organic compounds

2-O-Benzhydryl-3,4-(S)-O-benzylidene-D-lyxono-1,4-lactone

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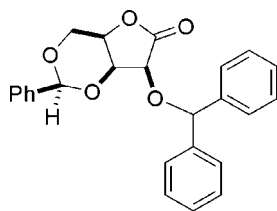
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X-ray crystallography unequivocally showed that protection of the free hydroxyl group of 3,5-O-benzylidene-D-lyxono-1,4-lactone with diphenyldiazomethane proceeded with retention of configuration to give the title compound, $C_{25}H_{22}O_5$. The crystal structure consists of layers of interlocked molecules lying parallel to the a axis.

Related literature

For related literature see: Jackson et al. (1982); Petursson & Webber (1982); Petursson et al. (2007); Petursson (2001, 2003); Draths et al. (1992); Collins & Ferrier (1995); Görbitz (1999); Larson (1970).

Experimental

Crystal data

$C_{25}H_{22}O_5$	$V = 2028.28$ (7) Å^3
$M_r = 402.45$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 9.2805$ (2) Å	$\mu = 0.09$ mm^{-1}
$b = 11.3538$ (2) Å	$T = 150$ K
$c = 19.2493$ (4) Å	$0.50 \times 0.25 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer	17577 measured reflections
Absorption correction: multi-scan	2610 independent reflections
(DENZO/SCALEPACK;	2218 reflections with $I > 2\sigma(I)$
Otwinowski & Minor, 1997)	$R_{int} = 0.036$
$T_{min} = 0.66$, $T_{max} = 0.99$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	272 parameters
$wR(F^2) = 0.077$	H-atom parameters constrained
$S = 0.97$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
2610 reflections	$\Delta\rho_{min} = -0.26$ e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H41···O21^i	0.98	2.59	3.502 (2)	155
C24—H242···O7^i	0.96	2.59	3.320 (2)	133

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

Data collection: COLLECT (Nonius, 1997); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO/SCALEPACK; program(s) used to solve structure: SIR92 (Altomare et al., 1994); program(s) used to refine structure: CRYSTALS (Betteridge et al., 2003); molecular graphics: CAMERON (Watkin et al., 1996); software used to prepare material for publication: CRYSTALS.

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supporting information

2-*O*-Benzhydryl-3,4-(*S*)-*O*-benzylidene-D-lyxono-1,4-lactone

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S1. Comment

Carbohydrates are relatively inexpensive and are useful starting materials for the synthesis of small chiral molecules (Collins & Ferrier, 1995) and chiral building blocks (Draths *et al.*, 1992). Much of their synthetic utility is however dependent on developing successful protecting group strategies. Diazodiphenylmethane has been found to be a useful protecting group in the synthesis of methyl 2,3,6-tri-*O*-methyl-[*α*]-*D*-glucopyranoside and kojibiose octa-acetate (Jackson *et al.*, 1982), and monoalkylations of vicinal diols have been achieved with this reagent and other diaryldiazoalkanes with high regioselectivities (Petursson & Webber, 1982; Petursson *et al.*, 2007; Petursson, 2003; Petursson, 2001). This is of particular interest as the reaction is carried out under neutral conditions.

The utility of the benzhydryl group as a protecting group in carbohydrate chemistry has here been demonstrated with the reaction of 3,5-*O*-benzylidene-D-lyxono-1,4-lactone **1** with diphenyldiazomethane (Fig. 1). Such lactones are susceptible to epimerization at C-2; however *x*-ray crystallography unequivocally showed that this had not occurred and the protection had proceeded with retention of stereochemistry (Fig. 2). The crystal structure consists of layers of interlocked molecules (Fig. 3 and Fig. 4), lying parallel to the *a*-axis. There are no short range intermolecular interactions and no unusual bond lengths or angles. The absolute configuration was determined by the use of D-lyxonolactone as the starting material.

S2. Experimental

The title compound was recrystallized from a 1:1 mixture of ethyl acetate and cyclohexane: m.p.: 461–463 K; $[\alpha]_D^{19}$ +75.6 (*c*, 0.87 in chloroform).

S3. Refinement

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from the starting material.

