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(1*R*,4*S*,8*R*,9*S*,12*S*,13*S*,14*R*,16*S*,19*R*)-19-Acetoxy-14-hydroxy-7,7-dimethyl-17-methylene-2,18-dioxo-3,10-dioxapentacyclo[14.2.1.0^{1,13}.0^{4,12}.0^{8,12}]nonadec-9-yl acetate

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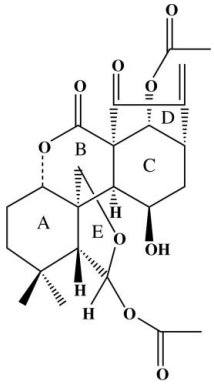
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.044; wR factor = 0.064; data-to-parameter ratio = 7.6.

The title compound, $C_{24}H_{30}O_9$, was prepared from the natural diterpenoid macrocalyxin J and is built from five fused rings. Cyclohexane ring A adopts a chair conformation, ring B exists in a screw-boat conformation and ring C adopts a boat conformation. The five-membered ring D adopts an envelope conformation, while ring E adopts a twist conformation. The crystal structure displays intermolecular O—H···O hydrogen bonds, which link molecules to form a chain parallel to the *a* axis. The absolute configuration was deduced from the chirality of macrocalyxin A, which was isolated from the same plant (*i.e. Rabdosia macrocalyx*) as macrocalyxin J. One of the carbonyl O atoms is disordered over two sites, with refined site occupancies of 0.794 (12):0.206 (12).

Related literature

For related literature, see: Cremer & Pople (1975); Shi *et al.* (2003, 2007).



Experimental

Crystal data

$C_{24}H_{30}O_9$
M_r = 462.48
Orthorhombic, $P2_12_12_1$
a = 7.5188 (6) Å
b = 9.7993 (13) Å
c = 30.876 (3) Å
V = 2274.9 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 (2) K
0.40 × 0.18 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.960, T_{max} = 0.983
10274 measured reflections
2324 independent reflections
1579 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.064
S = 1.16
2324 reflections
304 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O4^{i}	0.82	2.37	2.873 (3)	120

Symmetry code: (i) $x-1, y, z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2072).

References

Bruker (1999). *SMART* (Version 5.611), *SAINT* (Version 6.02a) and *SADABS* (Version 2.08). Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Shi, H., Guo, Y. W., Yu, J. L. & Sun, J. (2003). *Z. Kristallogr. New Cryst. Struct.* **218**, 328–330.
Shi, H., He, S., He, L. & Pan, Y. J. (2007). *Chem. J. Chin. Univ.* **28**, 100–102.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

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supplementary materials

Acta Cryst. (2007). E**63**, o4800 [**doi:10.1107/S1600536807059302**]

(1*R*,4*S*,8*R*,9*S*,12*S*,13*S*,14*R*,16*S*,19*R*)-19-Acetoxy-14-hydroxy-7,7-dimethyl-17-methylene-2,18-dioxo-3,10-dioxapentacyclo[14.2.1.$0^{1,13}$.$0^{4,12}$.$0^{8,12}$]nonadec-9-yl acetate

H. Shi

Comment

Since the natural diterpenoid Macrocalyxin J exhibits cytotoxicity *in vitro* against cultures of Hela cells (Shi *et al.*, 2007), I have derived the title compound from it.

The molecule is built up from five fused rings, three six membered and two five membered rings. Some geometrical features of these rings were investigated using *PLATON* (Spek, 2003).

Cyclohexane ring A (C4—C8/C12) adopts a chair conformation with puckering parameters (Cremer & Pople, 1975) Q = 0.542 (4) Å, and θ= 161.5 (3) and φ = 285.9 (12) °, ring B (O3/C2/C1/C13/C12/C4) exists in a screw-boat conformation (Q = 0.631 (3) Å, θ = 112.5 (3) and φ = 90.5 (3) °), ring C (C1/C13—C16/C19) adopt the boat conformation (Q = 0.847 (4) Å, θ = 81.0 (3) and φ = 292.0 (2) °). The two five-membered rings, ring D (C1/C18/C17/C16/C19) adopts an envelope conformation with puckering parameters Q2 = 0.472 (4) Å, and φ2 = 147.2 (5)° (envelope on C19), the ring E (O10/C9/C8/C12/C11) adopts a twisted conformation with puckering parameters Q2 = 0.368 (3) Å, and φ2 = 268.6 (5)° (twisted on C8 and C12).

