

The Structure of 12-Hydroxydaphnetoxin, a Poisonous Constituent of *Lasiosiphon Burchellii*: an X-ray Analysis of 12-Hydroxydaphnetoxin Tribromoacetate

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The crystal structure of the tribromoacetate of 12-hydroxydaphnetoxin, a $C_{27}H_{30}O_9$ toxic diterpene isolated from the plant species *Lasiosiphon burchellii*, has been solved by three-dimensional Patterson and Fourier techniques. The crystals are orthorhombic with space group $P2_12_12_1$. The unit cell of dimensions $a=14.51$, $b=10.65$ and $c=21.91$ Å contains four formula units. The final R index for 1698 observed reflexions was 0.074. 12-Hydroxydaphnetoxin is a tricyclic diterpene consisting of a five, a six and a seven-membered carbon ring structure. The functional groups include a primary, a tertiary and two secondary alcohols, an epoxide ring, an ortho ester of benzoic acid and an α,β -unsaturated ketone.

Introduction

Lasiosiphon burchellii, a shrub of widespread occurrence in Southern Africa is known for its highly toxic qualities and frequently causes the death of sheep (Terblance, Pieterse, Adelaar & Smit, 1966). Two toxic principles of formulae $C_{34}H_{34}O_{10}$ and $C_{36}H_{36}O_{10}$ have been isolated from extracts of the plant (Coetzer & Pieterse, 1971). Upon mild alkaline hydrolysis of either compound, a common residue of formula $C_{27}H_{30}O_9$ was obtained, accompanied by the elimination of benzoic acid and cinnamic acid respectively from the two toxic compounds. This common residue showed toxic properties which were comparable to those of the parent molecules. Bromoacetylation of the $C_{27}H_{30}O_9$ fragment yielded a crystalline tribromoacetate, the crystal structure of which is discussed in this paper.

Experimental

Colourless, rhombic needles of the tribromoacetate of the $C_{27}H_{30}O_9$ compound were obtained from a 1:1 mixture of ethyl acetate and petroleum spirit. Oscillation, Weissenberg and precession photographs showed the crystals to be orthorhombic with space group $P2_12_12_1$ (hkl , no conditions; $h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$). A least-squares procedure (Busing & Levy, 1967) was used to calculate the unit-cell dimensions from spot positions measured on a Hilger and Watts four-circle automatic diffractometer.

The crystal data are:

$$\begin{aligned} a &= 14.51 \pm 0.01 \text{ \AA} \\ b &= 10.65 \pm 0.01 \\ c &= 21.91 \pm 0.02 \\ D_m &= 1.67 \text{ g.cm}^{-3} \\ D_x &= 1.68 \end{aligned}$$

$Z=4$ molecules of $C_{33}H_{33}O_{12}Br_3$
M.W. 861.35.

A single crystal with dimensions of $0.15 \times 0.25 \times 0.40$ mm was used for the intensity measurements. Intensities were collected for 1698 independent reflexions using the automatic diffractometer with Mo $K\alpha$ (Zr, β -filtered) radiation in conjunction with the ω - 2θ scanning technique. A reference standard, the intense 004 reflexion, was measured after each set of 10 reflexions. Scans of intensity against θ were made in order to correct for the background. These scans were taken parallel to central lattice rows but far enough from them in ω to prevent intersection with the tails of diffraction peaks. The standard corrections were made for Lorentz and polarization factors but no corrections were applied for absorption ($\mu R \approx 0.10$).

