



Crystal structure of 6-deoxy- α -L-psico-furanose

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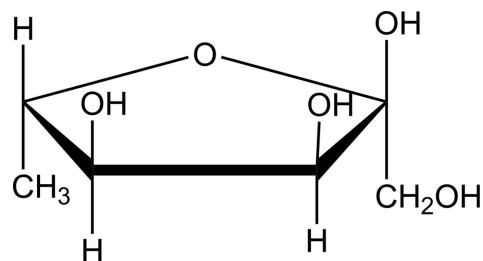
The title compound, C₆H₁₂O₅, was crystallized from an aqueous solution of 6-deoxy-L-psicose (6-deoxy-L-allulose, (3*S*,4*S*,5*S*)-1,3,4,5-tetrahydroxyhexan-2-one), and the molecule was confirmed as α -furanose with a ³T₄ (or E₄) conformation, which is a predominant tautomer in solution. This five-membered furanose ring structure is the second example in the field of the 6-deoxy-ketohexose family. The cell volume of the title compound [742.67 (7) Å³, Z = 4 at room temperature] is only 1.4% smaller than that of β -D-psicopyranose, C₆H₁₂O₆ (753.056 Å³, Z = 4 at room temperature).

Keywords: crystal structure; hydrogen bonding; deoxy compound; rare sugar.

CCDC reference: 1437931

1. Related literature

For the predominant tautomer, α -furanose, of 6-deoxy-L-psicose in aqueous solution, see: Yoshihara *et al.* (2015). For the crystal structure of chiral β -D-psicose, see: Kwiecień *et al.* (2008); Fukada *et al.* (2010). For the crystal structure of racemic β -D,L-psicose, see: Ishii *et al.* (2015). For the synthesis of 6-deoxy-L-psicose, see: Shompoosang *et al.* (2014). For the crystal structures of 6-deoxy- α -L-sorbofuranose and 6-deoxy- α -D-sorbofuranose, see: Swaminathan *et al.* (1979); Rao *et al.* (1981); Jones *et al.* (2006).



2. Experimental

2.1. Crystal data

C ₆ H ₁₂ O ₅	$V = 742.67 (7) \text{ \AA}^3$
$M_r = 164.16$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Cu $K\alpha$ radiation
$a = 5.7853 (3) \text{ \AA}$	$\mu = 1.12 \text{ mm}^{-1}$
$b = 8.9442 (5) \text{ \AA}$	$T = 296 \text{ K}$
$c = 14.3528 (8) \text{ \AA}$	$0.10 \times 0.10 \times 0.10 \text{ mm}$

2.2. Data collection

Rigaku R-AXIS RAPID diffractometer	13299 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	1358 independent reflections
$T_{\min} = 0.732$, $T_{\max} = 0.894$	1330 reflections with $F^2 > 2\sigma(F^2)$
	$R_{\text{int}} = 0.072$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{\min} = -0.14 \text{ e \AA}^{-3}$
$wR(F^2) = 0.065$	Absolute structure: Flack x determined using 521 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons & Flack, 2004)
$S = 1.08$	Absolute structure parameter: 0.03 (8)
1358 reflections	
105 parameters	
H-atom parameters constrained	
$\Delta\rho_{\max} = 0.15 \text{ e \AA}^{-3}$	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1A \cdots O5 ⁱ	0.82	2.02	2.839 (2)	177
O2—H2A \cdots O1 ⁱⁱ	0.82	2.13	2.819 (2)	142
O2—H2A \cdots O3	0.82	2.08	2.592 (2)	121
O3—H3A \cdots O2 ⁱⁱⁱ	0.82	1.93	2.732 (2)	166
O4—H4A \cdots O3 ^{iv}	0.82	2.24	2.902 (2)	138
O4—H4A \cdots O4 ^{iv}	0.82	2.26	2.987 (2)	148

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

Data collection: *RAPID-AUTO* (Rigaku, 2009); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *Il Milione* (Burla *et al.*, 2012); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *CrystalStructure* (Rigaku, 2014); software used to prepare material for publication: *CrystalStructure*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5433).