Intermolecular O—H···O hydrogen bond is present and link molecules to form a chain parallel to the *a* axis.

Since the title compound was prepared from Macrocalyxin J, which was isolated from the same plant (*i.e. Rabdosia macrocalyx*) as Macrocalyxin A, the configuration can be deduced from the known chirality of the Macrocalyxin A (Shi *et al.*, 2003),and thus Fig. 1 represents the correct absolute configuration.

Experimental

Macrocalyxin J (50 mg; isolated from Rabdosia macrocalyx) was dissolved in a mixture of pyridine (1.5 ml) and Ac_2O (1.5 ml) and the solution was stirred for 3 h at room temperature. MeOH (5 ml) was then added to the mixture and the solution was concentrated *in vacuo* to give a residue that was purified by column chromatography to give the title compound (I).

Crystals suitable for X-ray structure analysis were obtained by slow evaporation from a solution of methanol at room temperature.

Refinement

H atoms were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.96 Å (CH_3), 0.97 Å (CH_2) and 0.98(CH) and with the temperature factors U_{iso}= 1.5 U_{eq}(CH_3) and 1.2 U_{eq}(CH_2, CH).

In the absence of significant anomalous scattering, the absolute configuration could not be reliably determined from the X-ray analyses. The Friedel pairs were merged and any references to the Flack parameter was removed.

Figures

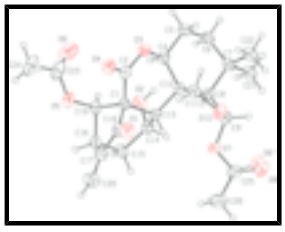

Fig. 1. Perspective view of the title compound, shown with 30% probability displacement ellipsoids.

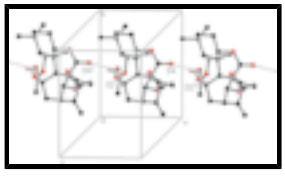

Fig. 2. Partial packing view of the title compound showing the formation of a chain parallel through O—H···O hydrogen bonding interactions. H atoms not involved in hydrogen bonds have been omitted for clarity. Symmetry codes: (i) $x-1,y,z$; (ii) $x+1,y,z$.

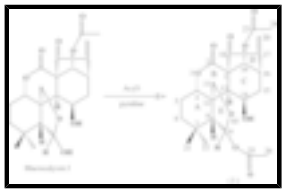

Fig. 3. The formation of the title compound.

(1*R*,4*S*,8*R*,9*S*,12*S*,13*S*,14*R*, 16*S*,19*R*)-19-acetoxy-14-hydroxy-7,7-dimethyl-17-methylene- 2,18-dioxo-3,10-dioxapentacyclo[14.2.1.$0^{1,13}$.$0^{4,12}$.$0^{8,12}$]nonadec-9-yl acetate

Crystal data

$C_{24}H_{30}O_9$	F_{000} = 984
M_r = 462.48	D_x = 1.350 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 1637 reflections
a = 7.5188 (6) Å	θ = 2.5–18.6º
b = 9.7993 (13) Å	μ = 0.10 mm^{-1}
c = 30.876 (3) Å	T = 298 (2) K
V = 2274.9 (4) Å^3	Needle, colorless
Z = 4	0.40 × 0.18 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2324 independent reflections
Radiation source: fine-focus sealed tube	1579 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.058
T = 298(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.2º
Absorption correction: multi-scan (SADABS; Bruker, 1999)	h = −8→8
T_{min} = 0.960, T_{max} = 0.983	k = −11→11

10274 measured reflections

$l = -36 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.064$

$S = 1.16$

2324 reflections

304 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0113P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.18$ e Å^{-3}

