Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-(7-Acetoxy-6-methoxy-4-methyl-2-oxo-2*H*-chromen-3-yl)phenyl acetate

Hao Jiang, Peng Xia and Qian Zhang*

Department of Medicinal Chemistry, School of Pharmacy, Fudan University, Shanghai 200032, People's Republic of China
Correspondence e-mail: zhangqian511@shmu.edu.cn

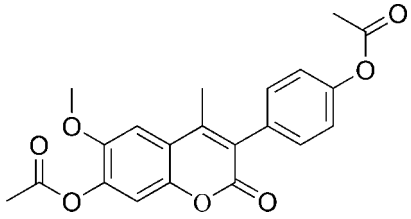
Received 29 April 2008; accepted 1 May 2008

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.074; wR factor = 0.254; data-to-parameter ratio = 12.2.

The title compound, $C_{21}H_{18}O_7$, is an important intermediate in the synthesis of 3-(4-hydroxyphenyl)-4-methyl-6-methoxy-7-hydroxycoumarin, which is a nonsteroidal analogue of 2-methoxyestradiol (2-ME). The substituent benzene ring is not in the same plane as the coumarin ring system, with a dihedral angle of 66.88 (10)°. There are some weak intermolecular C—H···O interactions. One carbonyl O atom is disordered over two sites, with occupancies of 0.6 and 0.4.

Related literature

For related literature, see: Gibanananda *et al.* (2006); Sutherland *et al.* (2007).



Experimental

Crystal data

$C_{21}H_{18}O_7$
M_r = 382.35
Triclinic, $P\overline{1}$
a = 8.142 (3) Å
b = 11.167 (4) Å
c = 11.756 (4) Å
α = 65.130 (4)°
β = 75.392 (4)°
γ = 79.055 (4)°
V = 934.1 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 (2) K
0.15 × 0.12 × 0.04 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.985, T_{max} = 0.996
3893 measured reflections
3245 independent reflections
2279 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.074
$wR(F^2)$ = 0.254
S = 1.09
3245 reflections
266 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C20—H20B···O2^{i}	0.96	2.47	3.362 (4)	154
C20—H20C···O4B^{i}	0.96	2.55	3.297 (9)	134
C11—H11B···O7^{ii}	0.96	2.74	3.349 (4)	122
C13—H13···O2^{iii}	0.93	2.74	3.331 (4)	122
C19—H19A···O7^{iii}	0.96	2.50	3.392 (5)	154
C17—H17···O2^{iv}	0.93	2.66	3.246 (3)	122

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was financed by the National Natural Science Foundation of China (grant No. 30500631, awarded to Qian Zhang) and the Postgraduate Innovative Research Foundation of Fudan University (grant awarded to Hao Jiang). The authors acknowledge Professor Minqin Chen, Center of Analysis and Measurement, Fudan University, for his kind help with the data analysis and his professional advice.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2199).

References

Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Gibanananda, R., Gopal, D., Veladhuizen, P. J. V., Banerjee, S., Saxena, N. K., Sengupta, K. & Banerjee, S. K. (2006). *Biochemistry*, **45**, 3703–3713.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sutherland, T. E., Anderson, R. L., Hughes, A. R., Altmann, E., Schliga, M., Ziogas, J. & Stewart, A. G. (2007). *Drug Discov. Today*, **12**, 577–584.

supporting information

Acta Cryst. (2008). E**64**, o1230 [doi:10.1107/S1600536808012890]