Table 1. Final atomic parameters (fractional coordinates and isotropic temperature factors)

Thermal parameters for Br atoms are of the form

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

The fractional coordinates and the β_{ij} 's are multiplied by 10^4 . (Standard deviations are given in parentheses.)

	x/a	y/b	z/c	B
Br(1)	845 (2)	11780 (2)	5011 (1)	
Br(2)	8015 (2)	4502 (3)	2795 (1)	
Br(3)	5055 (2)	10191 (3)	5191 (1)	
O(1)	1101 (16)	8572 (22)	4728 (10)	5.0 (5)
O(2)	2431 (15)	9639 (21)	4561 (10)	4.3 (5)
O(3)	6254 (17)	3071 (25)	3174 (11)	5.4 (6)
O(4)	5215 (15)	4583 (22)	2915 (10)	4.4 (5)
O(5)	2966 (17)	8361 (23)	5783 (10)	5.2 (5)
O(6)	3839 (13)	7858 (18)	4946 (10)	3.7 (4)
O(7)	2314 (12)	4983 (17)	2586 (8)	2.4 (4)
O(8)	2405 (13)	3818 (18)	3484 (9)	3.1 (4)
O(9)	2011 (14)	6784 (19)	3823 (9)	3.4 (4)
O(10)	4107 (16)	5713 (22)	5794 (10)	4.7 (5)

Table 1 (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>		
O(11)	4499 (13)	5833 (19)	4430 (9)	3·3 (4)		
O(12)	3036 (13)	3102 (17)	2547 (8)	2·9 (4)		
C(1)	2998 (22)	3577 (27)	4820 (14)	3·2 (6)		
C(2)	3305 (24)	3833 (33)	5384 (17)	4·7 (8)		
C(3)	3729 (21)	5181 (31)	5378 (15)	3·6 (7)		
C(4)	3604 (20)	5696 (29)	4702 (13)	3·0 (6)		
C(5)	3111 (19)	6981 (26)	4712 (13)	2·6 (6)		
C(6)	2771 (23)	7528 (31)	4072 (15)	3·8 (7)		
C(7)	2907 (20)	6864 (29)	3481 (13)	3·3 (6)		
C(8)	3430 (18)	5648 (26)	3350 (12)	2·3 (5)		
C(9)	3259 (20)	4428 (29)	3729 (13)	3·2 (6)		
C(10)	2987 (21)	4711 (27)	4368 (13)	3·0 (6)		
C(11)	4108 (21)	3564 (26)	3607 (13)	2·9 (6)		
C(12)	4484 (21)	3619 (30)	2917 (14)	3·3 (7)		
C(13)	3710 (20)	4068 (27)	2447 (13)	2·8 (6)		
C(14)	3268 (20)	5357 (28)	2633 (13)	3·2 (6)		
C(15)	4048 (24)	3957 (31)	1780 (15)	4·3 (7)		
C(16)	4841 (27)	3464 (35)	1588 (17)	5·3 (9)		
C(17)	3323 (28)	4418 (40)	1340 (17)	6·2 (9)		
C(18)	3935 (21)	2122 (29)	3771 (14)	3·7 (7)		
C(19)	3362 (26)	3050 (36)	5959 (17)	5·4 (9)		
C(20)	2707 (24)	8937 (32)	3991 (16)	4·2 (8)		
C(21)	2279 (19)	3757 (26)	2849 (13)	2·6 (6)		
C(22)	1382 (18)	3142 (27)	2729 (12)	2·6 (6)		
C(23)	854 (23)	3449 (31)	2186 (15)	4·4 (8)		
C(24)	16 (23)	2745 (31)	2063 (15)	4·1 (7)		
C(25)	-302 (26)	1831 (40)	2471 (19)	6·0 (10)		
C(26)	212 (28)	1543 (36)	3009 (17)	5·4 (9)		
C(27)	1031 (25)	2121 (36)	3173 (17)	5·2 (9)		
C(28)	6093 (27)	4153 (38)	3045 (17)	5·6 (9)		
C(29)	6781 (22)	5286 (32)	2943 (14)	4·2 (7)		
C(30)	1687 (24)	9402 (34)	4848 (15)	4·8 (8)		
C(31)	1472 (23)	10338 (33)	5408 (15)	4·6 (8)		
C(32)	3692 (26)	8390 (35)	5524 (16)	4·8 (8)		
C(33)	4558 (23)	8931 (32)	5771 (15)	4·2 (8)		
Br(1)	β_{11} 59 (1)	β_{22} 88 (2)	β_{33} 44 (1)	β_{12} 7 (2)	β_{13} 11 (1)	β_{23} 2 (1)
Br(2)	42 (1)	158 (3)	35 (1)	-6 (2)	4 (1)	-2 (1)
Br(3)	114 (2)	141 (3)	44 (1)	-57 (2)	-6 (1)	8 (2)