$\Delta\rho_{min} = -0.14$ e Å^{-3}

Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0023 (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 $F^2 > 2$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}	Occ. (<1)
O1	0.9266 (3)	0.3557 (3)	0.10199 (9)	0.0638 (8)	
O2	0.2850 (3)	0.4305 (2)	0.17675 (7)	0.0576 (7)	
H2	0.2533	0.5074	0.1697	0.086*	
O3	0.7029 (3)	0.6822 (2)	0.15932 (7)	0.0493 (6)	
O4	0.9468 (3)	0.5647 (2)	0.16904 (8)	0.0575 (7)	
O5	0.8068 (3)	0.3360 (3)	0.21771 (8)	0.0585 (7)	
O6	0.7301 (5)	0.5132 (4)	0.25961 (10)	0.0999 (12)	
O7	0.3183 (3)	0.4234 (2)	0.03846 (7)	0.0540 (7)	
O8	0.2005 (10)	0.4360 (5)	−0.0284 (2)	0.097 (2)	0.794 (12)
O8'	0.109 (4)	0.440 (2)	−0.0064 (7)	0.097 (2)	0.206 (12)
O10	0.5259 (3)	0.5940 (2)	0.03211 (7)	0.0536 (7)	
C1	0.6912 (4)	0.4326 (3)	0.15109 (10)	0.0381 (8)	
C2	0.7893 (5)	0.5633 (4)	0.16052 (10)	0.0440 (9)	
C4	0.5137 (4)	0.6782 (3)	0.14912 (11)	0.0421 (9)	

H4	0.4504	0.6345	0.1731	0.051*
C5	0.4536 (5)	0.8256 (3)	0.14586 (12)	0.0539 (11)
H5A	0.5275	0.8745	0.1253	0.065*
H5B	0.4640	0.8699	0.1738	0.065*
C6	0.2601 (5)	0.8270 (3)	0.13087 (11)	0.0517 (10)
H6A	0.1887	0.7737	0.1508	0.062*
H6B	0.2160	0.9201	0.1313	0.062*
C7	0.2398 (5)	0.7694 (3)	0.08555 (11)	0.0431 (10)
C8	0.3068 (4)	0.6184 (3)	0.08541 (10)	0.0359 (9)
H8	0.2158	0.5598	0.0985	0.043*
C9	0.3465 (5)	0.5686 (4)	0.04003 (10)	0.0439 (9)
H9	0.2714	0.6155	0.0188	0.053*
C11	0.6174 (5)	0.6268 (3)	0.07161 (11)	0.0464 (10)
H11A	0.6495	0.7226	0.0722	0.056*
H11B	0.7248	0.5727	0.0743	0.056*
C12	0.4870 (4)	0.5935 (3)	0.10847 (10)	0.0346 (8)
C13	0.5188 (4)	0.4418 (3)	0.12135 (10)	0.0367 (9)
H13	0.5496	0.3946	0.0944	0.044*
C14	0.3617 (5)	0.3632 (3)	0.14031 (11)	0.0463 (10)
H14	0.2702	0.3557	0.1178	0.056*
C15	0.4184 (5)	0.2188 (3)	0.15317 (12)	0.0558 (11)
H15A	0.4182	0.1616	0.1275	0.067*
H15B	0.3314	0.1819	0.1732	0.067*
C16	0.6038 (5)	0.2121 (4)	0.17436 (12)	0.0521 (10)
H16	0.6077	0.1417	0.1969	0.062*
C17	0.7514 (5)	0.1926 (4)	0.14214 (12)	0.0527 (11)
C18	0.8119 (5)	0.3301 (4)	0.12811 (12)	0.0481 (10)
C19	0.6474 (5)	0.3517 (3)	0.19292 (11)	0.0475 (10)
H19	0.5493	0.3914	0.2096	0.057*
C20	0.8287 (5)	0.0804 (4)	0.12796 (13)	0.0759 (13)
H20A	0.9235	0.0861	0.1087	0.091*
H20B	0.7884	−0.0045	0.1372	0.091*
C21	0.0411 (4)	0.7654 (3)	0.07380 (12)	0.0554 (11)
H21A	−0.0225	0.7145	0.0954	0.083*
H21B	0.0264	0.7225	0.0461	0.083*
H21C	−0.0046	0.8568	0.0726	0.083*
C22	0.3306 (5)	0.8651 (3)	0.05231 (12)	0.0629 (12)
H22A	0.3085	0.8322	0.0235	0.094*
H22B	0.4564	0.8669	0.0576	0.094*
H22C	0.2832	0.9556	0.0552	0.094*
C23	0.8354 (7)	0.4277 (6)	0.24981 (14)	0.0762 (14)
C24	1.0157 (6)	0.4049 (5)	0.26971 (12)	0.0957 (17)
H24A	1.1059	0.4180	0.2481	0.143*
H24B	1.0227	0.3135	0.2808	0.143*
H24C	1.0334	0.4687	0.2929	0.143*
C25	0.2385 (6)	0.3704 (4)	0.00398 (15)	0.0697 (13)
C26	0.2193 (6)	0.2209 (4)	0.00810 (14)	0.0904 (16)
H26A	0.1868	0.1829	−0.0194	0.136*
H26B	0.1286	0.2006	0.0290	0.136*

