

(1*R,5*R**,6*S**,7*R**)-6,7-Dihydroxy-6-hydroxy-methyl-2-oxabicyclo[3.2.0]heptan-3-one**

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.035

wR factor = 0.067

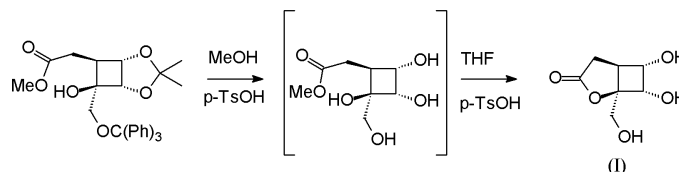
Data-to-parameter ratio = 8.3

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound $\text{C}_7\text{H}_{10}\text{O}_5$, crystallizes in the space group $P3_1$ as individual molecules on a three fold screw axis, and is stabilized by strong intermolecular hydrogen bonds between the methylene alcohol $[\text{O}-\text{H}\cdots\text{O}\ 1.75(5)\text{ \AA}]$ and the two secondary alcohol moieties $[\text{O}-\text{H}\cdots\text{O}\ 1.81(3)$ and $1.91(3)\text{ \AA}]$.

Comment

The title compound, (I), was synthesized as part of a larger effort in our laboratories directed towards the synthesis of carbohydrate derivatives with SmI_2 -mediated chemistry (Grové *et al.*, 1996*a, b*). In the preparation of the title compound, its precursor was subjected to two acid-catalysed steps (see Scheme), the first of which involved methanolysis in acidic methanol, and the second lactonization in acidic THF (see *Experimental*). The product was recrystallized from water to afford X-ray quality crystals (Fig. 1 and Table 1).



The title compound crystallizes as individual molecules on a threefold screw axis, showing three strong intermolecular hydrogen bonds of $\text{O5}^{\text{iii}}\cdots\text{H05} = 1.75(6)\text{ \AA}$, $\text{O4}^{\text{ii}}\cdots\text{H03} = 1.84(4)\text{ \AA}$ and $\text{O3}^{\text{i}}\cdots\text{H04} = 1.78(5)\text{ \AA}$ (symmetry codes as in Table 2). The hydrogen-bonding contacts lead to the formation of a layered structure in the 101 plane and channels defined by the threefold screw axis along the c axis (Fig. 2). These strong interactions result in well defined positions for the hydroxyl H atoms, enabling their positions to be obtained precisely from a difference Fourier map.

Similar to the previously published experimental method (Caddy *et al.*, 2003), ring closure as a result of acid-mediated lactonization was observed, affording a four and five-membered bicyclic system. In the present instance, however, the lactone formed from the tertiary alcohol O1.

It is also interesting to note that there is almost no distortion observed in the five membered ring (including the carbonyl moiety); C1 is twisted out of the plane formed by C1–C4–C5–C6–O1–O2 by $0.0308(17)\text{ \AA}$, whereas the mean deviation of the individual atoms is 0.02 \AA . This planarity is also manifested by the torsion angles ranging from $-4.0(3)$ to $4.4(3)^\circ$. The dihedral angle between the C1–C4–C5–C6–O1–O2 plane and the four-membered C1–C2–

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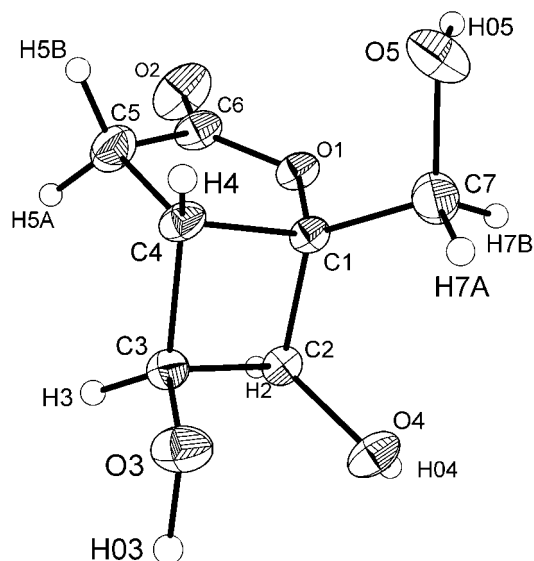


Figure 1
View of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level.

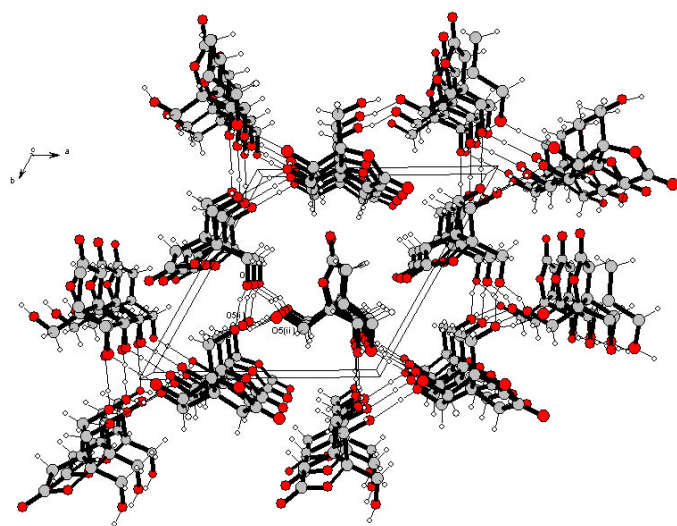


Figure 2
A view of the crystal packing of (I) along the *c* axis.

