IUCrData

ISSN 2414-3146

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*)-10,13-Dimethyl-17-[5-oxo-5-(prop-2-yn-1-yloxy)pentan-2-yl]hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triyl triacetate

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Received 22 February 2017
Accepted 20 March 2017

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

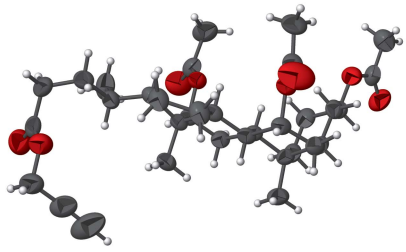
Keywords: crystal structure; cholic acid; terminal alkynes; hydrogen bonding.

CCDC reference: 1538917

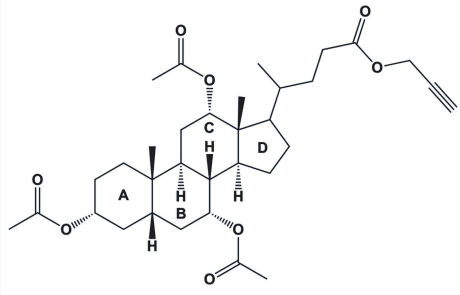
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{33}H_{48}O_8$, four terminal H atoms of cholic acid are replaced by three acetyl and one terminal alkyne group. All the acetyl residues are twisted with respect to the rings (*A*, *B* and *C*) to which they are attached. The cyclopentane ring *D* adopts an envelope conformation with the methyl-substituted C atom as the flap. Rings *A*, *B* and *C* have chair conformations. The dihedral angle between the mean planes of rings *C* and *D* is 4.70 (11)°. In the crystal, molecules are linked by C—H···O hydrogen bonds, forming a three-dimensional structure.

3D view



Chemical scheme



Structure description

Cholic acid is one of the two major bile acids produced by the liver (Suryanarayana Ch *et al.*, 2014; Yadav & Kumar, 2014). Combinations of bile acids and drugs can lead to cholesterol-lowering agents (Tamminen & Kolehmainen, 2001). The introduction of a bile acid group at the 20-position of camptochecin was found to decrease toxicity *in vivo* and improve selectivity for hepatoma cells (Li *et al.*, 2014). Bile acid esters may find applications in molecular recognition, supramolecular chemistry and in pharmacology (Pospieszny *et al.*, 2014). We report herein on the synthesis and crystal structure of the title cholic acid derivative.

In the title compound, Fig. 1, the acetyl residues are twisted with respect to the rings to which they are attached as shown by the torsion angles [C2—O2—C3—C4 = 147.4 (2)°, C20—O6—C18—C17 = −152.3 (2)°, C14—O3—C7—C8 = 130.8 (2)°]. Rings *A*, *B* and *C* have chair conformations. The cyclopentane (C16/C17/C22/C23/C25) ring *D* adopts an

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O4^{i}	0.96	2.58	3.521 (5)	166
C6—H6A···O1^{ii}	0.97	2.50	3.357 (4)	147
C21—H21C···O5^{iii}	0.96	2.50	3.450 (5)	171

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

envelope conformation with atom C17 [displacement = −0.7144 Å] as the flap. The puckering parameters are $Q(2)$ = 0.474 (3) Å, $\varphi(2)$ = 211.6 (3)°. The dihedral angle between the mean planes of rings C and D is 4.70 (11)°.

