

## Ethyl $\alpha$ -L-sorbose

Natsumi Nagayama,<sup>a</sup> Norito Taniguchi,<sup>a</sup> Mao Matsumoto,<sup>a</sup> Kei Takeshita<sup>b</sup> and Tomohiko Ishii<sup>a\*</sup>

<sup>a</sup>Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan, and <sup>b</sup>Fushimi Pharmaceutical Co Ltd, 307 Minatomachi, Marugame, Kagawa 763-8605, Japan. \*Correspondence e-mail: ishii.tomohiko@kagawa-u.ac.jp

Received 30 November 2020

Accepted 15 December 2020

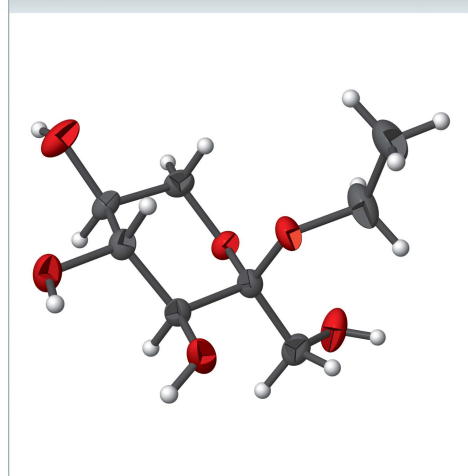
Edited by R. J. Butcher, Howard University, USA

Keywords: crystal structure; hydrogen bonding; rare sugar; alkyl sorboside.

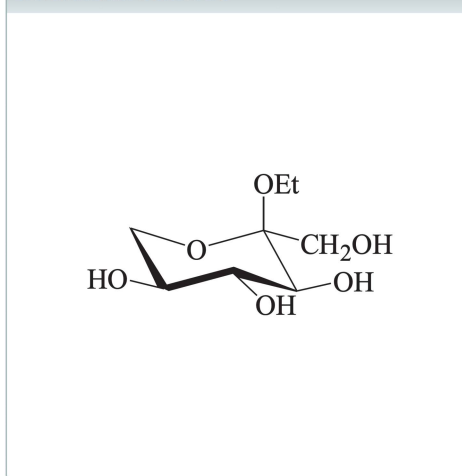
Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

Ethyl L-sorbose, C<sub>8</sub>H<sub>16</sub>O<sub>6</sub>, was prepared from the rare sugar L-sorbose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, and crystallized. It was confirmed that ethyl L-sorbose formed  $\alpha$ -pyranose with a <sup>2</sup>C<sub>5</sub> conformation. In the crystal, molecules are linked by O—H···O hydrogen bonds, forming a three-dimensional network. The unit-cell volume of the title ethyl  $\alpha$ -L-sorbose is 940.63 Å<sup>3</sup> (Z = 4), which is about 194.69 Å<sup>3</sup> (26.1%) bigger than that of L-sorbose [745.94 Å<sup>3</sup> (Z = 4)].

### 3D view



### Chemical scheme



### Structure description

The rare sugar L-sorbose is the first L-form hexose found in nature (Itoh *et al.*, 1995; Khan *et al.*, 1992; Nordenson *et al.*, 1979). Ethyl L-sorbose (Fig. 1) is an  $\alpha$ -pyranose form in which the OH group located on the C-2 position in the rare sugar L-sorbose is converted into the ethoxy group OC<sub>2</sub>H<sub>5</sub>. The molecular weight of C<sub>8</sub>H<sub>16</sub>O<sub>6</sub> is 208. On the other hand, the molecular weight of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> is 180. So, the increase in molecular weight is about 16%. In contrast, the volume has increased by 26%. This point is characteristic. In other words, sorbose is highly crystalline and has a high density. On the other hand, the addition of the ethoxy group, which is hydrophobic, weakens inter-molecular interactions between sugar molecules, resulting in a decrease in density and an increase in volume.

In this study, we aimed to create a single crystal of ethyl L-sorbose. The space group is non-centrosymmetric, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, and there are total of four sorboside molecules in the unit cell (Z = 4). The crystal structure of ethyl L-sorbose features a three-dimensional hydrogen-bonded network (Table 1), with each molecule interacting with six neighbours. There are four intermolecular hydrogen bonds and an additional intramolecular hydrogen bond (Fig. 2).