4-(7-Acetoxy-6-methoxy-4-methyl-2-oxo-2*H*-chromen-3-yl)phenyl acetate

Hao Jiang, Peng Xia and Qian Zhang

S1. Comment

2-ME, an endogenous metabolite of estrogen, was proved to be a potent antitumor and antiangiogenic compound (Gibanananda *et al.*, 2006). Currently 2-ME is in phase I–III clinical trials for treating a variety of solid cancers, especially breast cancer, prostate cancer and multiple myeloma (Sutherland *et al.*, 2007). Based on the structure and the bioactivity of 2-ME, 3-(*p*-hydroxyphenyl)-4-methyl-6-methoxyl-7-hydroxycoumarin, an non-steroidal analog of 2-ME, was designed, synthesized and evaluated on Human Umbilical Vein Endothelial Cells (HUVEC). The compound showed higher activity and much lower toxicity (EC_{50} = 5.69 μM; TI = 45.01) than 2-ME (EC_{50} = 8.59 μM; TI = 8.25) in the biological assay. Here we report the crystal structure of 3-(*p*-acetoxyphenyl)-4-methyl-6-methoxyl-7-acetoxycoumarin, which is an important intermediate in the synthesis of 3-(*p*-hydroxyphenyl)-4-methyl-6-methoxyl-7-hydroxycoumarin. The molecular structure of (I) is illustrated in Fig.1. The coumarin ring system (C1—C10) is essentially planar, with a mean deviation of 0.0153 Å from the least-squares plane defined by the ten constituent atoms. The coumarin ring system and the 3-aryl ring make a dihedral angle of 66.88 (10)°. The fact that the of C3—C12 bond [length 1.480 (4) Å] is a single bond also confirms that the coumarin ring system and the 3-substituent are not conjugated. The molecular packing (Fig. 2) is stabilized by weak intermolecular C—H···O hydrogen bonds.

S2. Experimental

A mixture of 1-(2,4-dihydroxyl-5-methoxyphenyl)ethanone (300 mg, 1.65 mmol), 4-hydroxyphenylacetic acid (501 mg, 3.29 mmol), Et_3N (6 ml) and Ac_2O (10 ml) was refluxed for 10 h. After cooling, the mixture was poured into 2 *N* HCl (20 ml) and extracted with acetyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a yellow oil, which was purified *via* chromatography on silica gel column with petroleum ether/acetone (10:3) as eluent. The title compound was recrystallized from acetyl acetate to give colorless crystals for the single-crystal X-ray diffraction analysis.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.93 Å for aromatic H atoms and 0.96 Å for methyl H atoms, and refined in riding mode with U_{iso}(H) = 1.2 U_{eq}(C) for aromatic H atoms and U_{iso}(H) = 1.5 U_{eq}(C) for methyl H atoms.

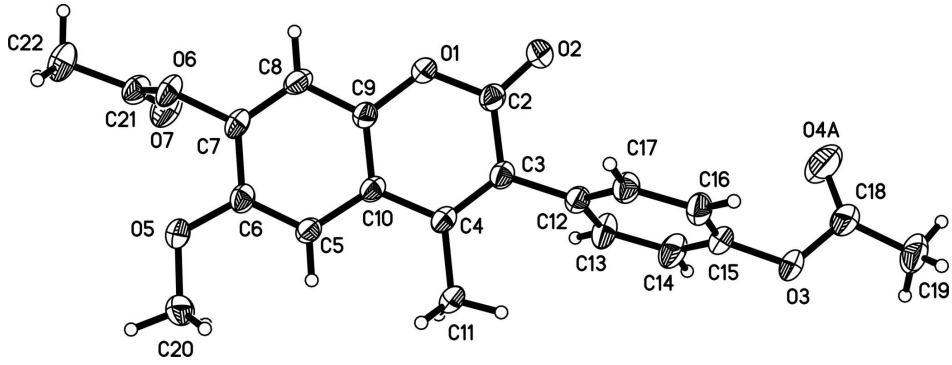


Figure 1

The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms. The minor disorder component is not shown.

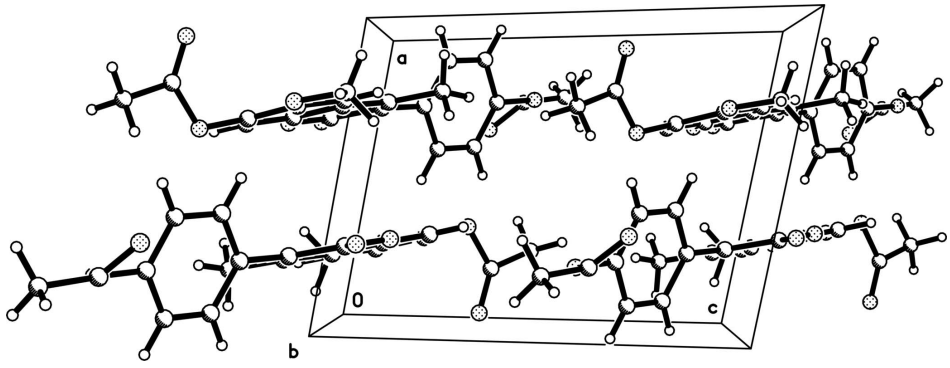


Figure 2

Packing diagram, viewed down the *b* axis.

