

(Takenaka, 1972). Programs for tangent refinement (*PHASE-III*) written by one of the authors (K.H.), bond dimensions (*BOND*) by Mr H. Yoshioka and stereoscopic drawing (*TECS*) by Dr F. Takusagawa were also used.

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The Crystal and Molecular Structure of the Bromolactone of Echinocystic Acid Diacetate, $C_{34}H_{51}O_6Br$

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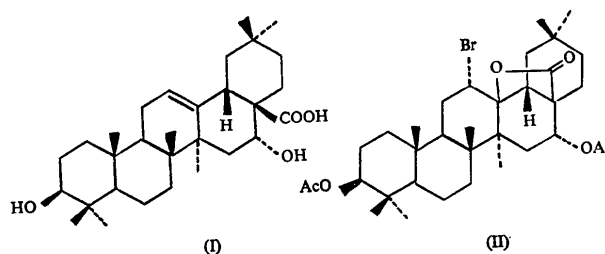
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The bromolactone of echinocystic acid diacetate crystallizes in the monoclinic system: $a=9.051$ (1), $b=10.229$ (1), $c=18.019$ (2) Å, $\beta=96.00$ (1)°, $Z=2$, space group $P2_1$. The structure has been solved with data collected on an automated diffractometer and refined by full-matrix least squares to $R=0.08$ for 3004 reflexions. The analysis confirms that the acetate group at C(16) is axial (α) and therefore *trans* to the lactone ring.

Introduction

Echinocystic acid (I) is related to the β -amyrin group of triterpenoids, a common feature of which is hydroxylation at the C(16) position (Boar & Allen, 1973). However, the precise stereochemistry at C(16) in echinocystic acid and several other 16-hydroxyoleananes has recently been under dispute (Segal & Taube, 1973). The present paper reports details of the X-ray single-crystal structure analysis of the bromolactone of echinocystic acid diacetate (II). The structure of (II) un-

equivocally establishes the presence of a *trans*-diaxial 16 α ,28-diol system in echinocystic acid (Carlisle, Lindley, Perales, Boar, McGhie & Barton, 1974).



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Experimental

The sample of the bromolactone of echinocystic acid diacetate used in this analysis was kindly supplied by Professor Sir Derek Barton, FRS, of Imperial College, University of London, and consisted of colourless sphenoidal crystals. A crystal fragment of approximate dimensions $0.47 \times 0.37 \times 0.19$ mm parallel to **a**, **b** and **c** and mounted about the *a* axis was used for the X-ray measurements. Preliminary cell dimensions and space-group information were obtained from precession and Weissenberg photographs taken with Cu radiation. Accurate cell dimensions were determined by least-squares refinement of the θ values of the Cu $K\alpha_1$ components ($\lambda = 1.5405$ Å) of 20 reflexions measured on a Hilger & Watts Y290 automated four-circle diffractometer. The crystal data are given in Table 1. The crystal density was measured by flotation in a mixture of benzene and carbon tetrachloride.

Table 1. *Crystal data*

$C_{34}H_{51}O_6Br$: M.W. 635.7; monoclinic, space group $P2_1$ (C_2^2 , No. 4).	
Cell dimensions measured at $20(\pm 1)^\circ C$	Cell volume = 1659.1 \AA^3
$a = 9.051$ (1) Å	$D_m^4 = 1.282 \text{ g cm}^{-3}$
$b = 10.229$ (1)	$D_c = 1.272$
$c = 18.019$ (2)	$Z = 2$
$\beta = 96.00$ (1°)	$\mu(\text{Cu } K\alpha) = 22.1 \text{ cm}^{-1}$
	$F(000) = 676$

Intensity data were also measured on the Y290 diffractometer using Ni-filtered Cu radiation. The $\omega/2\theta$ step-scanning technique was used with a step size of 0.01° in ω and a counting time of 1s per step. The width of scan for each reflexion as an integral number of steps was evaluated from the expression $(A + B \times \tan \theta)$ where *A* was based on a value of 90 steps for the $3\bar{2}7$ reflexion ($\theta = 23.81^\circ$) and *B*, a dispersion constant, was 0.142° for Cu $K\alpha$ radiation. A background count was taken at both ends of each scan for one tenth of the time taken for the scan. Decomposition of the crystal in the X-ray beam during data collection was monitored by measuring three reference reflexions after every 50 reflexions and the data were scaled to these reference reflexions; the overall decrease in the sum of the reference intensities was 10.5%. In this manner 3004 independent reflexions were measured within the range $0^\circ \leq \theta \leq 60^\circ$, of which 2778 had $I > 3\sigma(I)$. Lorentz and polarization corrections were applied to all reflexions but no corrections were made for absorption.