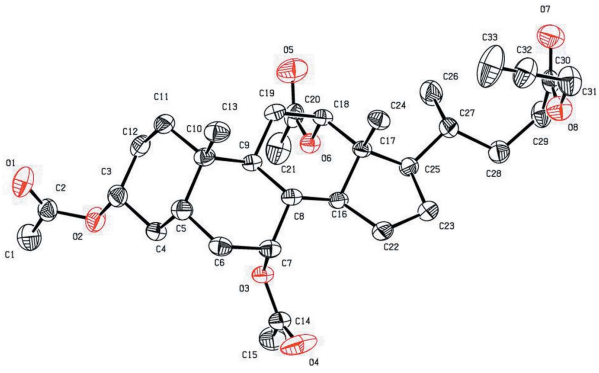


Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

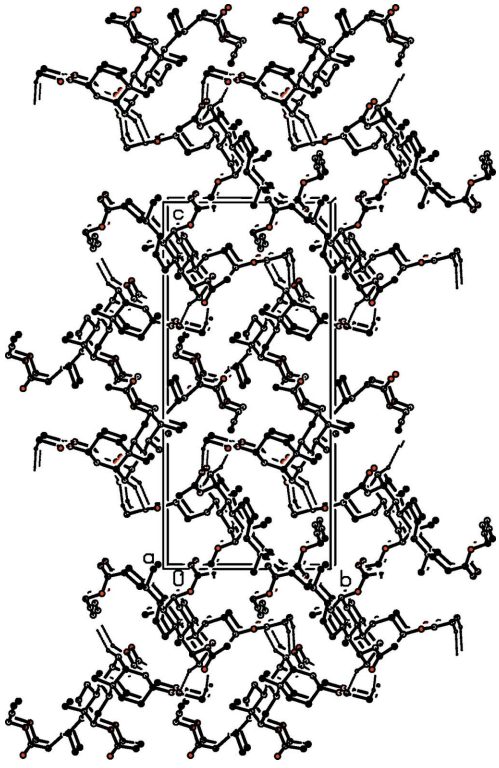


Figure 2
A view along the a axis of the crystal packing of the title compound. Hydrogen bonds are shown as dotted lines (see Table 1) and, for clarity, only H atoms H1B, H6A and H21C have been included.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{33}H_{48}O_8$
M_r	572.71
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, b, c (Å)	9.7437 (3), 12.2437 (3), 26.8215 (10)
V (Å^3)	3199.78 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.25 × 0.19 × 0.13
Data collection	
Diffractometer	Bruker SMART APEXII area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.785, 0.856
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38159, 5634, 4628
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.089, 0.98
No. of reflections	5634
No. of parameters	376
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.13, −0.12
Absolute structure	Flack x determined using 1758 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.0 (3)

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

In the crystal, molecules are linked by C—H···O hydrogen bonds, forming a three-dimensional structure (Table 1 and Fig. 2).

Synthesis and crystallization

This terminal alkyne was prepared by esterification of cholic acid (1 g, 2.4 mmol) in propargyl alcohol (5–10 ml), to which a catalytic amount (10 mol %) of *para*-toluene sulfonic acid (PTSA) was added. The reaction mixture was then heated at 328–333 K for 7 h to give the propargyl ester (yield 95%). Then the propargyl ester compound (2 g, 4.52 mmol) in CH_2Cl_2 was treated with acetic anhydride (1 ml) at 273 K, followed by a solution of trimethylsilyl trifluoromethanesulfonate (26 µl, 0.14 mmol) in CH_2Cl_2 to give the acetylated terminal alkyne title compound (yield 89%). Colourless block-like crystals were obtained by the slow evaporation method.

Refinement

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

Acknowledgements

The authors thank the Department of Chemistry, IIT, Chennai, for the data collection.

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full crystallographic data

IUCrData (2017). **2**, x170436 [https://doi.org/10.1107/S2414314617004369]