**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—H1...O3 <sup>i</sup>	0.82	2.00	2.811 (3)	169
O3—H3...O4 <sup>ii</sup>	0.82	1.94	2.750 (3)	167
O4—H4...O3	0.82	2.52	2.879 (2)	108
O4—H4...O5 <sup>ii</sup>	0.82	2.00	2.791 (2)	163
O5—H5...O6 <sup>iii</sup>	0.82	2.35	2.988 (2)	136

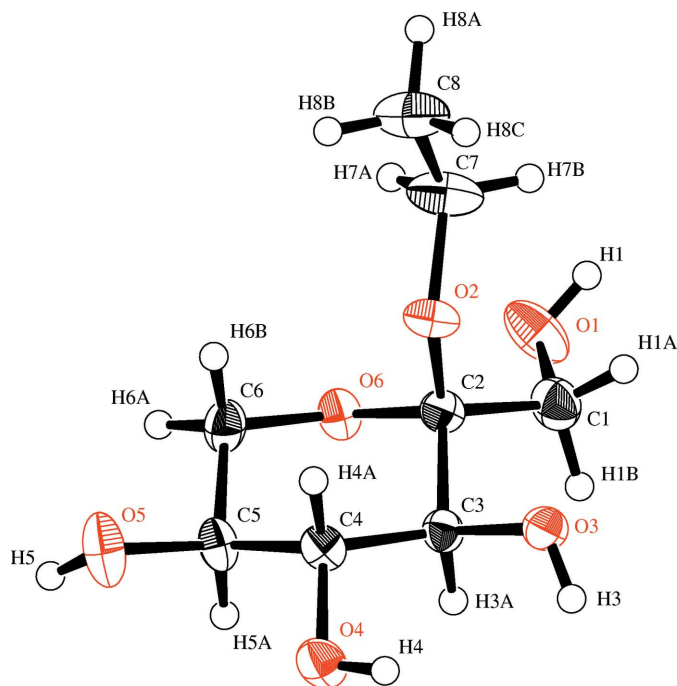
Symmetry codes: (i)  $-x, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .

### Synthesis and crystallization

Ethyl L-sorboside,  $\alpha$ -sorbopyranoside form, was prepared by Fischer glycosidation from L-sorbose and ethanol (Taguchi *et al.*, 2018). The Fisher method produces isomers such as  $\alpha$ -,  $\beta$ -, and furanose. Therefore, chromatographic separation using an ion-exchange resin was performed. After the separation step, the solution was evaporated to syrup. Small single crystals were obtained by keeping the flask at room temperature. It is obvious that the synthesized ethyl  $\alpha$ -L-sorbose is still in the L-form after dehydrative condensation, because L-sorbose is used as the starting material. The absolute structure were also confirmed by the Flack (1983) parameter.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.



**Figure 1**  
An ORTEP view of the title compound with the atom-labelling scheme. The displacement ellipsoids of all non-hydrogen atoms are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

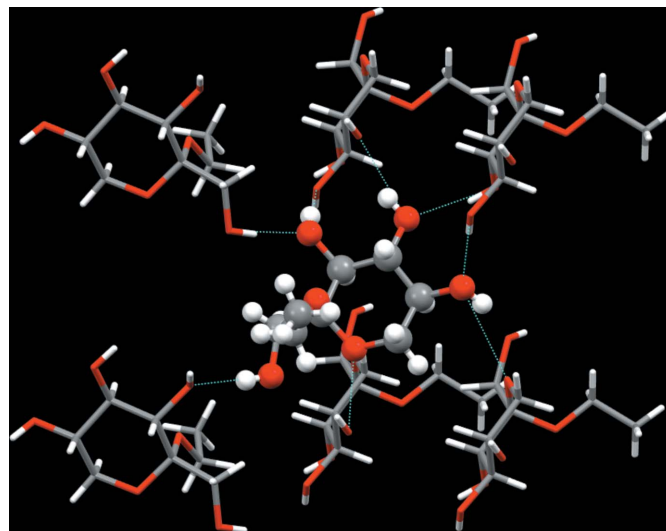
**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>8</sub> H <sub>16</sub> O <sub>6</sub>
<i>M<sub>r</sub></i>	208.21
Crystal system, space group	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.8203 (8), 8.6934 (10), 15.865 (2)
<i>V</i> (Å <sup>3</sup> )	940.63 (19)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	1.09
Crystal size (mm)	0.10 × 0.10 × 0.10
Data collection	
Diffractometer	Rigaku R-Axis RAPID
Absorption correction	Multi-scan ( <i>ABSCOR</i> ; Rigaku, 1995)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.462, 0.897
No. of measured, independent and observed [ <i>F</i> <sup>2</sup> > 2.0σ( <i>F</i> <sup>2</sup> )] reflections	10373, 1721, 1602
<i>R<sub>int</sub></i>	0.091
(sin $\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.602
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.037, 0.090, 1.07
No. of reflections	1721
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.20, -0.27
Absolute structure	Flack <i>x</i> determined using 581 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.06 (12)

Computer programs: *RAPID-AUTO* (Rigaku, 2009), *SIR2014* (Burla *et al.*, 2015), *SHELXL2018/3* (Sheldrick, 2015) and *CrystalStructure* (Rigaku, 2019).

