

2009

Methyl gallate

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Recommended Citation

Bebout, Deborah and Pagola, Silvina, Methyl gallate (2009). *Acta Crystallographica Section E-Structure Reports Online*, 65, O317-U2094.
10.1107/S1600536809001123

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Methyl gallate

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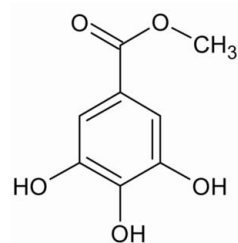
Received 31 December 2008; accepted 9 January 2009

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.033; wR factor = 0.093; data-to-parameter ratio = 11.2.

The crystal structure of the title compound (systematic name: methyl 3,4,5-trihydroxybenzoate), $\text{C}_8\text{H}_8\text{O}_5$, is composed of essentially planar molecules [maximum departures from the mean carbon and oxygen skeleton plane of 0.0348 (10) Å]. The H atoms of the three hydroxyl groups, which function as hydrogen-bond donors and acceptors simultaneously, are oriented in the same direction around the aromatic ring. In addition to two intramolecular hydrogen bonds, each molecule is hydrogen bonded to six others, creating a three-dimensional hydrogen-bonded network.

Related literature

For natural extracts containing gallic acid methyl ester, see: Saxena *et al.* (1994); Schmidt *et al.* (2003); Hawas (2007). For studies concerning antioxidant activity, see: Aruoma *et al.* (1993); Schmidt *et al.* (2003); Hawas (2007). For studies concerning anticancer properties, see: Fiuza *et al.* (2004) and for antimicrobial properties, see: Saxena *et al.* (1994); Landete *et al.* (2007). For cocrystals containing gallic acid methyl ester, see: Sekine *et al.* (2003); Martin *et al.* (1986). Similar gallate ester conformations are found in Parkin *et al.* (2002); Okabe & Kyoyama (2002a); Nomura *et al.* (2000); Mizuguchi *et al.* (2005). For structures with similar hydroxyl arrangements, see: Hitachi *et al.* (2005); Okabe *et al.* (2001); Okabe & Kyoyama (2002b). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$\text{C}_8\text{H}_8\text{O}_5$
 $M_r = 184.14$
Monoclinic, $P2_1/n$
 $a = 7.6963$ (2) Å
 $b = 9.9111$ (2) Å
 $c = 10.5625$ (2) Å
 $\beta = 95.9930$ (10)°

$V = 801.29$ (3) Å³
 $Z = 4$
Cu $K\alpha$ radiation
 $\mu = 1.12$ mm⁻¹
 $T = 100$ (2) K
 $0.31 \times 0.23 \times 0.21$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: numerical (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.723$, $T_{\max} = 0.799$

8192 measured reflections
1352 independent reflections
1311 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.093$
 $S = 0.69$
1352 reflections

121 parameters
All H-atom parameters refined
 $\Delta\rho_{\max} = 0.23$ e Å⁻³
 $\Delta\rho_{\min} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3}\cdots\text{O4}$	0.84	2.25	2.7075 (13)	115
$\text{O4}-\text{H4}\cdots\text{O5}$	0.84	2.29	2.7247 (12)	112
$\text{O4}-\text{H4}\cdots\text{O1}^{\text{i}}$	0.84	2.15	2.9470 (13)	159
$\text{O3}-\text{H3}\cdots\text{O1}^{\text{ii}}$	0.84	1.99	2.7007 (12)	142
$\text{O5}-\text{H5}\cdots\text{O3}^{\text{iii}}$	0.84	1.86	2.6859 (12)	166

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: WinGX (Farrugia, 1999); molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97 (Sheldrick, 2008).

We are indebted to the NSF (CHE-0443345) and The College of William and Mary for the purchase of X-ray equipment. This work was supported in part by the US National Science Foundation (CHE-0315934). Any opinions, findings and conclusions or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the National Science Foundation. SP gratefully acknowledges the Physics Department of the

College of William and Mary for funding and ICDD GIA 08–04.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2286).

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supporting information

Acta Cryst. (2009). E65, o317–o318 [doi:10.1107/S1600536809001123]

Methyl gallate

Deborah Bebout and Silvina Pagola

S1. Comment

Gallic acid methyl ester (**I**) is a polyphenolic compound present in grape seeds and other natural substrates (Saxena *et al.*, 1994; Schmidt *et al.*, 2003; Hawas, 2007). Like other polyphenols, **I** shows antioxidant activity (Aruoma *et al.*, 1993; Schmidt *et al.*, 2003; Hawas, 2007). Formerly used as an astringent and in ophthalmology, its anticancer (Fiuza *et al.*, 2004) and antimicrobial properties (Saxena *et al.*, 1994; Landete *et al.*, 2007) have also been studied. The molecular structure of **I** is shown below.