Structure refinement

The trial structure was deduced from three-dimensional Patterson and Fourier syntheses according to the heavy atom method. A full-matrix least-squares

Table 2. Bond distances (Å)

Standard deviations in parentheses.			
C=O bond lengths			
C(3)—O(10)	1·20 (2)		
C(28)—O(3)	1·21 (2)		
C(30)—O(1)	1·25 (2)		
C(32)—O(5)	1·20 (2)		
=C—O bond lengths			
C(30)—O(2)	1·28 (3)		
C(28)—O(4)	1·38 (2)		
C(32)—O(6)	1·40 (3)		
—C—O bond lengths			
C(20)—O(2)	1·51 (2)		
C(5)—O(6)	1·50 (2)		
C(12)—O(4)	1·48 (2)		
C(6)—O(9)	1·46 (2)		
C(7)—O(9)	1·50 (2)		
C(14)—O(7)	1·44 (2)		
C(21)—O(7)	1·43 (2)		
C(13)—O(12)	1·44 (2)		
C(21)—O(12)	1·46 (2)		
C(21)—O(8)	1·41 (2)		
C(9)—O(8)	1·50 (2)		
C(4)—O(11)	1·44 (2)		
C=C (olefinic)		C=C (aromatic)	
C(1)—C(2)	1·34 (2)	C(22)—C(23)	1·45 (3)
C(15)—C(16)	1·33 (2)	C(23)—C(24)	1·45 (3)
		C(24)—C(25)	1·40 (2)
		C(25)—C(26)	1·43 (2)
		C(26)—C(27)	1·39 (2)
		C(27)—C(22)	1·54 (4)
C-halogen			
Br(1)—C(31)	1·98 (3)		
Br(2)—C(29)	2·00 (3)		
Br(3)—C(33)	1·98 (3)		
Non-bonded interatomic distance O(6)···O(11)		2·61 (3)	

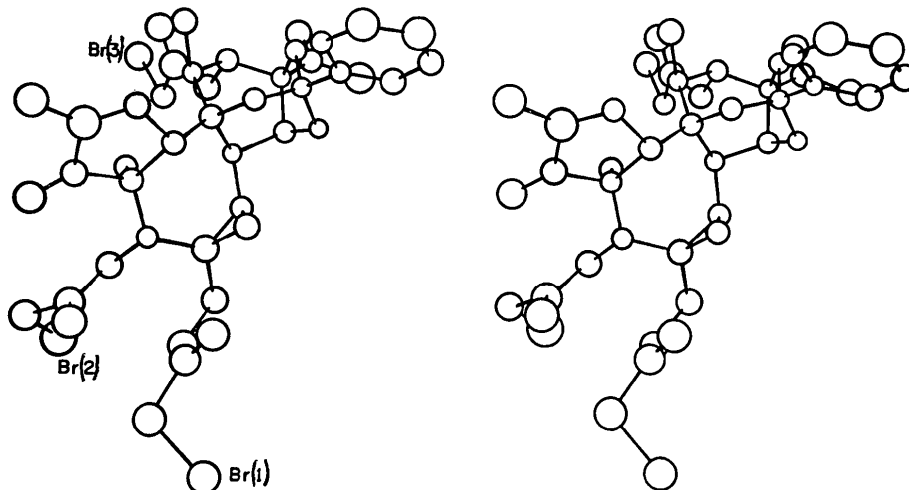
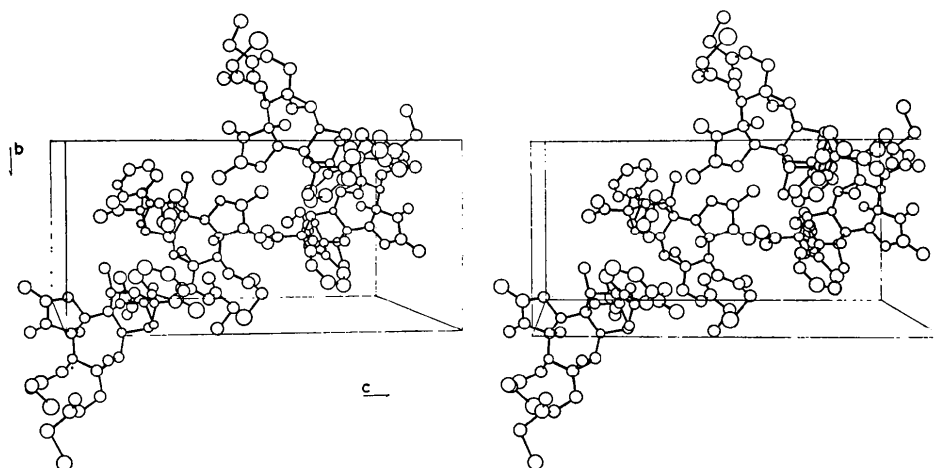