### Acknowledgements

The authors are sincerely grateful to Professor Genta Sakane (Okayama University of Science) for excellent discussion and useful technical advice.



**Figure 2**  
A packing diagram of the title compound, showing the hydrogen-bonding network (dotted lines).

### Funding information

The authors are grateful to Grants-in-Aid for Rare Sugar Research of Kagawa University and the Strategic Foundational Technology Improvement Support Operation (Supporting Industry Program) for financial support.

### References

- Burla, M. C., Caliandro, R., Carrozzini, B., Cascarano, G. L., Cuocci, C., Giacobazzo, C., Mallamo, M., Mazzone, A. & Polidori, G. (2015). *J. Appl. Cryst.* **48**, 306–309.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Itoh, H., Sato, T., Takeuchi, T., Khan, A. R. & Izumori, K. (1995). *J. Ferment. Bioeng.* **79**, 184–185.
- Khan, A. R., Takahata, S., Okaya, H., Tsumura, T. & Izumori, K. (1992). *J. Ferment. Bioeng.* **74**, 149–152.
- Nordenson, S., Takagi, S. & Jeffrey, G. A. (1979). *Acta Cryst.* **B35**, 1005–1007.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Rigaku (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2009). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2019). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Taguchi, H., Sogo, K., Ishii, T., Yoshihara, A. & Fukada, K. (2018). *IUCrData*, **3**, x180114.

## full crystallographic data

*IUCrData* (2020). 5, x201625 [https://doi.org/10.1107/S2414314620016259]

Ethyl  $\alpha$ -L-sorbose

Natsumi Nagayama, Norito Taniguchi, Mao Matsumoto, Kei Takeshita and Tomohiko Ishii

Ethyl  $\alpha$ -L-sorbose

## Crystal data

$C_8H_{16}O_6$	$D_x = 1.470 \text{ Mg m}^{-3}$
$M_r = 208.21$	Cu $K\alpha$ radiation, $\lambda = 1.54187 \text{ \AA}$
Orthorhombic, $P2_12_12_1$	Cell parameters from 9046 reflections
$a = 6.8203 (8) \text{ \AA}$	$\theta = 5.1\text{--}68.6^\circ$
$b = 8.6934 (10) \text{ \AA}$	$\mu = 1.09 \text{ mm}^{-1}$
$c = 15.865 (2) \text{ \AA}$	$T = 296 \text{ K}$
$V = 940.63 (19) \text{ \AA}^3$	Block, colorless
$Z = 4$	$0.10 \times 0.10 \times 0.10 \text{ mm}$
$F(000) = 448.00$	

## Data collection

Rigaku R-Axis RAPID diffractometer	1721 independent reflections
Detector resolution: $10.000 \text{ pixels mm}^{-1}$	1602 reflections with $F^2 > 2.0\sigma(F^2)$
$\omega$ scans	$R_{\text{int}} = 0.091$
Absorption correction: multi-scan (ABSCOR; Rigaku, 1995)	$\theta_{\text{max}} = 68.3^\circ$ , $\theta_{\text{min}} = 5.6^\circ$
$T_{\text{min}} = 0.462$ , $T_{\text{max}} = 0.897$	$h = -7 \rightarrow 8$
10373 measured reflections	$k = -10 \rightarrow 10$
	$l = -19 \rightarrow 18$

## Refinement

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.0827P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
1721 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
127 parameters	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack $x$ determined using 581 quotients $[(F^-)-(F)]/[(F^+)+(F)]$ (Parsons <i>et al.</i> , 2013)
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.06 (12)

## Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**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).