The relatively large ratio of minimum to maximum corrections applied in the multiscan process (1:1.5) reflect changes in the illuminated volume of the crystal. Changes in illuminated volume were kept to a minimum, and were taken into account (Görbitz, 1999) by the multi-scan inter-frame scaling (*DENZO/SCALEPACK*, Otwinowski & Minor, 1997).

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.
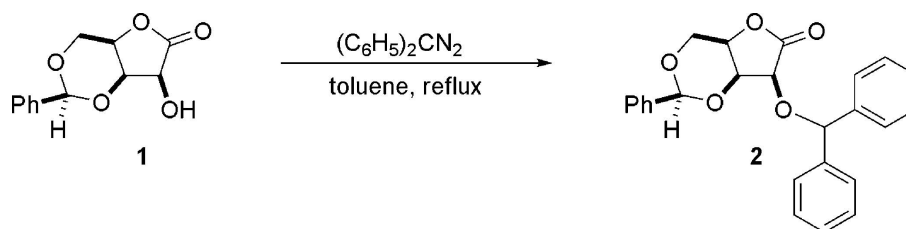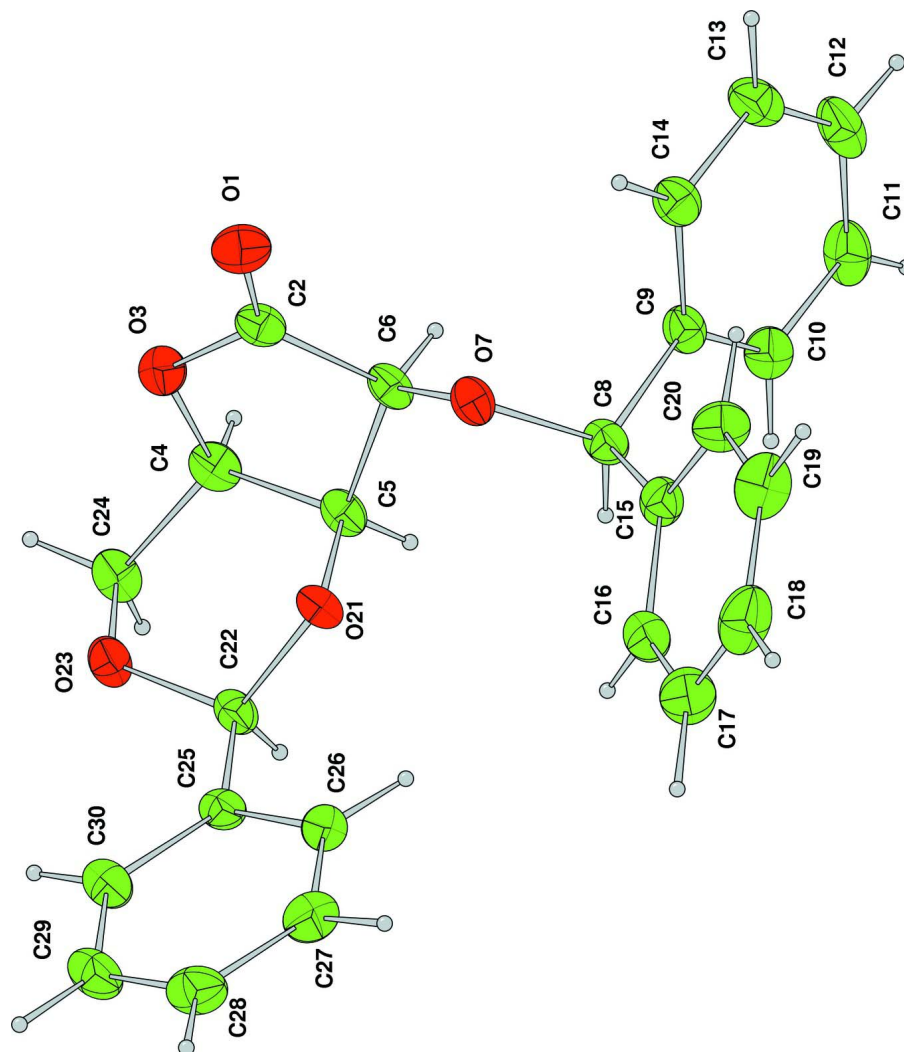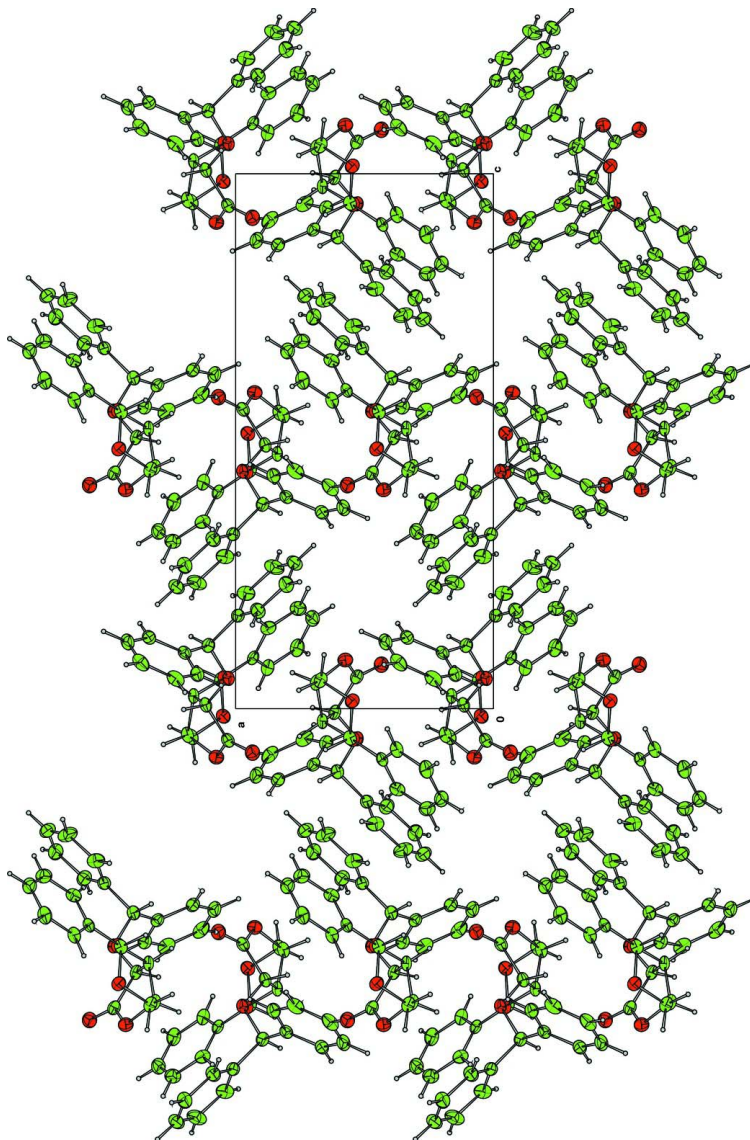
Figure 1