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Crystal data

$C_{33}H_{48}O_8$
M_r = 572.71
Orthorhombic, $P2_12_12_1$
a = 9.7437 (3) Å
b = 12.2437 (3) Å
c = 26.8215 (10) Å
V = 3199.78 (17) Å^3
Z = 4
$F(000)$ = 1240
D_x = 1.189 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5634 reflections
θ = 2.6–25.0°
μ = 0.08 mm^{-1}
T = 296 K
Block, colourless
0.25 × 0.19 × 0.13 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.785, T_{max} = 0.856
38159 measured reflections
5634 independent reflections
4628 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.0°, θ_{min} = 2.6°
h = −11→11
k = −14→14
l = −31→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.089
S = 0.98
5634 reflections
376 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
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.4364P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Absolute structure: Flack x determined using 1758 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.0 (3)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5885 (4)	−0.2288 (3)	0.14363 (14)	0.0804 (10)
H1A	0.514327	−0.280308	0.142339	0.121*
H1B	0.654138	−0.251852	0.168181	0.121*
H1C	0.632203	−0.225022	0.111588	0.121*
C2	0.5343 (3)	−0.1192 (2)	0.15724 (10)	0.0569 (7)
C3	0.5935 (3)	0.0648 (2)	0.17617 (11)	0.0562 (7)
H3	0.510928	0.060747	0.196949	0.067*
C4	0.7087 (3)	0.1118 (2)	0.20652 (10)	0.0531 (7)
H4A	0.792035	0.111983	0.186720	0.064*
H4B	0.724397	0.065947	0.235463	0.064*
C5	0.6772 (3)	0.2288 (2)	0.22377 (10)	0.0525 (6)
H5	0.596371	0.224091	0.245403	0.063*
C6	0.7930 (3)	0.2760 (2)	0.25562 (10)	0.0537 (7)
H6A	0.756985	0.337167	0.274516	0.064*
H6B	0.821930	0.220786	0.279329	0.064*
C7	0.9172 (3)	0.3142 (2)	0.22703 (9)	0.0478 (6)
H7	0.977081	0.355780	0.249454	0.057*
C8	0.8814 (2)	0.38515 (19)	0.18193 (9)	0.0434 (5)
H8	0.843531	0.453879	0.194652	0.052*
C9	0.7693 (2)	0.33099 (19)	0.14966 (9)	0.0411 (5)
H9	0.806441	0.260379	0.138980	0.049*
C10	0.6379 (2)	0.3056 (2)	0.18003 (9)	0.0478 (6)
C11	0.5276 (3)	0.2487 (2)	0.14848 (11)	0.0558 (7)
H11A	0.443514	0.245243	0.167790	0.067*
H11B	0.509348	0.293326	0.119328	0.067*
C12	0.5635 (3)	0.1341 (2)	0.13123 (11)	0.0575 (7)
H12A	0.487508	0.103252	0.112626	0.069*
H12B	0.643219	0.136406	0.109581	0.069*
C13	0.5717 (3)	0.4105 (2)	0.20055 (12)	0.0648 (8)
H13A	0.543922	0.456342	0.173301	0.097*
H13B	0.636889	0.448861	0.220882	0.097*
H13C	0.492849	0.391832	0.220257	0.097*