4-(7-Acetoxy-6-methoxy-4-methyl-2-oxo-2H-chromen-3-yl)phenyl acetate

Crystal data

$C_{21}H_{18}O_7$
M_r = 382.35
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.142 (3) Å
b = 11.167 (4) Å
c = 11.756 (4) Å
α = 65.130 (4)°
β = 75.392 (4)°
γ = 79.055 (4)°
V = 934.1 (5) Å^3
Z = 2
F(000) = 400
D_x = 1.359 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 954 reflections
θ = 2.6–26.3°
μ = 0.10 mm^{-1}
T = 293 K
Sheet, colorless
0.15 × 0.12 × 0.04 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.985, T_{max} = 0.996
3893 measured reflections
3245 independent reflections
2279 reflections with $I > 2\sigma(I)$

R_{int} = 0.031
θ_{max} = 25.1°, θ_{min} = 2.0°
h = −9→9
k = −13→10
l = −13→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.074
$wR(F^2)$ = 0.254
S = 1.10
3245 reflections
266 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
$w = 1/[\sigma^2(F_o^2) + (0.1741P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.3185 (3)	0.17959 (18)	0.16190 (17)	0.0502 (6)	
O2	0.3094 (3)	0.3939 (2)	0.1010 (2)	0.0586 (6)	
O3	0.2256 (3)	0.8533 (2)	−0.4110 (2)	0.0687 (7)	
O5	0.2670 (3)	−0.27608 (18)	0.10771 (19)	0.0563 (6)	
O6	0.3460 (2)	−0.28758 (18)	0.31855 (17)	0.0507 (6)	
O7	0.0661 (3)	−0.3060 (2)	0.3850 (2)	0.0736 (7)	
C2	0.2997 (4)	0.3052 (3)	0.0710 (3)	0.0461 (7)	
C3	0.2680 (3)	0.3215 (3)	−0.0519 (3)	0.0422 (7)	
C4	0.2529 (3)	0.2128 (3)	−0.0733 (2)	0.0405 (6)	
C5	0.2552 (3)	−0.0362 (3)	0.0142 (2)	0.0425 (7)	
H5	0.2329	−0.0317	−0.0613	0.051*	
C6	0.2753 (3)	−0.1569 (3)	0.1113 (3)	0.0442 (7)	
C7	0.3133 (3)	−0.1642 (3)	0.2232 (3)	0.0440 (7)	
C8	0.3266 (4)	−0.0521 (3)	0.2393 (3)	0.0481 (7)	
H8	0.3507	−0.0578	0.3148	0.058*	
C9	0.3036 (3)	0.0699 (3)	0.1407 (2)	0.0413 (6)	
C10	0.2678 (3)	0.0826 (3)	0.0268 (2)	0.0399 (6)	
C11	0.2208 (4)	0.2260 (3)	−0.1983 (3)	0.0527 (8)	
H11A	0.2364	0.3147	−0.2601	0.079*	
H11B	0.1061	0.2074	−0.1871	0.079*	
H11C	0.2992	0.1644	−0.2276	0.079*	
C12	0.2578 (3)	0.4597 (3)	−0.1475 (3)	0.0444 (7)	

