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Methyl 3-[(chloromethoxy)carbonyloxy]-7-hydroxycholan-24-oate

Jia-Liang Zhong,[a] Wen-Xia Sun,[a] Fu-Li Zhang,[a] Li-Hong Liu[b] and He Liu[b]*

[a]Shanghai Institute of Pharmaceutical Industry, Shanghai 200040, People's Republic of China, and [b]Beijing Chao-Yang Hospital Affiliated with Beijing Capital Medical University, Beijing 100020, People's Republic of China
Correspondence e-mail: liuheliuhe@126.com

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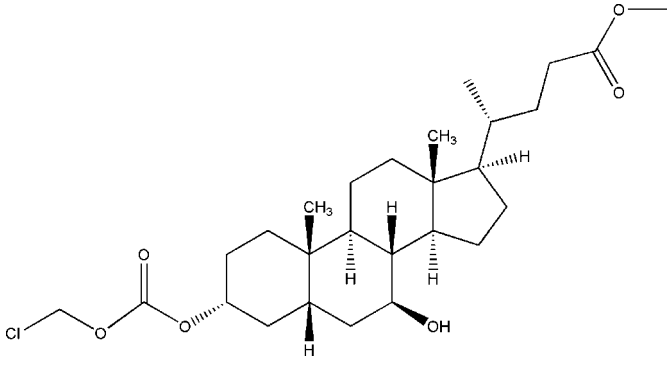
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.050; wR factor = 0.118; data-to-parameter ratio = 17.4.

The title compound, $C_{27}H_{43}ClO_6$, is a derivative of ursodeoxycholic acid, in which the OH group at the 3-position is substituted by a chloromethoxycarbonyloxy substituent and the carboxylic acid group at the 24-position is methylated. The *A* and *B* rings are *cis*-fused, while all other rings are *trans*-fused. In the crystal, two adjacent molecules located along the *b*-axis direction are interlocked head-to-tail due to weak C—H···O hydrogen bonds. Therefore each molecule is linked to four neighbouring molecules by four C—H···O hydrogen bonds, with the OH group at the 7-position and the carbonyl O atom of the ester group acting as the acceptor sites.

Related literature

For the synthesis of the title compound, see: von Geldern *et al.* (2004); For similar structures, see: Kannan *et al.* (2001); Lindley & Carey *et al.* (1987).



Experimental

Crystal data

$C_{27}H_{43}ClO_6$
M_r = 499.06
Orthorhombic, $P2_12_12_1$
a = 7.8896 (13) Å
b = 10.9493 (17) Å
c = 30.683 (5) Å
V = 2650.6 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.18 mm^{-1}
T = 294 K
0.24 × 0.20 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
15292 measured reflections
5411 independent reflections
3191 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.118
S = 0.94
5411 reflections
311 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Absolute structure: Flack (1983), 2309 Friedel pairs
Flack parameter: −0.10 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11B···O2^{i}	0.97	2.49	3.339 (4)	146
C27—H27B···O5^{ii}	0.97	2.40	3.270 (4)	149

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; 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: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2434).

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supplementary materials

Acta Cryst. (2013). E**69**, o1186 [doi:10.1107/S160053681301725X]

Methyl 3-[(chloromethoxy)carbonyloxy]-7-hydroxycholan-24-oate

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Comment

The title compound, (I) (Fig. 1), methyl 3-((chloromethoxy)carbonyloxy-7- hydroxycholan-24-oate was synthesized according to a general literature procedure (von Geldern *et al.*, 2004).

Bile acid is a widely studied and used pharmaceutical molecule (Kannan *et al.*, 2001). It can be used to treat jaundice, gallstones (Lindley & Carey, 1987) *etc*. Ursodeoxycholic acid (UDCA) and chenodeoxycholic acid (CDCA) are two most famous analogues of bile acid. Here we report the crystal structure of a UDCA derivative.