C14	1.1101 (3)	0.1914 (2)	0.22900 (12)	0.0594 (7)
C15	1.1751 (3)	0.1001 (3)	0.20203 (15)	0.0837 (10)
H15A	1.256589	0.077791	0.219362	0.125*
H15B	1.198688	0.123184	0.168920	0.125*
H15C	1.112209	0.039843	0.200255	0.125*
C16	1.0058 (2)	0.41322 (18)	0.15097 (9)	0.0433 (6)
H16	1.042056	0.344005	0.138204	0.052*

C17	0.9756 (2)	0.48537 (17)	0.10507 (9)	0.0411 (6)
C18	0.8705 (2)	0.42596 (18)	0.07285 (9)	0.0421 (5)
H18	0.846058	0.471411	0.044118	0.051*
C19	0.7419 (2)	0.3965 (2)	0.10197 (9)	0.0477 (6)
H19A	0.681662	0.354363	0.080561	0.057*
H19B	0.694182	0.463297	0.110802	0.057*
C20	0.8925 (3)	0.2823 (2)	0.01253 (11)	0.0560 (7)
C21	0.9587 (4)	0.1752 (3)	0.00386 (14)	0.0862 (11)
H21A	0.932733	0.148005	−0.028358	0.129*
H21B	0.929786	0.124532	0.029090	0.129*
H21C	1.056636	0.183456	0.005232	0.129*
C22	1.1252 (3)	0.4716 (2)	0.17613 (10)	0.0572 (7)
H22A	1.182561	0.420249	0.194105	0.069*
H22B	1.092184	0.526641	0.199237	0.069*
C23	1.2048 (3)	0.5244 (2)	0.13309 (11)	0.0593 (7)
H23A	1.296103	0.493308	0.130752	0.071*
H23B	1.213277	0.602487	0.138439	0.071*
C24	0.9133 (3)	0.5965 (2)	0.11969 (10)	0.0537 (7)
H24A	0.879219	0.632484	0.090400	0.081*
H24B	0.982551	0.640979	0.135032	0.081*
H24C	0.839266	0.585249	0.142751	0.081*
C25	1.1229 (2)	0.50142 (19)	0.08477 (10)	0.0454 (6)
H25	1.153732	0.430461	0.072099	0.054*
C26	1.0909 (3)	0.5427 (3)	−0.00699 (11)	0.0765 (9)
H26A	1.102330	0.598079	−0.032011	0.115*
H26B	0.995312	0.525056	−0.003841	0.115*
H26C	1.141134	0.478570	−0.016476	0.115*
C27	1.1448 (3)	0.5849 (2)	0.04282 (10)	0.0505 (6)
H27	1.092447	0.650629	0.051362	0.061*
C28	1.2958 (3)	0.6182 (2)	0.03765 (12)	0.0602 (7)
H28A	1.329722	0.641000	0.070015	0.072*
H28B	1.348602	0.554880	0.027381	0.072*
C29	1.3199 (3)	0.7103 (2)	0.00028 (12)	0.0654 (8)
H29A	1.416761	0.728445	0.000017	0.078*
H29B	1.295639	0.684623	−0.032781	0.078*
C30	1.2399 (3)	0.8103 (2)	0.01140 (12)	0.0578 (7)
C31	1.1945 (3)	0.9435 (3)	0.07318 (14)	0.0818 (10)
H31A	1.254016	0.984853	0.095180	0.098*
H31B	1.175473	0.988237	0.044156	0.098*
C32	1.0680 (4)	0.9200 (3)	0.09856 (15)	0.0825 (10)
C33	0.9674 (5)	0.9057 (4)	0.1203 (2)	0.129 (2)
H33	0.886332	0.894184	0.137835	0.155*
O1	0.4159 (2)	−0.09753 (19)	0.16330 (9)	0.0834 (7)
O2	0.63337 (18)	−0.04528 (15)	0.16157 (8)	0.0655 (5)
O3	0.99245 (17)	0.22008 (13)	0.20794 (6)	0.0498 (4)
O4	1.1558 (3)	0.2353 (2)	0.26508 (11)	0.1107 (9)
O5	0.8116 (3)	0.3256 (2)	−0.01447 (8)	0.0902 (7)
O6	0.93469 (17)	0.32513 (13)	0.05577 (6)	0.0472 (4)

