

Crystal structure of β -D,L-psicoseTomohiko Ishii,^{a*} Genta Sakane,^b Akihide Yoshihara,^c
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Received 19 March 2015; accepted 2 April 2015

Edited by H. Ishida, Okayama University, Japan

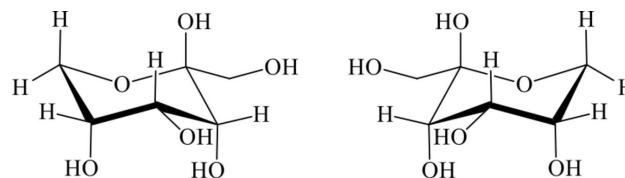
The title compound, C₆H₁₂O₆, a C-3 position epimer of fructose, was crystallized from an aqueous solution of equimolar mixture of D- and L-psicose (1,3,4,5,6-penta-hydroxyhexan-2-one, *ribo*-2-hexulose, allulose), and it was confirmed that D-psicose (or L-psicose) formed β -pyranose with a ²C₅ (or ⁵C₂) conformation. In the crystal, an O—H...O hydrogen bond between the hydroxy groups at the C-3 and C-2 positions connects homochiral molecules into a column along the *b* axis. The columns are linked by other O—H...O hydrogen bonds between D- and L-psicose molecules, forming a three-dimensional network. An intramolecular O—H...O hydrogen bond is also observed. The cell volume of racemic β -D,L-psicose [763.21 (6) Å³] is almost the same as that of chiral β -D-psicose [753.06 Å³].

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

CCDC reference: 1057484

1. Related literature

For the crystal structure of the chiral β -D-psicose, see: Kwiecien *et al.* (2008); Fukada *et al.* (2010). For the synthesis of the chiral D-psicose, see: Itoh *et al.* (1995); Takeshita *et al.* (2000). For the synthesis of the chiral L-psicose, see: Takeshita *et al.* (1996).



2. Experimental

2.1. Crystal data

C₆H₁₂O₆
M_r = 180.16
 Orthorhombic, *Pna*2₁
a = 11.2629 (5) Å
b = 5.3552 (3) Å
c = 12.6538 (6) Å

V = 763.21 (6) Å³
Z = 4
 Cu *K*α radiation
 μ = 1.25 mm⁻¹
T = 296 K
 0.10 × 0.10 × 0.10 mm

2.2. Data collection

Rigaku R-Axis RAPID
 diffractometer
 Absorption correction: multi-scan
 (*ABSCOR*; Higashi, 1995)
T_{min} = 0.442, *T_{max}* = 0.883

12119 measured reflections
 1400 independent reflections
 1295 reflections with *F*² > 2σ(*F*²)
R_{int} = 0.139

2.3. Refinement

R[*F*² > 2σ(*F*²)] = 0.048
wR(*F*²) = 0.102
S = 1.04
 1400 reflections
 116 parameters
 1 restraint
 H-atom parameters constrained

$\Delta\rho_{\max}$ = 0.25 e Å⁻³
 $\Delta\rho_{\min}$ = -0.23 e Å⁻³
 Absolute structure: Flack (1983),
 666 Friedel pairs
 Absolute structure parameter:
 0.1 (4)

Table 1
 Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O3 ⁱ	0.82	1.91	2.715 (3)	168
O2—H2A...O4 ⁱⁱ	0.82	1.92	2.724 (3)	166
O3—H3A...O2 ⁱⁱⁱ	0.82	2.20	2.874 (3)	140
O3—H3A...O5	0.82	2.36	2.822 (4)	117
O4—H4A...O6 ^{iv}	0.82	2.14	2.829 (3)	141
O5—H5A...O1 ^v	0.82	1.94	2.746 (4)	169

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $x - \frac{1}{2}, -y + \frac{5}{2}, z$; (iii) $x, y - 1, z$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, z + \frac{1}{2}$.

Data collection: *RAPID-AUTO* (Rigaku, 2009); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SIR2011* (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*.

