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Acta Cryst. (1995). **C51**, 1330–1333

2,3-Dideoxy-D-*erythro*-hex-2-enono-1,5-lactone and 1,4-Lactone Obtained from Tri-*O*-acetyl-D-glucal

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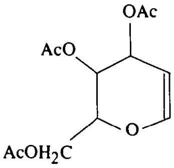
Abstract

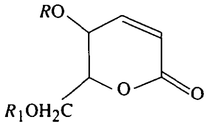
In the 1,5-lactone compound, $C_6H_8O_4$, the lactone ring adopts a conformation between sofa and half-chair. The five-membered ring in the 1,4-lactone, $C_6H_8O_4$, is planar and the side chain is in a staggered conformation. The crystal structure of the 1,5-lactone is stabilized by both O—H···O and C—H···O hydrogen bonds and that of the 1,4-lactone by O—H···O hydrogen bonds.

Comment

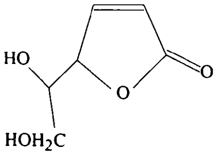
The title compounds have been prepared in high yield from tri-*O*-acetyl-D-glucal (1). Treatment of (1) with pyridinium chlorochromate in dichloroethane gave the acetate form of the δ-lactone, (2*a*) (R = R_1 = Ac) (Rollin & Sinay, 1981). This diacetate lactone, when treated with titanium tetraisopropoxide in 2-propanol for 72 h, gave 2,3-dideoxy-D-*erythro*-hex-2-enono-1,5-lactone (2*b*) (R = R_1 = H) and some of the γ-lactone (3). Prolonging the reaction for a further 24 h gave mainly the γ-lactone, 2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone, (3). Both the lactones are substructures for many natural products and have been synthesized with a view to elaborating them into some of these natural products (El-Zayat *et al.*, 1985). The crystal structure determination of these compounds was carried out to confirm the structures proposed from spectroscopic data.



(1)



(2*a*) $R = R_1$ = Ac
(2*b*) $R = R_1$ = H



(3)

Fig. 1 shows an *ORTEP* (Johnson, 1965) plot and the numbering scheme of the δ-lactone. The bond lengths and angles observed in this structure are comparable with those of other related naturally occurring lactones, such as asperlin, asperlinol (Fukuyama, Katsube, Noda, Hamasaki & Hatsuda, 1978) and goniotriol (Alkofahi, Ma, McKenzie, Byrn & McLaughlin, 1989). In general, the observed bond lengths are shorter than the normal values, *e.g.* the C1—C2 single-bond distance of 1.469 (3) Å is much less than the usual value and may be attributed to the effect of the neighbouring C═O and C═C bonds. The δ-lactone ring adopts a conformation in between sofa and half-chair, the corresponding asymmetry parameters are ΔC_s(C2) = 0.099 (1) and ΔC_2(C1—C2) = 0.045 (1) (Nardelli, 1983*a*), with more tendency towards half-chair conformation. This intermediate conformation of the lactone ring is observed in asperlin and in the chloro-derivative of asperlinol, but the sofa conformation is favoured in asperlinol and goniotriol. The two hydroxyl groups

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form intermolecular hydrogen bonds between themselves, leaving the carbonyl O2 atom to form a C—H···O hydrogen bond. This is quite different from the general observations where the carbonyl O atom always tries to form hydrogen bonds with the hydroxyl group. The molecular packing is shown in Fig. 3.

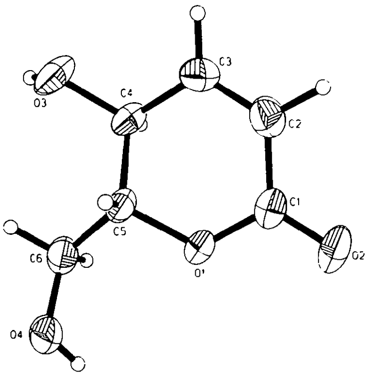

Fig. 1. Structure of the δ-lactone showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

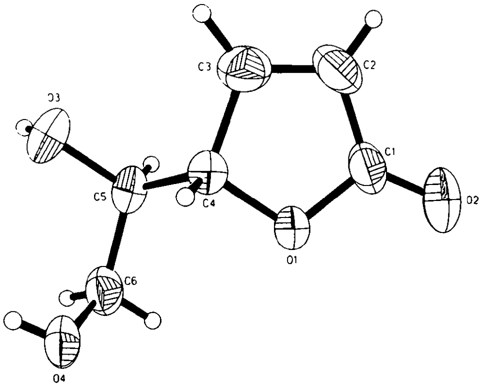

Fig. 2. Structure of the γ-lactone showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