Structure solution and refinement

The position of the Br atom was determined from a three-dimensional Patterson synthesis; the *y* coordinate was fixed at zero. The remaining non-hydrogen atoms

corresponding to the known stereoisomer were located by the iterative Fourier synthesis technique using weighted coefficients (Sim, 1959). However, although the position and orientation of the C(16) acetate group were clearly defined, the electron density maxima corresponding to the $-\text{CO.Me}$ moiety were not well resolved and it was not possible to distinguish geometrically between the carbonyl O and methyl C atoms. A conformation was assumed in which the carbonyl group was antiperiplanar with respect to C(16).

Table 2. *Atomic parameters with e.s.d.'s, where appropriate, in parentheses*

(a) Positional parameters of the non-hydrogen atoms excluding the 16α -acetate group

	<i>x</i>	<i>y</i>	<i>z</i>
Br(1)	0.0604 (1)	0.0000	0.1919 (1)
C(1)	0.3922 (9)	-0.2020 (8)	0.3516 (5)
C(2)	0.4874 (9)	-0.3111 (9)	0.3865 (5)
C(3)	0.6376 (9)	-0.3161 (8)	0.3598 (4)
C(4)	0.7271 (9)	-0.1887 (9)	0.3704 (3)
C(5)	0.6217 (9)	-0.0792 (8)	0.3328 (5)
C(6)	0.6976 (9)	0.0551 (9)	0.3298 (6)
C(7)	0.6071 (9)	0.1443 (8)	0.2764 (6)
C(8)	0.4482 (8)	0.1702 (8)	0.2989 (4)
C(9)	0.3750 (8)	0.0344 (7)	0.3108 (4)
C(10)	0.4671 (8)	-0.0652 (8)	0.3631 (4)
C(11)	0.2167 (8)	0.0575 (8)	0.3334 (4)
C(12)	0.1164 (8)	0.1250 (8)	0.2734 (4)
C(13)	0.1819 (9)	0.2503 (8)	0.2452 (5)
C(14)	0.3503 (9)	0.2444 (8)	0.2309 (5)
C(15)	0.4051 (10)	0.3894 (9)	0.2264 (7)
C(16)	0.2987 (12)	0.4852 (14)	0.1890 (8)
C(17)	0.1384 (10)	0.4685 (8)	0.2056 (7)
C(18)	0.0780 (10)	0.3299 (9)	0.1886 (5)
C(19)	0.0304 (14)	0.3030 (12)	0.1051 (6)
C(20)	-0.0896 (14)	0.4035 (15)	0.0732 (7)
C(21)	-0.0304 (15)	0.5433 (15)	0.0885 (8)
C(22)	0.0252 (13)	0.5718 (11)	0.1728 (10)
C(23)	0.7844 (11)	-0.1656 (11)	0.4500 (6)
C(24)	0.8602 (11)	-0.2011 (11)	0.3249 (7)
C(25)	0.4739 (9)	-0.0301 (8)	0.4455 (4)
C(26)	0.4683 (10)	0.2505 (10)	0.3710 (6)
C(27)	0.3656 (11)	0.1754 (11)	0.1569 (5)
C(28)	0.1492 (10)	0.4645 (10)	0.2885 (9)
C(29)	-0.2350 (13)	0.3798 (13)	0.1077 (6)
C(30)	-0.1218 (18)	0.3750 (19)	-0.0107 (7)
C(31)	0.7843 (9)	-0.5174 (10)	0.3676 (5)
C(32)	0.8690 (11)	-0.6040 (11)	0.4201 (7)
O(1)	0.1741 (6)	0.3378 (6)	0.3109 (4)
O(2)	0.1438 (9)	0.5500 (8)	0.3319 (7)
O(3)	0.7205 (7)	-0.4193 (6)	0.4022 (3)
O(4)	0.7704 (8)	-0.5320 (6)	0.3005 (4)

(b) Rigid-body refinement parameters for the 16α -acetate group (Doedens, 1969)

- (i) Fractional coordinates of group origin, taken at C(33)
 $x = 0.3761$ (12); $y = 0.5355$ (12); $z = 0.0623$ (6)
- (ii) Angular parameters in degrees
 $\phi = 157.4$ (10); $\theta = 133.6$ (6); $\rho = 72.3$ (10)
- (iii) Fractional coordinates of remaining group atoms

	<i>x</i>	<i>y</i>	<i>z</i>
C(34)	0.3670	0.4745	-0.0149
O(5)	0.2956	0.4679	0.1066
O(6)	0.4465	0.6317	0.0810