H26C	0.3302	0.1822	0.0174	0.136*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0483 (18)	0.0726 (19)	0.0705 (18)	0.0063 (15)	0.0176 (15)	0.0007 (16)
O2	0.0565 (17)	0.0549 (15)	0.0616 (15)	0.0084 (14)	0.0072 (14)	0.0112 (15)
O3	0.0370 (16)	0.0476 (15)	0.0633 (16)	−0.0001 (13)	−0.0105 (13)	−0.0090 (13)
O4	0.0351 (16)	0.0637 (16)	0.0737 (18)	−0.0027 (14)	−0.0131 (14)	0.0023 (16)
O5	0.0530 (18)	0.0747 (19)	0.0478 (16)	0.0041 (16)	−0.0117 (14)	0.0042 (15)
O6	0.087 (3)	0.131 (3)	0.082 (2)	0.002 (2)	0.000 (2)	−0.038 (2)
O7	0.0669 (19)	0.0443 (15)	0.0508 (16)	−0.0013 (15)	−0.0141 (14)	−0.0079 (14)
O8	0.149 (6)	0.086 (2)	0.055 (4)	0.010 (3)	−0.040 (4)	−0.013 (3)
O8'	0.149 (6)	0.086 (2)	0.055 (4)	0.010 (3)	−0.040 (4)	−0.013 (3)
O10	0.0485 (17)	0.0719 (18)	0.0404 (15)	−0.0043 (15)	0.0044 (13)	0.0009 (14)
C1	0.029 (2)	0.042 (2)	0.043 (2)	0.0020 (19)	−0.0021 (17)	0.0021 (19)
C2	0.040 (3)	0.053 (2)	0.039 (2)	0.000 (2)	−0.001 (2)	0.003 (2)
C4	0.031 (2)	0.048 (2)	0.047 (2)	−0.0017 (18)	−0.0044 (18)	−0.003 (2)
C5	0.051 (3)	0.046 (2)	0.065 (3)	0.005 (2)	−0.006 (2)	−0.018 (2)
C6	0.044 (3)	0.040 (2)	0.071 (3)	0.0091 (19)	−0.003 (2)	−0.008 (2)
C7	0.033 (2)	0.041 (2)	0.055 (2)	0.0015 (18)	−0.0008 (19)	0.0033 (19)
C8	0.031 (2)	0.033 (2)	0.044 (2)	−0.0046 (17)	−0.0001 (17)	0.0013 (17)
C9	0.035 (2)	0.049 (2)	0.047 (2)	0.003 (2)	−0.0100 (19)	0.002 (2)
C11	0.041 (2)	0.047 (2)	0.052 (2)	−0.0002 (19)	0.0001 (19)	0.006 (2)
C12	0.027 (2)	0.036 (2)	0.041 (2)	0.0007 (16)	0.0007 (17)	−0.0020 (19)
C13	0.029 (2)	0.041 (2)	0.040 (2)	−0.0036 (18)	−0.0019 (16)	0.0002 (19)
C14	0.039 (2)	0.051 (2)	0.050 (2)	−0.002 (2)	−0.0031 (19)	0.003 (2)
C15	0.050 (3)	0.047 (2)	0.070 (3)	−0.006 (2)	−0.005 (2)	0.011 (2)
C16	0.048 (3)	0.048 (2)	0.061 (3)	0.002 (2)	−0.006 (2)	0.010 (2)
C17	0.047 (3)	0.049 (2)	0.062 (3)	0.003 (2)	−0.009 (2)	−0.004 (2)
C18	0.038 (3)	0.054 (3)	0.052 (2)	0.005 (2)	−0.008 (2)	0.001 (2)
C19	0.039 (3)	0.055 (2)	0.048 (2)	0.002 (2)	−0.0060 (19)	0.009 (2)
C20	0.061 (3)	0.058 (3)	0.109 (3)	0.004 (3)	−0.004 (3)	−0.008 (3)
C21	0.040 (3)	0.053 (2)	0.074 (3)	0.005 (2)	−0.002 (2)	0.004 (2)
C22	0.056 (3)	0.048 (2)	0.085 (3)	−0.001 (2)	−0.001 (2)	0.015 (2)
C23	0.067 (4)	0.117 (5)	0.044 (3)	−0.011 (4)	0.000 (3)	0.006 (3)
C24	0.073 (4)	0.159 (5)	0.055 (3)	−0.024 (4)	−0.023 (3)	0.007 (3)
C25	0.072 (4)	0.065 (3)	0.072 (3)	0.008 (3)	−0.026 (3)	−0.015 (3)
C26	0.096 (4)	0.067 (3)	0.109 (4)	−0.011 (3)	−0.020 (3)	−0.022 (3)