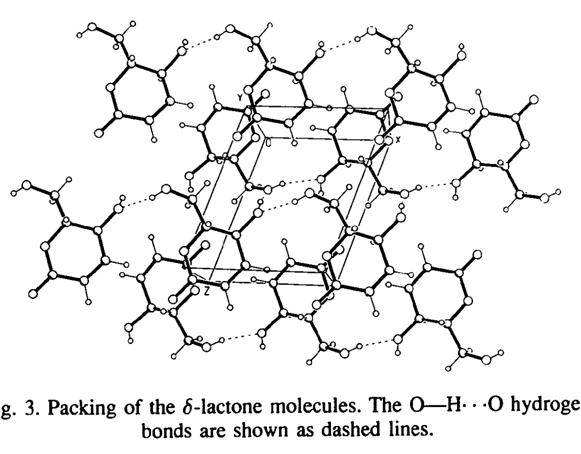

Fig. 3. Packing of the δ-lactone molecules. The O—H···O hydrogen bonds are shown as dashed lines.

A displacement ellipsoid plot with the numbering scheme of the γ-lactone is given in Fig. 2. The molecule consists of a five-membered ring system comprising the lactone group and an acyclic side chain. The bond lengths and angles are generally comparable to those values expected for the type of hybridization and also with those observed in related structures, such as L-ascorbic acid (Hvoslef, 1968), 2-acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone (Ruzic-Toros & Lazarini, 1978), D-*iso*-ascorbic acid (Azarnia, Berman & Rosenstein, 1972). The C—C bond lengths are in the range 1.448 (4)–1.526 (3) Å. The single bonds C1—C2 [1.448 (4) Å] and C3—C4 [1.484(4) Å] are shortened compared with the standard value of 1.54 Å, owing to the influence of the C═O and C═C double bonds. The asymmetric C—O bonds, C4—O1 [1.448 (3) Å] and C1—O1 [1.361 (3) Å] are common for this type of structure. The endocyclic bond angles are in the range 103.9 (2)–109.5 (3)°; the mean value of 108° is equal to the calculated angle in a regular pentagon. The five-membered ring is planar with a maximum deviation of 0.014 (3) Å for C1. The orientation of the side chain with respect to the planar moiety is governed by a rotation about the C4—C5 single bond. In the present case the conformation of the side chain is 'staggered', with O3 staggered between H(C4) and C3. Both the hydroxyl groups are involved in intermolecular hydrogen bonds; the O4H group acts as an acceptor in O3—H···O4 and as a donor in O4—H···O2. The hydrogen bonds are shown in the packing diagram in Fig. 4.

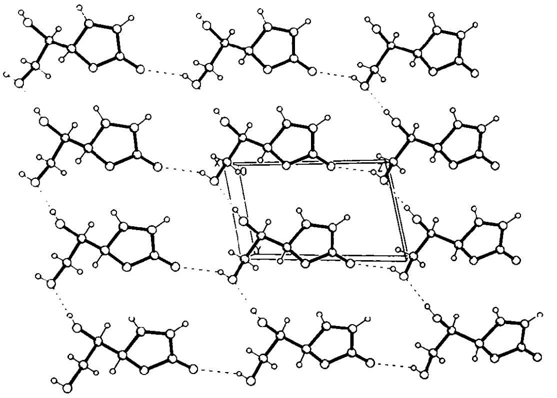

Fig. 4. Packing of the γ-lactone molecules. The hydrogen bonds are shown as dashed lines.

Experimental

The crystals of the two title compounds were obtained from ethyl acetate solution.

Compound (2*b*)

Crystal data

$C_6H_8O_4$

$M_r = 144.12$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Monoclinic
$P2_1$
$a = 6.361$ (1) Å
$b = 6.878$ (1) Å
$c = 7.801$ (1) Å
$\beta = 108.47$ (1)°
$V = 323.72$ (8) Å^3
$Z = 2$
$D_x = 1.479$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 8$–15°
$\mu = 0.126$ mm^{-1}
$T = 293$ (2) K
Transparent plates
0.54 × 0.42 × 0.12 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: none
1165 measured reflections
929 independent reflections
905 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0132$
$\theta_{\max} = 27.50°$
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 8$
$l = -10 \rightarrow 9$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0310$
$wR(F^2) = 0.0879$
$S = 1.080$
929 reflections
123 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 0.0279P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.214$ e Å^{-3}
$\Delta\rho_{\min} = -0.195$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2*b*)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.0339 (2)	0.4964 (2)	0.09899 (15)	0.0372 (3)
O2	−0.0213 (2)	0.5014 (3)	−0.1926 (2)	0.0490 (4)
O3	−0.3632 (2)	0.4479 (3)	0.3514 (2)	0.0477 (4)
O4	0.3035 (2)	0.6075 (3)	0.4557 (2)	0.0465 (4)
C1	−0.1035 (3)	0.4996 (3)	−0.0722 (2)	0.0347 (4)
C2	−0.3432 (3)	0.4938 (4)	−0.1015 (2)	0.0417 (4)
C3	−0.4199 (3)	0.4458 (3)	0.0318 (2)	0.0391 (4)
C4	−0.2646 (3)	0.4015 (3)	0.2159 (2)	0.0337 (4)
C5	−0.0564 (3)	0.5242 (3)	0.2469 (2)	0.0316 (4)
C6	0.1272 (3)	0.4717 (3)	0.4175 (2)	0.0395 (4)