Acknowledgements

The authors are grateful to Grants-in-Aid for Rare Sugar Research of Kagawa University.

Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5394).

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supporting information

Acta Cryst. (2015). E71, o289–o290 [doi:10.1107/S2056989015006623]

Crystal structure of β -D,L-psicose

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S1. Comment

In the crystal of the title compound, the *D*- and *L*-molecules are located alternatively in *a-c* plane, so that the main hydrogen bonding networks can be created between *D*- and *L*-molecules. An additional hydrogen bonding between two *D*-molecules (and two *L*-molecules) are observed along to the *b*-axis (O3—H3A \cdots O2ⁱⁱⁱ; Table 1). The molecular structure of *D*-psicose (or *L*-psicose) is β -pyranose form with a ²C₅ (or ⁵C₂) conformation. Orientations of two OH groups at C-3 and C-5 positions are axial, therefore an intramolecular hydrogen bonding can be observed (O3—H3A \cdots O5; 2.36 Å) [hereafter, (O3 \cdots O5)]. The intramolecular hydrogen bonding unit (O3 \cdots O5) shown in the racemic *D,L*-crystal has also observed in a chiral *D*-crystal (Fukada *et al.*, 2010). In the chiral one, one-dimensional hydrogen bonding chain, that is (O3 \cdots O5) \rightarrow (O3 \cdots O5) \rightarrow (O3 \cdots O5) $\rightarrow \cdots$, can be observed by connecting through an another hydrogen bonding between two *D*-molecule units (O5—H5 \cdots O3). On the other hand in the case of the racemic one, the *L*-molecule (or *D*-molecule) plays as a role of a bridging between two adjacent intramolecular hydrogen bonding in *D*-molecule (or *L*-molecule) (O3 \cdots O5) units, that is (*D* O3 \cdots O5) \rightarrow (*L* O1) \rightarrow (*D* O3 \cdots O5) \rightarrow (*L* O1) $\rightarrow \cdots$ (or, (*L* O3 \cdots O5) \rightarrow (*D* O1) \rightarrow (*L* O3 \cdots O5) \rightarrow (*D* O1) $\rightarrow \cdots$). Concerning the intermolecular hydrogen bonding, there are four kinds of bondings are also observed between *D*- and *L*- psicose molecules (O1—H1A \cdots O3 (*a*-axis), O2—H2A \cdots O4, O4—H4A \cdots O6 (*a*-axis), and O5—H5A \cdots O1 (*c*-axis)). The cell volume of racemic β -*D,L*-psicose [763.21 (6) Å³ at r.t.] is almost the same as that of chiral β -*D*-psicose [753.06 Å³ at r.t.].

S2. Experimental

D-Psicose was prepared from *D*-fructose by enzymatic epimerization using *D*-tagatose 3-epimerase (Itoh *et al.*, 1995; Takeshita *et al.*, 2000). *L*-Psicose was prepared from allitol by microbial oxidation using *Gluconobacter frateurii* IFO 3254 (Takeshita *et al.*, 1996). *D*-Psicose and *L*-psicose were mixed in equal amount and dissolved in hot water to give 60, 65, 70, 75, and 80 wt% solution. And these samples were kept at 10, 20, and 30 °C. After one day, small crystals were obtained in 65, 70, 75, and 80 wt% solution at 10, 20, and 30 °C.

S3. Refinement

H atoms bounded to methine-type C (H3B, H4B, H5B) were positioned geometrically and refined using a riding model with C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bounded to methylene-type C (H1B, H1C, H6A, H6B) were positioned geometrically and refined using a riding model with C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bounded to O (H1A, H2A, H3A, H4A, H5A) were positioned geometrically and refined using a riding model with O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$, allowing for free rotation of the OH groups.