Geometric parameters (Å, °)

O1—C18	1.207 (4)	C9—H9	0.9800
O2—C14	1.426 (4)	C11—C12	1.537 (4)
O2—H2	0.8200	C11—H11A	0.9700
O3—C2	1.334 (4)	C11—H11B	0.9700
O3—C4	1.458 (4)	C12—C13	1.557 (4)
O4—C2	1.213 (4)	C13—C14	1.527 (4)
O5—C23	1.355 (5)	C13—H13	0.9800

O5—C19	1.430 (4)	C14—C15	1.530 (4)
O6—C23	1.192 (5)	C14—H14	0.9800
O7—C25	1.328 (4)	C15—C16	1.542 (4)
O7—C9	1.439 (4)	C15—H15A	0.9700
O8—C25	1.223 (6)	C15—H15B	0.9700
O8'—C25	1.23 (2)	C16—C17	1.502 (5)
O10—C9	1.394 (3)	C16—C19	1.519 (4)
O10—C11	1.437 (4)	C16—H16	0.9800
C1—C2	1.507 (4)	C17—C20	1.319 (4)
C1—C18	1.528 (5)	C17—C18	1.487 (5)
C1—C19	1.551 (4)	C19—H19	0.9800
C1—C13	1.591 (4)	C20—H20A	0.9300
C4—C5	1.516 (4)	C20—H20B	0.9300
C4—C12	1.518 (4)	C21—H21A	0.9600
C4—H4	0.9800	C21—H21B	0.9600
C5—C6	1.527 (5)	C21—H21C	0.9600
C5—H5A	0.9700	C22—H22A	0.9600
C5—H5B	0.9700	C22—H22B	0.9600
C6—C7	1.517 (4)	C22—H22C	0.9600
C6—H6A	0.9700	C23—C24	1.505 (6)
C6—H6B	0.9700	C24—H24A	0.9600
C7—C21	1.538 (4)	C24—H24B	0.9600
C7—C22	1.549 (4)	C24—H24C	0.9600
C7—C8	1.563 (4)	C25—C26	1.477 (5)
C8—C9	1.513 (4)	C26—H26A	0.9600
C8—C12	1.550 (4)	C26—H26B	0.9600
C8—H8	0.9800	C26—H26C	0.9600
C14—O2—H2	109.5	C1—C13—H13	105.7
C2—O3—C4	117.3 (3)	O2—C14—C13	112.5 (3)
C23—O5—C19	117.0 (3)	O2—C14—C15	109.6 (3)
C25—O7—C9	118.7 (3)	C13—C14—C15	110.5 (3)
C9—O10—C11	110.8 (2)	O2—C14—H14	108.0
C2—C1—C18	111.0 (3)	C13—C14—H14	108.0
C2—C1—C19	112.2 (3)	C15—C14—H14	108.0
C18—C1—C19	100.2 (3)	C14—C15—C16	113.7 (3)
C2—C1—C13	117.5 (3)	C14—C15—H15A	108.8
C18—C1—C13	104.7 (3)	C16—C15—H15A	108.8
C19—C1—C13	109.7 (3)	C14—C15—H15B	108.8
O4—C2—O3	118.1 (3)	C16—C15—H15B	108.8
O4—C2—C1	122.0 (4)	H15A—C15—H15B	107.7
O3—C2—C1	119.9 (3)	C17—C16—C19	101.8 (3)
O3—C4—C5	106.3 (3)	C17—C16—C15	113.1 (3)
O3—C4—C12	108.8 (3)	C19—C16—C15	108.5 (3)
C5—C4—C12	115.2 (3)	C17—C16—H16	111.0
O3—C4—H4	108.8	C19—C16—H16	111.0
C5—C4—H4	108.8	C15—C16—H16	111.0
C12—C4—H4	108.8	C20—C17—C18	121.6 (4)
C4—C5—C6	108.2 (3)	C20—C17—C16	130.7 (4)
C4—C5—H5A	110.0	C18—C17—C16	107.7 (3)

