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(3*S*,5*R*,8*R*,9*R*,10*R*,13*S*,14*R*,17*S*)-Methyl 3β-acetoxy-17β-chloro-18-oxo-19,20,21,22,29,30-hexanorlupan-28-oate

Ivana Císařová,[a] Miroslav Kvasnica[b] and Jan Sarek[c]*

[a]Department of Inorganic Chemistry, Charles University, Hlavova 2030, Prague 128 40, Czech Republic, [b]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 166 10 Prague 6, Czech Republic, and [c]Department of Organic Chemistry, Charles University, Hlavova 2030, Prague 128 40, Czech Republic
Correspondence e-mail: cisarova@mail.natur.cuni.cz

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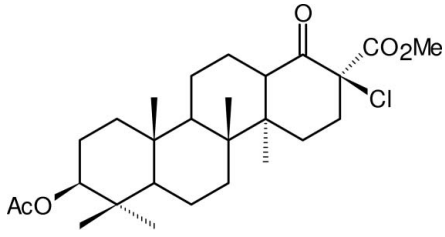
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.096; data-to-parameter ratio = 14.2.

In the title compound, $C_{27}H_{41}ClO_5$, all rings adopt chair conformations, giving the molecule the shape of a bow. In the crystal structure, the Cl atom is not involved in intermolecular interactions, as the packing is governed by C=O···H—C hydrogen bonds.

Related literature

For general background, see: Kim *et al.* (1998); Biedermann *et al.* (2005); Urban *et al.* (2005). For a related structure, see: Sarek *et al.* (2003). For related literature, see: Cremer & Pople (1975); Dzubak *et al.* (2006).



Experimental

Crystal data

$C_{27}H_{41}ClO_5$
M_r = 481.05
Monoclinic, $P2_1$
a = 11.331 (3) Å
b = 6.738 (1) Å
c = 16.366 (3) Å
β = 96.275 (10)°
V = 1242.0 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 150 (2) K
0.55 × 0.2 × 0.03 mm

Data collection

Bruker Nonius KappaCCD diffractometer
Absorption correction: none
8942 measured reflections
4320 independent reflections
3899 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.096
S = 1.10
4320 reflections
305 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), with 1923 Friedel pairs
Flack parameter: −0.01 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
C25—H25*C*···O2^{i}	0.96	2.55	3.407 (3)	148
C11—H11*B*···O3^{ii}	0.97	2.58	3.290 (3)	130

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

Data collection: *COLLECT* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); 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: LH2400).

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supplementary materials

Acta Cryst. (2007). E**63**, o3145 [**doi:10.1107/S1600536807026487**]

(3*S*,5*R*,8*R*,9*R*,10*R*,13*S*,14*R*,17*S*)-Methyl 3*β*-acetoxy-17*β*-chloro-18-oxo-19,20,21,22,29,30-hexanorlupan-28-oate

I. Císarová, M. Kvasnica and J. Sarek

Comment

Efforts have recently been exerted in order to synthesize new derivatives of natural compounds, especially terpenoides (Dzubak *et al.*, 2006; Kim *et al.*, 1998) with large number of functional groups (Kim *et al.*, 1998; Biedermann *et al.*, 2005; Urban *et al.*, 2005). Several years ago a group of new compounds called betulinines (Šarek *et al.*, 2003), was described. Betulinines have significant cytotoxic activity on broad scale of tumor lines including multidrug resistance. Among the most effective belulinines are β-ketoacids (**1**, Fig. 3) (Šarek *et al.*, 2003). The search for new degradable analogs of **1** with similar high cytotoxity resulted in a hexanorlupane derivatives (**I**) (Fig. 3) with cytotoxicity two times higher than **1**. The structure of **I** has been determined as a part of large study of structure-activity relationships.

The bond lengths and angles in **I** are unexceptional and very close to the pertinent ones in the parent molecule **1**. In both molecules the oxygen atom of the carbonyl substituent on D ring is slightly bend towards adjoining carboxyl moiety as follows from comparison of the angle around C18 (see Table I). All rings adopts chair conformations (Cremer & Pople, 1975) (Fig. 1), the deviation from ideal geometry (τ = 0, 180 °) can be discerned on ring D due its carbonyl substituent (τ = 164.6 (2) °). Without the possibility of classical hydrogen bonds, the role of weak C—H···O contacts in crystal packing is clearly revealed. Molecules are packed by *C*(methyl)-*H*···*O*(acetyl) hydrogen bonds forming columns along the *b* axis. Second parallel column related by operation of a 2_1 screw is attached to the first one in a zip-like way *via* a CH_2···*O*(carbonyl) interaction (see Fig. 2).

