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6β-Angeloyloxy-3β,8β-dihydroxy-eremophil-7(11)-en-12,8α-olide

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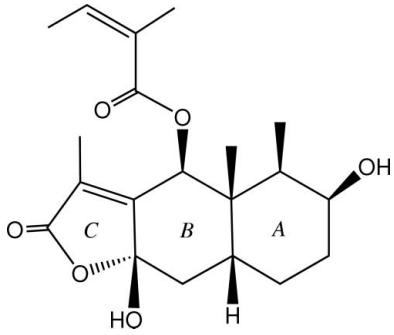
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.094; data-to-parameter ratio = 9.2.

The title compound, $C_{20}H_{28}O_6$, is an eremophilanolide which was isolated from the roots of *Petasites Hybridus*. The molecule contains three fused rings, of which two six-membered rings adopt chair conformations and are fused in a *cis* configuration. In the angeloyl group, the carbonyl and methyl groups display a *Z* configuration about the C=C bond. The crystal structure is stabilized by O—H···O and C—H···O hydrogen bonding.

Related literature

For general background, see: Agosti *et al.* (2006); Bodensieck *et al.* (2007); Cremer & Pople (1975); Fiebich *et al.* (2005); Gray *et al.* (2004); Jackson *et al.* (2004); Lipton *et al.* (2004); Neuenschwander, Neuenschwander & Steinegger (1979); Neuenschwander, Neuenschwander, Steinegger & Engel (1979); Saritas *et al.* (2002); Siegenthaler & Neuenschwander (1997); Sugama *et al.* (1985); Thomet & Simon (2002); Thomet *et al.* (2001); Yaoita & Kikuchi (1994); Yaoita *et al.* (1992).



Experimental

Crystal data

$C_{20}H_{28}O_6$
M_r = 364.42
Monoclinic, $P2_1$
a = 8.6160 (14) Å
b = 13.093 (2) Å
c = 9.2584 (15) Å
β = 112.499 (2)°
V = 964.9 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 (2) K
0.25 × 0.20 × 0.15 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: none
6181 measured reflections
2273 independent reflections
2027 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.094
S = 1.03
2273 reflections
248 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1X···O6^{i}	0.82 (2)	2.41 (4)	3.066 (3)	137 (4)
O3—H3X···O1^{ii}	0.827 (18)	1.900 (18)	2.726 (2)	178
C14—H14A···O5^{iii}	0.96	2.56	3.443 (3)	153
C14—H14B···O1	0.96	2.45	3.133 (3)	128
C19—H19B···O6	0.96	2.28	2.917 (3)	123
C18—H18···O3^{iv}	0.93	2.46	3.282 (3)	147

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

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXTL*.

We thank Professor Chuan-Zhuo Qiao (School of Pharmacy, Second Military Medical University, Shanghai 200433, China) for the identification of the plant material.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2247).

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supplementary materials

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6β-Angeloyloxy-3β,8β-dihydroxyeremophil-7(11)-en-12,8α-olide

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Comment

Petasites Hybridus (*L.*) is a medical plant belonging to the Compositae family. Its extracts were proved to have activities of anti-migraine (Lipton *et al.*, 2004; Agosti *et al.*, 2006), anti-allergy (Thomet & Simon, 2002; Gray *et al.*, 2004; Jackson *et al.*, 2004) and anti-inflammatory (Thomet *et al.*, 2001; Fiebich *et al.*, 2005). Many sesquiterpenes of the eremophilanolide type have been obtained from *P. Hybridus* (*L.*) (Neuenschwander, Neuenschwander & Steinegger, 1979; Neuenschwander, Neuenschwander, Steinegger & Engel, 1979;

Siegenthaler & Neuenschwander, 1997; Saritas *et al.*, 2002; Bodensieck *et al.*, 2007). Our investigation on the roots of this plant for bioactive components resulted in the isolation of the title compound (I), which was previously obtained from another plant *P. Japonicus* mixed together with its isomer, 6β-angeloyloxy-3β,8α-dihydroxyeremophil-7(11)-en-12,8β-olide (Sugama *et al.*, 1985). The structure elucidations of these two isomers were performed after acetylation because of the difficulty in separating them from each other (Sugama *et al.*, 1985; Yaoita *et al.*, 1992; Yaoita & Kikuchi, 1994). We now report here the isolation and the single-crystal X-ray structure of the title compound, (I).

