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7-(Hydroxymethyl)-2-(1-hydroxy-1-methylethyl)-4-methoxy-2,3-dihydro-5*H*-furo[3,2-*g*]chromen-5-one methanol hemisolvate

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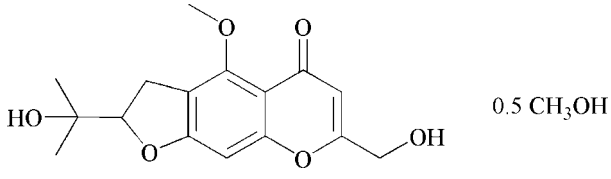
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; R factor = 0.039; wR factor = 0.108; data-to-parameter ratio = 7.8.

The title compound (cimifugin), $C_{16}H_{18}O_6\cdot0.5CH_3OH$, was isolated from the rhizome of *Actaea asiatica* Hara. The asymmetric unit contains two independent molecules and a solvent methanol molecule. The five-numbered ring adopts an envelope conformation in each molecule. Intra- and intermolecular O—H···O hydrogen bonds stabilize the crystal structure.

Related literature

For related literature, see: Kusano *et al.* (1998, 1999); Wan (1990).



Experimental

Crystal data

$C_{16}H_{18}O_6\cdot0.5CH_4O$
M_r = 322.33
Monoclinic, $P2_1$
a = 9.4092 (14) Å
b = 13.4176 (19) Å
c = 12.6903 (18) Å
β = 91.600 (2)°
V = 1601.5 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 294 (2) K
0.30 × 0.28 × 0.24 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.956, T_{max} = 0.976
9210 measured reflections
3408 independent reflections
2556 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.108
S = 1.03
3408 reflections
437 parameters
12 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O9^{i}	0.85 (3)	2.41 (4)	2.934 (3)	120 (4)
O12—H12···O11^{i}	0.85 (3)	1.99 (3)	2.812 (3)	162 (5)
O6—H6···O13^{ii}	0.85 (3)	1.80 (3)	2.618 (5)	159 (6)
O13—H13···O11	0.96 (3)	1.83 (4)	2.708 (4)	150 (6)
O7—H7···O6	0.87 (3)	1.92 (3)	2.779 (4)	169 (5)
O1—H1···O12	0.85 (3)	1.98 (3)	2.809 (4)	164 (5)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); 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, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG2062).

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7-(Hydroxymethyl)-2-(1-hydroxy-1-methylethyl)-4-methoxy-2,3-dihydro-5*H*-furo[3,2-*g*]chromen-5-one methanol hemisolvate

Ru Li, Pu Liu, Yu-Mei Gao, Lin-Lin Qin and Hua-Ning Yu

S1. Comment

Actaea asiatica Hara (Ranunculaceae) is widely distributed in the southwest and northwest of the People's Republic of China. As a Chinesa folk medicine, its rhizome is used to treat headache, sore throat, measles, pertussis, prolapse of uterus (Wan, 1990). Previous phytochemical investigations have reported in the isolation of cimiaceroside A and 26-deoxycimicifugoside from this plant (Kusano *et al.*, 1998, 1999). To investigate the bioactive natural products from A. asiatica, chemical studies of the rhizome of the plant were undertaken by screening using immunopotent tests *in vitro*, we obtained a compund, *viz*. cimifugin, from the petroleum ether extract. The structure of cimifugin was elucidated by extensive spectroscopic analysis, including two-dimensional NMR spectroscopy, and established unequivocally by single-crystal X-ray diffraction analysis.

The molecular structure of (I) and the atom-numbering scheme are shown in Fig. 1. The asymmetric unit of (I) contains two independent molecules and a methanol of solvation. The molecule is composed of a fused five-numbered ring and two fused six-numbered *viz*. A(C1–C3/C11/O2), B(C3–C5/C9–C11) and C(C5–C9/O4). In the two molecules, two fused six-numbered (B and C) are almost planar with the r.m.s. deviations of 0.0129 (4) and 1.0103 (4) Å, respectively, while ring C does not deviate form the chromone plane. The O5—C6—C5 and C7—C6—C5 angles are 123.3 (4)° and 115.8 (3)°, respectively, which indicates that carbonyl C6 atom slightly deviates from the ideal value of 120°. The similar deviation is also observed for the C22 with the angles of O11—C22—C21 [124.4 (3)°] and C23—C22—C21 [115.2 (3)°].

The hydroxy groups are attached at atoms C12, C16, C28 and C32. The methoxy group located at atoms C4 and C20. The interactions of intermolecular and intramolecular hydrogen bonds are formed between the hydroxy and carbonyl groups, which stablize the crystal structure.