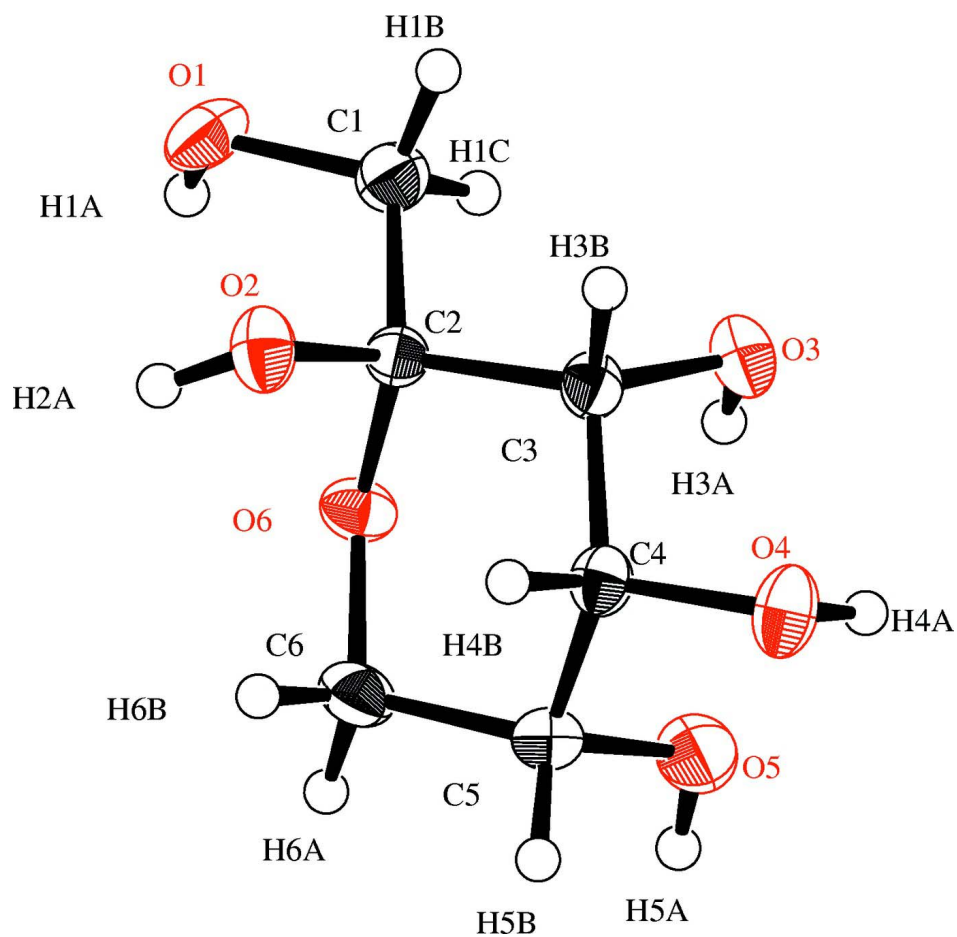


Figure 1

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.