Synthesis of the title compound.

Figure 2

The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

Figure 3

The packing of the title compound projected along the *b*-axis.
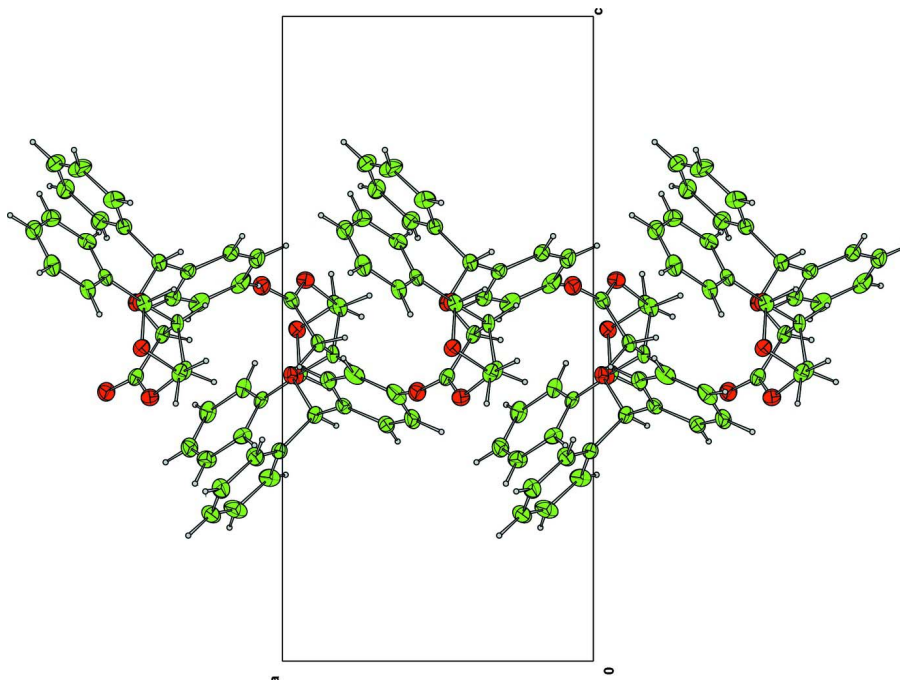
Figure 4