S2. Experimental

The rhizomes of Phlomis umbrosa turcz was collected in Jianshi county, Hubei province, China, January 2006. The plants were identified as Actaea asiatica Hara by Professor Ding-rong Wan, College of Life Science, South-Central University for Nationalities. A voucher specimen (No. D20050115) was deposited in the laboratory of Natural products, Tinjing Medical University. The rhizomes of Actaea asiatica Hara was dried at room temperature in the dark. The material (4.3 kg) was extracted three times with 95% ethanol under reflux. The 95% ethanol extract (500 g) was suspended in water, and then extracted with petroleum ether, ethyl acetate and n-butanol successively. The ethyl acetate layer (80 g) was absorbed on to silica gel (150 g) and chromatographed on a silica gel (1000 g) column eluted with petroleum ether–EtOAc with the increased polarity to give 25 fractions. Fraction 8 was further separated on Toyopear HW-40, pre. HPLC-ODS to afford 200 mg of cimifugin. ^{13}C NMR (300 MHz, CD_3OD, p.p.m.): 92.7, 28.8, 118.4, 167.1, 112.3, 179.7, 109.3, 168.7, 157.0, 94.5, 161.1, 72.3, 25.4, 25.5, 61.0, 61.2. Crystals suitable for X-ray structure analysis were obtained by

slow evaporation from methanol at room temperature.

S3. Refinement

H atoms of the hydroxy group were located in a difference density map and the atomic coordinates allowed to refine freely. Other H atoms were positioned geometrically and refined as riding with C—H = 0.95–0.98 Å). For the CH and CH_2 groups, U_{iso}(H) values are set equal to $1.2U_{eq}$(carrier atom) and for the methyl groups they are set equal to $1.5U_{eq}$(carrier atom). The absolute configuration could not be established because of the absence of significant anomalous effects. Friedel pairs were merged for the final cycles of refinement.

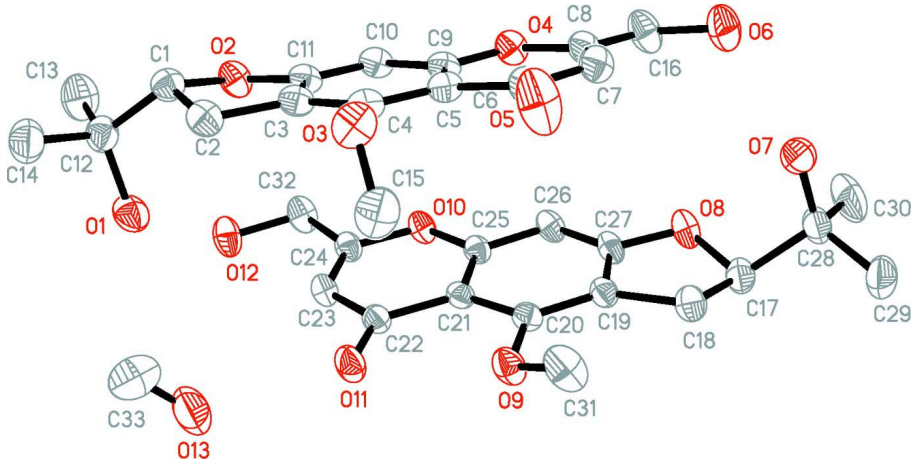

Figure 1

View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

7-(Hydroxymethyl)-2-(1-hydroxy-1-methylethyl)-4-methoxy-2,3-dihydro-5*H*- furo[3,2-*g*]chromen-5-one methanol hemisolvate