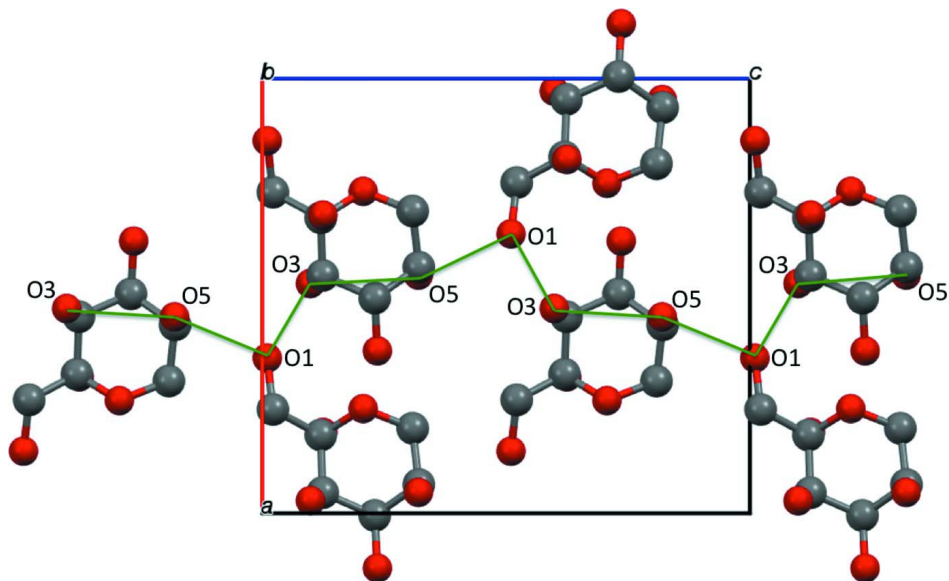


Figure 2

Figure 2

Part of the crystal structure of the title compound with hydrogen-bonding network represented as green solid lines, viewed down the *b*-axis. The hydrogen atoms are omitted for clarity.

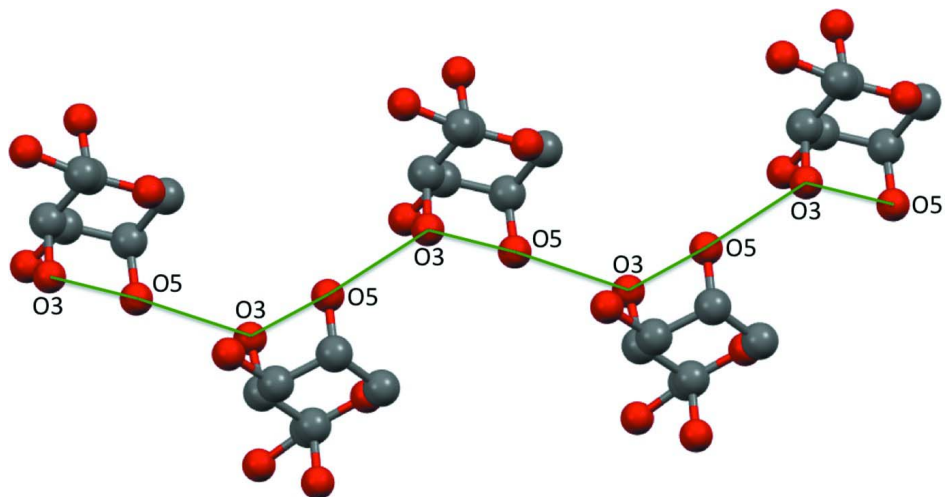


Figure 3

Figure 3

Part of the crystal structure of the chiral β -*D*-psicose (Fukada *et al.*, 2010) with hydrogen-bonding network represented as green solid lines. The hydrogen atoms are omitted for clarity.

(I)

*Crystal data*C₆H₁₂O₆*M_r* = 180.16Orthorhombic, *Pna*2₁*a* = 11.2629 (5) Å*b* = 5.3552 (3) Å*c* = 12.6538 (6) Å

$V = 763.21 (6) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 384.00$
 $D_x = 1.568 \text{ Mg m}^{-3}$
 Cu $K\alpha$ radiation, $\lambda = 1.54187 \text{ \AA}$
 Cell parameters from 5584 reflections

$\theta = 3.5\text{--}68.5^\circ$
 $\mu = 1.25 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Block, colorless
 $0.10 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Rigaku R-AXIS RAPID
 diffractometer
 Detector resolution: $10.000 \text{ pixels mm}^{-1}$
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.442$, $T_{\max} = 0.883$
 12119 measured reflections

1400 independent reflections
 1295 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.139$
 $\theta_{\max} = 68.2^\circ$, $\theta_{\min} = 7.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -6 \rightarrow 6$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.102$
 $S = 1.04$
 1400 reflections
 116 parameters
 1 restraint
 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
 $w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL
 Extinction coefficient: 0.039 (3)
 Absolute structure: Flack (1983), 666 Friedel
 pairs
 Absolute structure parameter: 0.1 (4)

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 $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R -factor (gt).