The crystal structure is comprised of layers of interlocked molecules lying parrallel to the *a*-axis.

2-*O*-Benzhydryl-3,4-(*S*)-*O*-benzylidene-d-lyxono-1,4-lactone

Crystal data

$C_{25}H_{22}O_5$	$D_x = 1.318$ Mg m^{-3}
$M_r = 402.45$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 2585 reflections
$a = 9.2805$ (2) Å	$\theta = 5–27°$
$b = 11.3538$ (2) Å	$\mu = 0.09$ mm^{-1}
$c = 19.2493$ (4) Å	$T = 150$ K
$V = 2028.28$ (7) Å^3	Plate, colourless
$Z = 4$	$0.50 \times 0.25 \times 0.10$ mm
$F(000) = 848$	

Data collection

Area diffractometer	17577 measured reflections
Graphite monochromator	2610 independent reflections
ω scans	2218 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)	$R_{int} = 0.036$
	$\theta_{max} = 27.5°$, $\theta_{min} = 5.1°$
	$h = -12 \rightarrow 12$
	$k = -14 \rightarrow 14$
$T_{min} = 0.66$, $T_{max} = 0.99$	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	2610 reflections
Least-squares matrix: full	272 parameters
$R[F^2 > 2\sigma(F^2)] = 0.031$	0 restraints
$wR(F^2) = 0.077$	Primary atom site location: structure-invariant
$S = 0.97$	direct methods

Hydrogen site location: inferred from neighbouring sites		$(\Delta/\sigma)_{max} = 0.001$	
H-atom parameters constrained		$\Delta\rho_{max} = 0.29$ e Å^{-3}	
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.05P)^2 + 0.05P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$		$\Delta\rho_{min} = -0.26$ e Å^{-3}	
		Extinction correction: Larson (1970), Equation 22	
		Extinction coefficient: 450 (70)	