C6—C5—H5A	110.0	O1—C18—C17	127.0 (4)
C4—C5—H5B	110.0	O1—C18—C1	126.7 (3)
C6—C5—H5B	110.0	C17—C18—C1	106.2 (3)
H5A—C5—H5B	108.4	O5—C19—C16	106.6 (3)
C7—C6—C5	111.8 (3)	O5—C19—C1	108.8 (3)
C7—C6—H6A	109.2	C16—C19—C1	101.1 (3)
C5—C6—H6A	109.2	O5—C19—H19	113.1
C7—C6—H6B	109.2	C16—C19—H19	113.1
C5—C6—H6B	109.2	C1—C19—H19	113.1
H6A—C6—H6B	107.9	C17—C20—H20A	120.0
C6—C7—C21	109.0 (3)	C17—C20—H20B	120.0
C6—C7—C22	109.9 (3)	H20A—C20—H20B	120.0
C21—C7—C22	106.7 (3)	C7—C21—H21A	109.5
C6—C7—C8	108.8 (3)	C7—C21—H21B	109.5
C21—C7—C8	106.8 (3)	H21A—C21—H21B	109.5
C22—C7—C8	115.4 (3)	C7—C21—H21C	109.5
C9—C8—C12	101.7 (3)	H21A—C21—H21C	109.5
C9—C8—C7	111.8 (3)	H21B—C21—H21C	109.5
C12—C8—C7	115.4 (3)	C7—C22—H22A	109.5
C9—C8—H8	109.2	C7—C22—H22B	109.5
C12—C8—H8	109.2	H22A—C22—H22B	109.5
C7—C8—H8	109.2	C7—C22—H22C	109.5
O10—C9—O7	108.3 (3)	H22A—C22—H22C	109.5
O10—C9—C8	107.2 (3)	H22B—C22—H22C	109.5
O7—C9—C8	108.7 (3)	O6—C23—O5	123.1 (5)
O10—C9—H9	110.8	O6—C23—C24	126.8 (5)
O7—C9—H9	110.8	O5—C23—C24	110.1 (5)
C8—C9—H9	110.8	C23—C24—H24A	109.5
O10—C11—C12	106.0 (3)	C23—C24—H24B	109.5
O10—C11—H11A	110.5	H24A—C24—H24B	109.5
C12—C11—H11A	110.5	C23—C24—H24C	109.5
O10—C11—H11B	110.5	H24A—C24—H24C	109.5
C12—C11—H11B	110.5	H24B—C24—H24C	109.5
H11A—C11—H11B	108.7	O8—C25—O7	123.7 (4)
C4—C12—C11	114.3 (3)	O8'—C25—O7	110.6 (10)
C4—C12—C8	114.2 (3)	O8—C25—C26	124.7 (4)
C11—C12—C8	100.6 (3)	O8'—C25—C26	119.4 (11)
C4—C12—C13	106.9 (3)	O7—C25—C26	111.3 (4)
C11—C12—C13	107.1 (3)	C25—C26—H26A	109.5
C8—C12—C13	113.7 (3)	C25—C26—H26B	109.5
C14—C13—C12	117.5 (3)	H26A—C26—H26B	109.5
C14—C13—C1	112.3 (3)	C25—C26—H26C	109.5
C12—C13—C1	109.1 (3)	H26A—C26—H26C	109.5
C14—C13—H13	105.7	H26B—C26—H26C	109.5
C12—C13—H13	105.7		
C4—O3—C2—O4	−179.9 (3)	C4—C12—C13—C1	−44.2 (3)
C4—O3—C2—C1	0.6 (4)	C11—C12—C13—C1	78.7 (3)
C18—C1—C2—O4	−33.5 (5)	C8—C12—C13—C1	−171.1 (3)
C19—C1—C2—O4	77.7 (4)	C2—C1—C13—C14	−132.9 (3)