O7	1.1635 (3)	0.8556 (2)	−0.01680 (9)	0.0875 (7)
O8	1.2641 (2)	0.84560 (17)	0.05769 (9)	0.0721 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.087 (2)	0.0656 (18)	0.089 (2)	−0.0076 (17)	−0.005 (2)	−0.0035 (18)
C2	0.0585 (18)	0.0649 (17)	0.0474 (17)	−0.0133 (14)	0.0018 (13)	0.0045 (14)
C3	0.0453 (14)	0.0542 (15)	0.0689 (19)	0.0010 (12)	0.0087 (13)	0.0061 (14)
C4	0.0492 (14)	0.0542 (15)	0.0560 (17)	0.0034 (12)	−0.0039 (12)	0.0117 (13)
C5	0.0479 (14)	0.0641 (16)	0.0456 (15)	0.0061 (12)	0.0075 (12)	0.0055 (13)
C6	0.0597 (16)	0.0596 (15)	0.0417 (15)	0.0102 (13)	−0.0011 (13)	0.0040 (13)
C7	0.0532 (14)	0.0489 (13)	0.0414 (14)	0.0091 (12)	−0.0075 (12)	−0.0034 (12)
C8	0.0453 (13)	0.0436 (12)	0.0413 (14)	0.0087 (11)	−0.0081 (11)	−0.0021 (11)
C9	0.0394 (12)	0.0436 (12)	0.0402 (13)	0.0068 (10)	−0.0050 (10)	−0.0004 (11)
C10	0.0412 (13)	0.0561 (14)	0.0461 (15)	0.0091 (11)	0.0010 (11)	0.0015 (12)
C11	0.0397 (13)	0.0681 (17)	0.0594 (17)	0.0019 (12)	−0.0002 (12)	0.0125 (14)
C12	0.0407 (13)	0.0712 (18)	0.0606 (18)	−0.0093 (13)	−0.0038 (13)	−0.0021 (15)
C13	0.0562 (15)	0.0718 (18)	0.0662 (19)	0.0211 (14)	0.0042 (14)	0.0016 (15)
C14	0.0479 (15)	0.0650 (17)	0.0654 (19)	0.0055 (13)	−0.0097 (14)	0.0143 (15)
C15	0.0627 (19)	0.071 (2)	0.117 (3)	0.0238 (16)	0.0014 (19)	0.009 (2)
C16	0.0435 (12)	0.0402 (12)	0.0462 (15)	0.0040 (10)	−0.0110 (11)	−0.0001 (11)
C17	0.0444 (13)	0.0359 (12)	0.0429 (14)	0.0041 (10)	−0.0081 (11)	0.0013 (11)
C18	0.0446 (12)	0.0406 (12)	0.0412 (14)	0.0072 (11)	−0.0072 (11)	0.0024 (11)
C19	0.0404 (13)	0.0555 (14)	0.0473 (15)	0.0059 (11)	−0.0097 (11)	0.0014 (12)
C20	0.0538 (16)	0.0635 (16)	0.0508 (17)	−0.0136 (14)	0.0042 (14)	−0.0096 (14)
C21	0.087 (2)	0.077 (2)	0.094 (3)	−0.0103 (19)	0.015 (2)	−0.035 (2)
C22	0.0571 (15)	0.0578 (15)	0.0567 (17)	−0.0071 (13)	−0.0207 (14)	0.0036 (13)
C23	0.0510 (15)	0.0601 (16)	0.0667 (19)	−0.0063 (13)	−0.0138 (14)	0.0076 (14)
C24	0.0626 (16)	0.0436 (14)	0.0550 (17)	0.0087 (12)	−0.0034 (13)	0.0013 (12)
C25	0.0452 (13)	0.0393 (12)	0.0515 (15)	0.0011 (11)	−0.0061 (12)	−0.0020 (11)
C26	0.087 (2)	0.087 (2)	0.0558 (19)	−0.0230 (19)	−0.0046 (17)	0.0114 (17)
C27	0.0500 (14)	0.0440 (13)	0.0574 (17)	−0.0007 (11)	−0.0002 (12)	0.0040 (12)
C28	0.0497 (15)	0.0532 (15)	0.078 (2)	0.0049 (12)	0.0063 (14)	0.0024 (15)
C29	0.0563 (17)	0.0644 (17)	0.075 (2)	−0.0052 (14)	0.0220 (15)	−0.0002 (16)
C30	0.0508 (16)	0.0577 (16)	0.065 (2)	−0.0120 (14)	0.0117 (14)	0.0120 (15)
C31	0.083 (2)	0.0592 (18)	0.104 (3)	0.0011 (17)	0.021 (2)	−0.0128 (19)
C32	0.069 (2)	0.079 (2)	0.099 (3)	−0.0073 (18)	0.008 (2)	−0.031 (2)
C33	0.091 (3)	0.142 (4)	0.154 (5)	−0.037 (3)	0.039 (3)	−0.074 (3)
O1	0.0550 (13)	0.0956 (16)	0.0996 (18)	−0.0194 (11)	0.0163 (12)	−0.0127 (13)
O2	0.0462 (10)	0.0583 (11)	0.0920 (15)	−0.0041 (9)	0.0068 (10)	−0.0036 (10)
O3	0.0472 (9)	0.0511 (9)	0.0512 (10)	0.0094 (8)	−0.0096 (8)	0.0028 (8)
O4	0.0982 (18)	0.128 (2)	0.106 (2)	0.0338 (16)	−0.0610 (17)	−0.0203 (18)
O5	0.1014 (18)	0.1056 (17)	0.0635 (14)	0.0045 (15)	−0.0307 (14)	−0.0190 (14)
O6	0.0518 (9)	0.0449 (9)	0.0449 (10)	−0.0001 (8)	−0.0045 (8)	−0.0066 (8)
O7	0.0863 (16)	0.0937 (17)	0.0826 (16)	0.0075 (14)	−0.0046 (14)	0.0205 (14)
O8	0.0758 (13)	0.0678 (13)	0.0728 (14)	0.0079 (11)	0.0006 (11)	−0.0074 (11)