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

	x	y	z	U_{iso}*/U_{eq}
O1	0.56592 (13)	0.07905 (11)	0.41774 (6)	0.0309
C2	0.47068 (18)	0.13932 (14)	0.44062 (8)	0.0235
O3	0.42559 (13)	0.23855 (10)	0.40913 (5)	0.0269
C4	0.31374 (18)	0.29565 (15)	0.45100 (8)	0.0256
C5	0.33742 (17)	0.24620 (13)	0.52366 (8)	0.0217
C6	0.38488 (17)	0.12108 (13)	0.50693 (8)	0.0217
O7	0.47250 (12)	0.06450 (9)	0.55632 (6)	0.0225
C8	0.39489 (18)	0.02870 (14)	0.61807 (8)	0.0231
C9	0.30274 (18)	−0.07850 (14)	0.60446 (7)	0.0226
C10	0.16512 (18)	−0.08515 (15)	0.63305 (8)	0.0268
C11	0.08162 (19)	−0.18516 (17)	0.62452 (9)	0.0330
C12	0.1333 (2)	−0.27901 (16)	0.58623 (9)	0.0343
C13	0.2677 (2)	−0.27227 (15)	0.55607 (9)	0.0317
C14	0.35179 (19)	−0.17234 (14)	0.56436 (8)	0.0256
C15	0.50938 (17)	0.01400 (14)	0.67385 (8)	0.0244
C16	0.5410 (2)	0.11037 (15)	0.71553 (8)	0.0322
C17	0.6506 (2)	0.10513 (18)	0.76443 (9)	0.0411
C18	0.7288 (2)	0.00261 (19)	0.77220 (9)	0.0398
C19	0.6970 (2)	−0.09474 (18)	0.73217 (9)	0.0374
C20	0.58660 (19)	−0.08899 (16)	0.68292 (8)	0.0307
O21	0.45628 (12)	0.30226 (9)	0.55734 (5)	0.0220
C22	0.44412 (18)	0.42778 (13)	0.55495 (8)	0.0222
O23	0.45259 (12)	0.46674 (9)	0.48571 (5)	0.0252
C24	0.33004 (18)	0.42708 (14)	0.44694 (9)	0.0266
C25	0.56836 (17)	0.47882 (14)	0.59490 (7)	0.0215
C26	0.62747 (18)	0.41894 (15)	0.65075 (8)	0.0271
C27	0.7432 (2)	0.46592 (16)	0.68709 (9)	0.0325
C28	0.7986 (2)	0.57411 (16)	0.66872 (8)	0.0324
C29	0.73958 (18)	0.63525 (15)	0.61357 (9)	0.0312
C30	0.62512 (17)	0.58803 (14)	0.57660 (9)	0.0259
H41	0.2201	0.2695	0.4329	0.0329*
H51	0.2482	0.2446	0.5518	0.0264*
H61	0.2989	0.0724	0.4983	0.0229*
H81	0.3272	0.0931	0.6347	0.0229*
H101	0.1291	−0.0182	0.6591	0.0311*
H111	−0.0116	−0.1921	0.6444	0.0416*
H121	0.0759	−0.3458	0.5822	0.0375*
H131	0.3037	−0.3345	0.5304	0.0389*
H141	0.4444	−0.1693	0.5436	0.0295*