References

- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Mallamo, M., Mazzone, A., Polidori, G. & Spagna, R. (2012). *J. Appl. Cryst.* **45**, 357–361.
- Fukada, K., Ishii, T., Tanaka, K., Yamaji, M., Yamaoka, Y., Kobashi, K. & Izumori, K. (2010). *Bull. Chem. Soc. Jpn.*, **83**, 1193–1197.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Ishii, T., Sakane, G., Yoshihara, A., Fukada, K. & Senoo, T. (2015). *Acta Cryst.* **E71**, o289–o290.
- Jones, N. A., Fanefjord, M., Jenkinson, S. F., Fleet, G. W. J. & Watkin, D. J. (2006). *Acta Cryst.* **E62**, o4663–o4665.
- Kwiecień, A., Ślepokura, K. & Lis, T. (2008). *Carbohydr. Res.* **343**, 2336–2339.
- Parsons, S. & Flack, H. (2004). *Acta Cryst.* **A60**, s61.
- Rao, S. T., Swaminathan, P. & Sundaralingam, M. (1981). *Carbohydr. Res.* **89**, 151–154.
- Rigaku (2009). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2014). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Shompoosang, S., Yoshihara, A., Uechi, K., Asada, Y. & Morimoto, K. (2014). *Biosci. Biotechnol. Biochem.* **78**, 317–325.
- Swaminathan, P., Anderson, L. & Sundaralingam, M. (1979). *Carbohydr. Res.* **75**, 1–10.
- Yoshihara, A., Sato, M. & Fukada, K. (2015). *Chem. Lett.* In the press.

supporting information

Acta Cryst. (2015). E71, o993–o994 [https://doi.org/10.1107/S2056989015022215]

Crystal structure of 6-deoxy- α -L-psicofuranose

Akihide Yoshihara, Tomohiko Ishii, Tatsuya Kamakura, Hiroaki Taguchi and Kazuhiro Fukada

S1. Comment

Psicose is classified into a rare sugar, and hardly exists in nature. In this study we prepare a single crystal of 6-deoxy-*L*-psicose (Fig. 1), which is obtained by enzymatic isomerization of *L*-rhamnose, and investigate the structure by X-ray crystal analysis. The space group of this compound is orthorhombic $P2_12_12_1$, which is the same as that of β -*D*-psicopyranose (*cf.* *D*-psicose; Kwiecień *et al.*, 2008; Fukada *et al.*, 2010). The molecular weight of 6-deoxy-*L*-psicose ($C_6H_{12}O_5$; *m.w.* = 164.16) is about 10 % smaller than that of *D*-psicose (180.16). On the other hand, the cell volume of 6-deoxy- α -*L*-psicofuranose is 742.67 (7) Å³ at r.t., which is a mere 1.4 % smaller than that of β -*D*-psicopyranose (753.056 Å³ at r.t., *cf.* *D*-psicose; Kwiecień *et al.*, 2008; Fukada *et al.*, 2010). This imbalance of decreasing suggests that a weaker intermolecular interaction caused by a smaller molecular density can be expected. The melting point of 6-deoxy- α -*L*-psicofuranose has been observed to be 76 °C, which is about 30 °C lower than that of psicose (107.6 °C). This lower melting point is consistent with the suggested weaker intermolecular interaction.