Geometric parameters (Å, º)

C1—C2	1.488 (4)	C16—H16	0.9800
C1—H1A	0.9600	C17—C18	1.524 (3)
C1—H1B	0.9600	C17—C24	1.540 (3)
C1—H1C	0.9600	C17—C25	1.548 (3)
C2—O1	1.194 (3)	C18—O6	1.458 (3)
C2—O2	1.328 (3)	C18—C19	1.520 (3)
C3—O2	1.456 (3)	C18—H18	0.9800
C3—C4	1.501 (4)	C19—H19A	0.9700
C3—C12	1.503 (4)	C19—H19B	0.9700
C3—H3	0.9800	C20—O5	1.195 (3)
C4—C5	1.536 (4)	C20—O6	1.337 (3)
C4—H4A	0.9700	C20—C21	1.480 (4)
C4—H4B	0.9700	C21—H21A	0.9600
C5—C6	1.529 (4)	C21—H21B	0.9600
C5—C10	1.552 (4)	C21—H21C	0.9600
C5—H5	0.9800	C22—C23	1.534 (4)
C6—C7	1.507 (4)	C22—H22A	0.9700
C6—H6A	0.9700	C22—H22B	0.9700
C6—H6B	0.9700	C23—C25	1.548 (4)
C7—O3	1.459 (3)	C23—H23A	0.9700
C7—C8	1.529 (3)	C23—H23B	0.9700
C7—H7	0.9800	C24—H24A	0.9600
C8—C16	1.509 (3)	C24—H24B	0.9600
C8—C9	1.543 (3)	C24—H24C	0.9600
C8—H8	0.9800	C25—C27	1.535 (3)
C9—C19	1.533 (3)	C25—H25	0.9800
C9—C10	1.549 (3)	C26—C27	1.526 (4)
C9—H9	0.9800	C26—H26A	0.9600
C10—C11	1.535 (4)	C26—H26B	0.9600
C10—C13	1.539 (4)	C26—H26C	0.9600
C11—C12	1.518 (4)	C27—C28	1.533 (4)
C11—H11A	0.9700	C27—H27	0.9800
C11—H11B	0.9700	C28—C29	1.527 (4)
C12—H12A	0.9700	C28—H28A	0.9700
C12—H12B	0.9700	C28—H28B	0.9700
C13—H13A	0.9600	C29—C30	1.482 (4)
C13—H13B	0.9600	C29—H29A	0.9700
C13—H13C	0.9600	C29—H29B	0.9700
C14—O4	1.193 (4)	C30—O7	1.197 (3)
C14—O3	1.325 (3)	C30—O8	1.336 (4)
C14—C15	1.475 (4)	C31—C32	1.437 (5)
C15—H15A	0.9600	C31—O8	1.438 (4)
C15—H15B	0.9600	C31—H31A	0.9700
C15—H15C	0.9600	C31—H31B	0.9700
C16—C22	1.523 (3)	C32—C33	1.154 (5)
C16—C17	1.543 (3)	C33—H33	0.9300

C2—C1—H1A	109.5	C18—C17—C24	107.54 (19)
C2—C1—H1B	109.5	C18—C17—C16	107.88 (18)
H1A—C1—H1B	109.5	C24—C17—C16	112.2 (2)
C2—C1—H1C	109.5	C18—C17—C25	118.9 (2)
H1A—C1—H1C	109.5	C24—C17—C25	110.05 (19)
H1B—C1—H1C	109.5	C16—C17—C25	100.16 (18)
O1—C2—O2	122.6 (3)	O6—C18—C19	108.32 (18)
O1—C2—C1	125.2 (3)	O6—C18—C17	107.13 (17)
O2—C2—C1	112.2 (3)	C19—C18—C17	112.0 (2)
O2—C3—C4	107.5 (2)	O6—C18—H18	109.8
O2—C3—C12	111.0 (2)	C19—C18—H18	109.8
C4—C3—C12	111.3 (2)	C17—C18—H18	109.8
O2—C3—H3	109.0	C18—C19—C9	114.15 (19)
C4—C3—H3	109.0	C18—C19—H19A	108.7
C12—C3—H3	109.0	C9—C19—H19A	108.7
C3—C4—C5	111.8 (2)	C18—C19—H19B	108.7
C3—C4—H4A	109.3	C9—C19—H19B	108.7
C5—C4—H4A	109.3	H19A—C19—H19B	107.6
C3—C4—H4B	109.3	O5—C20—O6	123.6 (3)
C5—C4—H4B	109.3	O5—C20—C21	125.9 (3)
H4A—C4—H4B	107.9	O6—C20—C21	110.5 (3)
C6—C5—C4	111.9 (2)	C20—C21—H21A	109.5
C6—C5—C10	112.0 (2)	C20—C21—H21B	109.5
C4—C5—C10	112.8 (2)	H21A—C21—H21B	109.5
C6—C5—H5	106.5	C20—C21—H21C	109.5
C4—C5—H5	106.5	H21A—C21—H21C	109.5
C10—C5—H5	106.5	H21B—C21—H21C	109.5
C7—C6—C5	115.2 (2)	C16—C22—C23	104.5 (2)
C7—C6—H6A	108.5	C16—C22—H22A	110.8
C5—C6—H6A	108.5	C23—C22—H22A	110.8
C7—C6—H6B	108.5	C16—C22—H22B	110.8
C5—C6—H6B	108.5	C23—C22—H22B	110.8
H6A—C6—H6B	107.5	H22A—C22—H22B	108.9
O3—C7—C6	109.7 (2)	C22—C23—C25	107.0 (2)
O3—C7—C8	106.60 (19)	C22—C23—H23A	110.3
C6—C7—C8	113.3 (2)	C25—C23—H23A	110.3
O3—C7—H7	109.1	C22—C23—H23B	110.3
C6—C7—H7	109.1	C25—C23—H23B	110.3
C8—C7—H7	109.1	H23A—C23—H23B	108.6
C16—C8—C7	112.40 (19)	C17—C24—H24A	109.5
C16—C8—C9	110.94 (19)	C17—C24—H24B	109.5
C7—C8—C9	111.19 (19)	H24A—C24—H24B	109.5
C16—C8—H8	107.3	C17—C24—H24C	109.5
C7—C8—H8	107.3	H24A—C24—H24C	109.5
C9—C8—H8	107.3	H24B—C24—H24C	109.5
C19—C9—C8	111.49 (19)	C27—C25—C23	114.9 (2)
C19—C9—C10	113.55 (19)	C27—C25—C17	118.1 (2)