Fig. 1. Stereoscopic drawing of the molecule of 12-hydroxydaphnetoxin tribromoacetate.

Table 3. Bond angles ($^{\circ}$)

Standard deviations in parentheses.

C(20)—O(2)—C(30)	122.3 (3)	C(9)—C(11)—C(18)	113.9 (4)
C(12)—O(4)—C(28)	115.6 (6)	C(12)—C(11)—C(18)	107.4 (2)
C(5)—O(6)—C(32)	116.9 (3)	C(11)—C(12)—C(13)	112.2 (5)
C(14)—O(7)—C(21)	104.9 (2)	C(11)—C(12)—O(4)	105.8 (2)
C(9)—O(8)—C(21)	118.8 (2)	O(4)—C(12)—C(13)	107.2 (4)
C(6)—O(9)—C(7)	60.2 (3)	C(12)—C(13)—C(14)	112.5 (3)
C(13)—O(12)—C(21)	103.9 (6)	C(12)—C(13)—C(15)	111.3 (5)
C(2)—C(1)—C(10)	115.5 (5)	C(12)—C(13)—O(12)	99.5 (5)
C(1)—C(2)—C(3)	108.1 (2)	C(14)—C(13)—C(15)	116.2 (1)
C(1)—C(2)—C(19)	132.3 (5)	C(14)—C(13)—O(12)	108.0 (6)
C(3)—C(2)—C(19)	119.4 (3)	C(15)—C(13)—O(12)	107.8 (2)
C(2)—C(3)—C(4)	106.2 (3)	C(8)—C(14)—C(13)	111.1 (1)
C(2)—C(3)—O(10)	127.3 (3)	C(8)—C(14)—O(7)	105.2 (1)
C(4)—C(3)—O(10)	126.5 (5)	C(13)—C(14)—O(7)	97.6 (4)
C(3)—C(4)—C(5)	110.1 (3)	C(13)—C(15)—C(16)	127.1 (1)
C(3)—C(4)—C(10)	105.7 (4)	C(13)—C(15)—C(17)	110.9 (5)
C(3)—C(4)—O(11)	108.6 (3)	C(16)—C(15)—C(17)	121.9 (5)
C(5)—C(4)—C(10)	109.6 (5)	C(6)—C(20)—O(2)	114.2 (4)
C(5)—C(4)—O(11)	109.6 (3)	O(7)—C(21)—C(22)	113.3 (3)
C(10)—C(4)—O(11)	113.1 (4)	O(8)—C(21)—C(22)	108.1 (1)
C(4)—C(5)—C(6)	116.9 (3)	O(12)—C(21)—C(22)	111.7 (5)
C(4)—C(5)—O(6)	103.3 (6)	O(7)—C(21)—O(8)	110.7 (3)
C(6)—C(5)—O(6)	106.9 (4)	O(7)—C(21)—O(12)	103.1 (4)
C(5)—C(6)—C(7)	123.4 (6)	O(8)—C(21)—O(12)	111.9 (3)
C(5)—C(6)—O(9)	111.3 (4)	C(21)—C(22)—C(23)	120.6 (3)
C(5)—C(6)—C(20)	118.9 (1)	C(21)—C(22)—C(27)	119.3 (3)