C13—C1—C2—O4	−153.8 (3)	C18—C1—C13—C14	103.5 (3)
C18—C1—C2—O3	146.1 (3)	C19—C1—C13—C14	−3.2 (4)
C19—C1—C2—O3	−102.8 (3)	C2—C1—C13—C12	−0.8 (4)
C13—C1—C2—O3	25.7 (4)	C18—C1—C13—C12	−124.4 (3)
C2—O3—C4—C5	−174.9 (3)	C19—C1—C13—C12	128.9 (3)
C2—O3—C4—C12	−50.3 (4)	C12—C13—C14—O2	−54.3 (4)
O3—C4—C5—C6	174.6 (3)	C1—C13—C14—O2	73.4 (3)
C12—C4—C5—C6	54.0 (4)	C12—C13—C14—C15	−177.2 (3)
C4—C5—C6—C7	−64.5 (4)	C1—C13—C14—C15	−49.5 (4)
C5—C6—C7—C21	176.4 (3)	O2—C14—C15—C16	−84.4 (4)
C5—C6—C7—C22	−67.0 (4)	C13—C14—C15—C16	40.1 (4)
C5—C6—C7—C8	60.3 (4)	C14—C15—C16—C17	−89.6 (4)
C6—C7—C8—C9	−161.7 (3)	C14—C15—C16—C19	22.6 (4)
C21—C7—C8—C9	80.8 (4)	C19—C16—C17—C20	150.7 (4)
C22—C7—C8—C9	−37.6 (4)	C15—C16—C17—C20	−93.1 (5)
C6—C7—C8—C12	−46.2 (4)	C19—C16—C17—C18	−26.5 (3)
C21—C7—C8—C12	−163.7 (3)	C15—C16—C17—C18	89.7 (4)
C22—C7—C8—C12	78.0 (4)	C20—C17—C18—O1	3.6 (6)
C11—O10—C9—O7	−103.6 (3)	C16—C17—C18—O1	−178.9 (4)
C11—O10—C9—C8	13.5 (4)	C20—C17—C18—C1	179.9 (4)
C25—O7—C9—O10	−105.0 (4)	C16—C17—C18—C1	−2.6 (4)
C25—O7—C9—C8	138.8 (3)	C2—C1—C18—O1	−35.2 (5)
C12—C8—C9—O10	−31.5 (3)	C19—C1—C18—O1	−153.9 (4)
C7—C8—C9—O10	92.2 (3)	C13—C1—C18—O1	92.5 (4)
C12—C8—C9—O7	85.3 (3)	C2—C1—C18—C17	148.5 (3)
C7—C8—C9—O7	−151.0 (3)	C19—C1—C18—C17	29.8 (3)
C9—O10—C11—C12	10.7 (4)	C13—C1—C18—C17	−83.8 (3)
O3—C4—C12—C11	−45.8 (4)	C23—O5—C19—C16	−155.6 (3)
C5—C4—C12—C11	73.3 (4)	C23—O5—C19—C1	96.1 (4)
O3—C4—C12—C8	−160.9 (3)	C17—C16—C19—O5	−69.0 (3)
C5—C4—C12—C8	−41.8 (4)	C15—C16—C19—O5	171.5 (3)
O3—C4—C12—C13	72.4 (3)	C17—C16—C19—C1	44.7 (3)
C5—C4—C12—C13	−168.4 (3)	C15—C16—C19—C1	−74.8 (3)
O10—C11—C12—C4	−152.1 (3)	C2—C1—C19—O5	−51.6 (4)
O10—C11—C12—C8	−29.3 (3)	C18—C1—C19—O5	66.2 (3)
O10—C11—C12—C13	89.8 (3)	C13—C1—C19—O5	175.9 (3)
C9—C8—C12—C4	158.8 (3)	C2—C1—C19—C16	−163.6 (3)
C7—C8—C12—C4	37.6 (4)	C18—C1—C19—C16	−45.9 (3)
C9—C8—C12—C11	35.9 (3)	C13—C1—C19—C16	63.8 (3)
C7—C8—C12—C11	−85.3 (3)	C19—O5—C23—O6	4.7 (6)
C9—C8—C12—C13	−78.2 (3)	C19—O5—C23—C24	−174.7 (3)
C7—C8—C12—C13	160.6 (3)	C9—O7—C25—O8	6.5 (8)
C4—C12—C13—C14	85.1 (3)	C9—O7—C25—O8'	−44.3 (15)
C11—C12—C13—C14	−152.0 (3)	C9—O7—C25—C26	−179.5 (3)
C8—C12—C13—C14	−41.8 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

O2—H2···O4^{i}	0.82	2.37	2.873 (3)	120

Symmetry codes: (i) $x-1, y, z$.