H161	0.4895	0.1815	0.7110	0.0385*
H171	0.6701	0.1722	0.7928	0.0503*
H181	0.8027	−0.0007	0.8051	0.0490*
H191	0.7479	−0.1668	0.7368	0.0442*
H201	0.5650	−0.1576	0.6565	0.0324*
H221	0.3486	0.4485	0.5766	0.0278*
H241	0.3431	0.4511	0.3995	0.0304*
H242	0.2454	0.4644	0.4657	0.0301*
H261	0.5900	0.3434	0.6651	0.0326*
H271	0.7810	0.4188	0.7246	0.0403*
H281	0.8757	0.6049	0.6915	0.0371*
H291	0.7803	0.7078	0.6024	0.0400*
H301	0.5885	0.6317	0.5379	0.0304*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0281 (6)	0.0319 (6)	0.0328 (6)	0.0032 (6)	−0.0004 (6)	−0.0061 (6)
C2	0.0221 (8)	0.0219 (8)	0.0267 (8)	−0.0032 (8)	−0.0045 (7)	−0.0031 (7)
O3	0.0295 (6)	0.0255 (6)	0.0259 (5)	−0.0002 (5)	−0.0004 (5)	0.0013 (5)
C4	0.0196 (8)	0.0247 (8)	0.0324 (8)	−0.0007 (7)	−0.0037 (7)	−0.0007 (7)
C5	0.0149 (7)	0.0200 (8)	0.0303 (8)	−0.0027 (7)	−0.0003 (7)	0.0007 (7)
C6	0.0189 (8)	0.0172 (7)	0.0290 (8)	−0.0031 (7)	−0.0036 (7)	0.0015 (7)
O7	0.0193 (6)	0.0208 (5)	0.0274 (5)	−0.0006 (5)	−0.0007 (5)	0.0031 (5)
C8	0.0225 (8)	0.0198 (7)	0.0272 (7)	−0.0021 (7)	0.0016 (7)	−0.0001 (7)
C9	0.0230 (8)	0.0214 (8)	0.0234 (7)	−0.0016 (7)	−0.0039 (7)	0.0035 (7)
C10	0.0242 (9)	0.0301 (9)	0.0262 (8)	−0.0011 (8)	−0.0030 (7)	0.0021 (7)
C11	0.0234 (9)	0.0414 (11)	0.0343 (8)	−0.0109 (9)	−0.0040 (8)	0.0100 (8)
C12	0.0366 (11)	0.0280 (9)	0.0383 (9)	−0.0130 (8)	−0.0142 (9)	0.0106 (8)
C13	0.0401 (10)	0.0211 (8)	0.0340 (8)	0.0005 (8)	−0.0103 (9)	0.0004 (8)
C14	0.0247 (9)	0.0234 (8)	0.0287 (8)	0.0005 (7)	−0.0020 (7)	0.0018 (7)
C15	0.0226 (8)	0.0274 (8)	0.0233 (7)	−0.0059 (7)	0.0007 (7)	0.0016 (7)
C16	0.0424 (11)	0.0264 (9)	0.0280 (8)	−0.0085 (9)	−0.0015 (9)	0.0021 (7)
C17	0.0514 (12)	0.0423 (11)	0.0297 (8)	−0.0159 (11)	−0.0102 (9)	0.0005 (8)
C18	0.0333 (10)	0.0584 (13)	0.0278 (8)	−0.0122 (10)	−0.0072 (8)	0.0076 (9)
C19	0.0290 (9)	0.0475 (12)	0.0358 (9)	0.0027 (10)	−0.0026 (8)	0.0066 (9)
C20	0.0288 (9)	0.0321 (9)	0.0313 (8)	0.0019 (8)	−0.0037 (8)	−0.0036 (8)
O21	0.0221 (6)	0.0156 (5)	0.0283 (5)	−0.0016 (5)	−0.0024 (5)	−0.0003 (5)
C22	0.0226 (8)	0.0158 (7)	0.0283 (8)	0.0007 (7)	0.0033 (7)	0.0007 (7)
O23	0.0260 (6)	0.0223 (5)	0.0272 (5)	−0.0045 (5)	−0.0028 (5)	0.0044 (5)
C24	0.0230 (8)	0.0244 (8)	0.0325 (8)	−0.0016 (8)	−0.0054 (8)	0.0038 (8)
C25	0.0188 (8)	0.0198 (7)	0.0261 (7)	0.0004 (7)	0.0056 (7)	−0.0043 (7)
C26	0.0316 (9)	0.0252 (8)	0.0246 (7)	−0.0035 (8)	0.0042 (8)	−0.0012 (7)
C27	0.0351 (10)	0.0353 (10)	0.0271 (8)	0.0007 (9)	−0.0012 (8)	−0.0033 (8)
C28	0.0261 (9)	0.0366 (10)	0.0345 (9)	−0.0067 (8)	−0.0009 (8)	−0.0098 (8)
C29	0.0266 (9)	0.0240 (9)	0.0428 (9)	−0.0057 (8)	0.0038 (9)	−0.0029 (8)
C30	0.0219 (8)	0.0214 (8)	0.0344 (8)	−0.0001 (7)	0.0038 (7)	−0.0007 (7)

Geometric parameters (Å, º)