We found that 6-deoxy-*L*-psicose molecules form a five-membered α -furanose ring structure in crystal. In the crystals of ketohexoses so far, six-membered pyranose ring structures have been mainly confirmed (*cf.* *D*-psicose; Kwiecień *et al.*, 2008; Fukada *et al.*, 2010, 1-deoxy-*L*-sorbitose; Jones *et al.*, 2006). Because of the deoxygenation in the 6-deoxy-*L*-psicose molecule, the carbonyl group at the C-2 position cannot form hemiacetal with the C-6 but with the C-5 hydroxyl group. It should be noted that the crystal structure of 6-deoxy-*L*-sorbitose, C-4 epimer of 6-deoxy-*L*-psicose, was reported to be α -furanose; C3'-exo-C4'-endo, 3T_4 (Swaminathan *et al.*, 1979). Therefore, the α -furanose structure observed in the crystal of 6-deoxy-*L*-psicose is the second example in 6-deoxy-ketohexose family, with 3T_4 (or E_4) conformation. An intramolecular hydrogen bond (O3—H3A \cdots O5) has been observed both in a chiral *D*-psicose (Kwiecień *et al.*, 2008; Fukada *et al.*, 2010) and a racemic *D,L*-psicose (Ishii *et al.*, 2015). This comes from two hydroxy groups located in a shorter distance from each other because of both axial conformations connecting to the C-3 and C-5 positions. On the other hand in the 6-deoxy-*L*-psicose, such an intramolecular hydrogen bond is not observed, because the hydroxy group at a C-5 position has been used for creating the ring structure. Intermolecular hydrogen bonds (O3—H3A \cdots O2 and O1—H1A \cdots O5) are also confirmed along the *b*-axis, and O4—H4A \cdots O4 along the *a*-axis, as shown in Fig. 2.

S2. Experimental

6-Deoxy-*L*-psicose was prepared from *L*-rhamnose by immobilized *L*-rhamnose isomerase and immobilized *D*-tagatose 3-epimerase in the batch reaction (Shompoosang *et al.*, 2014). After this reaction was reached equilibrium, the reaction mixture containing 6-deoxy-*L*-psicose was separated by column chromatography. The purified 6-deoxy-*L*-psicose solution was concentrated to 80% by evaporation. A seed crystal of 6-deoxy-*L*-psicose was added to the 80% 6-deoxy-*L*-psicose solution, which was kept at 30 °C. The tautomer ratio in aqueous solution at 30 °C is obtained as α -furanose : β -furanose : acyclic form = 72.9 : 24.5 : 2.69 (Yoshihara *et al.*, 2015). After one day, single crystals were obtained.

S3. Refinement

H atoms bounded to methine-type C (H3B, H4B, H5A) were positioned geometrically and refined using a riding model with $C-H = 0.98 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bounded to methylene-type C (H1B, H1C) were positioned geometrically and refined using a riding model with $C-H = 0.97 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bounded to methyl-type C (H6A, H6B, H6C) were positioned geometrically and refined using a riding model with $C-H = 0.96 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bounded to O (H1A, H2A, H3A, H4A) were positioned geometrically and refined using a riding model with $O-H = 0.82 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(O)$, allowing for free rotation of the OH groups.

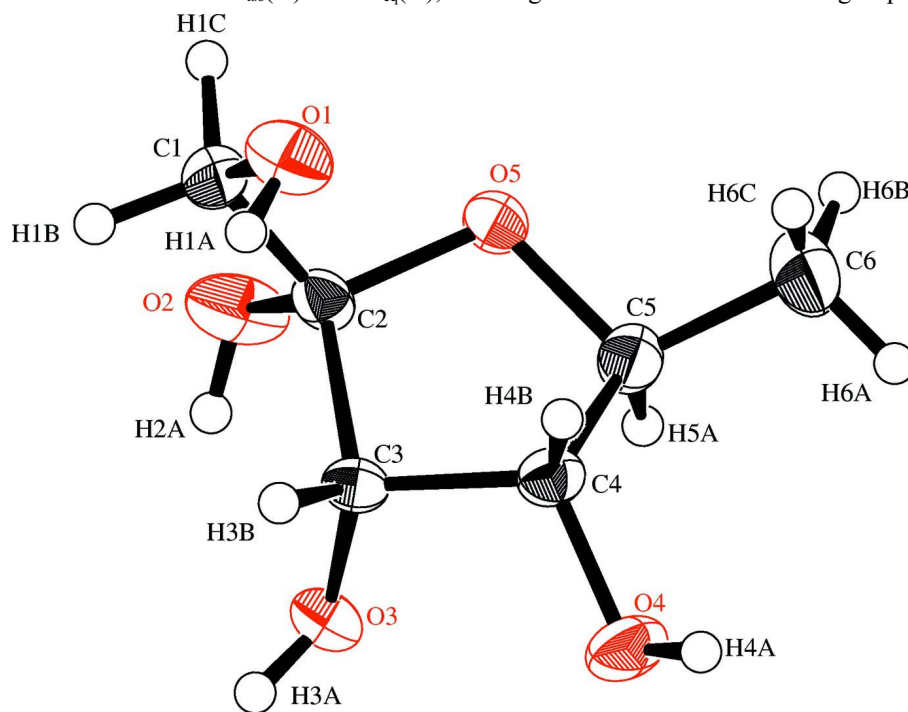


Figure 1

An ORTEP view of the title compound with the atom-labeling scheme. The thermal ellipsoids of all non-hydrogen atoms are drawn at the 50 % probability level. H atoms are shown as small spheres of arbitrary radius.

