Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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

Judy Caddy,* D. Bradley G. Williams, Andreas Roodt† and Alfred Muller

Department of Chemistry and Biochemistry,
Rand Afrikaans University, PO Box 524,
Aucklandpark, Johannesburg, 2006,
South Africa

† Additonal correspondence author; e-mail: aroo@rau.ac.za

Correspondence e-mail: dbgw@rau.ac.za

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.072
Data-to-parameter ratio = 8.7

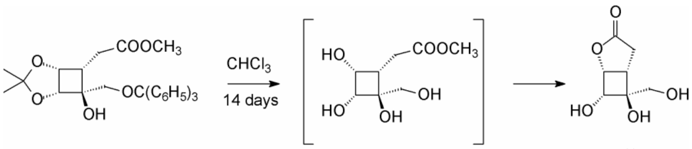
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 23 June 2003
Accepted 30 June 2003
Online 10 July 2003

The crystal structure analysis of the title compound, $C_7H_{10}O_5$, shows that a four–five lactonization instead of a four–six self condensation took place during the reaction sequence. The structure is stabilized by strong hydrogen-bonding interactions that serve to form a layer structure. The absolute configuration was assigned based on the chemical synthesis from a starting material of known chirality.

Comment

The title compound, (I), was prepared as part of a larger effort directed towards the synthesis of carbocyclic compounds from carbohydrate precursors (Grové *et al.*, 1996*a*,*b*). In the preparation of the title compound (see Scheme), its direct precursor, a product of SmI_2-mediated keto–olefin cyclization, underwent complete hydrolysis/deprotection in $CHCl_3$ at ambient temperature, affording the tetraol ester, which in turn underwent *in situ* lactonization. The product crystallized directly from $CHCl_3$, yielding single crystals of diffraction quality (Fig. 1).



(I)

Molecules of (I) crystallize as individual entities in the non-centrosymmetric space group $P2_12_12_1$ (Z = 4). The structure is stabilized by two strong and one weaker intermolecular hydrogen bonds, with 1.95 (2), 1.92 (2) and 2.21 (2) Å for $H02\cdots O1^{i}$, $H05\cdots O2^{ii}$, and $H01\cdots O4^{iii}$, respectively [symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $x, 1 + y, z$]. The hydrogen-bonding contacts lead to the formation of a layer structure stacked along the c direction. 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.

The absolute configuration could not be verified crystallographically due to the absence of significant anomalous scatters, but could be derived from the relative stereochemistry of atoms C1, C2, C3 and C4, as determined crystallographically, together with the known absolute stereochemistry of atoms C2 and C3 (from the lyxose-derived starting material).

The molecule displays a four-membered cyclobutane and a five-membered lactone ring and the mean calculated planes through the two rings form a dihedral angle of 112.8 (1)°. Atoms O2, C5, O1, C6 and C2 in the lactone ring (including the carbonyl group) deviate individually from coplanarity by

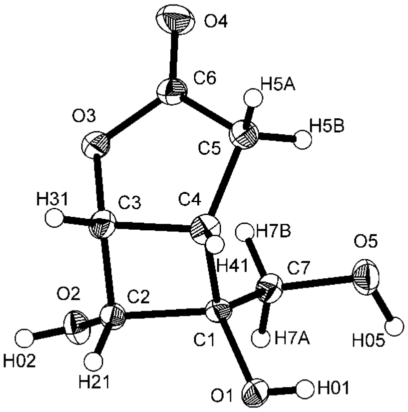


Figure 1
The structure of (I), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 30% probability level.

less than 0.04 Å, with C4 being twisted from this plane by 0.233 (3) Å. This distortion is further illustrated by the torsion angles within the ring, where the C4—C5—C6—O3 and C5—C6—O3—C3 angles are < 6.5°, while the C3—C4—C5—C6, C6—O3—C3—C4, and O3—C3—C4—C5 angles are 14.2 (2), 14.3 (2) and 17.2 (2)°, respectively.

Similarly, the individual atoms in the cyclobutane ring deviate from the mean plane by less than 0.08 Å, with the torsion angles ranging from 11.7 (2) to 12.0 (2)°.