Crystal data

$C_{16}H_{18}O_6 \cdot 0.5CH_4O$
$M_r = 322.33$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 9.4092$ (14) Å
$b = 13.4176$ (19) Å
$c = 12.6903$ (18) Å
$\beta = 91.600$ (2)°
$V = 1601.5$ (4) Å^3
$Z = 4$
$F(000) = 684$
$D_x = 1.337$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3898 reflections
$\theta = 2.6$–25.4°
$\mu = 0.10$ mm^{-1}
$T = 294$ K
Plate, colourless
0.30 × 0.28 × 0.24 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.956$, $T_{max} = 0.976$
9210 measured reflections
3408 independent reflections
2556 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 26.4°$, $\theta_{min} = 1.6°$
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.108$
$S = 1.03$
3408 reflections
437 parameters
12 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 0.2147P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.8781 (3)	0.6603 (2)	0.4785 (2)	0.0674 (7)
H1	0.820 (5)	0.621 (3)	0.508 (4)	0.101*
O2	0.9188 (3)	0.65092 (18)	0.70280 (17)	0.0545 (6)
O3	0.7862 (3)	0.97796 (18)	0.7545 (2)	0.0663 (7)
O4	0.6245 (3)	0.71772 (16)	0.98859 (17)	0.0499 (6)
O5	0.6128 (4)	1.0136 (2)	0.9273 (3)	0.1017 (12)
O6	0.4013 (3)	0.7906 (2)	1.1992 (2)	0.0779 (9)
H6	0.475 (4)	0.799 (5)	1.239 (4)	0.117*
O7	0.1990 (3)	0.9270 (2)	1.1264 (2)	0.0634 (7)
H7	0.254 (5)	0.878 (3)	1.147 (4)	0.095*
O8	0.1715 (3)	0.7605 (2)	0.98115 (17)	0.0566 (6)
O9	0.3011 (3)	0.93880 (18)	0.67958 (17)	0.0550 (6)
O10	0.4679 (2)	0.60625 (15)	0.73882 (16)	0.0445 (5)
O11	0.4630 (3)	0.84518 (19)	0.54207 (17)	0.0570 (6)
O12	0.6907 (3)	0.5091 (2)	0.53907 (19)	0.0619 (7)
H12	0.642 (5)	0.467 (3)	0.502 (3)	0.093*
C1	1.0036 (4)	0.7143 (3)	0.6349 (3)	0.0518 (8)
H1A	1.0994	0.7200	0.6668	0.062*
C2	0.9341 (4)	0.8170 (3)	0.6371 (3)	0.0553 (9)
H2A	1.0047	0.8694	0.6435	0.066*
H2B	0.8752	0.8284	0.5743	0.066*
C3	0.8461 (4)	0.8111 (3)	0.7335 (3)	0.0463 (8)
C4	0.7736 (4)	0.8812 (2)	0.7866 (3)	0.0468 (8)
C5	0.6943 (3)	0.8538 (2)	0.8758 (3)	0.0445 (7)

C6	0.6171 (4)	0.9232 (3)	0.9427 (3)	0.0554 (9)
C7	0.5464 (4)	0.8794 (3)	1.0296 (3)	0.0541 (9)
H7A	0.4959	0.9204	1.0743	0.065*
C8	0.5506 (4)	0.7821 (3)	1.0485 (3)	0.0505 (8)
C9	0.6955 (3)	0.7524 (2)	0.9032 (2)	0.0430 (7)
C10	0.7682 (4)	0.6792 (2)	0.8496 (3)	0.0460 (8)
H10	0.7662	0.6126	0.8696	0.055*
C11	0.8426 (4)	0.7116 (2)	0.7658 (2)	0.0447 (8)
C12	1.0158 (4)	0.6656 (3)	0.5284 (3)	0.0581 (9)
C13	1.0790 (6)	0.5624 (4)	0.5394 (4)	0.0854 (14)
H13A	1.0147	0.5203	0.5765	0.128*
H13B	1.1680	0.5662	0.5781	0.128*
H13C	1.0943	0.5351	0.4707	0.128*
C14	1.1047 (5)	0.7311 (4)	0.4586 (3)	0.0798 (13)
H14A	1.1128	0.7003	0.3908	0.120*
H14B	1.1976	0.7395	0.4904	0.120*
H14C	1.0598	0.7950	0.4504	0.120*
C15	0.6701 (5)	1.0182 (4)	0.6989 (4)	0.0815 (13)
H15A	0.6673	0.9923	0.6284	0.122*
H15B	0.6789	1.0894	0.6967	0.122*
H15C	0.5841	1.0005	0.7333	0.122*
C16	0.4762 (5)	0.7266 (3)	1.1319 (3)	0.0698 (11)
H16A	0.4100	0.6798	1.0990	0.084*
H16B	0.5453	0.6886	1.1734	0.084*
C17	0.0789 (4)	0.8478 (3)	0.9780 (3)	0.0529 (8)
H17	−0.0156	0.8272	0.9518	0.063*
C18	0.1425 (4)	0.9172 (3)	0.8981 (3)	0.0535 (9)
H18A	0.0691	0.9476	0.8536	0.064*
H18B	0.1984	0.9692	0.9325	0.064*
C19	0.2351 (3)	0.8488 (2)	0.8353 (2)	0.0414 (7)
C20	0.3053 (3)	0.8572 (2)	0.7426 (2)	0.0409 (7)
C21	0.3860 (3)	0.7750 (2)	0.7045 (2)	0.0373 (6)
C22	0.4621 (3)	0.7746 (3)	0.6053 (2)	0.0420 (7)
C23	0.5373 (4)	0.6851 (3)	0.5837 (2)	0.0459 (8)
H23	0.5869	0.6813	0.5214	0.055*
C24	0.5404 (3)	0.6068 (2)	0.6479 (2)	0.0425 (7)
C25	0.3925 (3)	0.6894 (2)	0.7668 (2)	0.0388 (7)
C26	0.3224 (4)	0.6792 (3)	0.8611 (2)	0.0453 (8)
H26	0.3272	0.6212	0.9010	0.054*
C27	0.2462 (3)	0.7599 (3)	0.8910 (2)	0.0452 (8)
C28	0.0656 (4)	0.8878 (3)	1.0900 (3)	0.0597 (10)
C29	−0.0371 (4)	0.9744 (4)	1.0879 (4)	0.0836 (15)
H29A	−0.0374	1.0053	1.1561	0.125*
H29B	−0.1309	0.9508	1.0697	0.125*
H29C	−0.0083	1.0223	1.0364	0.125*
C30	0.0158 (6)	0.8050 (4)	1.1621 (3)	0.0948 (17)
H30A	0.0848	0.7523	1.1640	0.142*
H30B	−0.0738	0.7795	1.1358	0.142*