Table 2. *Selected geometric parameters* (Å, °) *for* (2*b*)

O1—C1	1.345 (2)	C1—C2	1.469 (3)
O1—C5	1.455 (2)	C2—C3	1.323 (3)
O2—C1	1.211 (2)	C3—C4	1.494 (2)
O3—C4	1.426 (2)	C4—C5	1.523 (2)
O4—C6	1.417 (3)	C5—C6	1.510 (2)
C1—O1—C5	119.32 (13)	O3—C4—C5	108.8 (2)
O2—C1—O1	117.8 (2)	C3—C4—C5	108.47 (15)
O2—C1—C2	124.14 (15)	O1—C5—C6	106.13 (12)
O1—C1—C2	118.06 (14)	O1—C5—C4	110.04 (14)
C3—C2—C1	120.48 (15)	C6—C5—C4	113.5 (2)
C2—C3—C4	120.68 (15)	O4—C6—C5	111.6 (2)
O3—C4—C3	110.78 (14)		
C5—O1—C1—O2	170.6 (2)	C1—O1—C5—C4	45.4 (2)
C5—O1—C1—C2	−11.4 (3)	O3—C4—C5—O1	−173.54 (14)
O2—C1—C2—C3	163.7 (2)	C3—C4—C5—O1	−52.9 (2)
O1—C1—C2—C3	−14.0 (3)	O3—C4—C5—C6	67.7 (2)
C1—C2—C3—C4	1.6 (4)	C3—C4—C5—C6	−171.69 (15)
C2—C3—C4—O3	151.1 (2)	O1—C5—C6—O4	68.1 (2)
C2—C3—C4—C5	31.8 (3)	C4—C5—C6—O4	−170.98 (15)
C1—O1—C5—C6	168.5 (2)		

Table 3. *Hydrogen-bonding geometry* (Å, °) *for* (2*b*)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3B···O4$^{\rm i}$	0.84 (4)	1.94 (4)	2.744 (3)	161 (4)
O4—H4B···O3$^{\rm ii}$	0.78 (3)	1.97 (3)	2.730 (2)	165 (3)
C4—H4A···O2$^{\rm iii}$	0.95 (3)	2.46 (3)	3.336 (3)	152 (2)
C5—H5A···O2$^{\rm iv}$	0.96 (3)	2.56 (3)	3.366 (3)	142 (2)
C6—H6B···O2$^{\rm v}$	0.99 (3)	2.49 (2)	3.466 (2)	168 (2)

Symmetry codes: (i) $-x, y-\frac{1}{2}, 1-z$; (ii) $1+x, y, z$; (iii) $-x, y-\frac{1}{2}, -z$; (iv) $-x, \frac{1}{2}+y, -z$; (v) $x, y, 1+z$.

Compound (3)

Crystal data

$C_6H_8O_4$
$M_r = 144.12$
Triclinic
$P1$
$a = 4.558$ (1) Å
$b = 4.747$ (1) Å
$c = 8.150$ (2) Å
$\alpha = 76.92$ (2)°
$\beta = 75.61$ (2)°
$\gamma = 82.17$ (2)°
$V = 165.78$ (6) Å^3
$Z = 1$
$D_x = 1.444$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–15°
$\mu = 0.123$ mm^{-1}
$T = 293$ (2) K
Transparent needle
0.60 × 0.24 × 0.22 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: none
1153 measured reflections
1153 independent reflections
915 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 29.97°$
$h = -1 \rightarrow 5$
$k = -6 \rightarrow 6$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0372$
$wR(F^2) = 0.0916$
$S = 1.046$
1153 reflections
123 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.210$ e Å^{-3}
$\Delta\rho_{\min} = -0.184$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (3)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.0016 (4)	1.0357 (3)	0.3963 (2)	0.0427 (5)
O2	−0.2950 (6)	1.0448 (5)	0.6571 (2)	0.0745 (7)
O3	0.4817 (5)	0.5988 (4)	0.1053 (2)	0.0515 (5)