In the crystal structure, rings A and B are *cis* fused while rings B/C/D are *trans* fused. The dihedral angles of A/B, B/C, C/D are 62.89 (8)°, 2.70 (14)° and 5.05 (17)°, respectively. So the skeleton of the title compound exhibits a V shape with the 3-α and 17-β side chains stretched as the arms. In the crystal packing (Fig. 2), two adjacent molecules located along the *b* axis are interlocked head to tail due to weak hydrogen bondings (C11—H11B···O2 and C27—H27B···O5, Table 1). Therefore each molecule of the title compound is linked to four neighboring molecules by four C—H···O hydrogen bonds.

Experimental

Chloromethyl-chloroformate was slowly added to a solution of methyl 3,7- dihydroxycholan-24-oate and anhydrous pyridine in anhydrous CH_2Cl_2 under nitrogen at 273 K. The resulting mixture was allowed to warm to room temperature, was then stirred for 7 h and then extracted with CH_2Cl_2. The organic extract was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was washed with diethyl ether to afford the title compound as a white solid (>95% yield). No further purification was necessary. Crystals appropriate for X-ray diffraction data collection were obtained by slow evaporation of a saturated DMF/H_2O solution at room temperature.

Refinement

The H atom of the OH-group in 7-position was located from the difference Fourier map and restraind to ride on its parent O atom. All other H atoms were placed in geometically idealized positions and constrained to ride on their parent atoms with C—H distances of 0.93 Å (0.96 for methyl group) and U_{iso}(H) = 1.2 (1.5 for CH_3)U_{eq}(C) for CH.

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); 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: *publCIF* (Westrip, 2010).

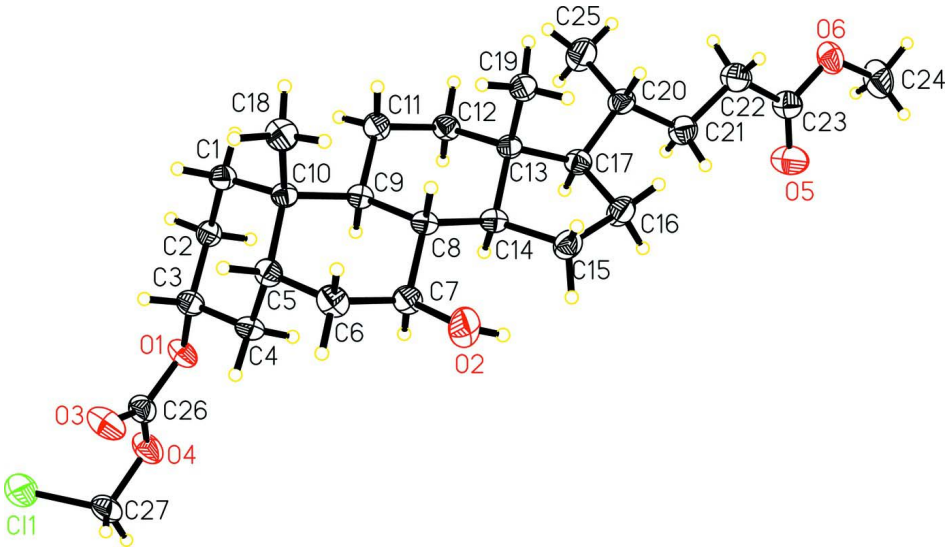

Figure 1

Molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

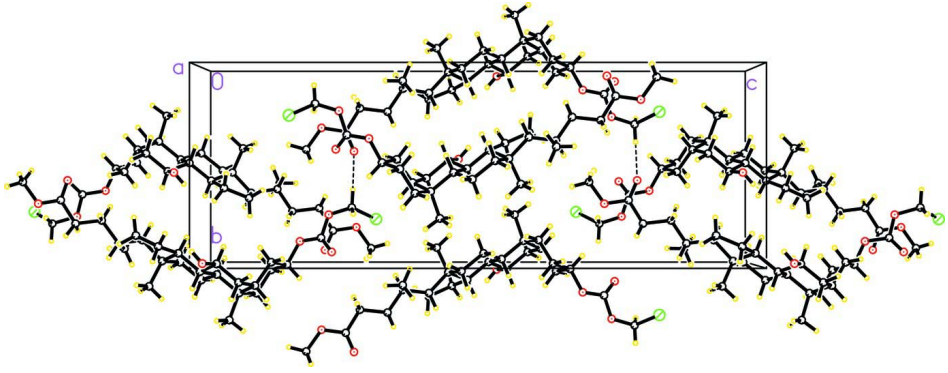

Figure 2

The packing of the title compound, viewed down the *a* axis. Dashed lines indicate the C—H···O hydrogen bonds.