(iv) Group isotropic thermal parameter, $U = 0.185$ (4) Å²

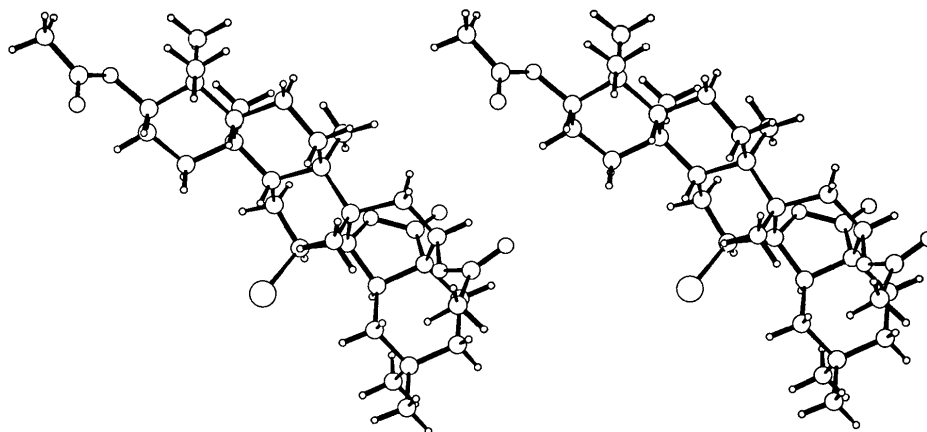


Fig. 1. A stereo drawing of the molecule of the bromolactone of echinocystic acid diacetate viewed along the normal to the plane defined by C(13), C(17) and C(18).

Full-matrix least-squares refinement with all atoms treated isotropically and using all 3004 reflexions gave an R value of 0.14. The $-\text{CO}_2\text{Me}$ moiety of the C(16) acetate group did not refine satisfactorily; the thermal vibration parameters of the individual atoms rose to unusually high values and the bond lengths and angles were stereochemically unacceptable. Refinement of models in which the methyl C atom was antiperiplanar with respect to C(16) or which combined both possibilities with the carbonyl O and methyl C atoms being given an occupancy of one half led to no significant improvement. Subsequently the complete $-\text{O}_2\text{CMe}$ group at C(16) was refined as a rigid body (Doedens, 1969).

A difference Fourier synthesis revealed diffuse electron density maxima ($0.2\text{--}0.5 \text{ e } \text{\AA}^{-3}$) corresponding to most of the non-methyl H atoms in the structure. In the remaining calculations a C-H bond distance of 1.0 \AA was assumed and the H atoms were placed in calculated positions, but no attempt was made to refine their positional or thermal parameters. Further refinement with all non-hydrogen atoms [with the exception of the C(16) acetate group] treated anisotropically proceeded by a partial full-matrix technique in which no more than 21 atoms (189 parameters) were permitted to vary in any one cycle, although an overall scale factor was always refined. Refinement was continued until all positional-parameter shifts were less than the corresponding standard deviations. The weighting scheme, $w = a_0$ for $|F_o| < 25.0$ else $w = [1 - \exp(-a_1 \sin^2 \theta / \lambda^2)] / (a_2 + |F_o| + a_3 |F_o|^2)$ with $a_0 = 0.003$, $a_1 = 5.0$, $a_2 = 50.0$ and $a_3 = 0.002$, was used to make the average values of $w\Delta^2$ uniform when analysed in terms of batches of increasing $|F_o|$ and $\sin \theta / \lambda$. The final values of R and $R' [= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}]$ were 0.078 and 0.096 respectively.

Throughout the structure factor calculations the atomic scattering factors of Hanson, Herman, Lea & Skillman (1964) were used. Allowance was made for anomalous scattering by the Br atom during the refinement with values of $\Delta f' = -0.90$ and $\Delta f'' = 1.50$

(Dauben & Templeton, 1955) for the real and imaginary dispersion corrections respectively. All calculations were performed on the CDC6600 computer at the University of London Computer Centre. The final atomic coordinates for the non-hydrogen atoms are given in Table 2.* A satisfactory tensor analysis of the anisotropic thermal-vibration parameters was obtained in all cases.

Discussion

The crystal structure of the bromolactone of echinocystic acid diacetate consists of discrete molecules, one of which is shown by a stereo drawing in Fig. 1. Fig. 2 is a schematic drawing of the molecule showing the atomic labelling. Intramolecular bond lengths and angles and further details of the molecular geometry are given in Table 3.

* A list of structure factors, anisotropic thermal parameters and the positional parameters for the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31902 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

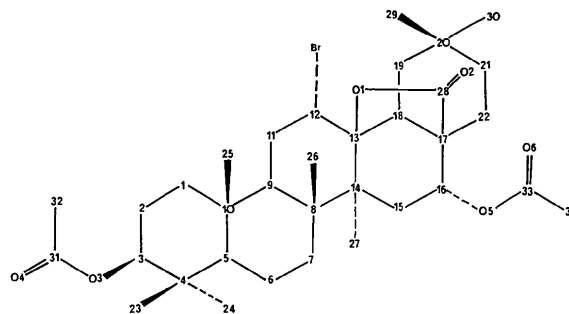


Fig. 2. A schematic drawing of the molecule of the bromolactone of echinocystic acid diacetate showing the atomic labelling.

Table 3. *Molecular geometry*

An asterisk denotes molecular parameters involved in 16 α -acetate group refinement.

(a) Bond lengths. All estimated standard deviations are less than 0.02 Å.