Experimental

A mixture of diketone (**2**) (Fig. 3) (0.93 mmol) and AcOOH (20 ml of a 32%aq soln) and Ru(IV)O_2·H_2O (0.15 mmol) in $CHCL_3$ (55 mL) was stirred at room temperature for one day. The extract was washed and evaporated. The resulting pale-yellow oil crystalization from $CHCl_3$/MeOH afforded chloroketone **I** as a colourless crystals. Yield 52%,

Refinement

All H atoms were positioned geometrically and refined as riding on their parent C atoms, with C—H = 0.98 Å, for CH, C—H = 0.97Å for –CH_2 and U_{iso}(H) = 1.2U_{eq}(C) or C—H = 0.96Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. The absolute configuration was assigned from the known absolute structure of parent compound and was confirmed by the Flack (1983) parameter. Optical rotation $[\alpha]_D$ +105$_o$. m.p. 495–498 K.

Figures

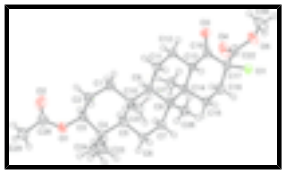


Fig. 1. The molecular structure of (I) showing 50% displacement ellipsoids and the atom-numbering scheme.

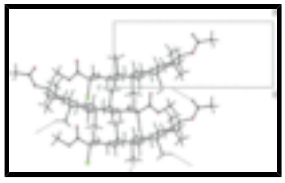


Fig. 2. A section of the crystal structure, showing hydrogen bonds as dashed lines.

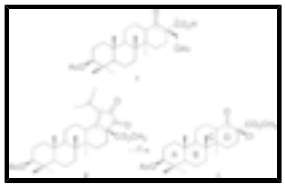


Fig. 3. Reagents and conditions: *a* AcO_2H, RuO_2,$CHCl_3$, r.t.

(3*S*,5*R*,8*R*,9*R*,10*R*,13*S*,14*R*,17*S*)-Methyl 3β-acetoxy-17β-chloro-18-oxo-19,20,21,22,29,30-hexanorlupan-28-oate

Crystal data

$C_{27}H_{41}ClO_5$	F_{000} = 520
M_r = 481.05	D_x = 1.286 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2yb	Cell parameters from 2233 reflections
a = 11.331 (3) Å	θ = 1–25º
b = 6.7380 (10) Å	μ = 0.19 mm^{-1}
c = 16.366 (3) Å	*T* = 150 (2) K
β = 96.275 (10)º	Bar, colourless
V = 1242.0 (4) Å^3	0.55 × 0.2 × 0.03 mm
Z = 2	

Data collection

Bruker Nonius KappaCCD diffractometer	4320 independent reflections
Radiation source: fine-focus sealed tube	3899 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.034
Detector resolution: 9.091 pixels mm^{-1}	θ_{max} = 25.0º
T = 150(2) K	θ_{min} = 2.5º
φ and ω scans to fill the Ewald sphere	*h* = −13→13
Absorption correction: none	*k* = −7→8
8942 measured reflections	*l* = −19→19

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.2905P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.10$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
4320 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}
305 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), with 1923 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.01 (6)
Secondary atom site location: difference Fourier map	

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}
C1	0.1096 (2)	0.3185 (4)	0.67922 (13)	0.0296 (5)
H1A	0.0379	0.2398	0.6790	0.035*
H1B	0.0964	0.4435	0.7062	0.035*
C2	0.1329 (2)	0.3596 (4)	0.59006 (13)	0.0315 (5)
H2A	0.1415	0.2351	0.5615	0.038*
H2B	0.0662	0.4310	0.5617	0.038*
C3	0.2446 (2)	0.4811 (4)	0.58938 (14)	0.0296 (5)
H3	0.2335	0.6068	0.6177	0.036*
C4	0.3569 (2)	0.3797 (4)	0.63145 (13)	0.0290 (5)
C5	0.32918 (19)	0.3257 (4)	0.72020 (13)	0.0247 (5)
H5	0.3168	0.4540	0.7461	0.030*
C6	0.4344 (2)	0.2339 (4)	0.77348 (14)	0.0292 (5)
H6A	0.4432	0.0960	0.7582	0.035*
H6B	0.5067	0.3036	0.7644	0.035*
C7	0.4148 (2)	0.2469 (4)	0.86420 (14)	0.0299 (6)