The molecular struture of (I) is shown in Fig. 1 and the bond lengths and angles are within normal ranges. The structure of (I) contains a fused three-ring system *A/B/C*. Two six-membered rings, i.e *A* and *B*, adopt the chair conformations and are fused in a *cis* configuration (Cremer & Pople, 1975). Ring *C*, a five-membered ring, deviates slightly from planarity indicated by the torsion angles C6—C7—C8—O of −173.77 (15)°, C8—C7—C11—C13 of −179.6 (3)°, C8—O4—C12—C11 of 0.8 (2)° and C11—C7—C8—O4 of −1.0 (2)°. The angeloyl group connects to O2 atom, the carbonyl and methyl groups have a *Z* configuration on the C═C bond. The dihedral angle of planar units in the angeloyl group (between plane defined by atoms O2, O6, C16 and C17 and the plane defined by C16, C17, C18, C19 and C20) is 20.95 (14)°.

The O–H···O and C–H···O hydrogen bonds help to stabilize the molecular conformation and crystal structure (Table 1).

Experimental

The roots of *P. hybridus* (*L.*) were collected from Zhejiang Province of China in March 2006. The identification was carried out by Professor Chuan-Zhuo Qiao at the School of Pharmacy, Second Military Medical University.

The air-dried powdered roots of *P. hybridus* (*L.*) (2.5 kg) were extracted with 95% EtOH at room temperature. After evaporation of the solvent under reduced pressure, the residue of the 95% EtOH extract was suspended in H_2O, and then extracted successively with petroleum ether, EtOAc and n-BuOH to give the petroleum ether fraction (30 g), the EtOAc fraction (120 g) and the n-BuOH fraction (55 g), respectively. The EtOAc fraction was subjected to vacuum liquid chromatography on silica gel, eluting with n-hexane-EtOAc in increasing polarity to yield 4 fractions (Fr.1~4). Fr.2 (36 g) was submitted to column chromatography on silica gel eluting with n-hexane-EtOAc in increasing polarity to afford 5 fractions (Fr·A~E). Fr·B (6 g) was purified repeatedly by column chromatography on Sephadex LH-20 and Silica gel affording the title compound (I) (5 mg). X-ray quality crystals were obtained by recrystallization from n-hexane-EtOAc solution (1:1).

Refinement

The hydroxyl H atoms were located in a difference Fourier map and isotropically refined with a constraint O—H distance 0.82 Å. The remaining H atoms were placed in calculated positions with C—H distances in the range 0.93–0.98 Å. The U_{iso} values were set equal to $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for the remaining H atoms. Friedel pairs were merged before the final refinement as there is no significant anomalous dispersion for the determination of the absolute configuration.

Figures

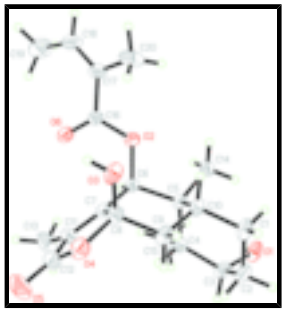

Fig. 1. The molecular structure of (I), showing the atom-labelling scheme with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radius.

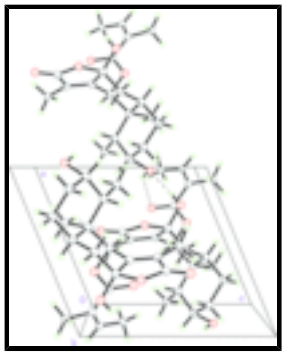

Fig. 2. The molecular packing of (I), viewed along the *b* axis.