(i) Triterpenoid nucleus

Ring A		Ring B	
C(1)—C(2)	1.51	C(5)—C(6)	1.54
C(2)—C(3)	1.49	C(6)—C(7)	1.51
C(3)—C(4)	1.53	C(7)—C(8)	1.56
C(4)—C(5)	1.58	C(8)—C(9)	1.56
C(5)—C(10)	1.56	C(9)—C(10)	1.57
C(1)—C(10)	1.56	C(5)—C(10)	1.56

Ring C		Ring D	
C(8)—C(9)	1.56	C(13)—C(14)	1.57
C(9)—C(11)	1.55	C(14)—C(15)	1.57
C(11)—C(12)	1.50	C(15)—C(16)	1.49
C(12)—C(13)	1.52	C(16)—C(17)	1.52
C(13)—C(14)	1.57	C(17)—C(18)	1.54
C(8)—C(14)	1.62	C(13)—C(18)	1.54

Ring E	
C(17)—C(18)	1.54
C(18)—C(19)	1.55
C(19)—C(20)	1.56

(ii) Extranuclear

C(3)—O(3)	1.46	C(12)—Br	1.975
C(4)—C(23)	1.49	C(14)—C(27)	1.53
C(4)—C(24)	1.53	C(16)—O(5)	1.49
C(10)—C(25)	1.52	C(20)—C(29)	1.53
C(8)—C(26)	1.53	C(20)—C(30)	1.54

(iii) Lactone moiety

C(13)—O(1)	1.49	O(1)—C(28)	1.37
C(17)—C(28)	1.49	C(28)—O(2)	1.18

(iv) 3 β -Acetate

C(31)—O(3)	1.34	C(33)—O(5)	1.33
C(31)—C(32)	1.45	C(33)—C(34)	1.52
C(31)—O(4)	1.21	C(33)—O(6)	1.20

(b) Bond angles. All estimated standard deviations are less than or equal to 1.0°.

(i) Triterpenoid nucleus

Ring A		Ring B	
C(10)—C(1)—C(2)	112.8	C(8)—C(9)—C(10)	117.0
C(1)—C(2)—C(3)	113.1	C(9)—C(10)—C(5)	106.8
C(2)—C(3)—C(4)	114.7	C(10)—C(5)—C(6)	110.5
C(3)—C(4)—C(5)	105.2	C(5)—C(6)—C(7)	110.4
C(4)—C(5)—C(10)	116.0	C(6)—C(7)—C(8)	113.1
C(5)—C(10)—C(1)	105.3	C(7)—C(8)—C(9)	107.5
C(1)—C(10)—C(9)	107.9	C(10)—C(9)—C(11)	112.9
C(4)—C(5)—C(6)	113.4	C(7)—C(8)—C(14)	109.3

Ring C		Ring D	
C(11)—C(12)—C(13)	113.6	C(13)—C(18)—C(17)	100.1
C(9)—C(11)—C(12)	112.7	C(14)—C(13)—C(18)	116.5
C(8)—C(9)—C(11)	108.6	C(13)—C(14)—C(15)	106.8
C(9)—C(8)—C(14)	108.3	C(14)—C(15)—C(16)	116.9
C(8)—C(14)—C(13)	110.9	C(15)—C(16)—C(17)	115.0
C(14)—C(13)—C(12)	116.1	C(16)—C(17)—C(18)	113.0
C(12)—C(13)—C(18)	115.6	C(13)—C(18)—C(19)	129.6
C(8)—C(14)—C(15)	109.3	C(16)—C(17)—C(22)	117.1

Ring E			
C(19)—C(20)—C(21)	109.3	C(18)—C(17)—C(22)	110.3
C(18)—C(19)—C(20)	110.7	C(17)—C(22)—C(21)	112.0
C(19)—C(18)—C(17)	114.5	C(22)—C(21)—C(20)	114.5

Table 3 (*cont.*)

(ii) Extranuclear

C(2)—C(3)—O(3)	107.0	C(15)—C(16)—O(5)	108.6
C(4)—C(3)—O(3)	108.2	C(17)—C(16)—O(5)	105.3
C(23)—C(4)—C(3)	112.3	C(26)—C(8)—C(14)	113.4
C(23)—C(4)—C(5)	115.7	C(27)—C(14)—C(8)	110.5
C(24)—C(4)—C(3)	107.3	C(27)—C(14)—C(13)	109.8
C(24)—C(4)—C(5)	107.7	C(27)—C(14)—C(15)	109.5
C(23)—C(4)—C(24)	108.3	C(29)—C(20)—C(19)	110.0
C(25)—C(10)—C(1)	108.3	C(29)—C(20)—C(21)	111.8
C(25)—C(10)—C(5)	114.6	C(30)—C(20)—C(19)	106.9
C(25)—C(10)—C(9)	113.4	C(30)—C(20)—C(21)	112.2
C(26)—C(8)—C(7)	106.4	C(29)—C(20)—C(30)	106.6
C(26)—C(8)—C(9)	111.9		