Methyl 3-[(chloromethoxy)carbonyloxy]-7-hydroxycholan-24-oate

Crystal data

$C_{27}H_{43}ClO_6$
$M_r = 499.06$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 7.8896\ (13)$ Å
$b = 10.9493\ (17)$ Å
$c = 30.683\ (5)$ Å
$V = 2650.6\ (7)$ Å^3
$Z = 4$

$F(000) = 1080$
$D_x = 1.251$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2869 reflections
$\theta = 2.3$–$20.2°$
$\mu = 0.18$ mm^{-1}
$T = 294$ K
Block, colorless
0.24 × 0.20 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
15292 measured reflections
5411 independent reflections
3191 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.0°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -38 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.118$
$S = 0.94$
5411 reflections
311 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.1843P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Absolute structure: Flack (1983), 2309 Friedel pairs
Flack parameter: −0.10 (9)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.32107 (15)	0.26524 (10)	0.18096 (3)	0.0899 (4)
O1	0.2665 (3)	0.37444 (17)	0.31505 (6)	0.0499 (5)
O2	−0.3225 (2)	0.4663 (2)	0.46546 (7)	0.0736 (7)
H2	−0.3270	0.4100	0.4831	0.110*
O3	0.1100 (3)	0.4228 (2)	0.25576 (7)	0.0717 (7)
O4	0.2450 (3)	0.24219 (18)	0.26367 (6)	0.0657 (7)
O5	0.1643 (4)	0.0724 (2)	0.72053 (8)	0.0823 (8)
O6	0.2415 (3)	0.18771 (19)	0.77669 (7)	0.0623 (6)
C1	0.3092 (4)	0.6337 (2)	0.39347 (9)	0.0435 (7)
H1A	0.3016	0.7011	0.3730	0.052*
H1B	0.3992	0.6527	0.4139	0.052*
C2	0.3587 (3)	0.5194 (2)	0.36840 (9)	0.0408 (7)
H2A	0.4639	0.5334	0.3528	0.049*
H2B	0.3758	0.4521	0.3885	0.049*
C3	0.2202 (3)	0.4882 (3)	0.33670 (9)	0.0416 (7)
H3	0.2097	0.5535	0.3150	0.050*