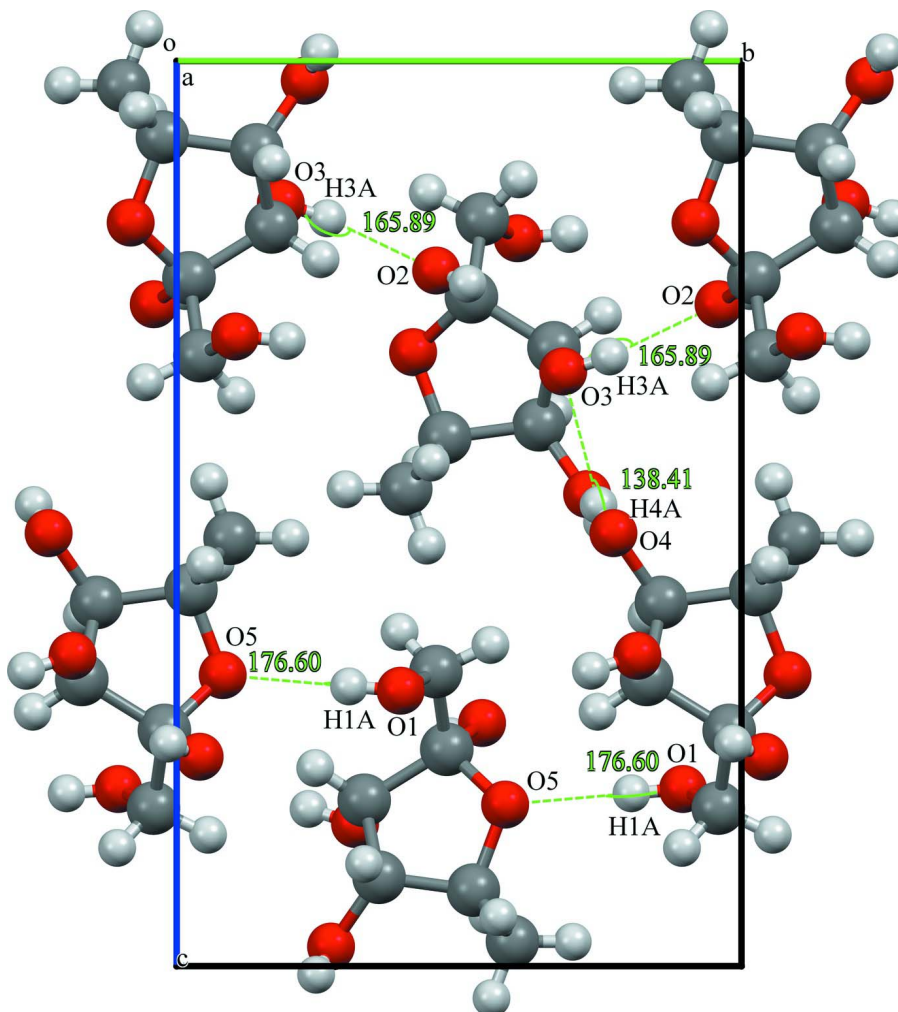


Figure 2

A packing diagram of the title compound viewed down the *a*-axis, showing the hydrogen-bonding network (green dashed lines).