(iii) Lactone moiety

C(12)—C(13)—O(1)	100.8	C(22)—C(17)—C(18)	112.0
C(14)—C(13)—O(1)	106.3	C(13)—O(1)—C(28)	110.7
C(18)—C(13)—O(1)	97.6	C(17)—C(28)—O(1)	108.4
C(16)—C(17)—C(28)	103.7	C(17)—C(28)—O(2)	130.1
C(18)—C(17)—C(28)	99.1	O(1)—C(28)—O(2)	121.6

(iv) 3 β -Acetate

C(3)—O(3)—O(31)	121.2	C(32)—C(31)—O(3)	112.1
O(3)—C(31)—O(4)	123.4	C(32)—C(31)—O(4)	124.6

(v) 16 α -Acetate*

C(16)—O(5)—C(33)	125.5	C(34)—C(33)—O(5)	110.8
O(5)—C(33)—O(6)	124.5	C(34)—C(33)—O(6)	124.7

(c) Torsion angles

(i) Triterpenoid nucleus

Ring A	
C(10)—C(1)—C(2)—C(3)	-56.7
C(1)—C(2)—C(3)—C(4)	56.1
C(2)—C(3)—C(4)—C(5)	-52.8
C(3)—C(4)—C(5)—C(10)	56.6
C(4)—C(5)—C(10)—C(1)	-57.6
C(5)—C(10)—C(1)—C(2)	54.8

Ring B

C(8)—C(9)—C(10)—C(5)	-53.6
C(9)—C(10)—C(5)—C(6)	57.1
C(10)—C(5)—C(6)—C(7)	-63.1
C(5)—C(6)—C(7)—C(8)	61.1
C(6)—C(7)—C(8)—C(9)	-52.7
C(7)—C(8)—C(9)—C(10)	50.9

Ring C

C(9)—C(11)—C(12)—C(13)	-52.2
C(8)—C(9)—C(11)—C(12)	63.0
C(11)—C(9)—C(8)—C(14)	-62.2
C(9)—C(8)—C(14)—C(13)	53.2
C(8)—C(14)—C(13)—C(12)	-44.1
C(11)—C(12)—C(13)—C(14)	43.3

Ring D

C(14)—C(13)—C(18)—C(17)	-67.3
C(18)—C(13)—C(14)—C(15)	55.4
C(13)—C(14)—C(15)—C(16)	-37.7
C(14)—C(15)—C(16)—C(17)	39.7
C(15)—C(16)—C(17)—C(18)	-54.7
C(16)—C(17)—C(18)—C(13)	63.3

Ring E

C(18)—C(19)—C(20)—C(21)	54.6
C(17)—C(18)—C(19)—C(20)	-57.2
C(19)—C(18)—C(17)—C(22)	54.1
C(18)—C(17)—C(22)—C(21)	-49.7
C(17)—C(22)—C(21)—C(20)	52.3
C(19)—C(20)—C(21)—C(22)	-53.7

Table 3 (cont.)

(ii) Extranuclear oxygen		
C(1)—C(2)—C(3)—O(3)	176.3	
C(5)—C(4)—C(3)—O(3)	-172.1	
C(14)—C(15)—C(16)—O(5)	-77.8	
C(18)—C(17)—C(16)—O(5)	64.8	
(iii) Lactone moiety		
C(17)—C(18)—C(13)—O(1)	45.2	φ_1
C(18)—C(13)—O(1)—C(28)	-29.1	φ_2
C(13)—O(1)—C(28)—C(17)	0.2	φ_3
O(1)—C(28)—C(17)—C(18)	29.1	φ_4
C(28)—C(17)—C(18)—C(13)	-45.9	φ_5
(iv) 3 β -Acetate		
C(2)—C(3)—O(3)—C(31)	126.5	
C(4)—C(3)—O(3)—C(31)	-109.8	
C(3)—O(3)—C(31)—C(32)	176.5	
C(3)—O(3)—C(31)—O(4)	-5.6	
(v) 16 α -Acetate		
C(15)—C(16)—O(5)—C(33)	-95.6	
C(17)—C(16)—O(5)—C(33)	141.9	
C(16)—O(5)—C(33)—C(34)	169.0*	
C(16)—O(5)—C(33)—O(6)	-11.0*	
(d) Least-squares planes defined by atomic positions and, in parentheses, distances of the atoms from the planes (Å)		
<i>X</i> , <i>Y</i> and <i>Z</i> refer to orthogonal coordinates obtained by the transformation		
$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a \sin \beta & 0 & 0 \\ 0 & b & 0 \\ a \cos \beta & 0 & c \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} .$		
Plane (i): C(2), C(3), C(5) and C(10)		
0.4376 <i>X</i> + 0.1839 <i>Y</i> + 0.8806 <i>Z</i> = 7.0737		
[C(2) -0.01, C(3) 0.01, C(5) -0.01, C(10) 0.01, C(1) -0.66, C(4) 0.70]		
Plane (ii): C(5), C(7), C(8) and C(10)		
0.4178 <i>X</i> + 0.4000 <i>Y</i> + 0.8157 <i>Z</i> = 6.4483		
[C(5) -0.02, C(7) 0.02, C(8) -0.02, C(10) 0.02, C(6) 0.72, C(9) -0.62]		
Plane (iii): C(9), C(11), C(13) and C(14)		
0.3071 <i>X</i> + 0.5824 <i>Y</i> + 0.7526 <i>Z</i> = 5.2484		
[C(9) -0.06, C(11) 0.06, C(13) -0.06, C(14) 0.06, C(8) 0.74, C(12) -0.56]		
Plane (iv): C(13), C(14), C(16) and C(17)		
0.2564 <i>X</i> + 0.3148 <i>Y</i> + 0.9139 <i>Z</i> = 5.0999		
[C(13) 0.01, C(14) -0.01, C(16) 0.01, C(17) -0.01, C(15) 0.47, C(18) -0.82]		
Plane (v): C(18), C(19), C(21) and C(22)		
0.9311 <i>X</i> + 0.1613 <i>Y</i> - 0.3272 <i>Z</i> = 0.1269		
[C(18) -0.02, C(19) 0.02, C(21) -0.02, C(22) 0.02, C(17) 0.64, C(20) -0.67]		
Plane (vi): C(17), C(28), O(1) and O(2)		
0.9878 <i>X</i> + 0.1384 <i>Y</i> - 0.0711 <i>Z</i> = 1.6362		
[C(17) 0.00, C(28) -0.01, O(1) 0.00, O(2) 0.00, C(13) 0.03, C(18) -0.71]		
Plane (vii): C(31), C(32), O(3) and O(4)		
0.8159 <i>X</i> + 0.5602 <i>Y</i> - 0.1432 <i>Z</i> = 1.9486		
[C(13) 0.01, C(32) 0.00, O(3) 0.00, O(4) 0.00, C(3) 0.08]		
Plane (viii): C(33), C(34), O(5) and O(6)*		
0.7951 <i>X</i> - 0.5692 <i>Y</i> + 0.2095 <i>Z</i> = -0.2656		
[C(16) 0.23]		