C4	0.0533 (3)	0.4714 (3)	0.35987 (9)	0.0439 (7)
H4A	0.0613	0.4012	0.3791	0.053*
H4B	−0.0342	0.4545	0.3385	0.053*
C5	0.0019 (3)	0.5833 (3)	0.38662 (10)	0.0415 (7)
H5	−0.0158	0.6502	0.3659	0.050*
C6	−0.1667 (4)	0.5618 (3)	0.40940 (9)	0.0508 (8)
H6A	−0.2474	0.5302	0.3884	0.061*
H6B	−0.2097	0.6394	0.4199	0.061*
C7	−0.1550 (3)	0.4733 (3)	0.44751 (9)	0.0462 (7)
H7	−0.1227	0.3926	0.4365	0.055*
C8	−0.0229 (3)	0.5153 (3)	0.48090 (9)	0.0351 (6)
H8	−0.0600	0.5940	0.4927	0.042*
C9	0.1503 (3)	0.5350 (2)	0.45808 (8)	0.0342 (6)
H9	0.1819	0.4558	0.4457	0.041*
C10	0.1415 (3)	0.6260 (2)	0.41883 (9)	0.0361 (6)
C11	0.2904 (4)	0.5677 (3)	0.49034 (9)	0.0459 (8)
H11A	0.2699	0.6494	0.5014	0.055*
H11B	0.3979	0.5688	0.4750	0.055*
C12	0.3042 (3)	0.4796 (3)	0.52914 (9)	0.0442 (7)
H12A	0.3393	0.3998	0.5188	0.053*
H12B	0.3897	0.5091	0.5492	0.053*
C13	0.1340 (3)	0.4681 (2)	0.55303 (9)	0.0359 (7)
C14	−0.0003 (3)	0.4264 (3)	0.51936 (9)	0.0380 (7)
H14	0.0433	0.3504	0.5067	0.046*
C15	−0.1512 (4)	0.3896 (3)	0.54761 (10)	0.0517 (8)
H15A	−0.2190	0.3277	0.5332	0.062*
H15B	−0.2223	0.4597	0.5539	0.062*
C16	−0.0713 (4)	0.3389 (3)	0.58960 (10)	0.0576 (9)
H16A	−0.0917	0.2517	0.5918	0.069*
H16B	−0.1206	0.3784	0.6149	0.069*
C17	0.1219 (4)	0.3648 (3)	0.58750 (9)	0.0426 (7)
H17	0.1754	0.2924	0.5748	0.051*
C18	0.1007 (4)	0.7560 (3)	0.43452 (10)	0.0541 (8)
H18A	0.1943	0.7871	0.4511	0.081*
H18B	0.0010	0.7543	0.4525	0.081*
H18C	0.0812	0.8078	0.4098	0.081*
C19	0.0859 (4)	0.5906 (2)	0.57389 (9)	0.0462 (8)
H19A	0.0679	0.6503	0.5515	0.069*
H19B	0.1758	0.6172	0.5927	0.069*
H19C	−0.0162	0.5809	0.5906	0.069*
C20	0.2012 (4)	0.3833 (3)	0.63295 (9)	0.0481 (8)
H20	0.1423	0.4517	0.6469	0.058*
C21	0.1710 (4)	0.2695 (3)	0.66091 (9)	0.0549 (8)
H21A	0.0532	0.2455	0.6580	0.066*
H21B	0.2399	0.2034	0.6495	0.066*
C22	0.2112 (5)	0.2856 (3)	0.70923 (10)	0.0659 (10)
H22A	0.3244	0.3192	0.7121	0.079*
H22B	0.1325	0.3441	0.7216	0.079*
C23	0.2014 (4)	0.1701 (3)	0.73474 (10)	0.0535 (8)