6-Deoxy- α -L-psicofuranose

Crystal data

$C_6H_{12}O_5$

$M_r = 164.16$

Orthorhombic, $P2_12_12_1$

$a = 5.7853$ (3) Å

$b = 8.9442$ (5) Å

$c = 14.3528$ (8) Å

$V = 742.69$ (7) Å³

$Z = 4$

$F(000) = 352.00$

$D_x = 1.468$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54187$ Å

Cell parameters from 7546 reflections

$\theta = 3.1$ – 68.3°

$\mu = 1.12$ mm⁻¹

$T = 296$ K

Block, colorless

$0.10 \times 0.10 \times 0.10$ mm

Data collection

Rigaku R-Axis RAPID
diffractometer

Detector resolution: 10.000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.732$, $T_{\max} = 0.894$

13299 measured reflections

1358 independent reflections

1330 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.072$

$\theta_{\max} = 68.2^\circ$, $\theta_{\min} = 5.8^\circ$

$h = -6 \rightarrow 6$

$k = -10 \rightarrow 10$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.065$

$S = 1.08$

1358 reflections

105 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 0.1732P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.14 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL*

Extinction coefficient: 0.0144 (15)

Absolute structure: Flack x determined using

521 quotients $[(I^-)-(I^+)]/[(I^-)+(I^+)]$ (Parsons &
Flack, 2004)

Absolute structure parameter: 0.03 (8)

Special details

Geometry. ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2 . R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0 \text{ sigma}(F^2)$ is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.1489 (3)	0.60359 (18)	0.19568 (11)	0.0370 (4)
O2	0.5730 (3)	0.45936 (18)	0.23138 (13)	0.0419 (4)
O3	0.5171 (2)	0.68432 (15)	0.34295 (10)	0.0274 (3)
O4	0.8265 (3)	0.72675 (18)	0.47842 (10)	0.0371 (4)
O5	0.8957 (3)	0.41852 (14)	0.32155 (9)	0.0297 (4)
C1	0.9314 (4)	0.5411 (2)	0.17460 (13)	0.0299 (5)
C2	0.7827 (3)	0.5218 (2)	0.26045 (13)	0.0239 (4)
C3	0.7513 (3)	0.6680 (2)	0.31678 (13)	0.0217 (4)
C4	0.9029 (3)	0.6417 (2)	0.40186 (13)	0.0243 (4)
C5	0.8846 (4)	0.4748 (2)	0.41607 (13)	0.0288 (5)
C6	1.0749 (5)	0.4055 (3)	0.47269 (18)	0.0472 (6)
H1A	1.14196	0.69485	0.19094	0.0444*
H1C	0.95355	0.44456	0.14516	0.0359*
H1B	0.85181	0.60539	0.13061	0.0359*
H2A	0.46647	0.5151	0.24595	0.0503*
H3A	0.47011	0.76663	0.32637	0.0328*
H3B	0.80479	0.75478	0.28114	0.0261*
H4A	0.93817	0.75318	0.50951	0.0445*

H4B	1.06309	0.66817	0.38712	0.0291*
H5A	0.73436	0.45008	0.44361	0.0346*
H6A	1.0678	0.44263	0.53538	0.0566*
H6B	1.05675	0.29881	0.47311	0.0566*
H6C	1.22165	0.4308	0.44577	0.0566*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0306 (8)	0.0317 (8)	0.0486 (9)	0.0022 (7)	0.0045 (7)	0.0026 (7)
O2	0.0265 (8)	0.0310 (9)	0.0683 (11)	-0.0008 (7)	-0.0091 (7)	-0.0203 (8)
O3	0.0221 (7)	0.0249 (8)	0.0351 (7)	0.0048 (6)	-0.0004 (6)	0.0008 (6)
O4	0.0320 (8)	0.0467 (10)	0.0325 (8)	0.0046 (8)	-0.0052 (6)	-0.0198 (7)
O5	0.0448 (9)	0.0177 (7)	0.0266 (7)	0.0073 (6)	-0.0022 (7)	0.0004 (5)
C1	0.0384 (11)	0.0263 (11)	0.0249 (10)	0.0058 (9)	-0.0033 (8)	-0.0040 (8)
C2	0.0267 (11)	0.0170 (9)	0.0282 (9)	0.0018 (8)	-0.0066 (8)	-0.0025 (7)
C3	0.0223 (9)	0.0165 (9)	0.0262 (9)	0.0002 (8)	0.0014 (8)	-0.0022 (7)
C4	0.0231 (9)	0.0244 (11)	0.0253 (9)	0.0001 (9)	-0.0000 (8)	-0.0055 (8)
C5	0.0333 (11)	0.0283 (11)	0.0248 (9)	0.0004 (9)	-0.0008 (8)	0.0004 (8)
C6	0.0607 (16)	0.0405 (14)	0.0404 (12)	0.0144 (12)	-0.0125 (12)	0.0049 (10)