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.6428 (2)	1.0475 (5)	0.0101 (2)	0.0321 (7)
O2	0.8138 (2)	1.3225 (4)	0.1244 (2)	0.0283 (6)
O3	0.9712 (2)	0.7407 (4)	0.0986 (2)	0.0278 (6)
O4	1.12635 (19)	0.9941 (5)	0.2360 (2)	0.0306 (7)
O5	0.9520 (3)	0.6941 (5)	0.3201 (2)	0.0368 (7)
O6	0.75926 (19)	0.9487 (5)	0.2068 (2)	0.0243 (6)
C1	0.7610 (3)	0.9600 (8)	0.0218 (3)	0.0275 (8)
C2	0.8199 (3)	1.0614 (6)	0.1199 (3)	0.0211 (7)
C3	0.9525 (3)	0.9956 (6)	0.1238 (3)	0.0223 (7)
C4	1.0049 (3)	1.0665 (7)	0.2306 (2)	0.0233 (8)
C5	0.9337 (3)	0.9564 (7)	0.3210 (3)	0.0266 (8)
C6	0.8044 (3)	1.0258 (7)	0.3083 (3)	0.0289 (8)

H1B	0.80695	1.00892	-0.03968	0.0330*
H1C	0.76042	0.77904	0.02497	0.0330*
H1A	0.59772	0.95756	0.04384	0.0386*
H2A	0.75043	1.36467	0.15074	0.0340*
H3A	0.92832	0.65324	0.13561	0.0333*
H3B	0.99273	1.0959	0.06985	0.0268*
H4B	1.00147	1.24872	0.23691	0.0280*
H4A	1.1313	0.84167	0.23198	0.0367*
H5A	0.92192	0.63218	0.37294	0.0442*
H5B	0.96322	1.0246	0.38792	0.0319*
H6A	0.75828	0.94707	0.36378	0.0347*
H6B	0.79566	1.20525	0.31544	0.0347*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0232 (14)	0.0431 (18)	0.0301 (13)	-0.0019 (11)	-0.0058 (11)	0.0126 (12)
O2	0.0238 (12)	0.0228 (13)	0.0384 (14)	0.0010 (9)	0.0057 (11)	0.0025 (13)
O3	0.0252 (12)	0.0240 (13)	0.0340 (14)	0.0013 (10)	0.0068 (10)	-0.0020 (11)
O4	0.0193 (12)	0.0265 (14)	0.0459 (17)	0.0004 (10)	-0.0022 (10)	0.0013 (12)
O5	0.0475 (17)	0.0309 (15)	0.0322 (15)	0.0064 (12)	0.0101 (11)	0.0101 (12)
O6	0.0230 (12)	0.0297 (14)	0.0203 (11)	-0.0057 (10)	0.0027 (10)	0.0002 (12)
C1	0.025 (2)	0.032 (2)	0.0254 (19)	-0.0001 (15)	-0.0001 (14)	0.0024 (18)
C2	0.0211 (17)	0.0228 (17)	0.0195 (16)	0.0012 (12)	0.0034 (14)	0.0043 (16)
C3	0.0197 (19)	0.0233 (17)	0.0239 (17)	0.0009 (12)	0.0038 (14)	0.0042 (14)
C4	0.0189 (17)	0.025 (2)	0.0265 (19)	0.0009 (13)	0.0000 (13)	0.0006 (15)
C5	0.030 (2)	0.030 (2)	0.0201 (17)	0.0027 (14)	-0.0011 (15)	-0.0001 (15)
C6	0.0272 (18)	0.039 (2)	0.0209 (17)	0.0006 (15)	0.0055 (15)	-0.0002 (15)

Geometric parameters (Å, °)