The molecular geometry is as expected from chemical bond rules (Figure 1) and it shows an almost planar conformation, with maximum departures from the mean carbon and oxygen skeleton plane of 0.0343 (9) and 0.0348 (10) Å for O4 and C8, respectively. The relative positions of the carbonyl and the three hydroxyls were also observed in a cocrystal of **I** and 5-chloro-2-methyl-4-isothiazoline-3-one (Sekine *et al.*, 2003). Four other compounds containing a gallic acid ester moiety have crystallized in an analogous conformation (Parkin *et al.*, 2002; Okabe & Kyoyama, 2002a; Nomura *et al.*, 2000; Mizuguchi *et al.*, 2005). Three other planar conformations of gallic acid esters are found in the Cambridge Structural Database (Allen, 2002). **I** has one of these other conformations in a cocrystal with caffeine (Martin *et al.*, 1986).

Crystallized **I** has intra- and intermolecular hydrogen bonding. The hydroxyl H atoms bound to O3 and O4 (donors) form intramolecular hydrogen bonds to O4 and O5 (acceptors), respectively. This is shown in Figure 1. Similar hydroxyl arrangements have been reported in other gallic acid derivatives, such as gallate ester solvates (Hitachi *et al.*, 2005), a gallic acid monohydrate polymorph (Okabe *et al.*, 2001) and 2,3,4-trihydroxybenzophenone monohydrate (Okabe & Kyoyama, 2002b).

Gallic acid methyl ester forms a three-dimensional H-bonded network lacking significant aromatic ring stacking interactions. There is one molecule of **I** in the asymmetric unit. The H-bonded network is shown in Figure 2. Using the carbonyl ester oxygen O1 (acceptor) and the hydroxyl O3 and O4 (donors), each molecule is linked to another four through two O1...H3—O3, and two O1...H4—O4 H-bonds. These H-bonds are likely relatively weak due to the spacial orientation of the H atoms with respect to the lone electron pairs of O1. In addition, there are two other O5—H5...O3 H-bonds. The three hydroxyl sites are used as hydrogen bond donors and acceptors simultaneously. In the ester group, only the carbonyl oxygen is used as an H-bond acceptor.

S2. Experimental

Gallic acid methyl ester was commercially obtained from Sigma-Aldrich (98% purity) and used as received. The crystal structure determination was carried out from a crystal with rhombic prismatic habit selected from the powder.

S3. Refinement

All hydrogen atoms were observed in the Fourier difference map. However, the torsion angle for the hydroxyl H was refined from the electron density and the methyl H was positioned in idealized staggered geometry. The H atoms were refined constrained to ride on their parent C or O atoms, with $U_{\text{iso}}(\text{H})=1.2 U_{\text{eq}}(\text{C})$ for aromatic H, and $U_{\text{iso}}(\text{H})=1.5 U_{\text{eq}}(\text{C or O})$ for methyl and hydroxyl H, respectively.

