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Phyllocladan-15-yl Bromoacetate

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Abstract. Orthorhombic, $P2_12_12_1$, $a=9{\cdot}000$ (2), $b=31{\cdot}46$ (1), $c=7{\cdot}313$ (8) Å, $C_{22}H_{35}O_2Br$, four molecules per cell, $D_m=1{\cdot}26$, $D_c=1{\cdot}31$ g cm^{-3}. The molecule has the expected conformation with all six-membered rings as chairs. Rings *B* and *C* are somewhat distorted, and the five-membered ring is in an 'envelope' conformation.

Introduction. Crystals were prepared by Professor B. R. Davis, from phyllocladan-15-one previously described (Buchanan & Davis, 1967). Data were collected on a Hilger–Watts automated diffractometer with Mo $K\alpha$ radiation, to a θ limit of 22°, giving a set of 1093 observed reflexions [$I>2\sigma(I)$]. Systematic absences were $h00$ h odd, $0k0$ k odd, $00l$ l odd. The structure was solved from Patterson and electron density syntheses, and all expected H atoms were located on a difference synthesis. Refinement by block-diagonal least-squares calculations, assuming anisotropic thermal motion for non-hydrogen atoms and an isotropic temperature factor of 5 Å^2 for H atoms, converged at $R=0{\cdot}064$. Atom coordinates and thermal parameters are listed

Table 1. *Atom coordinates and standard deviations for phyllocladan-15-yl bromoacetate*

	x	*y*	*z*
Br	0·09398 (24)	0·05837 (6)	0·07929 (27)
C(1)	0·3538 (16)	0·1695 (4)	0·8712 (18)
C(2)	0·0172 (18)	0·1932 (4)	0·8216 (24)
C(3)	0·1479 (17)	0·2170 (4)	0·7283 (22)
C(4)	0·1948 (19)	0·2554 (5)	0·8508 (24)
C(5)	0·2879 (17)	0·1892 (4)	0·7019 (18)
C(6)	0·1051 (18)	0·2353 (4)	0·5418 (22)
C(7)	0·0873 (20)	0·2024 (4)	0·3918 (20)
C(8)	0·2323 (17)	0·1768 (5)	0·3675 (19)
C(9)	0·2772 (16)	0·1543 (4)	0·5453 (18)
C(10)	0·4460 (15)	0·1383 (4)	0·5159 (18)
C(11)	0·1679 (15)	0·1180 (4)	0·5815 (25)
C(12)	0·4629 (17)	0·1048 (4)	0·3654 (19)
C(13)	0·6233 (20)	0·0937 (5)	0·3252 (21)
C(14)	0·7104 (18)	0·0856 (5)	0·5029 (23)
C(15)	0·7052 (16)	0·1254 (4)	0·6201 (21)
C(16)	0·5419 (16)	0·1263 (4)	0·6822 (19)
C(17)	0·5168 (17)	0·1578 (4)	0·8408 (19)
C(18)	0·5340 (17)	0·0789 (4)	0·7509 (20)
C(19)	0·6365 (16)	0·0527 (4)	0·6209 (20)
C(20)	0·7493 (21)	0·0248 (5)	0·7297 (26)
C(21)	0·3551 (17)	0·0351 (4)	0·8953 (20)
C(22)	0·1948 (20)	0·0229 (5)	0·8949 (25)
O(23)	0·4421 (14)	0·0229 (4)	0·0075 (16)
O(24)	0·3847 (10)	0·0621 (3)	0·7615 (12)
H(101)	0·289 (17)	0·144 (4)	0·910 (22)
H(201)	0·337 (16)	0·188 (5)	0·969 (22)
H(102)	0·042 (16)	0·180 (4)	0·930 (21)
H(202)	−0·014 (18)	0·169 (4)	0·734 (24)
H(302)	0·040 (17)	0·214 (4)	0·807 (20)
H(104)	0·194 (16)	0·246 (5)	0·991 (24)
H(204)	0·133 (16)	0·276 (4)	0·836 (20)
H(304)	0·306 (17)	0·267 (5)	0·816 (20)
H(105)	0·362 (16)	0·206 (4)	0·658 (20)
H(106)	0·179 (16)	0·258 (5)	0·501 (25)
H(206)	0·011 (16)	0·248 (5)	0·554 (22)
H(107)	0·052 (17)	0·220 (4)	0·289 (21)
H(207)	−0·017 (16)	0·185 (4)	0·415 (22)
H(108)	0·320 (17)	0·193 (5)	0·331 (21)
H(208)	0·208 (18)	0·157 (4)	0·258 (22)
H(110)	0·491 (16)	0·163 (4)	0·454 (22)
H(111)	0·181 (17)	0·104 (4)	0·708 (21)
H(211)	0·191 (16)	0·098 (4)	0·497 (21)
H(311)	0·069 (16)	0·130 (4)	0·563 (21)
H(112)	0·418 (18)	0·110 (4)	0·262 (21)
H(212)	0·408 (17)	0·080 (4)	0·394 (20)
H(113)	0·675 (16)	0·116 (4)	0·281 (22)
H(213)	0·616 (16)	0·068 (4)	0·254 (20)
H(114)	0·812 (17)	0·078 (4)	0·465 (21)
H(115)	0·733 (16)	0·147 (4)	0·562 (22)
H(215)	0·772 (18)	0·123 (4)	0·727 (22)
H(117)	0·580 (18)	0·179 (4)	0·803 (21)
H(217)	0·561 (16)	0·144 (4)	0·955 (21)
H(118)	0·578 (17)	0·076 (4)	0·860 (20)
H(119)	0·574 (17)	0·031 (4)	0·550 (21)
H(120)	0·836 (16)	0·021 (5)	0·666 (22)
H(220)	0·690 (17)	0·009 (5)	0·763 (23)
H(320)	0·767 (17)	0·041 (4)	0·838 (21)
H(122)	0·126 (16)	0·038 (4)	0·940 (21)
H(222)	0·173 (15)	0·002 (4)	0·941 (23)