H30C	0.0048	0.8309	1.2319	0.142*
C31	0.2736 (5)	1.0340 (3)	0.7232 (3)	0.0749 (12)
H31A	0.1729	1.0429	0.7292	0.112*
H31B	0.3105	1.0848	0.6782	0.112*
H31C	0.3188	1.0388	0.7918	0.112*
C32	0.6206 (4)	0.5121 (3)	0.6356 (3)	0.0550 (9)
H32A	0.6900	0.5056	0.6932	0.066*
H32B	0.5554	0.4563	0.6392	0.066*
O13	0.5854 (4)	0.7999 (3)	0.3575 (2)	0.0998 (12)
H13	0.569 (7)	0.802 (6)	0.432 (2)	0.150*
C33	0.7073 (6)	0.8399 (6)	0.3440 (5)	0.125 (2)
H33A	0.7379	0.8737	0.4073	0.187*
H33B	0.7004	0.8868	0.2870	0.187*
H33C	0.7750	0.7891	0.3274	0.187*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0728 (18)	0.077 (2)	0.0523 (14)	−0.0222 (15)	−0.0001 (12)	−0.0111 (13)
O2	0.0746 (16)	0.0410 (13)	0.0481 (12)	0.0016 (12)	0.0068 (11)	−0.0057 (11)
O3	0.0728 (17)	0.0358 (13)	0.0905 (19)	−0.0054 (13)	0.0057 (14)	0.0072 (13)
O4	0.0659 (15)	0.0334 (11)	0.0506 (12)	0.0051 (11)	0.0029 (11)	−0.0036 (10)
O5	0.178 (4)	0.0319 (15)	0.098 (2)	0.0235 (19)	0.049 (2)	0.0063 (15)
O6	0.105 (2)	0.0615 (19)	0.0684 (18)	0.0135 (18)	0.0215 (16)	−0.0086 (15)
O7	0.0598 (16)	0.0650 (17)	0.0650 (15)	0.0035 (13)	−0.0056 (12)	−0.0216 (13)
O8	0.0731 (15)	0.0553 (14)	0.0425 (12)	−0.0063 (13)	0.0191 (11)	−0.0037 (11)
O9	0.0782 (16)	0.0441 (13)	0.0431 (12)	0.0104 (12)	0.0091 (11)	0.0063 (10)
O10	0.0612 (14)	0.0357 (12)	0.0371 (11)	−0.0021 (10)	0.0088 (10)	−0.0013 (9)
O11	0.0722 (16)	0.0570 (15)	0.0426 (12)	0.0135 (13)	0.0156 (11)	0.0146 (11)
O12	0.0786 (18)	0.0524 (15)	0.0559 (15)	−0.0120 (13)	0.0216 (12)	−0.0181 (12)
C1	0.053 (2)	0.049 (2)	0.0533 (19)	−0.0027 (16)	−0.0018 (16)	−0.0045 (16)
C2	0.064 (2)	0.048 (2)	0.054 (2)	−0.0061 (18)	0.0000 (17)	−0.0041 (16)
C3	0.0536 (19)	0.0385 (17)	0.0464 (17)	−0.0031 (15)	−0.0063 (15)	−0.0035 (14)
C4	0.0505 (18)	0.0314 (17)	0.0579 (19)	−0.0038 (14)	−0.0081 (16)	−0.0023 (14)
C5	0.0491 (18)	0.0315 (16)	0.0524 (18)	0.0021 (14)	−0.0073 (15)	−0.0053 (14)
C6	0.074 (2)	0.0324 (19)	0.059 (2)	0.0060 (17)	−0.0028 (18)	−0.0057 (16)
C7	0.065 (2)	0.0394 (19)	0.058 (2)	0.0078 (16)	0.0020 (17)	−0.0101 (16)
C8	0.063 (2)	0.0402 (19)	0.0480 (17)	0.0059 (16)	−0.0013 (16)	−0.0070 (15)
C9	0.0505 (18)	0.0342 (17)	0.0438 (16)	−0.0018 (14)	−0.0078 (14)	−0.0030 (14)
C10	0.060 (2)	0.0303 (15)	0.0475 (17)	0.0044 (15)	−0.0068 (15)	−0.0023 (14)
C11	0.055 (2)	0.0351 (16)	0.0434 (17)	0.0049 (15)	−0.0076 (14)	−0.0068 (14)
C12	0.058 (2)	0.060 (2)	0.057 (2)	−0.0059 (19)	0.0067 (17)	−0.0110 (18)
C13	0.103 (4)	0.069 (3)	0.085 (3)	0.012 (3)	0.021 (3)	−0.018 (3)
C14	0.071 (3)	0.095 (4)	0.073 (3)	−0.013 (3)	0.016 (2)	−0.009 (3)
C15	0.087 (3)	0.061 (3)	0.097 (3)	0.012 (2)	0.018 (3)	0.025 (2)
C16	0.108 (3)	0.048 (2)	0.054 (2)	0.007 (2)	0.016 (2)	−0.0045 (18)
C17	0.0483 (19)	0.060 (2)	0.0508 (18)	−0.0060 (17)	0.0090 (15)	−0.0129 (17)
C18	0.058 (2)	0.051 (2)	0.0510 (19)	0.0027 (17)	0.0047 (16)	−0.0082 (16)