H7A	0.4130	0.3856	0.8799	0.036*
H7B	0.4816	0.1854	0.8968	0.036*
C8	0.29946 (19)	0.1467 (3)	0.88479 (13)	0.0235 (5)
C9	0.19388 (19)	0.2178 (3)	0.82254 (13)	0.0228 (5)
H9	0.1862	0.3597	0.8340	0.027*
C10	0.2134 (2)	0.2076 (3)	0.72883 (14)	0.0243 (5)
C11	0.0761 (2)	0.1264 (4)	0.84232 (13)	0.0276 (5)
H11A	0.0118	0.1778	0.8042	0.033*
H11B	0.0789	−0.0163	0.8351	0.033*
C12	0.05115 (19)	0.1728 (4)	0.93012 (13)	0.0256 (5)
H12A	0.0371	0.3141	0.9352	0.031*
H12B	−0.0202	0.1036	0.9417	0.031*
C13	0.15378 (19)	0.1115 (3)	0.99265 (13)	0.0230 (5)
H13	0.1629	−0.0325	0.9877	0.028*
C14	0.2738 (2)	0.2072 (3)	0.97524 (14)	0.0243 (5)
C15	0.3710 (2)	0.1300 (4)	1.04065 (14)	0.0285 (5)
H15A	0.3748	−0.0135	1.0370	0.034*
H15B	0.4472	0.1826	1.0291	0.034*
C16	0.3494 (2)	0.1879 (4)	1.12772 (14)	0.0316 (6)
H16A	0.3541	0.3311	1.1332	0.038*
H16B	0.4113	0.1307	1.1662	0.038*
C17	0.2285 (2)	0.1178 (4)	1.14980 (14)	0.0288 (5)
C18	0.1275 (2)	0.1525 (3)	1.07962 (14)	0.0259 (5)
C22	0.1959 (2)	0.2277 (4)	1.22574 (15)	0.0335 (6)
C23	0.3937 (2)	0.2028 (4)	0.58118 (15)	0.0379 (6)
H23A	0.4212	0.2498	0.5312	0.057*
H23B	0.3268	0.1167	0.5682	0.057*
H23C	0.4563	0.1309	0.6126	0.057*
C24	0.4572 (2)	0.5360 (4)	0.63727 (16)	0.0383 (6)
H24A	0.5303	0.4758	0.6602	0.057*
H24B	0.4376	0.6434	0.6719	0.057*
H24C	0.4662	0.5859	0.5834	0.057*
C25	0.2135 (2)	−0.0073 (4)	0.69583 (14)	0.0321 (6)
H25A	0.1617	−0.0878	0.7247	0.048*
H25B	0.2926	−0.0600	0.7041	0.048*
H25C	0.1862	−0.0077	0.6382	0.048*
C26	0.3176 (2)	−0.0803 (4)	0.88048 (15)	0.0338 (6)
H26A	0.3440	−0.1144	0.8285	0.051*
H26B	0.2439	−0.1464	0.8862	0.051*
H26C	0.3762	−0.1210	0.9241	0.051*
C27	0.2652 (2)	0.4347 (3)	0.98586 (15)	0.0290 (5)
H27A	0.2295	0.4637	1.0351	0.044*
H27B	0.2175	0.4901	0.9393	0.044*
H27C	0.3433	0.4914	0.9898	0.044*
C28	0.2175 (2)	0.6906 (4)	0.47046 (16)	0.0355 (6)
C29	0.2527 (3)	0.7223 (5)	0.38621 (16)	0.0434 (7)
H29A	0.1834	0.7170	0.3469	0.065*
H29B	0.3074	0.6204	0.3740	0.065*
H29C	0.2899	0.8498	0.3835	0.065*