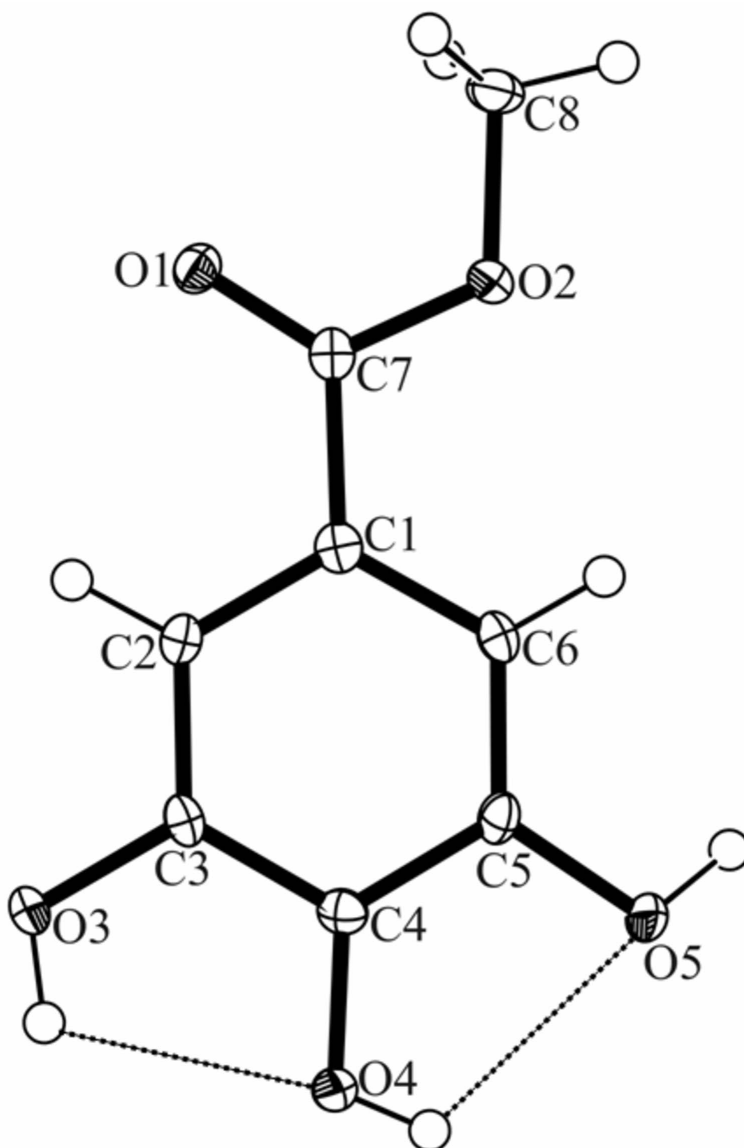
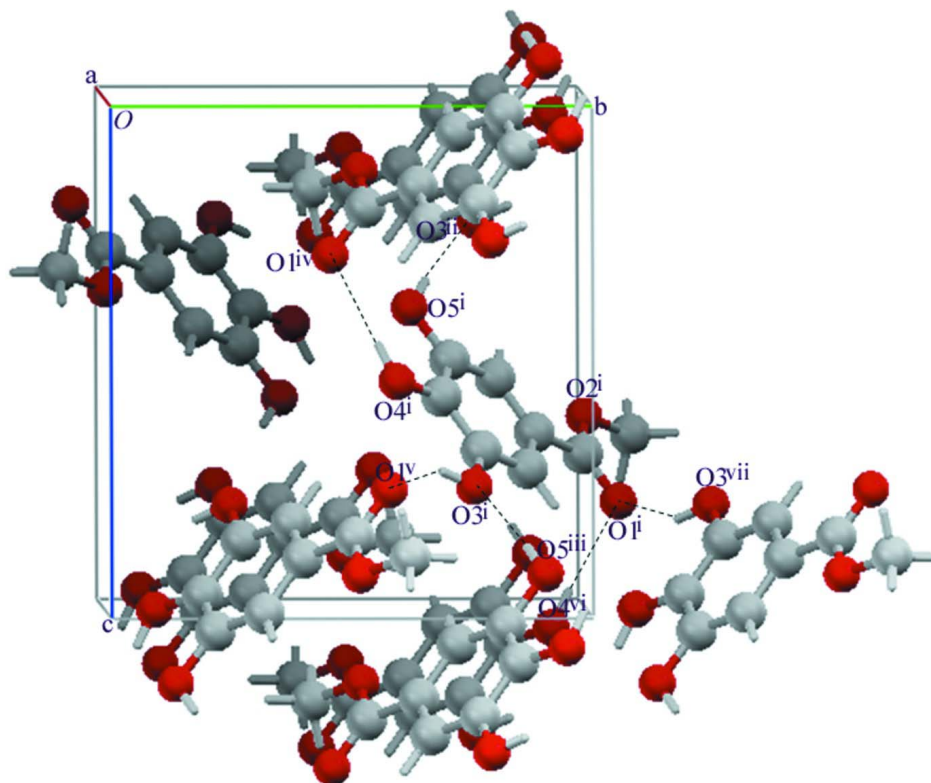


Figure 1

Thermal ellipsoid plot of gallic acid methyl ester with the atomic numbering scheme. Non-H atoms are represented at 50% probability level. Intramolecular hydrogen bonds are shown with dashed lines.