O4	0.3391 (4)	1.1911 (4)	−0.0442 (2)	0.0477 (5)
C1	−0.0826 (7)	0.9249 (5)	0.5688 (3)	0.0478 (6)
C2	0.1187 (8)	0.6690 (6)	0.6104 (4)	0.0558 (7)
C3	0.3220 (8)	0.6302 (6)	0.4686 (4)	0.0526 (7)
C4	0.2669 (6)	0.8631 (5)	0.3212 (3)	0.0370 (5)
C5	0.2037 (6)	0.7533 (5)	0.1723 (3)	0.0381 (5)
C6	0.1122 (7)	0.9958 (6)	0.0339 (3)	0.0438 (6)

Table 5. *Selected geometric parameters* (Å, °) *for* (3)

O1—C1	1.361 (3)	C1—C2	1.448 (4)
O1—C4	1.448 (3)	C2—C3	1.321 (4)
O2—C1	1.212 (3)	C3—C4	1.484 (4)
O3—C5	1.423 (3)	C4—C5	1.526 (3)
O4—C6	1.415 (3)	C5—C6	1.512 (4)
C1—O1—C4	109.1 (2)	O1—C4—C5	109.7 (2)
O2—C1—O1	119.5 (2)	C3—C4—C5	114.2 (2)
O2—C1—C2	132.1 (2)	O3—C5—C6	110.9 (2)
O1—C1—C2	108.4 (2)	O3—C5—C4	104.4 (2)
C3—C2—C1	109.0 (3)	C6—C5—C4	112.9 (2)
C2—C3—C4	109.5 (3)	O4—C6—C5	113.0 (2)
O1—C4—C3	103.9 (2)		
C4—O1—C1—O2	177.5 (3)	C2—C3—C4—C5	−120.8 (2)
C4—O1—C1—C2	−2.2 (3)	O1—C4—C5—O3	177.7 (2)
O2—C1—C2—C3	−178.3 (3)	C3—C4—C5—O3	−66.1 (3)
O1—C1—C2—C3	1.4 (3)	O1—C4—C5—C6	57.0 (3)
C1—C2—C3—C4	0.0 (3)	C3—C4—C5—C6	173.2 (3)
C1—O1—C4—C3	2.2 (3)	O3—C5—C6—O4	−56.1 (3)
C1—O1—C4—C5	124.7 (2)	C4—C5—C6—O4	60.8 (3)
C2—C3—C4—O1	−1.3 (3)		

Table 6. *Hydrogen-bonding geometry* (Å, °) *for* (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···O4^{i}	0.83 (6)	1.91 (5)	2.730 (3)	172 (4)
O4—H4A···O2^{ii}	0.72 (3)	2.11 (3)	2.761 (3)	150 (3)

Symmetry codes: (i) $x, y-1, z$; (ii) $1+x, y, z-1$.

Both structures were solved by direct methods and refined by full-matrix least-squares technique. All the H atoms in the two structures were located from difference Fourier maps and refined isotropically.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELX*90 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*93; *PARST* (Nardelli, 1983*b*).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grants R&D 123-3417-2201 and 123-3104-2502. KS and H-BA acknowledge the Visiting Post Doctoral Research Fellowship and Postgraduate Fellowship from Universiti Sains Malaysia, respectively.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1333–1335

3-Phenyl-1,3(4*H*)-benzoselenazine-2,4(3*H*)-dione

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(*Received* 30 *August* 1994; *accepted* 13 *December* 1994)

Abstract

The title compound, 3-phenyl-1,3(4*H*)-benzoselenazine-2,4(3*H*)-dione, $C_{14}H_9NO_2Se$, was found to crystallize in space group $P2_12_12_1$. The ten atoms in the benzoselenazine ring system are planar to within 0.040 (3) Å, with both carbonyl O atoms being slightly out of this plane. The dihedral angle between the phenyl ring and benzoselenazine system is 87.41 (8)°.

Comment

Work in our laboratories has been directed towards the design and understanding of synthetic methods involving free-radical homolytic substitution at selenium. Recently, we began to explore the use of pyridine-2-thionoxycarbonyl (PTOC) carbamates as precursors to amidyl radicals for the preparation of analogues of the anti-inflammatory compound ebselen. Following the procedure described by Esker & Newcomb (1994), we reacted 2-benzylseleno-*N*-trimethylsilylbenzanilide with phosgene. To our surprise, we were unable to observe the expected carbamoyl chloride, rather a crystalline solid was isolated in 60% yield which proved to be the title compound, (1) (Fong & Schiesser, 1995). This