C24	0.2399 (5)	0.0802 (3)	0.80385 (11)	0.0825 (12)
H24A	0.1299	0.0429	0.8027	0.124*
H24B	0.2653	0.1028	0.8334	0.124*
H24C	0.3236	0.0234	0.7936	0.124*
C25	0.3888 (4)	0.4142 (4)	0.63165 (12)	0.0798 (12)
H25A	0.4474	0.3547	0.6143	0.120*
H25B	0.4336	0.4135	0.6607	0.120*
H25C	0.4038	0.4938	0.6191	0.120*
C26	0.1968 (4)	0.3558 (3)	0.27627 (10)	0.0494 (8)
C27	0.1876 (5)	0.2065 (3)	0.22191 (9)	0.0642 (10)
H27A	0.0731	0.2362	0.2174	0.077*
H27B	0.1854	0.1181	0.2201	0.077*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1037 (8)	0.1095 (8)	0.0566 (5)	−0.0270 (6)	0.0159 (6)	−0.0190 (5)
O1	0.0637 (13)	0.0502 (12)	0.0358 (11)	0.0123 (10)	−0.0067 (11)	−0.0087 (10)
O2	0.0304 (11)	0.126 (2)	0.0641 (15)	−0.0057 (12)	0.0029 (12)	0.0148 (14)
O3	0.0891 (18)	0.0694 (15)	0.0566 (14)	0.0211 (14)	−0.0233 (15)	−0.0142 (12)
O4	0.1050 (19)	0.0487 (12)	0.0433 (12)	0.0106 (13)	−0.0066 (13)	−0.0096 (10)
O5	0.124 (2)	0.0533 (14)	0.0699 (16)	−0.0114 (15)	−0.0356 (17)	0.0132 (13)
O6	0.0814 (17)	0.0611 (13)	0.0445 (12)	0.0078 (12)	0.0031 (13)	0.0078 (11)
C1	0.0495 (19)	0.0389 (16)	0.0421 (16)	−0.0033 (14)	−0.0036 (15)	−0.0019 (14)
C2	0.0362 (15)	0.0453 (16)	0.0410 (16)	−0.0001 (14)	0.0027 (14)	−0.0016 (14)
C3	0.0423 (16)	0.0417 (16)	0.0407 (16)	0.0044 (14)	−0.0009 (15)	−0.0064 (13)
C4	0.0414 (17)	0.0485 (17)	0.0417 (18)	−0.0028 (14)	−0.0091 (15)	−0.0070 (15)
C5	0.0396 (17)	0.0435 (17)	0.0414 (17)	0.0053 (14)	−0.0066 (15)	0.0038 (15)
C6	0.0355 (16)	0.066 (2)	0.0505 (18)	0.0099 (15)	−0.0055 (16)	−0.0017 (16)
C7	0.0289 (15)	0.063 (2)	0.0468 (18)	0.0007 (15)	−0.0016 (15)	−0.0029 (16)
C8	0.0299 (14)	0.0360 (15)	0.0395 (16)	0.0043 (12)	−0.0013 (13)	−0.0072 (13)
C9	0.0304 (14)	0.0336 (15)	0.0387 (15)	0.0060 (12)	−0.0013 (13)	−0.0043 (12)
C10	0.0365 (15)	0.0327 (15)	0.0392 (15)	0.0028 (13)	0.0012 (14)	−0.0045 (13)
C11	0.0340 (16)	0.0604 (19)	0.0434 (17)	−0.0018 (15)	−0.0007 (15)	−0.0012 (15)
C12	0.0372 (16)	0.0516 (17)	0.0438 (17)	0.0012 (14)	−0.0047 (15)	−0.0025 (14)
C13	0.0360 (15)	0.0339 (15)	0.0379 (16)	0.0008 (13)	−0.0009 (14)	−0.0016 (13)
C14	0.0327 (16)	0.0367 (15)	0.0444 (17)	0.0038 (13)	−0.0021 (15)	−0.0075 (14)
C15	0.0417 (17)	0.058 (2)	0.0554 (19)	−0.0081 (15)	−0.0026 (17)	0.0066 (16)
C16	0.0531 (19)	0.063 (2)	0.057 (2)	−0.0165 (16)	−0.0101 (18)	0.0185 (18)
C17	0.0471 (17)	0.0352 (16)	0.0455 (17)	0.0026 (13)	−0.0017 (16)	−0.0015 (14)
C18	0.065 (2)	0.0400 (17)	0.0569 (19)	0.0126 (16)	−0.0005 (18)	−0.0009 (15)
C19	0.0553 (19)	0.0382 (17)	0.0452 (18)	0.0000 (15)	0.0015 (16)	−0.0002 (14)
C20	0.0547 (19)	0.0418 (16)	0.0478 (18)	−0.0083 (15)	−0.0081 (17)	0.0067 (14)
C21	0.059 (2)	0.0509 (19)	0.0547 (19)	−0.0017 (16)	−0.0068 (18)	0.0086 (15)
C22	0.096 (3)	0.050 (2)	0.0516 (19)	−0.0089 (19)	−0.014 (2)	0.0100 (16)
C23	0.055 (2)	0.051 (2)	0.054 (2)	0.0046 (17)	−0.0109 (18)	0.0041 (17)
C24	0.121 (3)	0.072 (2)	0.054 (2)	0.017 (2)	0.002 (2)	0.0246 (19)
C25	0.069 (2)	0.105 (3)	0.065 (2)	−0.031 (2)	−0.023 (2)	0.026 (2)
C26	0.058 (2)	0.049 (2)	0.0415 (18)	0.0017 (17)	0.0030 (18)	−0.0060 (16)
C27	0.091 (3)	0.060 (2)	0.0418 (18)	−0.0061 (19)	0.000 (2)	−0.0203 (16)

Geometric parameters (Å, º)