C30	0.1176 (3)	0.2194 (5)	1.35275 (17)	0.0531 (8)
H30A	0.1875	0.2789	1.3809	0.080*
H30B	0.0847	0.1267	1.3886	0.080*
H30C	0.0602	0.3209	1.3367	0.080*
Cl1	0.23243 (5)	−0.14730 (8)	1.16448 (3)	0.03141 (15)
O1	0.26597 (15)	0.5253 (3)	0.50489 (9)	0.0340 (4)
O2	0.15200 (19)	0.7987 (3)	0.50365 (12)	0.0512 (5)
O3	0.03047 (15)	0.2038 (3)	1.09674 (10)	0.0339 (4)
O4	0.2100 (2)	0.4038 (3)	1.23222 (11)	0.0525 (6)
O5	0.14850 (17)	0.1160 (3)	1.27991 (10)	0.0406 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0247 (11)	0.0379 (15)	0.0257 (11)	0.0015 (11)	0.0013 (9)	0.0014 (11)
C2	0.0314 (12)	0.0386 (14)	0.0243 (11)	0.0007 (13)	0.0028 (9)	0.0019 (12)
C3	0.0366 (13)	0.0333 (13)	0.0197 (11)	0.0025 (12)	0.0066 (10)	0.0007 (10)
C4	0.0279 (12)	0.0330 (14)	0.0271 (11)	−0.0006 (11)	0.0069 (9)	0.0020 (11)
C5	0.0255 (11)	0.0250 (12)	0.0239 (11)	−0.0013 (10)	0.0046 (9)	−0.0020 (10)
C6	0.0251 (12)	0.0330 (13)	0.0301 (12)	−0.0004 (10)	0.0062 (10)	0.0019 (11)
C7	0.0225 (12)	0.0384 (14)	0.0284 (12)	0.0004 (11)	0.0015 (10)	0.0054 (11)
C8	0.0222 (11)	0.0234 (12)	0.0248 (11)	−0.0015 (10)	0.0018 (9)	0.0021 (10)
C9	0.0243 (11)	0.0193 (11)	0.0246 (11)	−0.0012 (9)	0.0020 (9)	−0.0003 (9)
C10	0.0255 (11)	0.0254 (12)	0.0225 (11)	−0.0012 (10)	0.0044 (9)	−0.0007 (10)
C11	0.0250 (12)	0.0316 (13)	0.0255 (11)	−0.0046 (10)	−0.0001 (9)	0.0034 (10)
C12	0.0243 (11)	0.0258 (12)	0.0265 (11)	0.0010 (10)	0.0024 (9)	0.0035 (10)
C13	0.0238 (11)	0.0210 (11)	0.0242 (11)	−0.0002 (9)	0.0023 (9)	0.0021 (9)
C14	0.0250 (12)	0.0233 (12)	0.0240 (11)	−0.0006 (10)	0.0009 (9)	0.0030 (10)
C15	0.0251 (12)	0.0309 (12)	0.0288 (12)	−0.0019 (11)	−0.0007 (10)	0.0037 (10)
C16	0.0345 (13)	0.0310 (13)	0.0279 (12)	−0.0044 (11)	−0.0023 (10)	0.0060 (10)
C17	0.0350 (13)	0.0237 (12)	0.0269 (12)	−0.0015 (11)	−0.0003 (10)	0.0042 (10)
C18	0.0334 (13)	0.0165 (11)	0.0280 (12)	−0.0002 (10)	0.0044 (10)	0.0034 (9)
C22	0.0420 (15)	0.0326 (15)	0.0256 (13)	−0.0030 (12)	0.0020 (11)	0.0029 (11)
C23	0.0407 (15)	0.0422 (16)	0.0329 (13)	0.0077 (13)	0.0135 (11)	−0.0021 (12)
C24	0.0361 (14)	0.0447 (16)	0.0351 (14)	−0.0056 (12)	0.0078 (12)	0.0064 (12)
C25	0.0375 (14)	0.0309 (14)	0.0283 (12)	−0.0038 (12)	0.0049 (11)	−0.0053 (11)
C26	0.0402 (15)	0.0277 (13)	0.0338 (13)	0.0071 (11)	0.0052 (11)	0.0010 (10)
C27	0.0365 (14)	0.0231 (12)	0.0275 (12)	−0.0045 (10)	0.0031 (10)	−0.0006 (10)
C28	0.0418 (14)	0.0331 (14)	0.0301 (13)	−0.0047 (13)	−0.0022 (11)	0.0005 (11)
C29	0.0464 (16)	0.0484 (17)	0.0358 (15)	−0.0052 (14)	0.0061 (12)	0.0093 (13)
C30	0.072 (2)	0.0530 (18)	0.0378 (15)	−0.0152 (17)	0.0215 (15)	−0.0093 (14)
Cl1	0.0375 (3)	0.0236 (3)	0.0324 (3)	0.0000 (3)	0.0006 (2)	0.0054 (2)
O1	0.0445 (10)	0.0351 (10)	0.0236 (8)	0.0032 (8)	0.0099 (8)	0.0034 (7)
O2	0.0684 (13)	0.0474 (13)	0.0364 (10)	0.0190 (11)	−0.0002 (10)	−0.0016 (9)
O3	0.0365 (10)	0.0343 (10)	0.0314 (9)	0.0079 (8)	0.0062 (7)	0.0007 (8)
O4	0.0908 (16)	0.0313 (11)	0.0377 (10)	−0.0103 (10)	0.0169 (10)	−0.0042 (8)
O5	0.0574 (12)	0.0367 (10)	0.0297 (9)	−0.0097 (9)	0.0140 (8)	−0.0025 (8)