C13	0.1053 (4)	0.5256 (3)	−0.1852 (3)	0.0592 (8)	
H13	0.0075	0.4810	−0.1518	0.071*	
C14	0.0962 (4)	0.6549 (3)	−0.2704 (3)	0.0641 (9)	
H14	−0.0067	0.6966	−0.2953	0.077*	
C15	0.2384 (4)	0.7232 (3)	−0.3192 (3)	0.0524 (8)	
C16	0.3906 (4)	0.6615 (3)	−0.2841 (3)	0.0540 (8)	
H16	0.4875	0.7072	−0.3181	0.065*	
C17	0.3995 (4)	0.5314 (3)	−0.1982 (3)	0.0497 (7)	
H17	0.5028	0.4907	−0.1737	0.060*	
C18	0.2305 (6)	0.9555 (4)	−0.3829 (4)	0.0864 (13)	
O4A	0.1775 (16)	0.9331 (7)	−0.2672 (6)	0.159 (4)	0.55
O4B	0.3254 (11)	0.9405 (7)	−0.3076 (8)	0.094 (2)	0.45
C19	0.2078 (6)	1.0852 (3)	−0.4860 (4)	0.0876 (12)	
H19A	0.1643	1.1509	−0.4506	0.131*	
H19B	0.1287	1.0822	−0.5329	0.131*	
H19C	0.3155	1.1075	−0.5424	0.131*	
C20	0.2417 (4)	−0.2736 (3)	−0.0087 (3)	0.0571 (8)	
H20A	0.1307	−0.2306	−0.0234	0.086*	
H20B	0.2502	−0.3627	−0.0032	0.086*	
H20C	0.3270	−0.2258	−0.0781	0.086*	
C21	0.2086 (4)	−0.3556 (3)	0.3919 (3)	0.0515 (8)	
C22	0.2624 (5)	−0.4899 (3)	0.4777 (3)	0.0720 (10)	
H22A	0.2921	−0.4860	0.5500	0.108*	
H22B	0.3596	−0.5265	0.4327	0.108*	
H22C	0.1707	−0.5449	0.5065	0.108*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0708 (14)	0.0396 (11)	0.0404 (11)	−0.0112 (9)	−0.0212 (9)	−0.0075 (9)
O2	0.0779 (15)	0.0445 (12)	0.0597 (13)	−0.0139 (10)	−0.0268 (11)	−0.0153 (10)
O3	0.113 (2)	0.0374 (12)	0.0452 (12)	−0.0105 (12)	−0.0248 (12)	0.0010 (9)
O5	0.0827 (15)	0.0348 (11)	0.0463 (12)	−0.0121 (10)	−0.0177 (10)	−0.0054 (9)
O6	0.0515 (12)	0.0402 (11)	0.0424 (11)	−0.0096 (9)	−0.0125 (9)	0.0050 (9)
O7	0.0529 (14)	0.0680 (16)	0.0697 (16)	−0.0088 (12)	−0.0070 (11)	0.0002 (12)
C2	0.0489 (16)	0.0437 (16)	0.0429 (16)	−0.0153 (12)	−0.0139 (12)	−0.0068 (13)
C3	0.0420 (15)	0.0379 (15)	0.0410 (15)	−0.0089 (11)	−0.0109 (12)	−0.0064 (12)
C4	0.0398 (14)	0.0402 (15)	0.0345 (14)	−0.0074 (11)	−0.0094 (11)	−0.0052 (11)
C5	0.0492 (16)	0.0401 (15)	0.0345 (14)	−0.0087 (12)	−0.0120 (12)	−0.0072 (12)
C6	0.0464 (15)	0.0364 (15)	0.0426 (15)	−0.0107 (12)	−0.0077 (12)	−0.0062 (12)
C7	0.0437 (15)	0.0378 (14)	0.0361 (14)	−0.0081 (11)	−0.0069 (11)	0.0005 (11)
C8	0.0555 (17)	0.0502 (17)	0.0336 (14)	−0.0113 (14)	−0.0154 (12)	−0.0053 (12)
C9	0.0469 (15)	0.0372 (14)	0.0371 (14)	−0.0089 (11)	−0.0092 (11)	−0.0093 (11)
C10	0.0402 (14)	0.0402 (15)	0.0336 (14)	−0.0096 (11)	−0.0089 (11)	−0.0057 (11)
C11	0.073 (2)	0.0404 (15)	0.0380 (15)	−0.0088 (14)	−0.0198 (14)	−0.0027 (12)
C12	0.0499 (16)	0.0397 (15)	0.0401 (15)	−0.0092 (12)	−0.0122 (12)	−0.0084 (12)
C13	0.0510 (17)	0.0442 (17)	0.065 (2)	−0.0106 (14)	−0.0162 (15)	0.0009 (14)
C14	0.0596 (19)	0.0531 (19)	0.063 (2)	−0.0022 (15)	−0.0246 (16)	−0.0007 (15)

C15	0.072 (2)	0.0405 (16)	0.0363 (15)	−0.0119 (14)	−0.0124 (14)	−0.0031 (12)
C16	0.0615 (19)	0.0416 (16)	0.0510 (17)	−0.0156 (14)	−0.0083 (14)	−0.0075 (13)
C17	0.0490 (16)	0.0442 (16)	0.0510 (17)	−0.0111 (13)	−0.0130 (13)	−0.0092 (13)
C18	0.153 (4)	0.045 (2)	0.057 (2)	−0.003 (2)	−0.040 (3)	−0.0074 (16)
O4A	0.341 (14)	0.060 (4)	0.057 (4)	0.018 (7)	−0.045 (6)	−0.017 (3)
O4B	0.162 (7)	0.044 (3)	0.087 (5)	−0.015 (4)	−0.069 (5)	−0.009 (3)
C19	0.128 (4)	0.0412 (19)	0.070 (2)	−0.002 (2)	−0.020 (2)	−0.0011 (16)
C20	0.071 (2)	0.0475 (17)	0.0543 (18)	−0.0161 (14)	−0.0085 (15)	−0.0191 (14)
C21	0.0548 (19)	0.0492 (17)	0.0397 (16)	−0.0136 (14)	−0.0073 (13)	−0.0047 (13)
C22	0.077 (2)	0.0501 (19)	0.061 (2)	−0.0128 (17)	−0.0088 (17)	0.0060 (16)