Fig. 1

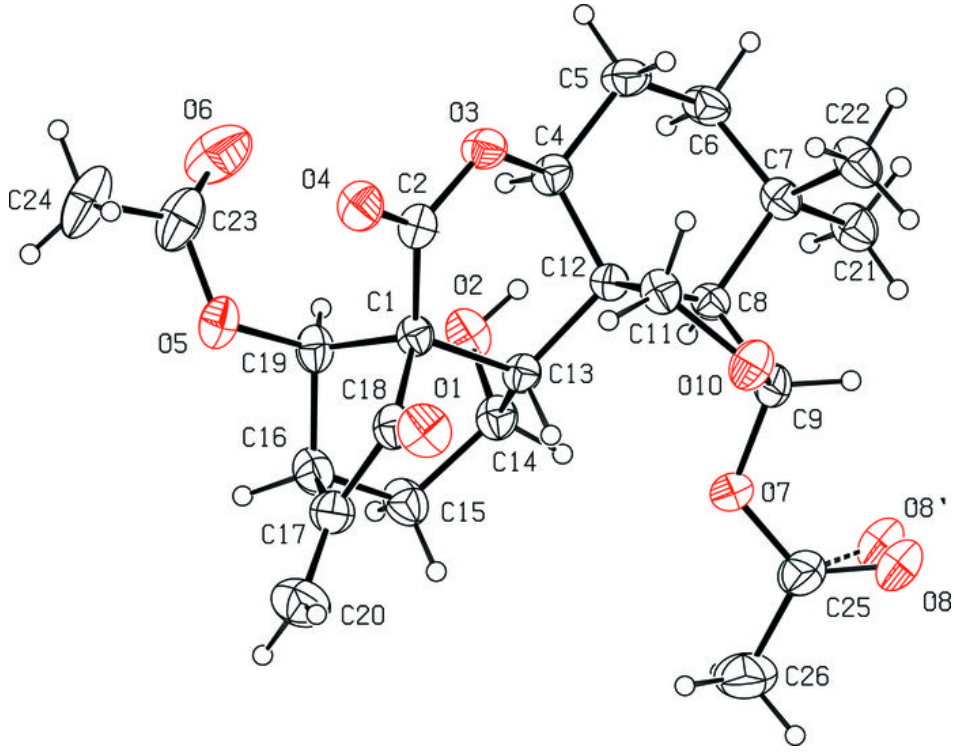

Fig. 2

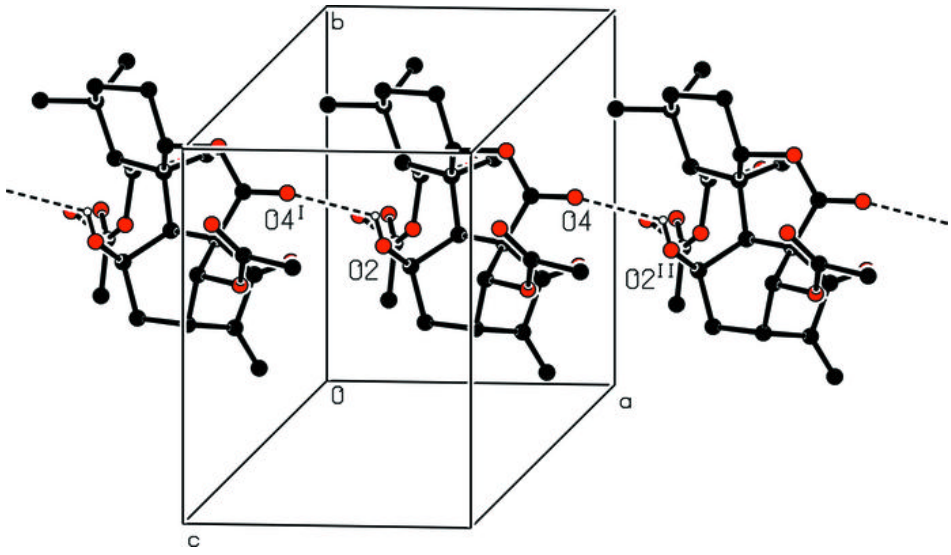

Fig. 3