C8—C9—C10	112.09 (19)	C23—C25—C17	101.9 (2)
C19—C9—H9	106.4	C27—C25—H25	107.1
C8—C9—H9	106.4	C23—C25—H25	107.1
C10—C9—H9	106.4	C17—C25—H25	107.1
C11—C10—C13	106.4 (2)	C27—C26—H26A	109.5
C11—C10—C9	112.3 (2)	C27—C26—H26B	109.5
C13—C10—C9	111.6 (2)	H26A—C26—H26B	109.5
C11—C10—C5	108.3 (2)	C27—C26—H26C	109.5
C13—C10—C5	109.8 (2)	H26A—C26—H26C	109.5
C9—C10—C5	108.37 (19)	H26B—C26—H26C	109.5
C12—C11—C10	115.2 (2)	C26—C27—C28	109.9 (2)
C12—C11—H11A	108.5	C26—C27—C25	111.6 (2)
C10—C11—H11A	108.5	C28—C27—C25	112.1 (2)
C12—C11—H11B	108.5	C26—C27—H27	107.6
C10—C11—H11B	108.5	C28—C27—H27	107.6
H11A—C11—H11B	107.5	C25—C27—H27	107.6
C3—C12—C11	108.8 (2)	C29—C28—C27	113.8 (2)
C3—C12—H12A	109.9	C29—C28—H28A	108.8
C11—C12—H12A	109.9	C27—C28—H28A	108.8
C3—C12—H12B	109.9	C29—C28—H28B	108.8
C11—C12—H12B	109.9	C27—C28—H28B	108.8
H12A—C12—H12B	108.3	H28A—C28—H28B	107.7
C10—C13—H13A	109.5	C30—C29—C28	113.4 (2)
C10—C13—H13B	109.5	C30—C29—H29A	108.9
H13A—C13—H13B	109.5	C28—C29—H29A	108.9
C10—C13—H13C	109.5	C30—C29—H29B	108.9
H13A—C13—H13C	109.5	C28—C29—H29B	108.9
H13B—C13—H13C	109.5	H29A—C29—H29B	107.7
O4—C14—O3	123.3 (3)	O7—C30—O8	123.2 (3)
O4—C14—C15	125.4 (3)	O7—C30—C29	125.6 (3)
O3—C14—C15	111.3 (3)	O8—C30—C29	111.2 (3)
C14—C15—H15A	109.5	C32—C31—O8	112.0 (3)
C14—C15—H15B	109.5	C32—C31—H31A	109.2
H15A—C15—H15B	109.5	O8—C31—H31A	109.2
C14—C15—H15C	109.5	C32—C31—H31B	109.2
H15A—C15—H15C	109.5	O8—C31—H31B	109.2
H15B—C15—H15C	109.5	H31A—C31—H31B	107.9
C8—C16—C22	118.5 (2)	C33—C32—C31	176.6 (4)
C8—C16—C17	114.59 (19)	C32—C33—H33	180.0
C22—C16—C17	103.31 (19)	C2—O2—C3	117.4 (2)
C8—C16—H16	106.6	C14—O3—C7	119.6 (2)
C22—C16—H16	106.6	C20—O6—C18	118.2 (2)
C17—C16—H16	106.6	C30—O8—C31	117.0 (3)
O2—C3—C4—C5	179.8 (2)	C16—C17—C18—O6	−63.5 (2)
C12—C3—C4—C5	58.0 (3)	C25—C17—C18—O6	49.5 (3)
C3—C4—C5—C6	178.8 (2)	C24—C17—C18—C19	−66.0 (2)
C3—C4—C5—C10	−53.8 (3)	C16—C17—C18—C19	55.2 (2)