Geometric parameters (Å, º)

O1—C2	1.369 (3)	C11—H11C	0.960
O1—C9	1.380 (3)	C12—C17	1.389 (4)
O2—C2	1.205 (3)	C12—C13	1.392 (4)
O3—C18	1.324 (4)	C13—C14	1.369 (4)
O3—C15	1.402 (3)	C13—H13	0.930
O5—C6	1.364 (3)	C14—C15	1.372 (5)
O5—C20	1.423 (4)	C14—H14	0.930
O6—C21	1.363 (3)	C15—C16	1.369 (5)
O6—C7	1.392 (3)	C16—C17	1.378 (4)
O7—C21	1.194 (4)	C16—H16	0.930
C2—C3	1.461 (4)	C17—H17	0.930
C3—C4	1.371 (4)	C18—O4A	1.248 (7)
C3—C12	1.480 (4)	C18—O4B	1.257 (7)
C4—C10	1.442 (3)	C18—C19	1.461 (5)
C4—C11	1.498 (4)	C19—H19A	0.960
C5—C6	1.364 (4)	C19—H19B	0.960
C5—C10	1.421 (4)	C19—H19C	0.960
C5—H5	0.930	C20—H20A	0.960
C6—C7	1.392 (4)	C20—H20B	0.960
C7—C8	1.369 (4)	C20—H20C	0.960
C8—C9	1.386 (4)	C21—C22	1.470 (4)
C8—H8	0.930	C22—H22A	0.960
C9—C10	1.386 (4)	C22—H22B	0.960
C11—H11A	0.960	C22—H22C	0.960
C11—H11B	0.960		

C2—O1—C9	121.4 (2)	C14—C13—H13	119.3
C18—O3—C15	120.8 (2)	C12—C13—H13	119.3
C6—O5—C20	116.9 (2)	C13—C14—C15	120.2 (3)
C21—O6—C7	116.7 (2)	C13—C14—H14	119.9
O2—C2—O1	115.9 (2)	C15—C14—H14	119.9
O2—C2—C3	125.5 (3)	C16—C15—C14	120.0 (3)
O1—C2—C3	118.6 (2)	C16—C15—O3	121.5 (3)
C4—C3—C2	120.2 (2)	C14—C15—O3	118.4 (3)
C4—C3—C12	124.4 (2)	C15—C16—C17	119.7 (3)

C2—C3—C12	115.4 (2)	C15—C16—H16	120.1
C3—C4—C10	119.3 (2)	C17—C16—H16	120.1
C3—C4—C11	121.6 (2)	C16—C17—C12	121.6 (3)
C10—C4—C11	119.1 (2)	C16—C17—H17	119.2
C6—C5—C10	121.0 (2)	C12—C17—H17	119.2
C6—C5—H5	119.5	O4A—C18—O3	113.0 (5)
C10—C5—H5	119.5	O4B—C18—O3	117.6 (5)
O5—C6—C5	125.2 (2)	O4A—C18—C19	123.9 (5)
O5—C6—C7	115.1 (2)	O4B—C18—C19	119.1 (5)
C5—C6—C7	119.6 (2)	O3—C18—C19	114.7 (3)
C8—C7—O6	119.0 (2)	C18—C19—H19A	109.5
C8—C7—C6	121.2 (2)	C18—C19—H19B	109.5
O6—C7—C6	119.7 (2)	H19A—C19—H19B	109.5
C7—C8—C9	118.6 (2)	C18—C19—H19C	109.5
C7—C8—H8	120.7	H19A—C19—H19C	109.5
C9—C8—H8	120.7	H19B—C19—H19C	109.5
O1—C9—C10	121.3 (2)	O5—C20—H20A	109.5
O1—C9—C8	116.2 (2)	O5—C20—H20B	109.5
C10—C9—C8	122.5 (2)	H20A—C20—H20B	109.5
C9—C10—C5	117.0 (2)	O5—C20—H20C	109.5
C9—C10—C4	119.1 (2)	H20A—C20—H20C	109.5
C5—C10—C4	123.8 (2)	H20B—C20—H20C	109.5
C4—C11—H11A	109.5	O7—C21—O6	121.7 (3)
C4—C11—H11B	109.5	O7—C21—C22	127.3 (3)
H11A—C11—H11B	109.5	O6—C21—C22	111.0 (3)
C4—C11—H11C	109.5	C21—C22—H22A	109.5
H11A—C11—H11C	109.5	C21—C22—H22B	109.5
H11B—C11—H11C	109.5	H22A—C22—H22B	109.5
C17—C12—C13	117.1 (3)	C21—C22—H22C	109.5
C17—C12—C3	120.9 (2)	H22A—C22—H22C	109.5
C13—C12—C3	121.9 (2)	H22B—C22—H22C	109.5
C14—C13—C12	121.4 (3)		