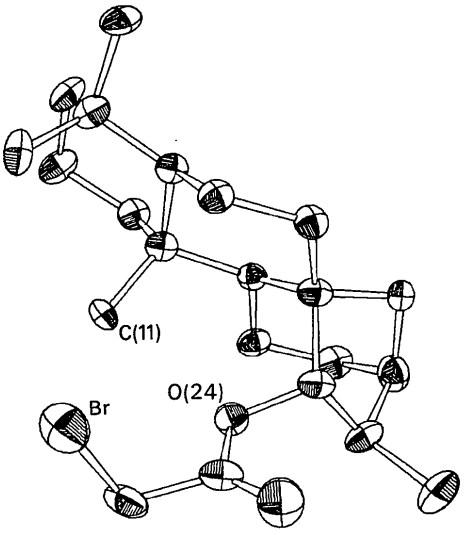

Fig. 1. An *ORTEP* diagram of the phyllocladan-15-yl bromoacetate molecule, non-hydrogen atoms only.

in Table 1, thermal parameters in Table 2.* H atoms are numbered according to the heavy atom to which they are attached. The molecule is depicted in Fig. 1, and bond lengths and angles are shown in Fig. 2. The packing of the molecules is shown in Fig. 3.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31444 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

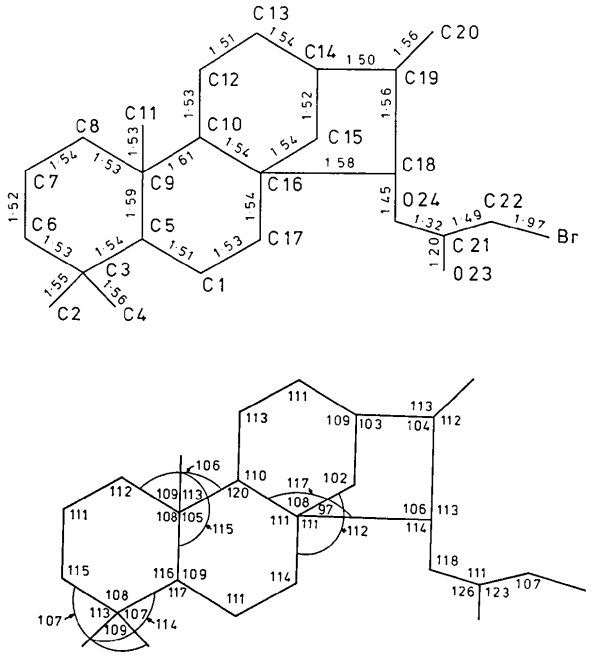

Fig. 2. Bond lengths and angles.

Table 3. *Least-squares planes*

The equations of the plane are given in the form: $Ax+By+Cz+D=0$ where A, B, C are the direction cosines with respect to the crystallographic axes. All displacements are given in Å.