C19	0.0442 (17)	0.0448 (18)	0.0354 (15)	−0.0032 (14)	0.0028 (13)	−0.0050 (14)
C20	0.0435 (17)	0.0416 (17)	0.0372 (15)	−0.0011 (14)	−0.0026 (13)	−0.0022 (13)
C21	0.0388 (15)	0.0413 (17)	0.0317 (13)	−0.0056 (13)	−0.0012 (11)	−0.0013 (13)
C22	0.0420 (17)	0.0484 (19)	0.0354 (15)	−0.0031 (15)	0.0013 (13)	0.0025 (14)
C23	0.0535 (19)	0.0487 (19)	0.0360 (15)	−0.0007 (16)	0.0089 (14)	−0.0018 (14)
C24	0.0480 (18)	0.0421 (17)	0.0375 (16)	−0.0053 (15)	0.0034 (13)	−0.0057 (14)
C25	0.0430 (17)	0.0380 (17)	0.0354 (15)	−0.0053 (14)	0.0010 (13)	−0.0059 (13)
C26	0.060 (2)	0.0402 (17)	0.0364 (15)	−0.0103 (16)	0.0064 (14)	−0.0016 (13)
C27	0.0515 (19)	0.0509 (19)	0.0335 (15)	−0.0111 (16)	0.0074 (13)	−0.0092 (15)
C28	0.054 (2)	0.077 (3)	0.0486 (18)	−0.0041 (19)	0.0108 (16)	−0.0169 (19)
C29	0.065 (2)	0.108 (4)	0.078 (3)	0.016 (3)	0.008 (2)	−0.040 (3)
C30	0.110 (4)	0.120 (5)	0.056 (2)	−0.026 (3)	0.033 (2)	−0.009 (3)
C31	0.117 (4)	0.049 (2)	0.059 (2)	0.004 (2)	0.006 (2)	0.0002 (19)
C32	0.078 (2)	0.0362 (17)	0.0510 (19)	−0.0038 (17)	0.0131 (17)	−0.0068 (15)
O13	0.126 (3)	0.113 (3)	0.0614 (18)	0.022 (2)	0.0245 (19)	0.0038 (19)
C33	0.081 (3)	0.163 (6)	0.130 (4)	0.015 (4)	−0.012 (3)	0.014 (5)

Geometric parameters (Å, º)