O1—C2	1.2015 (19)	C15—C20	1.382 (2)
C2—O3	1.3461 (19)	C16—C17	1.387 (3)
C2—C6	1.519 (2)	C16—H161	0.942
O3—C4	1.465 (2)	C17—C18	1.380 (3)
C4—C5	1.523 (2)	C17—H171	0.955
C4—C24	1.502 (2)	C18—C19	1.379 (3)
C4—H41	0.982	C18—H181	0.934
C5—C6	1.522 (2)	C19—C20	1.397 (2)
C5—O21	1.4291 (18)	C19—H191	0.948
C5—H51	0.990	C20—H201	0.952
C6—O7	1.4063 (18)	O21—C22	1.4303 (18)
C6—H61	0.984	C22—O23	1.4065 (18)
O7—C8	1.4482 (19)	C22—C25	1.502 (2)
C8—C9	1.510 (2)	C22—H221	1.008
C8—C15	1.520 (2)	O23—C24	1.4329 (19)
C8—H81	1.016	C24—H241	0.961
C9—C10	1.393 (2)	C24—H242	0.962
C9—C14	1.392 (2)	C25—C26	1.385 (2)
C10—C11	1.385 (2)	C25—C30	1.393 (2)
C10—H101	0.970	C26—C27	1.388 (2)
C11—C12	1.382 (3)	C26—H261	0.966
C11—H111	0.949	C27—C28	1.378 (2)
C12—C13	1.377 (3)	C27—H271	0.965
C12—H121	0.930	C28—C29	1.382 (2)
C13—C14	1.386 (2)	C28—H281	0.909
C13—H131	0.925	C29—C30	1.386 (2)
C14—H141	0.949	C29—H291	0.931
C15—C16	1.388 (2)	C30—H301	0.958
O1—C2—O3	122.70 (15)	C16—C15—C20	118.96 (15)
O1—C2—C6	128.04 (15)	C15—C16—C17	120.88 (17)
O3—C2—C6	109.25 (13)	C15—C16—H161	121.0
C2—O3—C4	110.05 (12)	C17—C16—H161	118.1
O3—C4—C5	103.88 (12)	C16—C17—C18	119.71 (17)
O3—C4—C24	109.85 (14)	C16—C17—H171	119.6
C5—C4—C24	113.54 (14)	C18—C17—H171	120.7
O3—C4—H41	107.3	C17—C18—C19	120.16 (17)
C5—C4—H41	110.0	C17—C18—H181	119.6
C24—C4—H41	111.8	C19—C18—H181	120.3
C4—C5—C6	101.04 (12)	C18—C19—C20	119.92 (18)
C4—C5—O21	111.33 (13)	C18—C19—H191	122.1
C6—C5—O21	106.76 (12)	C20—C19—H191	118.0
C4—C5—H51	112.9	C19—C20—C15	120.35 (17)
C6—C5—H51	109.9	C19—C20—H201	118.6
O21—C5—H51	114.0	C15—C20—H201	121.1
C5—C6—C2	101.68 (12)	C5—O21—C22	111.61 (12)

C5—C6—O7	116.79 (13)	O21—C22—O23	109.84 (12)
C2—C6—O7	109.11 (12)	O21—C22—C25	107.90 (13)
C5—C6—H61	109.0	O23—C22—C25	108.72 (13)
C2—C6—H61	111.1	O21—C22—H221	106.8
O7—C6—H61	109.0	O23—C22—H221	111.6
C6—O7—C8	113.30 (11)	C25—C22—H221	111.9
O7—C8—C9	111.43 (12)	C22—O23—C24	110.51 (12)
O7—C8—C15	105.25 (12)	C4—C24—O23	111.41 (13)
C9—C8—C15	115.46 (13)	C4—C24—H241	110.2
O7—C8—H81	111.4	O23—C24—H241	107.8
C9—C8—H81	106.5	C4—C24—H242	109.6
C15—C8—H81	106.8	O23—C24—H242	108.3
C8—C9—C10	119.62 (14)	H241—C24—H242	109.5
C8—C9—C14	121.86 (14)	C22—C25—C26	120.79 (14)
C10—C9—C14	118.52 (15)	C22—C25—C30	120.28 (14)
C9—C10—C11	120.72 (16)	C26—C25—C30	118.92 (15)
C9—C10—H101	118.6	C25—C26—C27	120.58 (16)
C11—C10—H101	120.7	C25—C26—H261	121.1
C10—C11—C12	120.09 (17)	C27—C26—H261	118.4
C10—C11—H111	122.1	C26—C27—C28	120.13 (17)
C12—C11—H111	117.8	C26—C27—H271	116.4
C11—C12—C13	119.76 (17)	C28—C27—H271	123.4
C11—C12—H121	118.3	C27—C28—C29	119.82 (17)
C13—C12—H121	121.9	C27—C28—H281	120.9
C12—C13—C14	120.44 (16)	C29—C28—H281	119.3
C12—C13—H131	120.7	C28—C29—C30	120.25 (16)
C14—C13—H131	118.9	C28—C29—H291	117.4
C9—C14—C13	120.39 (15)	C30—C29—H291	122.3
C9—C14—H141	120.1	C25—C30—C29	120.29 (16)
C13—C14—H141	119.5	C25—C30—H301	121.6
C8—C15—C16	117.99 (15)	C29—C30—H301	118.1
C8—C15—C20	123.00 (14)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C4—H41···O21[i]	0.98	2.59	3.502 (2)	155
C24—H242···O7[i]	0.96	2.59	3.320 (2)	133

Symmetry code: (i) $x-1/2$, $-y+1/2$, $-z+1$.