C3—C4 ring is $64.35(13)^\circ$. The latter ring displays a slightly puckered geometry, with individual atom distances from the average plane of $0.067(1) \text{ \AA}$. This effect is further illustrated by torsion angles of $-10.0(2)$ to $10.0(2)^\circ$ in the four-membered ring.

The carbonyl group (C6—O2) is well defined, with a short bond distance of $1.198(4) \text{ \AA}$. Somewhat large displacement parameters are observed for the carbonyl O atom, indicating some degree of freedom around the C5—O1 axis. The other bonds and angles in the title compound are typical of sp^3 hybridization (Table 1).

The absolute structure could not be verified crystallographically due to the absence of anomalous scatters, but could be derived from the crystallographically determined relative stereochemistry of the product in combination with

the known absolute stereochemistry of the ribose-derived starting material (specifically the known stereochemistry at C2 and C3).

Experimental

To the ethyl ester precursor (100 mg) dissolved in MeOH (5 ml) was added *p*-TsOH (20 mg). The reaction mixture was stirred at ambient temperature for 24 h, after which it was neutralized by the addition of Et_3N . The solvent was rigorously removed *in vacuo*, and the residue dissolved in THF (5 ml, to which 3 drops of water had been added). *p*-TsOH (20 mg) was added and the resulting solution was stirred at room temperature for another 24 h. Neutralization and chromatography afforded the pure title compound, which was recrystallized from water.

Crystal data

$\text{C}_7\text{H}_{10}\text{O}_5$
 $M_r = 174.15$
Trigonal, $P3_1$
 $a = 11.532(5) \text{ \AA}$
 $c = 5.328(5) \text{ \AA}$
 $V = 613.6(7) \text{ \AA}^3$
 $Z = 3$
 $D_x = 1.414 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 293 reflections
 $\theta = 4\text{--}21^\circ$
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
Cuboid, colorless
 $0.26 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1K CCD diffractometer
 ω scans
Absorption correction: none
4357 measured reflections
1009 independent reflections

586 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -15 \rightarrow 15$
 $k = -15 \rightarrow 13$
 $l = -5 \rightarrow 7$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.067$
 $S = 0.90$
1009 reflections
121 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.027P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (\AA , $^\circ$).

O1—C6	1.358 (4)	C4—C1	1.542 (4)
O1—C1	1.453 (3)	C1—C7	1.497 (4)
O3—C3	1.413 (3)	C1—C2	1.538 (4)
O4—C2	1.404 (3)	C2—C3	1.543 (4)
O5—C7	1.428 (4)	O2—C6	1.198 (4)
C4—C5	1.521 (4)	C6—C5	1.493 (5)
C4—C3	1.536 (4)		
C6—O1—C1	110.7 (2)	O4—C2—C3	116.0 (2)
C5—C4—C3	119.0 (3)	C1—C2—C3	89.6 (2)
C5—C4—C1	104.3 (2)	O3—C3—C4	110.0 (2)
C3—C4—C1	89.6 (2)	O3—C3—C2	113.8 (2)
O1—C1—C7	108.6 (2)	C4—C3—C2	89.5 (2)
O1—C1—C2	112.9 (2)	O2—C6—O1	120.7 (3)
C7—C1—C2	118.7 (2)	O2—C6—C5	127.9 (3)
O1—C1—C4	107.4 (2)	O1—C6—C5	111.4 (3)
C7—C1—C4	118.4 (2)	O5—C7—C1	109.7 (2)
C2—C1—C4	89.5 (2)	C6—C5—C4	106.0 (3)
O4—C2—C1	117.7 (2)		
C6—O1—C1—C4	-4.4 (3)	C1—C2—C3—C4	10.0 (2)
C5—C4—C1—O1	4.0 (3)	C1—O1—C6—C5	2.9 (3)
C3—C4—C1—C2	10.0 (2)	O1—C6—C5—C4	-0.3 (4)
C4—C1—C2—C3	-10.0 (2)	C1—C4—C5—C6	-2.3 (3)
C1—C4—C3—C2	-10.0 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H04 \cdots O3 ⁱ	0.85 (4)	1.84 (4)	2.688 (4)	178 (4)
O3—H03 \cdots O4 ⁱⁱ	0.93 (4)	1.78 (5)	2.706 (3)	173 (4)
O5—H05 \cdots O5 ⁱⁱⁱ	0.94 (6)	1.75 (6)	2.673 (3)	165 (4)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - y, x - y - 1, \frac{1}{3} + z$; (iii) $2 - x + y, 2 - x, z - \frac{1}{3}$.

The methylene and methine H atoms were placed in geometrically idealized positions ($C-H = 0.97-0.98$) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The positions of the hydroxyl H atoms were determined from a Fourier difference map and the coordinates were refined with isotropic displacement parameters constrained to $U_{iso}(H) = 1.2U_{eq}(C)$.

Refinement of the Flack parameter (Flack, 1983) led to an inconclusive value (Flack & Bernardinelli, 2000) of 10 (10). The 386 Friedel equivalents were therefore merged before final refinement. The conformation of the title compound was assigned to agree with the chirality as established by synthesis.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Brendt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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