H atoms were positioned geometrically (C—H = 0.98, 0.97 or 0.96 Å, and O—H = 0.82 Å) and refined using as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or O})$ , allowing for free rotation of the OH groups.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.0029 (3)	0.18389 (19)	0.69407 (12)	0.0427 (6)
H1	−0.027589	0.171200	0.743583	0.051*
O2	0.3056 (3)	0.46513 (18)	0.70305 (10)	0.0272 (4)
O3	0.0535 (3)	0.66379 (18)	0.63075 (10)	0.0309 (5)
H3	−0.023262	0.711551	0.600806	0.037*
O4	0.2892 (3)	0.71889 (18)	0.48325 (11)	0.0313 (5)
H4	0.222838	0.785460	0.506192	0.038*
O5	0.6053 (3)	0.51250 (18)	0.46175 (12)	0.0393 (6)
H5	0.633778	0.456529	0.421987	0.047*
O6	0.2702 (3)	0.28944 (17)	0.59356 (11)	0.0257 (4)
C1	−0.0118 (4)	0.3405 (3)	0.67368 (18)	0.0331 (6)
H1A	−0.052757	0.397130	0.723326	0.040*
H1B	−0.111982	0.353631	0.630877	0.040*
C2	0.1802 (4)	0.4074 (3)	0.64149 (16)	0.0238 (6)
C3	0.1421 (4)	0.5445 (3)	0.58310 (15)	0.0225 (5)
H3A	0.050371	0.512312	0.538941	0.027*
C4	0.3292 (4)	0.5991 (2)	0.54174 (16)	0.0242 (6)
H4A	0.420080	0.636598	0.584961	0.029*
C5	0.4209 (4)	0.4673 (3)	0.49524 (16)	0.0251 (6)
H5A	0.334371	0.435115	0.449203	0.030*
C6	0.4498 (4)	0.3347 (3)	0.55571 (16)	0.0283 (6)
H6A	0.505486	0.248021	0.525599	0.034*
H6B	0.541691	0.364895	0.599347	0.034*
C7	0.3484 (6)	0.3705 (3)	0.77397 (18)	0.0434 (8)
H7A	0.392720	0.269868	0.755600	0.052*
H7B	0.232444	0.357408	0.808608	0.052*
C8	0.5050 (5)	0.4492 (4)	0.8224 (2)	0.0500 (9)
H8A	0.538256	0.388699	0.870993	0.060*
H8B	0.618825	0.461344	0.787445	0.060*
H8C	0.459315	0.548465	0.840200	0.060*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0666 (16)	0.0315 (10)	0.0301 (10)	−0.0161 (9)	0.0115 (10)	0.0011 (8)
O2	0.0373 (11)	0.0233 (9)	0.0210 (9)	−0.0029 (8)	−0.0068 (8)	0.0021 (7)
O3	0.0390 (12)	0.0297 (9)	0.0241 (9)	0.0174 (8)	0.0028 (9)	0.0013 (7)
O4	0.0418 (12)	0.0220 (8)	0.0299 (10)	0.0040 (8)	0.0069 (9)	0.0058 (7)
O5	0.0410 (12)	0.0257 (9)	0.0512 (13)	−0.0061 (8)	0.0240 (10)	−0.0085 (9)

O6	0.0287 (10)	0.0190 (8)	0.0292 (10)	-0.0008 (7)	0.0060 (8)	-0.0011 (6)
C1	0.0334 (16)	0.0325 (14)	0.0335 (15)	-0.0032 (12)	0.0054 (13)	0.0051 (11)
C2	0.0277 (14)	0.0217 (12)	0.0221 (13)	0.0013 (10)	0.0001 (11)	-0.0003 (9)
C3	0.0250 (14)	0.0213 (11)	0.0213 (12)	0.0031 (10)	0.0019 (10)	-0.0016 (10)
C4	0.0292 (15)	0.0196 (11)	0.0239 (13)	-0.0014 (10)	0.0021 (11)	-0.0001 (9)
C5	0.0260 (14)	0.0215 (12)	0.0279 (14)	-0.0037 (10)	0.0088 (11)	-0.0035 (9)
C6	0.0268 (16)	0.0236 (12)	0.0344 (15)	0.0044 (11)	0.0057 (12)	-0.0015 (10)
C7	0.066 (2)	0.0321 (14)	0.0324 (16)	-0.0072 (14)	-0.0163 (16)	0.0080 (12)
C8	0.057 (2)	0.0532 (18)	0.0398 (18)	-0.0050 (16)	-0.0183 (17)	0.0121 (14)