6β-angeloyloxy-3β,8β-dihydroxyeremophil-7(11)-en-12,8α-olide

Crystal data

$C_{20}H_{28}O_6$	F_{000} = 392
M_r = 364.42	D_x = 1.254 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2yb	Cell parameters from 2840 reflections
a = 8.6160 (14) Å	θ = 2.3–27.2º
b = 13.093 (2) Å	μ = 0.09 mm^{-1}
c = 9.2584 (15) Å	T = 296 (2) K
β = 112.499 (2)º	Prismatic, colorless
V = 964.9 (3) Å^3	0.25 × 0.20 × 0.15 mm
Z = 2	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	2027 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.020$
Monochromator: graphite	$\theta_{max} = 27.5°$
$T = 296(2)$ K	$\theta_{min} = 2.3°$
φ and ω scans	$h = -11 \rightarrow 10$
Absorption correction: none	$k = -13 \rightarrow 16$
6181 measured reflections	$l = -11 \rightarrow 11$
2273 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.094$	$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.0461P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
2273 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
248 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
3 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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}
O1	1.0234 (2)	1.03673 (14)	0.2920 (2)	0.0550 (4)
H1X	1.066 (6)	0.987 (3)	0.347 (5)	0.121 (17)*
O2	0.37308 (15)	0.93739 (11)	0.20428 (14)	0.0371 (3)
O3	0.24117 (18)	1.14429 (14)	0.20077 (19)	0.0489 (4)

H3X	0.173 (3)	1.112 (2)	0.227 (3)	0.067 (9)*
O4	0.3663 (2)	1.22014 (12)	0.4432 (2)	0.0533 (4)
O5	0.4027 (4)	1.20759 (19)	0.6941 (3)	0.0886 (7)
O6	0.27831 (19)	0.86145 (14)	0.37027 (17)	0.0513 (4)
C1	0.7171 (3)	1.1679 (2)	0.1344 (3)	0.0514 (6)
H1A	0.7441	1.1217	0.0656	0.062*
H1B	0.6742	1.2307	0.0776	0.062*
C2	0.8745 (3)	1.19068 (19)	0.2761 (3)	0.0535 (6)
H2A	0.9590	1.2187	0.2420	0.064*
H2B	0.8492	1.2419	0.3396	0.064*
C3	0.9447 (3)	1.09694 (19)	0.3746 (3)	0.0470 (5)
H3	1.0322	1.1192	0.4732	0.056*
C4	0.8132 (2)	1.03547 (16)	0.4139 (2)	0.0382 (4)
H4	0.7841	1.0777	0.4873	0.046*
C5	0.6461 (2)	1.01715 (15)	0.2720 (2)	0.0328 (4)
C6	0.5169 (2)	0.97456 (14)	0.3373 (2)	0.0307 (4)
H6	0.5672	0.9185	0.4105	0.037*
C7	0.4592 (2)	1.05701 (15)	0.4167 (2)	0.0326 (4)
C8	0.3918 (2)	1.15371 (16)	0.3272 (2)	0.0385 (4)
C9	0.5214 (3)	1.19837 (16)	0.2726 (3)	0.0441 (5)
H9A	0.6170	1.2221	0.3623	0.053*
H9B	0.4736	1.2567	0.2057	0.053*
C10	0.5808 (2)	1.11928 (16)	0.1824 (2)	0.0393 (4)
H10	0.4847	1.1028	0.0863	0.047*
C11	0.4737 (3)	1.06644 (18)	0.5636 (3)	0.0430 (5)
C12	0.4125 (3)	1.1694 (2)	0.5809 (3)	0.0550 (6)
C13	0.5344 (4)	0.9937 (2)	0.6964 (3)	0.0689 (8)
H13A	0.6413	1.0161	0.7705	0.103*
H13B	0.5461	0.9270	0.6585	0.103*
H13C	0.4551	0.9908	0.7462	0.103*
C14	0.6657 (3)	0.93699 (18)	0.1583 (2)	0.0446 (5)
H14A	0.6868	0.8713	0.2081	0.067*
H14B	0.7580	0.9556	0.1299	0.067*
H14C	0.5643	0.9342	0.0662	0.067*
C15	0.8943 (3)	0.9388 (2)	0.5040 (3)	0.0560 (6)
H15A	0.9990	0.9560	0.5865	0.084*
H15B	0.9143	0.8911	0.4341	0.084*
H15C	0.8206	0.9085	0.5477	0.084*
C16	0.2616 (2)	0.88123 (16)	0.2383 (2)	0.0355 (4)
C17	0.1146 (3)	0.85431 (18)	0.0947 (2)	0.0451 (5)
C18	0.0138 (3)	0.7783 (2)	0.0942 (3)	0.0618 (7)
H18	−0.0762	0.7679	−0.0002	0.074*
C19	0.0222 (5)	0.7076 (3)	0.2203 (4)	0.0898 (11)
H19A	−0.0892	0.6860	0.2061	0.135*
H19B	0.0730	0.7415	0.3193	0.135*
H19C	0.0883	0.6491	0.2179	0.135*
C20	0.0845 (4)	0.9185 (3)	−0.0477 (3)	0.0704 (8)
H20A	−0.0193	0.8984	−0.1292	0.106*
H20B	0.1751	0.9089	−0.0826	0.106*