O1—C12	1.428 (5)	C14—H14A	0.9600
O1—H1	0.85 (3)	C14—H14B	0.9600
O2—C11	1.359 (4)	C14—H14C	0.9600
O2—C1	1.464 (4)	C15—H15A	0.9600
O3—C4	1.367 (4)	C15—H15B	0.9600
O3—C15	1.393 (5)	C15—H15C	0.9600
O4—C8	1.356 (4)	C16—H16A	0.9700
O4—C9	1.370 (4)	C16—H16B	0.9700
O5—C6	1.229 (4)	C17—C18	1.512 (5)
O6—C16	1.415 (5)	C17—C28	1.527 (5)
O6—H6	0.85 (3)	C17—H17	0.9800
O7—C28	1.426 (5)	C18—C19	1.509 (4)
O7—H7	0.87 (3)	C18—H18A	0.9700
O8—C27	1.359 (4)	C18—H18B	0.9700
O8—C17	1.459 (5)	C19—C20	1.369 (4)
O9—C20	1.356 (4)	C19—C27	1.389 (5)
O9—C31	1.419 (5)	C20—C21	1.431 (4)
O10—C24	1.356 (4)	C21—C25	1.395 (4)
O10—C25	1.375 (4)	C21—C22	1.465 (4)
O11—C22	1.242 (4)	C22—C23	1.424 (5)
O12—C32	1.409 (4)	C23—C24	1.330 (4)
O12—H12	0.85 (3)	C23—H23	0.9300
C1—C12	1.508 (5)	C24—C32	1.488 (5)
C1—C2	1.526 (5)	C25—C26	1.388 (4)
C1—H1A	0.9800	C26—C27	1.358 (5)
C2—C3	1.498 (5)	C26—H26	0.9300
C2—H2A	0.9700	C28—C29	1.511 (6)
C2—H2B	0.9700	C28—C30	1.522 (6)
C3—C4	1.354 (5)	C29—H29A	0.9600

C3—C11	1.397 (5)	C29—H29B	0.9600
C4—C5	1.421 (5)	C29—H29C	0.9600
C5—C9	1.403 (4)	C30—H30A	0.9600
C5—C6	1.467 (5)	C30—H30B	0.9600
C6—C7	1.430 (5)	C30—H30C	0.9600
C7—C8	1.328 (5)	C31—H31A	0.9600
C7—H7A	0.9300	C31—H31B	0.9600
C8—C16	1.485 (5)	C31—H31C	0.9600
C9—C10	1.386 (4)	C32—H32A	0.9700
C10—C11	1.361 (5)	C32—H32B	0.9700
C10—H10	0.9300	O13—C33	1.283 (7)
C12—C13	1.512 (6)	O13—H13	0.96 (3)
C12—C14	1.515 (6)	C33—H33A	0.9600
C13—H13A	0.9600	C33—H33B	0.9600
C13—H13B	0.9600	C33—H33C	0.9600
C13—H13C	0.9600		

C12—O1—H1	115 (4)	H16A—C16—H16B	107.9
C11—O2—C1	107.7 (3)	O8—C17—C18	105.4 (3)
C4—O3—C15	116.4 (3)	O8—C17—C28	108.7 (3)
C8—O4—C9	119.7 (3)	C18—C17—C28	116.8 (3)
C16—O6—H6	91 (4)	O8—C17—H17	108.5
C28—O7—H7	109 (4)	C18—C17—H17	108.5
C27—O8—C17	107.7 (3)	C28—C17—H17	108.5
C20—O9—C31	119.9 (3)	C19—C18—C17	103.0 (3)
C24—O10—C25	119.4 (2)	C19—C18—H18A	111.2
C32—O12—H12	104 (3)	C17—C18—H18A	111.2
O2—C1—C12	109.4 (3)	C19—C18—H18B	111.2
O2—C1—C2	105.8 (3)	C17—C18—H18B	111.2
C12—C1—C2	116.8 (3)	H18A—C18—H18B	109.1
O2—C1—H1A	108.2	C20—C19—C27	118.5 (3)
C12—C1—H1A	108.2	C20—C19—C18	134.7 (3)
C2—C1—H1A	108.2	C27—C19—C18	106.8 (3)
C3—C2—C1	102.4 (3)	O9—C20—C19	124.5 (3)
C3—C2—H2A	111.3	O9—C20—C21	115.4 (2)
C1—C2—H2A	111.3	C19—C20—C21	120.0 (3)
C3—C2—H2B	111.3	C25—C21—C20	117.2 (2)
C1—C2—H2B	111.3	C25—C21—C22	118.0 (3)
H2A—C2—H2B	109.2	C20—C21—C22	124.8 (3)
C4—C3—C11	120.1 (3)	O11—C22—C23	120.4 (3)
C4—C3—C2	131.9 (3)	O11—C22—C21	124.4 (3)
C11—C3—C2	107.9 (3)	C23—C22—C21	115.2 (3)
C3—C4—O3	117.6 (3)	C24—C23—C22	123.4 (3)
C3—C4—C5	120.0 (3)	C24—C23—H23	118.3
O3—C4—C5	122.4 (3)	C22—C23—H23	118.3
C9—C5—C4	116.6 (3)	C23—C24—O10	121.6 (3)
C9—C5—C6	118.2 (3)	C23—C24—C32	127.8 (3)
C4—C5—C6	125.2 (3)	O10—C24—C32	110.7 (3)