**Figure 2**

The packing of gallic acid methyl ester molecules along the *a*-axis showing the unit cell and the hydrogen bonded network formed (dashed lines). Symmetry codes: (i) x, y, z ; (ii) $1/2 + x, 1.5 - y, -1/2 + z$; (iii) $-1/2 + x, 1.5 - y, 1/2 + z$; (iv) $-1/2 + x, 1.5 - y, -1/2 + z$; (v) $-1/2 - x, -1/2 + y, 1.5 - z$; (vi) $1/2 + x, 1.5 - y, 1/2 + z$; (vii) $-1/2 - x, 1/2 + y, 1.5 - z$.

methyl 3,4,5-trihydroxybenzoate

Crystal data

$C_8H_8O_5$

$M_r = 184.14$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 7.6963\ (2)\ \text{\AA}$

$b = 9.9111\ (2)\ \text{\AA}$

$c = 10.5625\ (2)\ \text{\AA}$

$\beta = 95.993\ (1)^\circ$

$V = 801.29\ (3)\ \text{\AA}^3$

$Z = 4$

$F(000) = 384$

$D_x = 1.526\ \text{Mg m}^{-3}$

Melting point: 474 K

Cu $K\alpha$ radiation, $\lambda = 1.54178\ \text{\AA}$

Cell parameters from 1352 reflections

$\theta = 6.1\text{--}67.0^\circ$

$\mu = 1.12\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Rhombic prism, colourless

$0.31 \times 0.23 \times 0.21\ \text{mm}$

Data collection

Bruker SMART APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ψ scans

Absorption correction: numerical

(*SADABS*; Sheldrick, 2004)

$T_{\min} = 0.723$, $T_{\max} = 0.799$

8192 measured reflections

1352 independent reflections

1311 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 67.0^\circ$, $\theta_{\min} = 6.1^\circ$

$h = -8 \rightarrow 9$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.033$ $wR(F^2) = 0.093$ $S = 0.69$

1352 reflections

121 parameters

0 restraints

32 constraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

 $w = 1/[\sigma^2(F_o^2) + (0.0834P)^2 + 0.9466P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.004$ $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$ *Special details*

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

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	0.14003 (11)	1.05605 (9)	0.77633 (8)	0.0145 (2)
O2	0.29090 (12)	0.99023 (9)	0.61631 (8)	0.0156 (3)
O3	−0.38148 (12)	0.74067 (10)	0.72722 (9)	0.0189 (3)
H3	−0.4389	0.6742	0.6963	0.028*
O4	−0.33530 (12)	0.58249 (9)	0.52444 (9)	0.0167 (2)
H4	−0.314	0.5462	0.4559	0.025*
O5	−0.05442 (13)	0.61740 (10)	0.39075 (9)	0.0185 (3)
H5	0.0127	0.6524	0.3422	0.028*
C7	0.15489 (17)	0.98352 (13)	0.68447 (12)	0.0121 (3)
C1	0.02736 (17)	0.87858 (13)	0.63777 (12)	0.0126 (3)
C2	−0.11958 (17)	0.85957 (13)	0.70290 (12)	0.0126 (3)
H2	−0.1378	0.9145	0.774	0.015*
C3	−0.23803 (17)	0.75983 (13)	0.66260 (12)	0.0129 (3)
C4	−0.21306 (17)	0.67861 (13)	0.55808 (12)	0.0129 (3)
C5	−0.06683 (17)	0.69987 (13)	0.49284 (12)	0.0134 (3)
C6	0.05370 (16)	0.79838 (13)	0.53249 (12)	0.0134 (3)
H6	0.1539	0.8116	0.4885	0.016*
C8	0.42258 (18)	1.09026 (14)	0.65644 (13)	0.0182 (3)
H8A	0.5161	1.0867	0.6003	0.027*
H8B	0.4712	1.0715	0.7441	0.027*
H8C	0.3695	1.1802	0.6521	0.027*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0147 (5)	0.0147 (5)	0.0141 (5)	0.0011 (4)	0.0010 (4)	−0.0023 (4)
O2	0.0135 (5)	0.0186 (5)	0.0153 (5)	−0.0048 (4)	0.0040 (4)	−0.0030 (4)
O3	0.0171 (5)	0.0206 (5)	0.0209 (5)	−0.0067 (4)	0.0108 (4)	−0.0070 (4)