Cl1—C27	1.761 (3)	C11—H11B	0.9700
O1—C26	1.327 (3)	C12—C13	1.535 (4)
O1—C3	1.458 (3)	C12—H12A	0.9700
O2—C7	1.433 (3)	C12—H12B	0.9700
O2—H2	0.8200	C13—C19	1.534 (4)
O3—C26	1.185 (4)	C13—C14	1.549 (4)
O4—C26	1.357 (3)	C13—C17	1.551 (4)
O4—C27	1.414 (3)	C14—C15	1.526 (4)
O5—C23	1.191 (4)	C14—H14	0.9800
O6—C23	1.340 (4)	C15—C16	1.538 (4)
O6—C24	1.442 (3)	C15—H15A	0.9700
C1—C2	1.520 (4)	C15—H15B	0.9700
C1—C10	1.537 (4)	C16—C17	1.552 (4)
C1—H1A	0.9700	C16—H16A	0.9700
C1—H1B	0.9700	C16—H16B	0.9700
C2—C3	1.502 (3)	C17—C20	1.542 (4)
C2—H2A	0.9700	C17—H17	0.9800
C2—H2B	0.9700	C18—H18A	0.9600
C3—C4	1.508 (4)	C18—H18B	0.9600
C3—H3	0.9800	C18—H18C	0.9600
C4—C5	1.530 (4)	C19—H19A	0.9600
C4—H4A	0.9700	C19—H19B	0.9600
C4—H4B	0.9700	C19—H19C	0.9600
C5—C6	1.521 (4)	C20—C25	1.519 (4)
C5—C10	1.552 (4)	C20—C21	1.531 (4)
C5—H5	0.9800	C20—H20	0.9800
C6—C7	1.522 (4)	C21—C22	1.526 (4)
C6—H6A	0.9700	C21—H21A	0.9700
C6—H6B	0.9700	C21—H21B	0.9700
C7—C8	1.533 (4)	C22—C23	1.489 (4)
C7—H7	0.9800	C22—H22A	0.9700
C8—C14	1.540 (4)	C22—H22B	0.9700
C8—C9	1.550 (4)	C24—H24A	0.9600
C8—H8	0.9800	C24—H24B	0.9600
C9—C11	1.526 (4)	C24—H24C	0.9600
C9—C10	1.564 (4)	C25—H25A	0.9600
C9—H9	0.9800	C25—H25B	0.9600
C10—C18	1.537 (4)	C25—H25C	0.9600
C11—C12	1.536 (4)	C27—H27A	0.9700
C11—H11A	0.9700	C27—H27B	0.9700
C26—O1—C3	115.8 (2)	C12—C13—C17	116.1 (2)
C7—O2—H2	109.5	C14—C13—C17	101.4 (2)
C26—O4—C27	114.9 (3)	C15—C14—C8	120.8 (2)
C23—O6—C24	115.8 (3)	C15—C14—C13	103.4 (2)
C2—C1—C10	115.6 (2)	C8—C14—C13	113.8 (2)
C2—C1—H1A	108.4	C15—C14—H14	105.9
C10—C1—H1A	108.4	C8—C14—H14	105.9