O1—C1	1.419 (4)	O1—H1A	0.820
O2—C2	1.401 (4)	O2—H2A	0.820
O3—C3	1.418 (4)	O3—H3A	0.820
O4—C4	1.423 (4)	O4—H4A	0.820
O5—C5	1.419 (4)	O5—H5A	0.820
O6—C2	1.428 (4)	C1—H1B	0.970
O6—C6	1.442 (4)	C1—H1C	0.970
C1—C2	1.509 (5)	C3—H3B	0.980
C2—C3	1.535 (5)	C4—H4B	0.980
C3—C4	1.523 (5)	C5—H5B	0.980
C4—C5	1.516 (5)	C6—H6A	0.970
C5—C6	1.512 (5)	C6—H6B	0.970
C2—O6—C6	113.3 (2)	C4—O4—H4A	109.469
O1—C1—C2	112.3 (3)	C5—O5—H5A	109.469
O2—C2—O6	111.6 (3)	O1—C1—H1B	109.152
O2—C2—C1	111.8 (3)	O1—C1—H1C	109.152

O2—C2—C3	106.0 (3)	C2—C1—H1B	109.145
O6—C2—C1	105.7 (3)	C2—C1—H1C	109.145
O6—C2—C3	110.1 (3)	H1B—C1—H1C	107.867
C1—C2—C3	111.8 (3)	O3—C3—H3B	107.581
O3—C3—C2	111.0 (3)	C2—C3—H3B	107.578
O3—C3—C4	112.5 (3)	C4—C3—H3B	107.580
C2—C3—C4	110.4 (3)	O4—C4—H4B	107.757
O4—C4—C3	110.3 (3)	C3—C4—H4B	107.761
O4—C4—C5	111.5 (3)	C5—C4—H4B	107.767
C3—C4—C5	111.6 (3)	O5—C5—H5B	109.099
O5—C5—C4	107.5 (3)	C4—C5—H5B	109.103
O5—C5—C6	112.5 (3)	C6—C5—H5B	109.093
C4—C5—C6	109.5 (3)	O6—C6—H6A	109.357
O6—C6—C5	111.4 (3)	O6—C6—H6B	109.357
C1—O1—H1A	109.471	C5—C6—H6A	109.358
C2—O2—H2A	109.471	C5—C6—H6B	109.358
C3—O3—H3A	109.470	H6A—C6—H6B	107.992
C2—O6—C6—C5	-60.7 (3)	C1—C2—C3—C4	-171.7 (2)
C6—O6—C2—O2	-58.2 (3)	O3—C3—C4—O4	52.5 (3)
C6—O6—C2—C1	-179.9 (2)	O3—C3—C4—C5	-72.0 (3)
C6—O6—C2—C3	59.2 (3)	C2—C3—C4—O4	177.1 (2)
O1—C1—C2—O2	-53.5 (4)	C2—C3—C4—C5	52.6 (3)
O1—C1—C2—O6	68.1 (3)	O4—C4—C5—O5	-54.2 (3)
O1—C1—C2—C3	-172.1 (2)	O4—C4—C5—C6	-176.7 (2)
O2—C2—C3—O3	-168.2 (2)	C3—C4—C5—O5	69.6 (3)
O2—C2—C3—C4	66.4 (3)	C3—C4—C5—C6	-52.9 (3)
O6—C2—C3—O3	71.0 (3)	O5—C5—C6—O6	-63.8 (4)
O6—C2—C3—C4	-54.4 (3)	C4—C5—C6—O6	55.7 (4)
C1—C2—C3—O3	-46.2 (4)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O3 ⁱ	0.82	1.91	2.715 (3)	168
O2—H2A \cdots O4 ⁱⁱ	0.82	1.92	2.724 (3)	166
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O3—H3A \cdots O5	0.82	2.36	2.822 (4)	117
O4—H4A \cdots O6 ^{iv}	0.82	2.14	2.829 (3)	141
O5—H5A \cdots O1 ^v	0.82	1.94	2.746 (4)	169

Symmetry codes: (i) $x-1/2, -y+3/2, z$; (ii) $x-1/2, -y+5/2, z$; (iii) $x, y-1, z$; (iv) $x+1/2, -y+3/2, z$; (v) $-x+3/2, y-1/2, z+1/2$.