C9—O1—C2—O2	177.5 (2)	C8—C9—C10—C4	−177.3 (2)
C9—O1—C2—C3	−1.8 (4)	C6—C5—C10—C9	0.9 (4)
O2—C2—C3—C4	−177.4 (3)	C6—C5—C10—C4	178.1 (2)
O1—C2—C3—C4	1.8 (4)	C3—C4—C10—C9	−2.5 (4)
O2—C2—C3—C12	3.8 (4)	C11—C4—C10—C9	177.7 (2)
O1—C2—C3—C12	−177.0 (2)	C3—C4—C10—C5	−179.6 (2)
C2—C3—C4—C10	0.3 (4)	C11—C4—C10—C5	0.6 (4)
C12—C3—C4—C10	179.0 (2)	C4—C3—C12—C17	−113.2 (3)
C2—C3—C4—C11	−179.9 (2)	C2—C3—C12—C17	65.6 (4)
C12—C3—C4—C11	−1.2 (4)	C4—C3—C12—C13	70.4 (4)
C20—O5—C6—C5	2.5 (4)	C2—C3—C12—C13	−110.8 (3)
C20—O5—C6—C7	−175.2 (2)	C17—C12—C13—C14	1.2 (5)
C10—C5—C6—O5	−179.4 (2)	C3—C12—C13—C14	177.8 (3)
C10—C5—C6—C7	−1.8 (4)	C12—C13—C14—C15	−1.0 (5)
C21—O6—C7—C8	106.7 (3)	C13—C14—C15—C16	0.9 (5)

C21—O6—C7—C6	−76.1 (3)	C13—C14—C15—O3	176.9 (3)
O5—C6—C7—C8	179.6 (2)	C18—O3—C15—C16	−74.4 (5)
C5—C6—C7—C8	1.7 (4)	C18—O3—C15—C14	109.6 (4)
O5—C6—C7—O6	2.5 (4)	C14—C15—C16—C17	−1.0 (5)
C5—C6—C7—O6	−175.4 (2)	O3—C15—C16—C17	−176.9 (3)
O6—C7—C8—C9	176.3 (2)	C15—C16—C17—C12	1.1 (5)
C6—C7—C8—C9	−0.8 (4)	C13—C12—C17—C16	−1.2 (4)
C2—O1—C9—C10	−0.4 (4)	C3—C12—C17—C16	−177.8 (3)
C2—O1—C9—C8	179.4 (2)	C15—O3—C18—O4A	−27.7 (9)
C7—C8—C9—O1	−180.0 (2)	C15—O3—C18—O4B	35.1 (8)
C7—C8—C9—C10	−0.1 (4)	C15—O3—C18—C19	−177.3 (3)
O1—C9—C10—C5	179.9 (2)	C7—O6—C21—O7	−8.4 (4)
C8—C9—C10—C5	0.0 (4)	C7—O6—C21—C22	173.1 (3)
O1—C9—C10—C4	2.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C20—H20*B*···O2^{i}	0.96	2.47	3.362 (4)	154
C20—H20*C*···O4*B*^{i}	0.96	2.55	3.297 (9)	134
C11—H11*B*···O7^{ii}	0.96	2.74	3.349 (4)	122
C13—H13···O2^{iii}	0.93	2.74	3.331 (4)	122
C19—H19*A*···O7^{iii}	0.96	2.50	3.392 (5)	154
C17—H17···O2^{iv}	0.93	2.66	3.246 (3)	122

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, −*y*, −*z*; (iii) −*x*, −*y*+1, −*z*; (iv) −*x*+1, −*y*+1, −*z*.