C2—C1—H1B	108.4	C13—C14—H14	105.9
C10—C1—H1B	108.4	C14—C15—C16	104.6 (2)
H1A—C1—H1B	107.4	C14—C15—H15A	110.8
C3—C2—C1	109.2 (2)	C16—C15—H15A	110.8
C3—C2—H2A	109.9	C14—C15—H15B	110.8
C1—C2—H2A	109.9	C16—C15—H15B	110.8
C3—C2—H2B	109.9	H15A—C15—H15B	108.9
C1—C2—H2B	109.9	C15—C16—C17	107.5 (2)
H2A—C2—H2B	108.3	C15—C16—H16A	110.2
O1—C3—C2	107.9 (2)	C17—C16—H16A	110.2
O1—C3—C4	109.2 (2)	C15—C16—H16B	110.2
C2—C3—C4	111.0 (2)	C17—C16—H16B	110.2
O1—C3—H3	109.6	H16A—C16—H16B	108.5
C2—C3—H3	109.6	C20—C17—C13	119.8 (2)
C4—C3—H3	109.6	C20—C17—C16	112.6 (2)
C3—C4—C5	112.7 (2)	C13—C17—C16	102.8 (2)
C3—C4—H4A	109.0	C20—C17—H17	107.0
C5—C4—H4A	109.0	C13—C17—H17	107.0
C3—C4—H4B	109.0	C16—C17—H17	107.0
C5—C4—H4B	109.0	C10—C18—H18A	109.5
H4A—C4—H4B	107.8	C10—C18—H18B	109.5
C6—C5—C4	110.8 (2)	H18A—C18—H18B	109.5
C6—C5—C10	112.0 (2)	C10—C18—H18C	109.5
C4—C5—C10	113.3 (2)	H18A—C18—H18C	109.5
C6—C5—H5	106.8	H18B—C18—H18C	109.5
C4—C5—H5	106.8	C13—C19—H19A	109.5
C10—C5—H5	106.8	C13—C19—H19B	109.5
C5—C6—C7	113.5 (2)	H19A—C19—H19B	109.5
C5—C6—H6A	108.9	C13—C19—H19C	109.5
C7—C6—H6A	108.9	H19A—C19—H19C	109.5
C5—C6—H6B	108.9	H19B—C19—H19C	109.5
C7—C6—H6B	108.9	C25—C20—C21	110.3 (3)
H6A—C6—H6B	107.7	C25—C20—C17	113.6 (3)
O2—C7—C6	105.9 (2)	C21—C20—C17	109.7 (2)
O2—C7—C8	112.7 (2)	C25—C20—H20	107.7
C6—C7—C8	111.3 (2)	C21—C20—H20	107.7
O2—C7—H7	108.9	C17—C20—H20	107.7
C6—C7—H7	108.9	C22—C21—C20	114.7 (2)
C8—C7—H7	108.9	C22—C21—H21A	108.6
C7—C8—C14	113.6 (2)	C20—C21—H21A	108.6
C7—C8—C9	109.8 (2)	C22—C21—H21B	108.6
C14—C8—C9	109.4 (2)	C20—C21—H21B	108.6
C7—C8—H8	107.9	H21A—C21—H21B	107.6
C14—C8—H8	107.9	C23—C22—C21	113.7 (3)
C9—C8—H8	107.9	C23—C22—H22A	108.8
C11—C9—C8	112.2 (2)	C21—C22—H22A	108.8
C11—C9—C10	112.5 (2)	C23—C22—H22B	108.8
C8—C9—C10	113.4 (2)	C21—C22—H22B	108.8
C11—C9—H9	106.0	H22A—C22—H22B	107.7

C8—C9—H9	106.0	O5—C23—O6	122.6 (3)
C10—C9—H9	106.0	O5—C23—C22	125.6 (3)
C18—C10—C1	106.7 (2)	O6—C23—C22	111.7 (3)
C18—C10—C5	109.3 (2)	O6—C24—H24A	109.5
C1—C10—C5	107.8 (2)	O6—C24—H24B	109.5
C18—C10—C9	111.0 (2)	H24A—C24—H24B	109.5
C1—C10—C9	112.7 (2)	O6—C24—H24C	109.5
C5—C10—C9	109.3 (2)	H24A—C24—H24C	109.5
C9—C11—C12	114.0 (2)	H24B—C24—H24C	109.5
C9—C11—H11A	108.7	C20—C25—H25A	109.5
C12—C11—H11A	108.7	C20—C25—H25B	109.5
C9—C11—H11B	108.7	H25A—C25—H25B	109.5
C12—C11—H11B	108.7	C20—C25—H25C	109.5
H11A—C11—H11B	107.6	H25A—C25—H25C	109.5
C13—C12—C11	111.1 (2)	H25B—C25—H25C	109.5
C13—C12—H12A	109.4	O3—C26—O1	128.4 (3)
C11—C12—H12A	109.4	O3—C26—O4	125.3 (3)
C13—C12—H12B	109.4	O1—C26—O4	106.3 (3)
C11—C12—H12B	109.4	O4—C27—Cl1	110.7 (2)
H12A—C12—H12B	108.0	O4—C27—H27A	109.5
C19—C13—C12	110.1 (2)	Cl1—C27—H27A	109.5
C19—C13—C14	111.5 (2)	O4—C27—H27B	109.5
C12—C13—C14	107.7 (2)	Cl1—C27—H27B	109.5
C19—C13—C17	109.7 (2)	H27A—C27—H27B	108.1