O4	0.0188 (5)	0.0180 (5)	0.0141 (5)	−0.0071 (4)	0.0058 (4)	−0.0043 (4)
O5	0.0237 (5)	0.0196 (5)	0.0140 (5)	−0.0080 (4)	0.0103 (4)	−0.0057 (4)
C1	0.0135 (6)	0.0127 (6)	0.0114 (6)	0.0019 (5)	0.0004 (5)	0.0028 (5)
C2	0.0147 (7)	0.0130 (6)	0.0104 (6)	0.0023 (5)	0.0021 (5)	−0.0002 (5)
C3	0.0127 (6)	0.0147 (6)	0.0120 (6)	0.0012 (5)	0.0041 (5)	0.0025 (5)
C4	0.0137 (6)	0.0123 (6)	0.0124 (6)	−0.0012 (5)	0.0000 (5)	0.0022 (5)
C5	0.0176 (7)	0.0129 (6)	0.0100 (6)	0.0012 (5)	0.0032 (5)	0.0002 (5)
C6	0.0127 (6)	0.0159 (7)	0.0121 (6)	0.0004 (5)	0.0040 (5)	0.0024 (5)
C7	0.0129 (7)	0.0122 (6)	0.0111 (6)	0.0037 (5)	0.0006 (5)	0.0030 (5)
C8	0.0157 (7)	0.0203 (7)	0.0185 (7)	−0.0071 (5)	0.0015 (6)	−0.0010 (5)

Geometric parameters (Å, °)

O1—C7	1.2225 (16)	C1—C6	1.3988 (19)
O2—C7	1.3327 (15)	C2—C3	1.3815 (18)
O2—C8	1.4491 (16)	C2—H2	0.95
O3—C3	1.3705 (15)	C3—C4	1.3957 (18)
O3—H3	0.84	C4—C5	1.3956 (18)
O4—C4	1.3598 (16)	C5—C6	1.3813 (18)
O4—H4	0.84	C6—H6	0.95
O5—C5	1.3644 (16)	C8—H8A	0.98
O5—H5	0.84	C8—H8B	0.98
C7—C1	1.4790 (19)	C8—H8C	0.98
C1—C2	1.3965 (17)		
C7—O2—C8	116.16 (10)	O4—C4—C5	123.25 (11)
C3—O3—H3	109.5	O4—C4—C3	117.52 (11)
C4—O4—H4	109.5	C5—C4—C3	119.22 (12)
C5—O5—H5	109.5	O5—C5—C6	124.25 (11)
O1—C7—O2	122.91 (12)	O5—C5—C4	115.24 (12)
O1—C7—C1	124.36 (11)	C6—C5—C4	120.51 (11)
O2—C7—C1	112.72 (11)	C5—C6—C1	119.62 (12)
C2—C1—C6	120.47 (12)	C5—C6—H6	120.2
C2—C1—C7	118.29 (11)	C1—C6—H6	120.2
C6—C1—C7	121.24 (12)	O2—C8—H8A	109.5
C3—C2—C1	119.15 (12)	O2—C8—H8B	109.5
C3—C2—H2	120.4	H8A—C8—H8B	109.5
C1—C2—H2	120.4	O2—C8—H8C	109.5
O3—C3—C2	119.06 (11)	H8A—C8—H8C	109.5
O3—C3—C4	119.91 (12)	H8B—C8—H8C	109.5
C2—C3—C4	121.03 (12)		
C8—O2—C7—O1	−0.42 (18)	C2—C3—C4—O4	179.88 (11)
C8—O2—C7—C1	−179.68 (10)	O3—C3—C4—C5	179.65 (11)
O1—C7—C1—C2	−0.53 (19)	C2—C3—C4—C5	−0.7 (2)
O2—C7—C1—C2	178.71 (11)	O4—C4—C5—O5	0.45 (19)
O1—C7—C1—C6	−179.44 (12)	C3—C4—C5—O5	−178.97 (11)
O2—C7—C1—C6	−0.19 (17)	O4—C4—C5—C6	−179.37 (11)

C6—C1—C2—C3	0.47 (19)	C3—C4—C5—C6	1.21 (19)
C7—C1—C2—C3	−178.44 (11)	O5—C5—C6—C1	179.28 (12)
C1—C2—C3—O3	179.52 (11)	C4—C5—C6—C1	−0.92 (19)
C1—C2—C3—C4	−0.17 (19)	C2—C1—C6—C5	0.07 (19)
O3—C3—C4—O4	0.19 (18)	C7—C1—C6—C5	178.95 (11)

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>
O3—H3 $\cdots$ O4	0.84	2.25	2.7075 (13)	115
O4—H4 $\cdots$ O5	0.84	2.29	2.7247 (12)	112
O4—H4 $\cdots$ O1 ⁱ	0.84	2.15	2.9470 (13)	159
O3—H3 $\cdots$ O1 ⁱⁱ	0.84	1.99	2.7007 (12)	142
O5—H5 $\cdots$ O3 ⁱⁱⁱ	0.84	1.86	2.6859 (12)	166

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