H20C	0.0785	0.9891	−0.0225	0.106*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0436 (8)	0.0512 (10)	0.0839 (12)	0.0060 (7)	0.0397 (9)	0.0061 (9)
O2	0.0351 (6)	0.0395 (7)	0.0342 (6)	−0.0078 (6)	0.0106 (5)	−0.0028 (6)
O3	0.0317 (7)	0.0544 (10)	0.0596 (9)	0.0073 (7)	0.0163 (6)	0.0176 (8)
O4	0.0536 (9)	0.0371 (8)	0.0798 (12)	0.0058 (7)	0.0374 (9)	−0.0041 (8)
O5	0.129 (2)	0.0699 (14)	0.0916 (16)	0.0024 (14)	0.0692 (16)	−0.0273 (12)
O6	0.0460 (8)	0.0636 (11)	0.0428 (8)	−0.0186 (8)	0.0154 (6)	0.0009 (8)
C1	0.0532 (12)	0.0454 (13)	0.0675 (14)	0.0025 (10)	0.0363 (11)	0.0173 (11)
C2	0.0448 (12)	0.0397 (12)	0.0898 (18)	−0.0054 (9)	0.0411 (12)	0.0017 (12)
C3	0.0326 (9)	0.0483 (13)	0.0640 (13)	−0.0047 (9)	0.0227 (9)	−0.0042 (11)
C4	0.0301 (8)	0.0431 (12)	0.0422 (9)	−0.0001 (8)	0.0148 (7)	−0.0010 (9)
C5	0.0318 (8)	0.0302 (9)	0.0388 (9)	−0.0002 (8)	0.0159 (7)	0.0017 (8)
C6	0.0295 (8)	0.0290 (9)	0.0327 (8)	−0.0030 (7)	0.0107 (7)	0.0017 (7)
C7	0.0281 (8)	0.0295 (9)	0.0415 (9)	−0.0037 (7)	0.0146 (7)	−0.0015 (8)
C8	0.0329 (9)	0.0340 (10)	0.0512 (11)	0.0036 (8)	0.0188 (8)	0.0024 (9)
C9	0.0378 (10)	0.0333 (10)	0.0656 (13)	0.0040 (8)	0.0249 (10)	0.0108 (10)
C10	0.0354 (9)	0.0372 (11)	0.0475 (10)	0.0006 (8)	0.0184 (8)	0.0097 (9)
C11	0.0471 (11)	0.0411 (11)	0.0439 (10)	−0.0039 (9)	0.0209 (9)	−0.0058 (9)
C12	0.0613 (14)	0.0471 (13)	0.0678 (15)	−0.0048 (11)	0.0372 (12)	−0.0149 (12)
C13	0.101 (2)	0.0663 (18)	0.0436 (12)	0.0057 (15)	0.0318 (14)	0.0025 (12)
C14	0.0519 (11)	0.0432 (11)	0.0458 (10)	−0.0029 (10)	0.0267 (9)	−0.0044 (10)
C15	0.0392 (10)	0.0651 (16)	0.0578 (13)	0.0042 (11)	0.0121 (10)	0.0167 (13)
C16	0.0331 (8)	0.0318 (9)	0.0407 (10)	−0.0016 (7)	0.0132 (7)	−0.0043 (8)
C17	0.0399 (10)	0.0445 (12)	0.0461 (10)	−0.0039 (9)	0.0111 (8)	−0.0129 (10)
C18	0.0541 (13)	0.0620 (16)	0.0614 (14)	−0.0196 (12)	0.0133 (12)	−0.0236 (13)
C19	0.107 (3)	0.063 (2)	0.100 (2)	−0.0419 (19)	0.039 (2)	−0.0163 (18)
C20	0.0734 (16)	0.0700 (19)	0.0439 (12)	−0.0058 (15)	−0.0041 (11)	−0.0050 (13)

Geometric parameters (Å, °)