*Geometric parameters (Å, °)*

O1—C1	1.403 (3)	C2—C3	1.532 (3)
O1—H1	0.8200	C3—C4	1.512 (3)
O2—C2	1.392 (3)	C3—H3A	0.9800
O2—C7	1.424 (3)	C4—C5	1.499 (3)
O3—C3	1.418 (3)	C4—H4A	0.9800
O3—H3	0.8200	C5—C6	1.512 (3)
O4—C4	1.421 (3)	C5—H5A	0.9800
O4—H4	0.8200	C6—H6A	0.9700
O5—C5	1.420 (3)	C6—H6B	0.9700
O5—H5	0.8200	C7—C8	1.483 (4)
O6—C2	1.416 (3)	C7—H7A	0.9700
O6—C6	1.419 (3)	C7—H7B	0.9700
C1—C2	1.521 (4)	C8—H8A	0.9600
C1—H1A	0.9700	C8—H8B	0.9600
C1—H1B	0.9700	C8—H8C	0.9600
C1—O1—H1	109.5	O4—C4—H4A	109.5
C2—O2—C7	118.2 (2)	C5—C4—H4A	109.5
C3—O3—H3	109.5	C3—C4—H4A	109.5
C4—O4—H4	109.5	O5—C5—C4	109.99 (19)
C5—O5—H5	109.5	O5—C5—C6	109.5 (2)
C2—O6—C6	113.59 (17)	C4—C5—C6	108.94 (19)
O1—C1—C2	112.8 (2)	O5—C5—H5A	109.5
O1—C1—H1A	109.0	C4—C5—H5A	109.5
C2—C1—H1A	109.0	C6—C5—H5A	109.5
O1—C1—H1B	109.0	O6—C6—C5	111.6 (2)
C2—C1—H1B	109.0	O6—C6—H6A	109.3
H1A—C1—H1B	107.8	C5—C6—H6A	109.3
O2—C2—O6	111.8 (2)	O6—C6—H6B	109.3
O2—C2—C1	115.5 (2)	C5—C6—H6B	109.3
O6—C2—C1	106.1 (2)	H6A—C6—H6B	108.0
O2—C2—C3	104.35 (19)	O2—C7—C8	106.9 (2)
O6—C2—C3	108.20 (18)	O2—C7—H7A	110.3
C1—C2—C3	110.8 (2)	C8—C7—H7A	110.3
O3—C3—C4	111.19 (19)	O2—C7—H7B	110.3
O3—C3—C2	108.60 (18)	C8—C7—H7B	110.3

C4—C3—C2	111.3 (2)	H7A—C7—H7B	108.6
O3—C3—H3A	108.6	C7—C8—H8A	109.5
C4—C3—H3A	108.6	C7—C8—H8B	109.5
C2—C3—H3A	108.6	H8A—C8—H8B	109.5
O4—C4—C5	108.6 (2)	C7—C8—H8C	109.5
O4—C4—C3	110.6 (2)	H8A—C8—H8C	109.5
C5—C4—C3	109.02 (19)	H8B—C8—H8C	109.5
C7—O2—C2—O6	-71.6 (3)	C1—C2—C3—C4	-172.6 (2)
C7—O2—C2—C1	49.9 (3)	O3—C3—C4—O4	-63.0 (2)
C7—O2—C2—C3	171.7 (2)	C2—C3—C4—O4	175.78 (17)
C6—O6—C2—O2	-55.5 (2)	O3—C3—C4—C5	177.69 (19)
C6—O6—C2—C1	177.7 (2)	C2—C3—C4—C5	56.5 (3)
C6—O6—C2—C3	58.9 (3)	O4—C4—C5—O5	64.3 (3)
O1—C1—C2—O2	-88.5 (3)	C3—C4—C5—O5	-175.1 (2)
O1—C1—C2—O6	36.0 (3)	O4—C4—C5—C6	-175.7 (2)
O1—C1—C2—C3	153.2 (2)	C3—C4—C5—C6	-55.2 (3)
O2—C2—C3—O3	-60.3 (2)	C2—O6—C6—C5	-60.9 (3)
O6—C2—C3—O3	-179.47 (19)	O5—C5—C6—O6	177.60 (19)
C1—C2—C3—O3	64.7 (3)	C4—C5—C6—O6	57.3 (3)
O2—C2—C3—C4	62.5 (2)	C2—O2—C7—C8	172.0 (2)
O6—C2—C3—C4	-56.7 (3)		

*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—H1...O3 <sup>i</sup>	0.82	2.00	2.811 (3)	169
O3—H3...O4 <sup>ii</sup>	0.82	1.94	2.750 (3)	167
O4—H4...O3	0.82	2.52	2.879 (2)	108
O4—H4...O5 <sup>ii</sup>	0.82	2.00	2.791 (2)	163
O5—H5...O6 <sup>iii</sup>	0.82	2.35	2.988 (2)	136

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