Table 3 (cont.)

Dihedral angles between normals to planes (°)					
Plane A	Plane B	Angle	Plane A	Plane B	Angle
(i)	(ii)	13.0	(iv)	(v)	90.5
(i)	(vii)	70.5	(iv)	(vi)	76.6
(ii)	(iii)	12.8	(iv)	(viii)	77.5
(iii)	(iv)	18.2			

The C—C single-bond lengths in the triterpenoid nucleus range between 1.49 and 1.62 Å with a mean value of 1.547 Å. There are significant deviations from this mean, notably the C(8)—C(14) distance of 1.62 Å. Long C(8)—C(14) bonds have also been found in several other triterpenoid structures, for example 1.609 (10) Å in 3 β -acetoxy-20-hydroxylupane (Watson, Ting & Dominguez, 1972) and 1.67 (2) Å in the bromolactone of platycodigenin (Akiyama, Tanaka & Iitaka, 1970), and are probably caused by strain in the molecule. The strain is partially caused by non-bonded repulsions between the β -methyl groups, and the part of the triterpenoid nucleus involving rings *A*, *B*, *C* and *D* distorts in order to maximize the separations of these groups. The distortion involves a twist about the long direction of the molecule [parallel to the C(10)—C(13) vector] and a bend along that direction as shown in Fig. 3, a view of the molecule parallel to the least-squares plane through atoms C(1)—C(18) inclusive. Similar distortion is found in the structure of gymnemagenin (Hoge & Nordman, 1974). The C(23)—C(25) and C(25)—C(26) β -methyl separations in the bromolactone of echinocystic acid diacetate are 3.15 and 3.16 Å respectively; the van der Waals radius of a methyl group is 2.0 Å (Pauling, 1960). Additional causes of strain in the bromolactone of echinocystic acid diacetate (and similarly for the bromolactone of platycodigenin) are non-bonded interactions between the 12 α -bromine atom and the 14 α -methyl group and the presence of the lactone group bridging C(13) and C(18). The Br—C(27) separation is 3.41 Å compared with the value of 3.95 Å for the sum of the van der Waals radii (Pauling, 1960).

The conformations of the five six-membered rings in the triterpenoid nucleus are best described in terms of asymmetry parameters (Duax & Norton, 1975); torsion angles and least-squares planes are listed in Table 3. All five rings have chair conformations, although that for ring *D* is highly distorted due to the presence of the lactone group bridging C(13) and C(17). In ring *A* rotational symmetry is dominant with $\Delta C_3^{3-4} = 0.7$ and $\Delta C_5^2 = 1.3^\circ$; ΔC_5^2 is orthogonal to ΔC_3^{3-4} . In ring *B* rotational symmetry is again dominant with $\Delta C_5^{5-6} = 2.9$, $\Delta C_5^6 = 3.2$ and $\Delta C_5^7 = 8.8^\circ$. Rings *A* and *B* are *trans* coupled and the sum of the endocyclic ring junction torsion angles $T_1 = 114.7^\circ$. In ring *C* mirror symmetry is dominant with $\Delta C_5^{11} = 0.9$, $\Delta C_2^{8-9} = 9.0$ and $\Delta C_2^{8-14} = 18.9^\circ$; the *B/C* ring junction is *trans* with $T_2 = 113.1^\circ$. In ring *D* mirror symmetry is again dominant with $\Delta C_5^{15} = 2.6$, $\Delta C_2^{13-18} = 13.3$ and $\Delta C_2^{13-14} = 26.8^\circ$; the *C/D* ring junction is *trans* with $T_3 = 99.5^\circ$. In ring *E* the relevant asymmetry parameters are