O5—C6—C7	120.9 (4)	O10—C25—C26	113.8 (3)
O5—C6—C5	123.3 (4)	O10—C25—C21	122.4 (2)
C7—C6—C5	115.8 (3)	C26—C25—C21	123.7 (3)
C8—C7—C6	122.1 (3)	C27—C26—C25	115.5 (3)
C8—C7—H7A	119.0	C27—C26—H26	122.3
C6—C7—H7A	119.0	C25—C26—H26	122.3
C7—C8—O4	122.6 (3)	C26—C27—O8	122.0 (3)
C7—C8—C16	127.6 (3)	C26—C27—C19	125.1 (3)
O4—C8—C16	109.8 (3)	O8—C27—C19	112.9 (3)
O4—C9—C10	113.9 (3)	O7—C28—C29	106.2 (3)
O4—C9—C5	121.7 (3)	O7—C28—C30	110.9 (3)
C10—C9—C5	124.4 (3)	C29—C28—C30	111.4 (4)
C11—C10—C9	115.4 (3)	O7—C28—C17	109.7 (3)
C11—C10—H10	122.3	C29—C28—C17	108.8 (3)
C9—C10—H10	122.3	C30—C28—C17	109.7 (3)
O2—C11—C10	124.1 (3)	C28—C29—H29A	109.5
O2—C11—C3	112.5 (3)	C28—C29—H29B	109.5
C10—C11—C3	123.4 (3)	H29A—C29—H29B	109.5
O1—C12—C1	109.1 (3)	C28—C29—H29C	109.5
O1—C12—C13	110.2 (4)	H29A—C29—H29C	109.5
C1—C12—C13	110.7 (3)	H29B—C29—H29C	109.5
O1—C12—C14	106.2 (3)	C28—C30—H30A	109.5
C1—C12—C14	109.2 (3)	C28—C30—H30B	109.5
C13—C12—C14	111.3 (4)	H30A—C30—H30B	109.5
C12—C13—H13A	109.5	C28—C30—H30C	109.5
C12—C13—H13B	109.5	H30A—C30—H30C	109.5
H13A—C13—H13B	109.5	H30B—C30—H30C	109.5
C12—C13—H13C	109.5	O9—C31—H31A	109.5
H13A—C13—H13C	109.5	O9—C31—H31B	109.5
H13B—C13—H13C	109.5	H31A—C31—H31B	109.5
C12—C14—H14A	109.5	O9—C31—H31C	109.5
C12—C14—H14B	109.5	H31A—C31—H31C	109.5
H14A—C14—H14B	109.5	H31B—C31—H31C	109.5
C12—C14—H14C	109.5	O12—C32—C24	111.5 (3)
H14A—C14—H14C	109.5	O12—C32—H32A	109.3
H14B—C14—H14C	109.5	C24—C32—H32A	109.3
O3—C15—H15A	109.5	O12—C32—H32B	109.3
O3—C15—H15B	109.5	C24—C32—H32B	109.3
H15A—C15—H15B	109.5	H32A—C32—H32B	108.0
O3—C15—H15C	109.5	C33—O13—H13	107 (4)
H15A—C15—H15C	109.5	O13—C33—H33A	109.5
H15B—C15—H15C	109.5	O13—C33—H33B	109.5
O6—C16—C8	112.2 (3)	H33A—C33—H33B	109.5
O6—C16—H16A	109.2	O13—C33—H33C	109.5
C8—C16—H16A	109.2	H33A—C33—H33C	109.5
O6—C16—H16B	109.2	H33B—C33—H33C	109.5
C8—C16—H16B	109.2		