C(7)—C(6)—O(9)	61.2 (3)	C(23)—C(22)—C(27)	120.0 (4)
C(7)—C(6)—C(20)	112.1 (4)	C(22)—C(23)—C(24)	118.4 (3)
C(20)—C(6)—O(9)	116.5 (4)	C(23)—C(24)—C(25)	121.1 (4)
C(6)—C(7)—C(8)	129.2 (2)	C(24)—C(25)—C(26)	120.3 (4)
C(6)—C(7)—O(9)	58.6 (2)	C(25)—C(26)—C(27)	124.5 (3)
C(8)—C(7)—O(9)	118.4 (3)	C(26)—C(27)—C(22)	115.6 (4)
C(7)—C(8)—C(9)	121.7 (5)	O(3)—C(28)—C(29)	129.6 (4)
C(7)—C(8)—C(14)	105.8 (1)	O(3)—C(28)—O(4)	122.8 (1)
C(9)—C(8)—C(14)	109.4 (5)	O(4)—C(28)—C(29)	107.5 (5)
C(8)—C(9)—C(10)	111.9 (5)	Br(2)—C(29)—C(28)	105.6 (9)
C(8)—C(9)—C(11)	105.9 (4)	O(1)—C(30)—C(31)	117.7 (4)
C(8)—C(9)—O(8)	107.6 (4)	O(1)—C(30)—O(2)	127.5 (4)
C(10)—C(9)—O(8)	101.9 (4)	O(2)—C(30)—C(31)	114.7 (3)
C(10)—C(9)—C(11)	119.3 (1)	Br(1)—C(31)—C(30)	103.5 (9)
C(11)—C(9)—O(8)	109.7 (5)	O(5)—C(32)—C(33)	125.7 (5)
C(1)—C(10)—C(4)	102.5 (6)	O(5)—C(32)—O(6)	123.4 (2)
C(1)—C(10)—C(9)	115.9 (5)	O(6)—C(32)—C(33)	110.8 (3)
C(4)—C(10)—C(9)	115.2 (3)	Br(3)—C(33)—C(32)	109.7 (9)
C(9)—C(11)—C(12)	113.9 (2)		

Fig. 2. Stereoscopic diagram of the molecular packing in the unit cell viewed along the c axis.

reflexions of magnitude greater than 3 × the background count, while the others (the unobserved) were omitted (Dunning & Vand, 1969). Refinement with individual isotropic thermal parameters for all the atoms yielded an *R* index [$R = (\sum |F_o| - |\sum F_c|) / \sum |F_o|$] of 0.116. Refinement with individual anisotropic thermal parameters for the 3 bromine atoms resulted in the *R* index reducing to 0.074. The form factors used were those of Hansen, Herman, Lea & Skillman (1964).