1. Ring *A*: through C(5), C(6), C(7), C(9)
$-0{\cdot}737x-0{\cdot}442y+0{\cdot}510z+1{\cdot}941=0$

C(5)	0·013	C(6)	−0·013	C(7)	0·013
C(9)	−0·012	C(3)	0·675	C(8)	−0·690

2. Ring *B*: through C(1), C(9), C(10), C(17)
$-0{\cdot}234x-0{\cdot}932y+0{\cdot}277z+3{\cdot}971=0$

C(1)	0·028	C(9)	−0·026	C(10)	0·026
C(17)	−0·027	C(5)	−0·758	C(16)	0·511

3. Ring *C*: through C(10), C(13), C(14), C(16)
$-0{\cdot}560x-0{\cdot}812y+0{\cdot}165z+5{\cdot}145=0$

C(10)	−0·010	C(13)	0·010	C(14)	−0·011
C(16)	0·011	C(12)	0·581	C(15)	−0·858

4. Ring *D*: through C(14), C(16), C(18), C(19)
$0{\cdot}733x+0{\cdot}144y+0{\cdot}664z-7{\cdot}490=0$

C(14)	0·027	C(16)	−0·027	C(18)	0·041
C(19)	−0·041	C(15)	0·751		

Discussion. The molecule shows the expected configuration, as in Fig. 1. The detail of the conformation is best revealed by the deviations from planes calculated through various groups of atoms (Table 3), and by the bond angles. Ring *A* is in almost perfect chair conformation, the 1,3-diaxial repulsion between C(2) and C(11) (3·24 Å) reflecting only in the significantly greater than tetrahedral value (115°) for angle C(3)–C(5)–C(9).

Table 2. *Anisotropic thermal parameters* ($\times 10^4$) *for phyllocladan-15-yl bromoacetate*

The scattering factor for an atom is expressed as: $f=f_0 \exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Br	212 (2)	18 (0·1)	275 (3)	−18 (1·6)	88 (7)	−17 (2)
C(1)	129 (22)	8 (1)	139 (27)	−1 (9)	17 (42)	−18 (11)
C(2)	96 (21)	17 (2)	282 (39)	1 (11)	7 (55)	−7 (17)
C(3)	136 (24)	9 (2)	188 (32)	10 (10)	47 (52)	2 (14)
C(4)	170 (25)	9 (2)	336 (41)	5 (11)	149 (63)	−54 (14)
C(5)	123 (21)	7 (1)	102 (26)	−1 (9)	−47 (44)	9 (11)
C(6)	154 (22)	10 (2)	256 (36)	37 (10)	−5 (64)	−6 (13)
C(7)	202 (24)	11 (2)	152 (29)	39 (11)	−51 (61)	17 (13)
C(8)	138 (23)	10 (2)	138 (30)	4 (10)	−38 (48)	−4 (12)
C(9)	128 (21)	7 (1)	95 (27)	−2 (9)	−22 (45)	7 (11)
C(10)	93 (20)	6 (1)	127 (25)	−2 (9)	36 (39)	5 (10)
C(11)	86 (18)	9 (1)	240 (34)	−11 (9)	−39 (54)	−15 (15)
C(12)	153 (23)	7 (1)	131 (29)	9 (10)	−47 (46)	−1 (11)
C(13)	199 (28)	12 (2)	159 (29)	10 (12)	−38 (61)	−7 (14)
C(14)	104 (22)	12 (2)	238 (34)	−9 (11)	−27 (51)	10 (14)
C(15)	82 (18)	8 (1)	219 (34)	0 (9)	−9 (47)	−10 (13)
C(16)	139 (24)	7 (1)	128 (26)	−1 (9)	−58 (45)	−4 (11)
C(17)	115 (21)	10 (2)	142 (26)	−5 (10)	−7 (45)	−16 (12)
C(18)	154 (24)	6 (1)	138 (26)	−6 (9)	−29 (48)	3 (11)
C(19)	168 (24)	8 (2)	216 (32)	23 (10)	−56 (50)	16 (13)
C(20)	185 (29)	17 (2)	259 (40)	41 (13)	−23 (64)	34 (17)
C(21)	201 (26)	7 (1)	152 (28)	−6 (10)	14 (52)	1 (12)
C(22)	182 (25)	8 (2)	287 (39)	−31 (11)	117 (63)	2 (15)
O(23)	192 (21)	19 (1)	284 (25)	−12 (9)	−29 (40)	75 (10)
O(24)	114 (13)	9 (1)	157 (16)	−3 (7)	−10 (31)	22 (8)