C15—O3—C4—C3	105.4 (4)	C7—C8—C16—O6	−3.9 (6)
C15—O3—C4—C5	−78.1 (4)	O4—C8—C16—O6	177.9 (3)
C31—O9—C20—C19	26.1 (5)	C27—O8—C17—C18	−19.7 (3)
C31—O9—C20—C21	−156.1 (3)	C27—O8—C17—C28	−145.7 (3)
C11—O2—C1—C12	−145.4 (3)	O8—C17—C18—C19	19.3 (3)
C11—O2—C1—C2	−18.8 (3)	C28—C17—C18—C19	140.1 (3)
O2—C1—C2—C3	18.2 (3)	C17—C18—C19—C20	168.0 (3)
C12—C1—C2—C3	140.2 (3)	C17—C18—C19—C27	−12.7 (3)
C1—C2—C3—C4	170.2 (4)	C27—C19—C20—O9	178.6 (3)
C1—C2—C3—C11	−11.7 (4)	C18—C19—C20—O9	−2.2 (6)
C11—C3—C4—O3	177.0 (3)	C27—C19—C20—C21	0.9 (4)
C2—C3—C4—O3	−5.1 (6)	C18—C19—C20—C21	−179.9 (3)
C11—C3—C4—C5	0.3 (5)	O9—C20—C21—C25	−179.7 (3)
C2—C3—C4—C5	178.2 (3)	C19—C20—C21—C25	−1.9 (4)
C3—C4—C5—C9	−0.6 (4)	O9—C20—C21—C22	0.4 (4)
O3—C4—C5—C9	−177.0 (3)	C19—C20—C21—C22	178.3 (3)
C3—C4—C5—C6	177.0 (3)	C25—C21—C22—O11	178.8 (3)
O3—C4—C5—C6	0.5 (5)	C20—C21—C22—O11	−1.4 (5)
C9—C5—C6—O5	178.0 (4)	C25—C21—C22—C23	−0.7 (4)
C4—C5—C6—O5	0.5 (6)	C20—C21—C22—C23	179.1 (3)
C9—C5—C6—C7	−1.5 (5)	O11—C22—C23—C24	−179.9 (3)
C4—C5—C6—C7	−178.9 (3)	C21—C22—C23—C24	−0.3 (5)
O5—C6—C7—C8	−179.3 (4)	C22—C23—C24—O10	1.6 (5)
C5—C6—C7—C8	0.1 (5)	C22—C23—C24—C32	−176.9 (3)
C6—C7—C8—O4	1.5 (6)	C25—O10—C24—C23	−1.8 (4)
C6—C7—C8—C16	−176.4 (4)	C25—O10—C24—C32	176.9 (3)
C9—O4—C8—C7	−1.7 (5)	C24—O10—C25—C26	179.6 (3)
C9—O4—C8—C16	176.6 (3)	C24—O10—C25—C21	0.7 (4)
C8—O4—C9—C10	179.2 (3)	C20—C21—C25—O10	−179.3 (3)
C8—O4—C9—C5	0.2 (4)	C22—C21—C25—O10	0.5 (4)
C4—C5—C9—O4	179.1 (3)	C20—C21—C25—C26	1.9 (4)
C6—C5—C9—O4	1.4 (5)	C22—C21—C25—C26	−178.3 (3)
C4—C5—C9—C10	0.2 (5)	O10—C25—C26—C27	−179.7 (3)
C6—C5—C9—C10	−177.5 (3)	C21—C25—C26—C27	−0.8 (4)
O4—C9—C10—C11	−178.5 (3)	C25—C26—C27—O8	179.7 (3)
C5—C9—C10—C11	0.5 (5)	C25—C26—C27—C19	−0.3 (5)
C1—O2—C11—C10	−169.7 (3)	C17—O8—C27—C26	−167.8 (3)
C1—O2—C11—C3	11.7 (4)	C17—O8—C27—C19	12.1 (3)
C9—C10—C11—O2	−179.1 (3)	C20—C19—C27—C26	0.2 (5)
C9—C10—C11—C3	−0.7 (5)	C18—C19—C27—C26	−179.2 (3)
C4—C3—C11—O2	178.9 (3)	C20—C19—C27—O8	−179.7 (3)
C2—C3—C11—O2	0.5 (4)	C18—C19—C27—O8	0.9 (4)
C4—C3—C11—C10	0.3 (5)	O8—C17—C28—O7	67.5 (4)
C2—C3—C11—C10	−178.0 (3)	C18—C17—C28—O7	−51.5 (4)
O2—C1—C12—O1	64.8 (4)	O8—C17—C28—C29	−176.7 (3)
C2—C1—C12—O1	−55.4 (4)	C18—C17—C28—C29	64.3 (4)
O2—C1—C12—C13	−56.6 (4)	O8—C17—C28—C30	−54.6 (4)
C2—C1—C12—C13	−176.8 (4)	C18—C17—C28—C30	−173.6 (4)

O2—C1—C12—C14	−179.6 (3)	C23—C24—C32—O12	−4.5 (5)
C2—C1—C12—C14	60.3 (4)	O10—C24—C32—O12	176.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H12···O9^{i}	0.85 (3)	2.41 (4)	2.934 (3)	120 (4)
O12—H12···O11^{i}	0.85 (3)	1.99 (3)	2.812 (3)	162 (5)
O6—H6···O13^{ii}	0.85 (3)	1.80 (3)	2.618 (5)	159 (6)
O13—H13···O11	0.96 (3)	1.83 (4)	2.708 (4)	150 (6)
O7—H7···O6	0.87 (3)	1.92 (3)	2.779 (4)	169 (5)
O1—H1···O12	0.85 (3)	1.98 (3)	2.809 (4)	164 (5)

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