In Table 1 are listed the refined positional and ther-

Table 4. Observed and calculated structure factors

The columns are *k*, *l*, *F*_{obs} × 10 and *F*_{calc} × 10.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _{obs} × 10	<i>F</i> _{calc} × 10
0	0	0	1000	1000
0	0	1	1000	1000
0	0	2	1000	1000
0	0	3	1000	1000
0	0	4	1000	1000
0	0	5	1000	1000
0	0	6	1000	1000
0	0	7	1000	1000
0	0	8	1000	1000
0	0	9	1000	1000
0	0	10	1000	1000
0	0	11	1000	1000
0	0	12	1000	1000
0	0	13	1000	1000
0	0	14	1000	1000
0	0	15	1000	1000
0	0	16	1000	1000
0	0	17	1000	1000
0	0	18	1000	1000
0	0	19	1000	1000
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0	0	30	1000	1000
0	0	31	1000	1000
0	0	32	1000	1000
0	0	33	1000	1000
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0	0	35	1000	1000
0	0	36	1000	1000
0	0	37	1000	1000
0	0	38	1000	1000
0	0	39	1000	1000
0	0	40	1000	1000
0	0	41	1000	1000
0	0	42	1000	1000
0	0	43	1000	1000
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0	0	45	1000	1000
0	0	46	1000	1000
0	0	47	1000	1000
0	0	48	1000	1000
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0	0	50	1000	1000
0	0	51	1000	1000
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0	0	97	1000	1000
0	0	98	1000	1000
0	0	99	1000	1000
0	0	100	1000	1000

Table 4 (cont.)

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1	0	1	1000	1000
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1	0	11	1000	1000
1	0	12	1000	1000
1	0	13	1000	1000
1	0	14	1000	1000
1	0	15	1000	1000
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1	0	18	1000	1000
1	0	19	1000	1000
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1	0	76	1000	1000
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1	0	81	1000	1000
1	0	82	1000	1000
1	0	83	1000	1000
1	0	84	1000	1000
1	0	85	1000	1000
1	0	86	1000	1000
1	0	87	1000	1000
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1	0	89	1000	1000
1	0	90	1000	1000
1	0	91	1000	1000
1	0	92	1000	1000
1	0	93	1000	1000
1	0	94	1000	1000
1	0	95	1000	1000
1	0	96	1000	1000
1	0	97	1000	1000
1	0	98	1000	1000
1	0	99	1000	1000
1	0	100	1000	1000

Table 5. Equations for least-squares planes

X, *Y* and *Z* (in Å units) refer to the crystallographic axes *a*, *b* and *c* respectively.

Atoms
 C(1), C(2), C(3), C(4), C(10)
 C(22), C(23), C(24), C(25), C(26), C(27)
 O(3), O(4), C(28), C(29)
 O(1), O(2), C(30), C(31)
 O(5), O(6), C(32), C(33)

$$\begin{aligned}
 &0.8710X - 0.3779Y - 0.3138Z = -1.0400 \\
 &-0.5162X + 0.6911Y + 0.5058Z = 4.3079 \\
 &-0.1059X + 0.2425Y + 0.9644Z = 6.5480 \\
 &-0.4838X + 0.6238Y - 0.6139Z = -1.4430 \\
 &-0.2347X + 0.8772Y - 0.4190Z = 1.497
 \end{aligned}$$

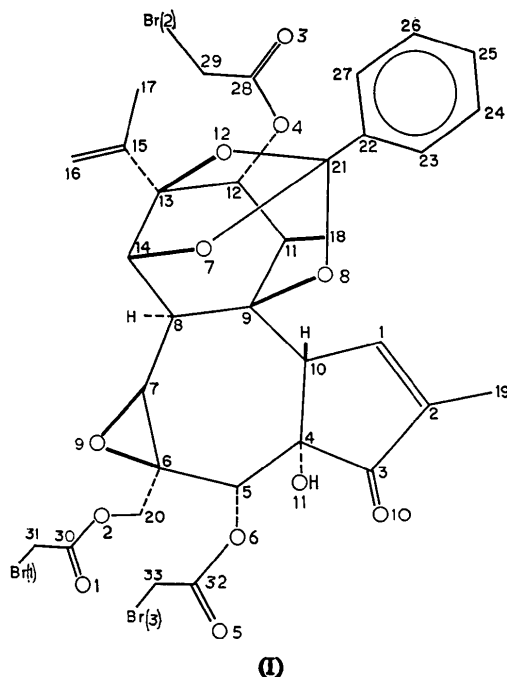
Maximum deviation from plane

- 0.08 (1)
- 0.01 (2)
- 0.02 (3)
- 0.02 (4)
- 0.01 (5)

mal parameters. The interatomic distances and bond angles given in Tables 2 and 3 were calculated using the crystallographic program *ORFFE* of Busing, Martin & Levy (1964). Observed and calculated structure factors are listed in Table 4.