O1—C3	1.436 (3)	C7—C8	1.503 (3)
O1—H1X	0.82 (2)	C8—C9	1.509 (3)
O2—C16	1.340 (2)	C9—C10	1.536 (3)
O2—C6	1.456 (2)	C9—H9A	0.9700
O3—C8	1.381 (3)	C9—H9B	0.9700
O3—H3X	0.827 (18)	C10—H10	0.9800
O4—C12	1.355 (3)	C11—C12	1.479 (3)
O4—C8	1.462 (3)	C11—C13	1.484 (3)
O5—C12	1.193 (3)	C13—H13A	0.9599
O6—C16	1.203 (2)	C13—H13B	0.9599
C1—C2	1.512 (4)	C13—H13C	0.9599
C1—C10	1.543 (3)	C14—H14A	0.9599
C1—H1A	0.9700	C14—H14B	0.9599
C1—H1B	0.9700	C14—H14C	0.9599
C2—C3	1.510 (4)	C15—H15A	0.9599

C2—H2A	0.9700	C15—H15B	0.9599
C2—H2B	0.9700	C15—H15C	0.9599
C3—C4	1.543 (3)	C16—C17	1.485 (3)
C3—H3	0.9800	C17—C18	1.320 (3)
C4—C15	1.530 (3)	C17—C20	1.500 (4)
C4—C5	1.552 (3)	C18—C19	1.470 (4)
C4—H4	0.9800	C18—H18	0.9300
C5—C14	1.540 (3)	C19—H19A	0.9599
C5—C6	1.559 (2)	C19—H19B	0.9599
C5—C10	1.560 (3)	C19—H19C	0.9599
C6—C7	1.494 (3)	C20—H20A	0.9599
C6—H6	0.9800	C20—H20B	0.9599
C7—C11	1.323 (3)	C20—H20C	0.9599
C3—O1—H1X	107 (3)	C10—C9—H9B	109.4
C16—O2—C6	116.06 (14)	H9A—C9—H9B	108.0
C8—O3—H3X	110 (2)	C9—C10—C1	109.09 (18)
C12—O4—C8	109.08 (16)	C9—C10—C5	114.61 (16)
C2—C1—C10	111.11 (18)	C1—C10—C5	110.31 (16)
C2—C1—H1A	109.4	C9—C10—H10	107.5
C10—C1—H1A	109.4	C1—C10—H10	107.5
C2—C1—H1B	109.4	C5—C10—H10	107.5
C10—C1—H1B	109.4	C7—C11—C12	107.4 (2)
H1A—C1—H1B	108.0	C7—C11—C13	131.1 (2)
C3—C2—C1	112.5 (2)	C12—C11—C13	121.5 (2)
C3—C2—H2A	109.1	O5—C12—O4	121.8 (3)
C1—C2—H2A	109.1	O5—C12—C11	128.7 (3)
C3—C2—H2B	109.1	O4—C12—C11	109.49 (19)
C1—C2—H2B	109.1	C11—C13—H13A	109.5
H2A—C2—H2B	107.8	C11—C13—H13B	109.5
O1—C3—C2	106.65 (19)	H13A—C13—H13B	109.5
O1—C3—C4	112.24 (19)	C11—C13—H13C	109.5
C2—C3—C4	113.94 (17)	H13A—C13—H13C	109.5
O1—C3—H3	107.9	H13B—C13—H13C	109.5
C2—C3—H3	107.9	C5—C14—H14A	109.5
C4—C3—H3	107.9	C5—C14—H14B	109.5
C15—C4—C3	109.66 (17)	H14A—C14—H14B	109.5
C15—C4—C5	114.57 (18)	C5—C14—H14C	109.5
C3—C4—C5	114.05 (17)	H14A—C14—H14C	109.5
C15—C4—H4	105.9	H14B—C14—H14C	109.5
C3—C4—H4	105.9	C4—C15—H15A	109.5
C5—C4—H4	105.9	C4—C15—H15B	109.5
C14—C5—C4	112.04 (16)	H15A—C15—H15B	109.5
C14—C5—C6	107.58 (16)	C4—C15—H15C	109.5
C4—C5—C6	107.18 (14)	H15A—C15—H15C	109.5
C14—C5—C10	109.42 (15)	H15B—C15—H15C	109.5
C4—C5—C10	110.28 (16)	O6—C16—O2	122.63 (17)
C6—C5—C10	110.29 (14)	O6—C16—C17	126.02 (19)
O2—C6—C7	108.78 (14)	O2—C16—C17	111.23 (17)
O2—C6—C5	107.12 (14)	C18—C17—C16	121.1 (2)