$\Delta C_5^{19} = 2.1$, $\Delta C_2^{17-22} = 2.8$ and $\Delta C_2^{17-18} = 5.5^\circ$, but the *D/E* ring junction is *cis* with $C_4 = 117.4^\circ$.

The conformation of the five-membered ring formed by the lactone group bridging C(13) and C(17) can be described in terms of pseudorotational phase parameters (Altona, Geise & Romers, 1968). The ring adopts a C(18)-envelope conformation with $\Delta = 35.6^\circ$ and $\varphi_m = -48.2^\circ$; the torsion angle C(13)–C(18)–C(17)–C(28) is taken as φ_0 . The atom O(2) is coplanar with C(28), O(1) and C(17).

In the 3β -acetate group the atoms O(3), C(31), O(4) and C(32) are coplanar and the group is anticlinal to the C(2)–C(3) bond, the torsion angle C(2)–C(3)–O(3)–C(31) = 126.5° . The carbonyl group C(31)–O(4) is syn-periplanar to C(3), the torsion angle C(3)–O(3)–C(31)–O(4) = -5.6° . Similarly in the 16α -acetate group the torsion angle C(15)–C(16)–O(5)–C(33) = -94.5° indicating an anticlinal conformation of the group with respect to the C(15)–C(16) bond and the carbonyl

group C(33)–O(6) is periplanar with respect to C(16) [whether the conformation is *syn* or *anti* cannot be determined due to the uncertainty of the O(6) and C(34) atomic positions].

The molecular packing is shown by a stereo drawing along the *a* axis in Fig. 4. The molecules lie in layers approximately parallel to the *b* axis. Each layer can be considered as composed of two sublayers, of thickness $c/2$, which are related to one another by the twofold screw axes at $z = 0$. The 16α -acetate groups are oriented towards the centre of these sublayers and there are no close intermolecular contacts involving these groups. The crystal packing may therefore allow conformational mobility of the 16α -acetate groups which is consistent with the difficulty in determining the positions of the individual atoms with any degree of precision. In the remainder of the structure there are no intermolecular separations significantly less than the sum of the respective van der Waals radii.

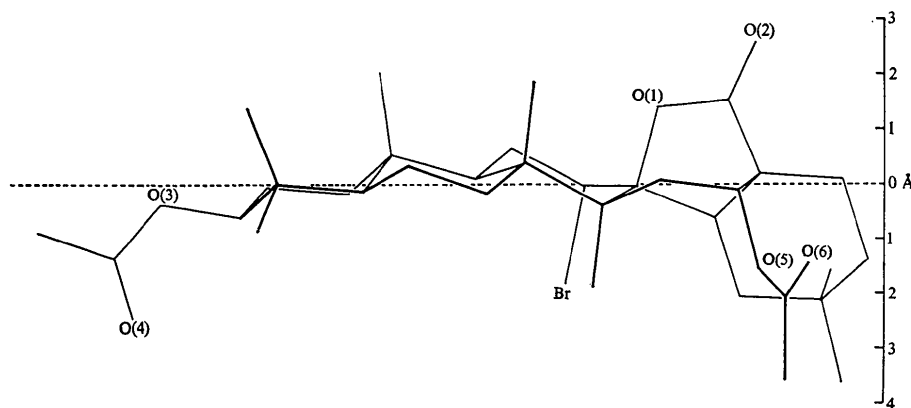


Fig. 3. A view of the molecule of the bromolactone of echinocystic acid diacetate parallel to the least-squares plane through atoms C(1)–C(18) inclusive.

