·6802			

Plane 5

Atom	O(8)	C(12)	O(12)	C(11)	
Devn.	0·00	0·00	0·00	0·00	$\sum|d_4| = 0·005$ Å
Coeffs.	−0·3202	−0·2300	0·9190	3·5586	

Plane 6

Atom	C(7)	C(11)	C(12)	C(13)	
Devn.	0·00	0·00	0·00	0·00	$\sum|d_4| = 0·006$ Å
Coeffs.	−0·3545	−0·2384	0·9042	3·3515	

Plane 7

Atom	C(7)	C(8)	O(8)	C(11)	C(12)	C(13)	O(12)
Devn.	−0·06	0·06	−0·01	−0·01	−0·01	0·04	−0·01
Coeffs.	−0·3200	−0·2287	0·9194	3·5582	$\sum|d_7| = 0·20$ Å		

Plane 8

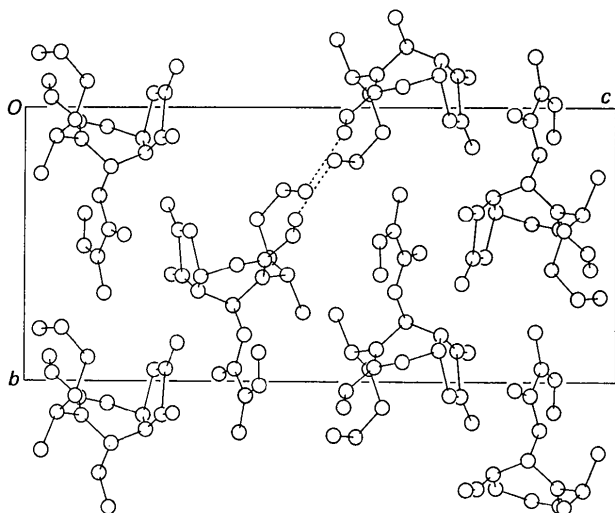| Atom	C(14)	C(10)	C(5)	C(9)	C(6)	C(4)
Devn.	−0·05	0·01	0·03	0·04	−0·05	0·03
Coeffs.	0·3914	0·7302	0·5599	10·7696	$\sum|d_6| = 0·20$ Å	

Fig. 5. Arrangement of molecules in the crystal seen in projection down a. The hydrogen bonds are indicated by broken lines. The lower of the two bonds is from the left molecule to the molecule on the right translated by a.

zoate, where the stereochemistry of ring fusion is 7,8-*trans* to a ten-membered ring, and in euparotin bromoacetate where the fusion is 6,7-*trans* to a seven-membered ring. It has been suggested that flattening of the lactone ring is more likely with fusion to larger ring systems (McPhail & Sim, 1972), but it seems clear that we are still far from being able to make useful generalizations on such systems. Least-squares mean planes through selected atomic groupings are shown in Table 4.

In the crystal the molecules are apparently linked in chains along **a** by pairs of hydrogen bonds between the hydroxyl and aldehyde oxygen atoms of adjacent molecules. The hydroxyl hydrogen atom has not been found, but the geometry of the contact is compatible with hydrogen bonding, having $C(1)-O(1)\cdots O(14)$ 104° and $O(1)\cdots O(14)$ 2·87 Å. Tables of shorter intra- and intermolecular contacts are given with the supplementary material,* and a view of the molecular packing is shown in Fig. 5.

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* See footnote on p. 2216.

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