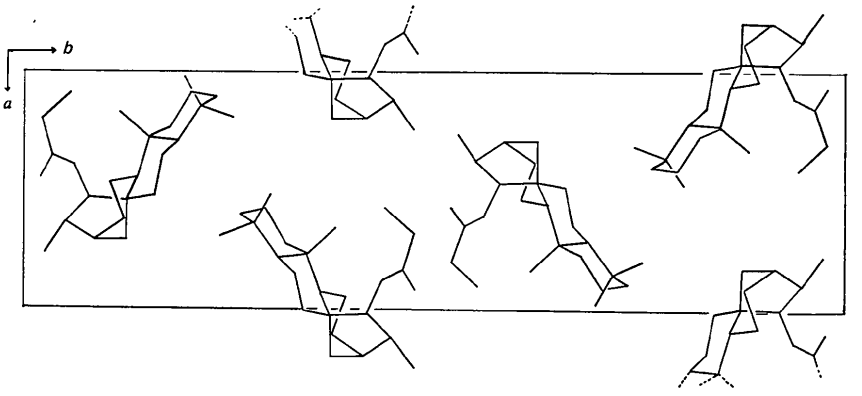

Fig. 3. Projection of the unit cell on (001).

The non-bonded intramolecular approach of 2·94 Å between C(11) and O(24) of the bromoacetate group, causes ring *B* to be slightly flattened, so that C(16) is only 0·51 Å from the central plane, and angle C(9)–C(10)–C(16) assumes the value 120°. This flattening of ring *B* together with the constraint imposed by closure of the five-membered ring *D*, results in a distinct distortion of ring *C*, as demonstrated by the displacements of C(12) and C(15) from the central plane, 0·58 and 0·86 Å respectively. Ring *D* itself is forced to adopt the 'envelope' conformation, four atoms coplanar and one distinctly out of plane, and the strain in this ring is evidenced by the fact that all internal angles are significantly less than tetrahedral.

Within error bond lengths are normal, other than C(9)–C(10) which is unusually long. There are no intermolecular approaches likely to affect the molecular stereochemistry.

Reference

BUCHANAN, J. G. ST. C. & DAVIS, B. R. (1967). *Chem. Commun.* pp. 1142–1143.

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The *exo* Isomer of Methyl 3,4-*O*-Ethylidene-β-D-galactopyranoside

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Abstract. $C_9H_{16}O_6$, orthorhombic, $P2_12_12_1$, $a=16{\cdot}678$ (1), $b=12{\cdot}828$ (2), $c=4{\cdot}9165$ (9) Å, $Z=4$.

Introduction. In studies (Garegg, Lindberg & Swahn, 1974) of the extracellular M-antigen, which can be isolated from the mutant *Salmonella typhimurium* 395 MRO-M1, it was found that there exists an asymmetric acetal carbon of the ethylidene group linked to the terminal D-galactose residue. To elucidate the configuration about the asymmetric carbon, a crystal structure determination of one of the two isomers of methyl 3,4-*O*-ethylidene-β-D-galactopyranoside was performed.

The cell dimensions were obtained from a powder photograph taken at 25 °C in a Guiner–Hägg focusing camera with monochromatized Cu $K\alpha_1$ radiation ($\lambda=1{\cdot}54051$ Å) and KCl ($a=6{\cdot}29300$ Å; Hambling, 1953) as an internal standard. The film was measured with a SAAB film-scanner (Abrahamsson, 1966) connected to an IBM 1800 computer. Data were evaluated by the program *PILT* (Malmros & Werner, 1973).

A prismatic crystal ($0{\cdot}02\times0{\cdot}03\times0{\cdot}2$ mm) was mounted on a goniometer head approximately along the *c* axis. Three-dimensional data were collected on a computer-controlled single-crystal diffractometer (Philips PW 1100) with graphite-monochromatized Cu $K\alpha$ radiation. The 1185 available independent data within $\theta<60°$ were collected with θ–2θ scan of 2° scan width; background intensities were measured on each side. The 944 data with $\sigma(I_{net})/I_{net}<0{\cdot}5$ were considered observable and used in the subsequent calculations. The calculations of $\sigma(I_{net})$ were based on conventional counter statistics. Lorentz and polarization factors were applied, but not absorption corrections.