C7—C6—C5	110.71 (15)	C18—C17—C20	121.8 (2)
O2—C6—H6	110.1	C16—C17—C20	117.1 (2)
C7—C6—H6	110.1	C17—C18—C19	129.8 (2)
C5—C6—H6	110.1	C17—C18—H18	115.1
C11—C7—C6	130.91 (19)	C19—C18—H18	115.1
C11—C7—C8	110.64 (18)	C18—C19—H19A	109.5
C6—C7—C8	117.95 (15)	C18—C19—H19B	109.5
O3—C8—O4	108.62 (15)	H19A—C19—H19B	109.5
O3—C8—C7	115.58 (17)	C18—C19—H19C	109.5
O4—C8—C7	103.36 (15)	H19A—C19—H19C	109.5
O3—C8—C9	109.06 (17)	H19B—C19—H19C	109.5
O4—C8—C9	110.72 (18)	C17—C20—H20A	109.5
C7—C8—C9	109.36 (15)	C17—C20—H20B	109.5
C8—C9—C10	111.35 (18)	H20A—C20—H20B	109.5
C8—C9—H9A	109.4	C17—C20—H20C	109.5
C10—C9—H9A	109.4	H20A—C20—H20C	109.5
C8—C9—H9B	109.4	H20B—C20—H20C	109.5
C10—C1—C2—C3	56.7 (2)	C6—C7—C8—C9	−55.8 (2)
C1—C2—C3—O1	74.9 (2)	O3—C8—C9—C10	−74.2 (2)
C1—C2—C3—C4	−49.5 (3)	O4—C8—C9—C10	166.32 (16)
O1—C3—C4—C15	54.8 (3)	C7—C8—C9—C10	53.1 (2)
C2—C3—C4—C15	176.2 (2)	C8—C9—C10—C1	−178.10 (17)
O1—C3—C4—C5	−75.2 (2)	C8—C9—C10—C5	−53.9 (2)
C2—C3—C4—C5	46.2 (3)	C2—C1—C10—C9	66.8 (2)
C15—C4—C5—C14	−54.1 (2)	C2—C1—C10—C5	−59.9 (2)
C3—C4—C5—C14	73.5 (2)	C14—C5—C10—C9	168.00 (16)
C15—C4—C5—C6	63.7 (2)	C4—C5—C10—C9	−68.3 (2)
C3—C4—C5—C6	−168.75 (17)	C6—C5—C10—C9	49.8 (2)
C15—C4—C5—C10	−176.21 (17)	C14—C5—C10—C1	−68.4 (2)
C3—C4—C5—C10	−48.7 (2)	C4—C5—C10—C1	55.2 (2)
C16—O2—C6—C7	−71.9 (2)	C6—C5—C10—C1	173.42 (17)
C16—O2—C6—C5	168.37 (16)	C6—C7—C11—C12	173.02 (18)
C14—C5—C6—O2	−47.61 (19)	C8—C7—C11—C12	1.5 (2)
C4—C5—C6—O2	−168.28 (15)	C6—C7—C11—C13	−8.0 (4)
C10—C5—C6—O2	71.66 (19)	C8—C7—C11—C13	−179.6 (3)
C14—C5—C6—C7	−166.08 (15)	C8—O4—C12—O5	−179.7 (2)
C4—C5—C6—C7	73.25 (19)	C8—O4—C12—C11	0.8 (2)
C10—C5—C6—C7	−46.8 (2)	C7—C11—C12—O5	179.1 (3)
O2—C6—C7—C11	124.4 (2)	C13—C11—C12—O5	0.0 (4)
C5—C6—C7—C11	−118.1 (2)	C7—C11—C12—O4	−1.4 (3)
O2—C6—C7—C8	−64.51 (19)	C13—C11—C12—O4	179.5 (2)
C5—C6—C7—C8	52.9 (2)	C6—O2—C16—O6	−0.5 (3)
C12—O4—C8—O3	123.31 (19)	C6—O2—C16—C17	175.72 (16)
C12—O4—C8—C7	0.1 (2)	O6—C16—C17—C18	−22.5 (4)
C12—O4—C8—C9	−116.96 (19)	O2—C16—C17—C18	161.4 (2)
C11—C7—C8—O3	−119.53 (19)	O6—C16—C17—C20	156.3 (3)
C6—C7—C8—O3	67.7 (2)	O2—C16—C17—C20	−19.8 (3)
C11—C7—C8—O4	−1.0 (2)	C16—C17—C18—C19	−1.3 (5)
C6—C7—C8—O4	−173.77 (15)	C20—C17—C18—C19	180.0 (3)