Discussion

The structure of the tribromoacetate of D (I) shows the relative stereochemistry and the atomic numbering used.



A stereoscopic drawing of the molecule is given in Fig. 1.

The structural detail shows the compound D to be the 12-hydroxy analogue of daphnetoxin, the poisonous constituent of the plant species *Daphne mezereum* (Stout, Balkenhol, Poling & Hickernell, 1970). The molecular framework is that of a tricyclic diterpene consisting of a five, a six and a seven membered carbon ring structure. The ortho ester of benzoic acid is attached by cross-linking at the 9, 13 and 14 carbon atom positions of the cyclohexane ring. The remaining oxygen functions are present in the form of an epoxide [O(9)], a primary alcohol [O(2)], two secondary alcohols [O(4) and O(6)], a tertiary alcohol [O(11)] and a cyclic ketone [O(10)].

Referring to the stereopair in Fig. 1, it is seen that the cyclohexane ring adopts a slightly twisted boat conformation. The cyclopentene ring is almost flat with a maximum atomic deviation (σ) of 0.08 Å from the least-squares plane [Table 5, equation (1)] through the atoms C(1), C(2), C(3), C(4) and C(10).

The C(1)=C(2) and C(3)=O(10) bond lengths of 1.34 ± 0.02 and 1.20 ± 0.02 Å agree well with the corresponding values of 1.34 and 1.23 Å reported for these distances (Brown, McPhail & Sim, 1966). The one primary and two secondary alcohols provided the active sites for bromoacetylation of the compound D. Steric crowding of the tertiary hydroxyl group, [O(11)], apparently prevented a fourth bromoacetyl function from adding onto the molecule. The bromoacetate groups show averaged sp^3C-O , sp^2C-O and $C=O$ bond lengths of 1.49 ± 0.02 , 1.35 ± 0.03 and 1.22 ± 0.02 Å respectively, which compare favourably with the corresponding literature values of 1.47, 1.33 and 1.21 Å

(McPhail & Sim, 1966; Grant, Hamilton, Hamor-Robertson & Sim, 1963).

The best planes passing through the trigonally hybridized carbonyl carbon atom and its three bonded neighbours are given by equations (2), (3) and (4) in Table 5 for the three acetate functions. The perpendicular distances from these atoms to the corresponding planes are all < 0.02 Å showing the functional groups to be planar.

The mean aromatic C=C bond length of 1.44 ± 0.03 Å for the phenyl ring is slightly larger than the average value of 1.395 Å found in aromatic compounds. The least-squares plane [Table 5, equation (5)] through the six carbon atoms of the benzene ring shows them to be coplanar to within 0.02 Å. Both the averaged values of 1.56 ± 0.02 and 1.44 ± 0.02 Å obtained for the sp^3C-sp^3C and sp^3C-O (*o*-benzoate) bond lengths agree satisfactorily with the values of 1.545 Å in diamond and 1.43 Å respectively in saturated heterocyclic compounds (Sutton, 1965).

In the epoxide ring the mean of the C-O bond length is 1.48 ± 0.02 Å compared to the value of 1.49 Å quoted for this distance by Grant *et al.* (1963). Intramolecular hydrogen bonding is indicated between O(6) and O(11) on account of their separation of 2.61 Å.

The stereoscopic diagram in Fig. 2 illustrates the molecular packing in the unit cell viewed along the *a*-axis. Atoms O(10) and C(23) show the closest contact distance of 3.17 ± 0.03 Å. These atoms belong to parent molecules related by a *c* screw axis at $a=0.25$.

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