The carbonyl group (C6/O4) is well defined, with a short bond distance of 1.205 (2) Å. The other bonds and angles in (I) (Table 1) are typical of sp^3 hybridization. Of interest is the fact that the C1—C4 bond [1.568 (3) Å] in the cyclobutyl ring is *ca* 0.03 Å longer than the other three bonds, C1—C2, C2—C3 and C3—C4 [mean 1.535 (4) Å].

Of additional interest is the fact that lactonization took place between O3 and C6, forming a four–five ring-fused product and not between O5 and C6 to form a four–six bicyclic system. The reason for this outcome presumably lies in the fact that in the theoretical four–six bicyclic lactone, the torque exerted by/on the four-membered ring as a result of one of its bonds being forced into an equatorial position (because of the *cis* relative stereochemistry around C1 and C4) renders such an outcome thermodynamically unfavourable.

Experimental

The protected hydroxy ester (15 mg) was dissolved in ‘wet’ $CHCl_3$ (0.5 ml) containing 10 µl 16% aqueous HCl (see Scheme). The solution was allowed to stand at ambient temperature for 14 d, during which time the lactone product (I) crystallized as single crystals (quantitative yield), which were used for the crystallograpic study.

Crystal data

$C_7H_{10}O_5$
$M_r = 174.15$
Orthorhombic, $P2_12_12_1$
$a = 6.5888 (9)$ Å
$b = 7.4342 (10)$ Å
$c = 15.303 (2)$ Å
$V = 749.59 (17)$ Å^3
$Z = 4$
$D_x = 1.543$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 698 reflections
$\theta = 3.8$–26.9°
$\mu = 0.13$ mm^{-1}
$T = 293 (2)$ K
Cuboid, colourless
0.46 × 0.26 × 0.18 mm

Data collection

Bruker SMART CCD 1K area-detector diffractometer
ω scans
Absorption correction: none
5322 measured reflections
1107 independent reflections

897 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\rm max} = 28.3°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 9$
$l = -18 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.072$
$S = 1.00$
1107 reflections
127 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O5—C7	1.424 (2)	C1—C2	1.536 (2)
O1—C1	1.425 (2)	C1—C4	1.568 (2)
O2—C2	1.411 (2)	C5—C6	1.493 (3)
O3—C6	1.350 (2)	C5—C4	1.521 (3)
O3—C3	1.447 (2)	C2—C3	1.531 (3)
O4—C6	1.205 (2)	C4—C3	1.544 (3)
C1—C7	1.514 (3)		
C6—O3—C3	111.52 (15)	C3—C2—C1	90.56 (14)
O1—C1—C7	109.49 (15)	C5—C4—C3	104.55 (14)
O1—C1—C2	111.21 (15)	C5—C4—C1	119.27 (16)
C7—C1—C2	115.06 (14)	C3—C4—C1	88.91 (14)
O1—C1—C4	114.46 (15)	O3—C3—C2	113.75 (16)
C7—C1—C4	116.79 (15)	O3—C3—C4	105.24 (14)
C2—C1—C4	88.52 (13)	C2—C3—C4	89.55 (13)
C6—C5—C4	104.50 (15)	O4—C6—O3	120.02 (17)
O5—C7—C1	109.87 (14)	O4—C6—C5	128.73 (17)
O2—C2—C3	120.59 (16)	O3—C6—C5	111.24 (17)
O2—C2—C1	116.71 (15)		

The methylene H atoms were placed in geometrically idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The positions of the hydroxyl and methine H atoms were determined from a Fourier difference map and the coordinates were refined with isotropic displacement parameters constrained to $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Refinement of the Flack (1983) parameter led to an inconclusive value (Flack & Bernardinelli, 2000) of −10 (10). The 744 Friedel pairs were therefore merged before final refinement. The absolute configuration of (I) 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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Brendt, 2000); software used to prepare material for publication: *SHELXL*97.

Financial assistance from the Research Fund of the RAU is gratefully acknowledged and the University of the Witwatersrand (Professor D. Levendis, Dr D. Billing and Mr M. Fernandez) is thanked for the use of its diffractometer. Part of this material is based on work supported by the South African National Research Foundation (NRF) under grant numbers GUN 2053397 and 2053664. Opinions, findings, conclusions or

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recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NRF.

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