C4—C5—C6—C7	77.4 (3)	C25—C17—C18—C19	168.15 (19)
C10—C5—C6—C7	−50.4 (3)	O6—C18—C19—C9	63.7 (3)
C5—C6—C7—O3	−71.7 (3)	C17—C18—C19—C9	−54.3 (3)
C5—C6—C7—C8	47.3 (3)	C8—C9—C19—C18	49.9 (3)
O3—C7—C8—C16	−53.6 (2)	C10—C9—C19—C18	177.7 (2)
C6—C7—C8—C16	−174.3 (2)	C8—C16—C22—C23	−159.5 (2)
O3—C7—C8—C9	71.4 (2)	C17—C16—C22—C23	−31.6 (3)
C6—C7—C8—C9	−49.3 (3)	C16—C22—C23—C25	3.9 (3)
C16—C8—C9—C19	−49.1 (2)	C22—C23—C25—C27	154.0 (2)
C7—C8—C9—C19	−174.9 (2)	C22—C23—C25—C17	25.0 (3)
C16—C8—C9—C10	−177.62 (19)	C18—C17—C25—C27	72.5 (3)
C7—C8—C9—C10	56.5 (2)	C24—C17—C25—C27	−52.1 (3)
C19—C9—C10—C11	54.2 (3)	C16—C17—C25—C27	−170.4 (2)
C8—C9—C10—C11	−178.35 (18)	C18—C17—C25—C23	−160.6 (2)
C19—C9—C10—C13	−65.2 (3)	C24—C17—C25—C23	74.8 (2)
C8—C9—C10—C13	62.3 (3)	C16—C17—C25—C23	−43.5 (2)
C19—C9—C10—C5	173.8 (2)	C23—C25—C27—C26	165.7 (2)
C8—C9—C10—C5	−58.7 (2)	C17—C25—C27—C26	−73.9 (3)
C6—C5—C10—C11	176.7 (2)	C23—C25—C27—C28	41.9 (3)
C4—C5—C10—C11	49.3 (3)	C17—C25—C27—C28	162.3 (2)
C6—C5—C10—C13	−67.5 (3)	C26—C27—C28—C29	61.6 (3)
C4—C5—C10—C13	165.1 (2)	C25—C27—C28—C29	−173.6 (2)
C6—C5—C10—C9	54.5 (3)	C27—C28—C29—C30	56.5 (4)
C4—C5—C10—C9	−72.8 (3)	C28—C29—C30—O7	−125.2 (3)
C13—C10—C11—C12	−170.7 (2)	C28—C29—C30—O8	55.2 (3)
C9—C10—C11—C12	67.0 (3)	O1—C2—O2—C3	2.4 (4)
C5—C10—C11—C12	−52.7 (3)	C1—C2—O2—C3	−178.3 (3)
O2—C3—C12—C11	−178.0 (2)	C4—C3—O2—C2	147.4 (2)
C4—C3—C12—C11	−58.3 (3)	C12—C3—O2—C2	−90.6 (3)
C10—C11—C12—C3	57.6 (3)	O4—C14—O3—C7	4.2 (4)
C7—C8—C16—C22	−57.2 (3)	C15—C14—O3—C7	−175.6 (2)
C9—C8—C16—C22	177.6 (2)	C6—C7—O3—C14	−106.3 (2)
C7—C8—C16—C17	−179.65 (19)	C8—C7—O3—C14	130.8 (2)
C9—C8—C16—C17	55.2 (2)	O5—C20—O6—C18	5.1 (4)
C8—C16—C17—C18	−57.6 (2)	C21—C20—O6—C18	−174.3 (2)
C22—C16—C17—C18	172.10 (19)	C19—C18—O6—C20	86.6 (2)
C8—C16—C17—C24	60.7 (3)	C17—C18—O6—C20	−152.3 (2)
C22—C16—C17—C24	−69.6 (2)	O7—C30—O8—C31	−0.6 (4)
C8—C16—C17—C25	177.35 (19)	C29—C30—O8—C31	179.1 (2)
C22—C16—C17—C25	47.1 (2)	C32—C31—O8—C30	93.7 (4)
C24—C17—C18—O6	175.33 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···O4^{i}	0.96	2.58	3.521 (5)	166

C6—H6*A*···O1^{ii}	0.97	2.50	3.357 (4)	147
C21—H21*C*···O5^{iii}	0.96	2.50	3.450 (5)	171

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