C10—C1—C2—C3	57.9 (3)	C11—C12—C13—C14	56.6 (3)
C26—O1—C3—C2	−156.1 (2)	C11—C12—C13—C17	169.4 (2)
C26—O1—C3—C4	83.2 (3)	C7—C8—C14—C15	−56.4 (3)
C1—C2—C3—O1	−176.6 (2)	C9—C8—C14—C15	−179.6 (2)
C1—C2—C3—C4	−57.1 (3)	C7—C8—C14—C13	179.6 (2)
O1—C3—C4—C5	175.3 (2)	C9—C8—C14—C13	56.4 (3)
C2—C3—C4—C5	56.5 (3)	C19—C13—C14—C15	−71.7 (3)
C3—C4—C5—C6	−179.9 (2)	C12—C13—C14—C15	167.4 (2)
C3—C4—C5—C10	−53.1 (3)	C17—C13—C14—C15	45.0 (3)
C4—C5—C6—C7	72.7 (3)	C19—C13—C14—C8	61.2 (3)
C10—C5—C6—C7	−54.9 (3)	C12—C13—C14—C8	−59.7 (3)
C5—C6—C7—O2	178.7 (2)	C17—C13—C14—C8	177.9 (2)
C5—C6—C7—C8	55.9 (3)	C8—C14—C15—C16	−161.5 (3)
O2—C7—C8—C14	63.5 (3)	C13—C14—C15—C16	−32.8 (3)
C6—C7—C8—C14	−177.7 (2)	C14—C15—C16—C17	8.1 (3)
O2—C7—C8—C9	−173.5 (2)	C19—C13—C17—C20	−46.8 (3)
C6—C7—C8—C9	−54.7 (3)	C12—C13—C17—C20	78.8 (3)
C7—C8—C9—C11	−175.7 (2)	C14—C13—C17—C20	−164.8 (2)
C14—C8—C9—C11	−50.3 (3)	C19—C13—C17—C16	79.0 (3)
C7—C8—C9—C10	55.5 (3)	C12—C13—C17—C16	−155.4 (2)
C14—C8—C9—C10	−179.1 (2)	C14—C13—C17—C16	−39.0 (3)
C2—C1—C10—C18	−170.0 (2)	C15—C16—C17—C20	149.8 (3)
C2—C1—C10—C5	−52.7 (3)	C15—C16—C17—C13	19.5 (3)
C2—C1—C10—C9	67.9 (3)	C13—C17—C20—C25	−56.5 (4)

C6—C5—C10—C18	−69.4 (3)	C16—C17—C20—C25	−177.5 (3)
C4—C5—C10—C18	164.4 (2)	C13—C17—C20—C21	179.5 (3)
C6—C5—C10—C1	175.0 (2)	C16—C17—C20—C21	58.5 (3)
C4—C5—C10—C1	48.8 (3)	C25—C20—C21—C22	65.9 (4)
C6—C5—C10—C9	52.2 (3)	C17—C20—C21—C22	−168.2 (3)
C4—C5—C10—C9	−74.0 (3)	C20—C21—C22—C23	−172.9 (3)
C11—C9—C10—C18	−62.0 (3)	C24—O6—C23—O5	1.0 (5)
C8—C9—C10—C18	66.7 (3)	C24—O6—C23—C22	−178.4 (3)
C11—C9—C10—C1	57.7 (3)	C21—C22—C23—O5	−0.9 (5)
C8—C9—C10—C1	−173.7 (2)	C21—C22—C23—O6	178.5 (3)
C11—C9—C10—C5	177.5 (2)	C3—O1—C26—O3	5.0 (5)
C8—C9—C10—C5	−53.9 (3)	C3—O1—C26—O4	−175.2 (2)
C8—C9—C11—C12	51.3 (3)	C27—O4—C26—O3	1.9 (5)
C10—C9—C11—C12	−179.4 (2)	C27—O4—C26—O1	−177.9 (2)
C9—C11—C12—C13	−55.0 (3)	C26—O4—C27—Cl1	82.3 (3)
C11—C12—C13—C19	−65.2 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*B*···O2^{i}	0.97	2.49	3.339 (4)	146
C27—H27*B*···O5^{ii}	0.97	2.40	3.270 (4)	149

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+1/2, −*y*, *z*−1/2.