Geometric parameters (Å, °)

O1—C1	1.410 (3)	O2—H2A	0.820
O2—C2	1.399 (2)	O3—H3A	0.820
O3—C3	1.414 (2)	O4—H4A	0.820
O4—C4	1.408 (2)	C1—H1C	0.970
O5—C2	1.432 (2)	C1—H1B	0.970
O5—C5	1.448 (2)	C3—H3B	0.980
C1—C2	1.512 (3)	C4—H4B	0.980
C2—C3	1.548 (3)	C5—H5A	0.980
C3—C4	1.522 (3)	C6—H6A	0.960
C4—C5	1.510 (3)	C6—H6B	0.960
C5—C6	1.502 (3)	C6—H6C	0.960
O1—H1A	0.820		
C2—O5—C5	109.24 (14)	O1—C1—H1C	109.164
O1—C1—C2	112.20 (16)	O1—C1—H1B	109.167
O2—C2—O5	108.73 (15)	C2—C1—H1C	109.166
O2—C2—C1	107.19 (16)	C2—C1—H1B	109.170
O2—C2—C3	113.01 (16)	H1C—C1—H1B	107.872
O5—C2—C1	108.26 (16)	O3—C3—H3B	111.067
O5—C2—C3	106.18 (14)	C2—C3—H3B	111.068
C1—C2—C3	113.31 (16)	C4—C3—H3B	111.066
O3—C3—C2	109.81 (15)	O4—C4—H4B	109.543
O3—C3—C4	110.80 (15)	C3—C4—H4B	109.538
C2—C3—C4	102.75 (15)	C5—C4—H4B	109.537
O4—C4—C3	111.22 (16)	O5—C5—H5A	109.822

O4—C4—C5	114.02 (16)	C4—C5—H5A	109.816
C3—C4—C5	102.76 (15)	C6—C5—H5A	109.811
O5—C5—C4	102.34 (14)	C5—C6—H6A	109.470
O5—C5—C6	109.33 (18)	C5—C6—H6B	109.472
C4—C5—C6	115.43 (18)	C5—C6—H6C	109.471
C1—O1—H1A	109.468	H6A—C6—H6B	109.472
C2—O2—H2A	109.470	H6A—C6—H6C	109.470
C3—O3—H3A	109.471	H6B—C6—H6C	109.473
C4—O4—H4A	109.477		
C2—O5—C5—C4	-34.64 (18)	O5—C2—C3—C4	12.06 (17)
C2—O5—C5—C6	-157.50 (14)	C1—C2—C3—O3	135.42 (15)
C5—O5—C2—O2	-107.81 (16)	C1—C2—C3—C4	-106.65 (16)
C5—O5—C2—C1	136.05 (14)	O3—C3—C4—O4	-37.4 (2)
C5—O5—C2—C3	14.07 (18)	O3—C3—C4—C5	85.02 (16)
O1—C1—C2—O2	-179.95 (14)	C2—C3—C4—O4	-154.60 (14)
O1—C1—C2—O5	-62.8 (2)	C2—C3—C4—C5	-32.21 (16)
O1—C1—C2—C3	54.7 (2)	O4—C4—C5—O5	161.44 (14)
O2—C2—C3—O3	13.2 (2)	O4—C4—C5—C6	-79.9 (2)
O2—C2—C3—C4	131.17 (15)	C3—C4—C5—O5	40.95 (18)
O5—C2—C3—O3	-105.88 (16)	C3—C4—C5—C6	159.59 (14)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1A \cdots O5 ⁱ	0.82	2.02	2.839 (2)	177
O2—H2A \cdots O1 ⁱⁱ	0.82	2.13	2.819 (2)	142
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