C11—C7—C8—C9	117.0 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1X···O6^{i}	0.82 (2)	2.41 (4)	3.066 (3)	137 (4)
O3—H3X···O1^{ii}	0.827 (18)	1.900 (18)	2.726 (2)	178
C14—H14A···O5^{iii}	0.96	2.56	3.443 (3)	153
C14—H14B···O1	0.96	2.45	3.133 (3)	128
C19—H19B···O6	0.96	2.28	2.917 (3)	123
C18—H18···O3^{iv}	0.93	2.46	3.282 (3)	147

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

Fig. 1

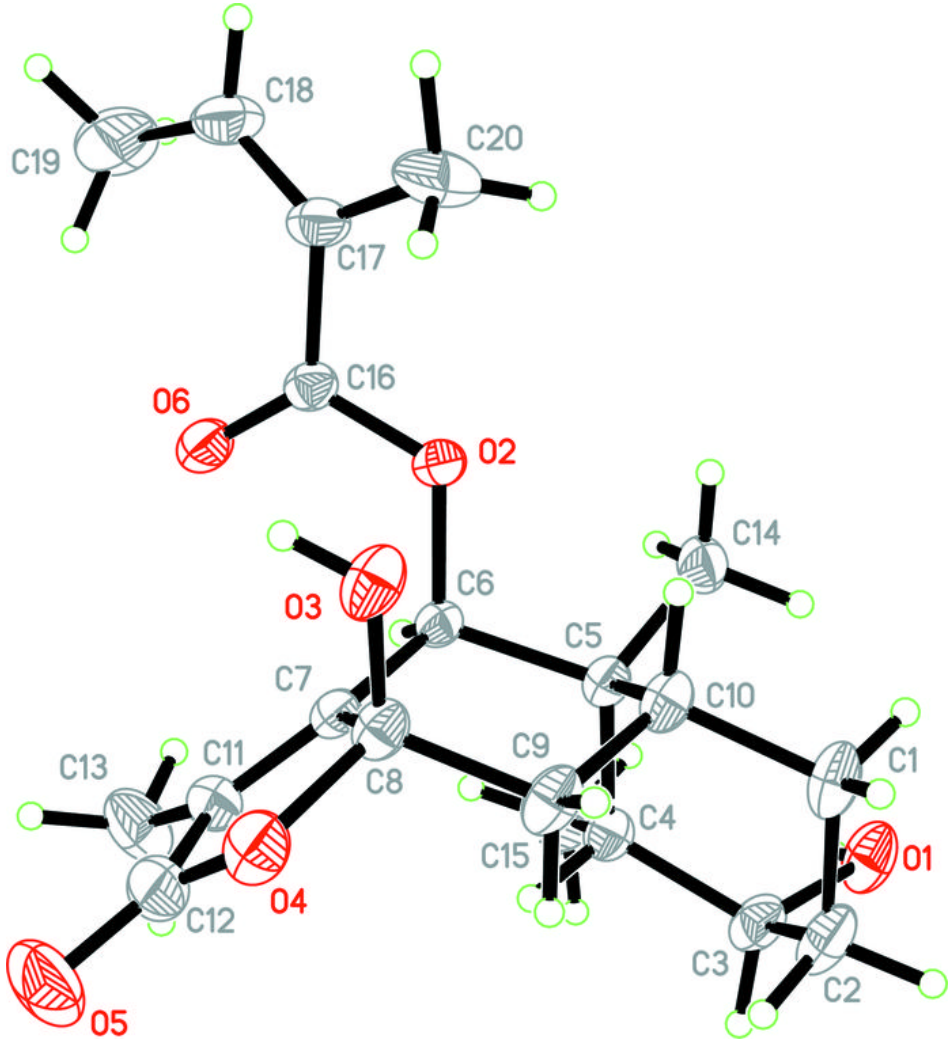
C18
C19
C20
C17
C16
O6
O2
C14
O3
C6
C5
C7
C10
C13
C11
C8
C9
C1
C4
C15
O1
O4
C12
C3
C2
O5

Fig. 2