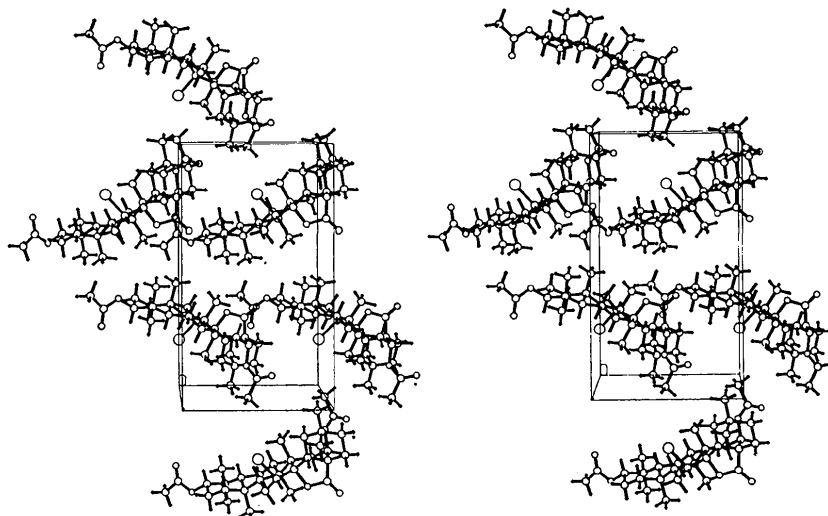


Fig. 4. A stereo drawing of the unit-cell contents viewed along the *a* axis.

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Die Kristallstruktur des Thallium(I)thio germanats $\text{Tl}_4\text{Ge}_4\text{S}_{10}$

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$\text{Tl}_4\text{Ge}_4\text{S}_{10}$ is monoclinic, space group $C2/c$, with $a=14.967$ (2), $b=14.980$ (2), $c=8.812$ (1) Å, $\beta=106.98$ (1)° and $Z=4$. The structure was determined by means of direct methods from diffractometer intensity data. The refinement yielded an R value of 0.081 for 1846 unique observed reflexions. The structure is characterized by nearly tetrahedral $[\text{Ge}_4\text{S}_{10}]^{4-}$ ions held together by Tl^+ ions. The tetrahedral anions are composed of four GeS_4 tetrahedra sharing vertices (mean Ge-S distance 2.210 Å). The Tl atoms are surrounded by nine S atoms at distances between 3.029 and 3.868 Å (mean distance 3.441 Å). The coordination polyhedra of Tl(1) and Tl(2) are similar. Six of the S atoms form a distorted pentagonal pyramid, and three further S atoms a triangle situated approximately parallel to the base of the pentagonal pyramid.

Einleitung

Kürzlich wurde über die Verbindung $\text{Tl}_2\text{Ge}_2\text{S}_5$ neben anderen Thallium(I)thio germanaten berichtet (Eulenberger & Müller, 1974). Die Thio germanate $\text{Cs}_4\text{Ge}_4\text{S}_{10} \cdot 4\text{H}_2\text{O}$ (Krebs & Pohl, 1971), $\text{Na}_4\text{Ge}_4\text{S}_{10}$ (Philippot, Ribes & Lindqvist, 1971) und $\text{Ba}_2\text{Ge}_4\text{S}_{10}$ (Ribes, Olivier-Fourcade, Philippot & Maurin, 1973), welche wie $\text{Tl}_2\text{Ge}_2\text{S}_5$ ein Ge:S-Verhältnis von 2:5 aufweisen, sind strukturchemisch durch das adamantanähnlich gebaute, aus vier über Ecken verknüpften GeS_4 -Tetraedern bestehende Anion $[\text{Ge}_4\text{S}_{10}]^{4-}$ charakterisiert. Zur Klärung der Frage, ob dies auch für $\text{Tl}_2\text{Ge}_2\text{S}_5$ trotz der $6s^2$ -Konfiguration des Tl^+ -Ions zutrifft, wurde eine Röntgenstrukturanalyse dieser Verbindung durchgeführt.

Experimentelles

Die Darstellung der Verbindung erfolgte durch Zusammenschmelzen eines stöchiometrischen Gemenges von Tl_2S und GeS_2 in einer evakuierten und abge-

schmolzenen Quarzglasampulle (10d, ca 500°C) und anschliessendes Tempern bei 300°C. Aus dem homogenen gelben Reaktionsprodukt konnte ein Einkristall mit den Dimensionen $0,06 \times 0,02 \times 0,33$ mm isoliert werden. Der Kristall wurde so montiert, dass die Richtung der Längsachse des Kristalls mit der Achse des Goniometerkopfes näherungsweise zusammenfiel.

Die aus Weissenberg-, Präzessions- und Drehkristallaufnahmen bestimmten Gitterkonstanten der monoklinen Elementarzelle wurden auf einem automatischen Vierkreis-Einkristalldiffraktometer des Typs Philips PW 1100 nach Zentrierung von 24 Reflexen nach der Methode der kleinsten Quadrate verfeinert (Mo $K\alpha$ -Strahlung, $\lambda=0,71069$ Å). Die experimentelle Dichte

Tabelle 1. Kristallographische Daten von $\text{Tl}_4\text{Ge}_4\text{S}_{10}$

Monoklin, Raumgruppe $C2/c$ (Nr 15)
 $a=14,967$ (2), $b=14,980$ (2), $c=8,812$ (1) Å
 $\beta=106,98$ (1)°
 $V=1889,6$ Å³, $Z=4$
 $D_m=4,96$, $D_x=5,03$ g cm⁻³
 $\mu(\text{Mo } K\alpha)=416$ cm⁻¹