Geometric parameters (Å, °)

C1—C2	1.536 (3)	C14—C27	1.547 (3)
C1—C10	1.547 (3)	C15—C16	1.523 (3)
C1—H1A	0.9700	C15—H15A	0.9700
C1—H1B	0.9700	C15—H15B	0.9700
C2—C3	1.508 (3)	C16—C17	1.529 (3)
C2—H2A	0.9700	C16—H16A	0.9700
C2—H2B	0.9700	C16—H16B	0.9700
C3—O1	1.460 (3)	C17—C22	1.526 (4)
C3—C4	1.539 (3)	C17—C18	1.549 (3)
C3—H3	0.9800	C17—Cl1	1.802 (2)
C4—C23	1.532 (4)	C18—O3	1.214 (3)
C4—C24	1.545 (4)	C22—O4	1.200 (3)
C4—C5	1.562 (3)	C22—O5	1.321 (3)
C5—C6	1.529 (3)	C23—H23A	0.9600
C5—C10	1.554 (3)	C23—H23B	0.9600
C5—H5	0.9800	C23—H23C	0.9600
C6—C7	1.528 (3)	C24—H24A	0.9600
C6—H6A	0.9700	C24—H24B	0.9600
C6—H6B	0.9700	C24—H24C	0.9600
C7—C8	1.541 (3)	C25—H25A	0.9600
C7—H7A	0.9700	C25—H25B	0.9600
C7—H7B	0.9700	C25—H25C	0.9600
C8—C26	1.546 (3)	C26—H26A	0.9600
C8—C9	1.560 (3)	C26—H26B	0.9600
C8—C14	1.593 (3)	C26—H26C	0.9600
C9—C11	1.536 (3)	C27—H27A	0.9600
C9—C10	1.575 (3)	C27—H27B	0.9600
C9—H9	0.9800	C27—H27C	0.9600
C10—C25	1.546 (3)	C28—O2	1.210 (3)
C11—C12	1.527 (3)	C28—O1	1.339 (3)
C11—H11A	0.9700	C28—C29	1.492 (4)
C11—H11B	0.9700	C29—H29A	0.9600
C12—C13	1.520 (3)	C29—H29B	0.9600
C12—H12A	0.9700	C29—H29C	0.9600
C12—H12B	0.9700	C30—O5	1.456 (3)
C13—C18	1.511 (3)	C30—H30A	0.9600
C13—C14	1.559 (3)	C30—H30B	0.9600
C13—H13	0.9800	C30—H30C	0.9600
C14—C15	1.540 (3)		
C2—C1—C10	112.70 (18)	C15—C14—C27	107.8 (2)
C2—C1—H1A	109.1	C15—C14—C13	107.78 (18)
C10—C1—H1A	109.1	C27—C14—C13	108.8 (2)
C2—C1—H1B	109.1	C15—C14—C8	111.72 (18)
C10—C1—H1B	109.1	C27—C14—C8	112.23 (19)
H1A—C1—H1B	107.8	C13—C14—C8	108.40 (18)
C3—C2—C1	109.66 (19)	C16—C15—C14	112.8 (2)

C3—C2—H2A	109.7	C16—C15—H15A	109.0
C1—C2—H2A	109.7	C14—C15—H15A	109.0
C3—C2—H2B	109.7	C16—C15—H15B	109.0
C1—C2—H2B	109.7	C14—C15—H15B	109.0
H2A—C2—H2B	108.2	H15A—C15—H15B	107.8
O1—C3—C2	110.11 (19)	C15—C16—C17	112.46 (19)
O1—C3—C4	107.44 (17)	C15—C16—H16A	109.1
C2—C3—C4	114.2 (2)	C17—C16—H16A	109.1
O1—C3—H3	108.3	C15—C16—H16B	109.1
C2—C3—H3	108.3	C17—C16—H16B	109.1
C4—C3—H3	108.3	H16A—C16—H16B	107.8
C23—C4—C3	111.4 (2)	C22—C17—C16	110.2 (2)
C23—C4—C24	108.74 (19)	C22—C17—C18	107.8 (2)
C3—C4—C24	107.0 (2)	C16—C17—C18	112.78 (19)
C23—C4—C5	114.3 (2)	C22—C17—Cl1	112.13 (17)
C3—C4—C5	106.22 (17)	C16—C17—Cl1	109.15 (18)
C24—C4—C5	108.83 (19)	C18—C17—Cl1	104.69 (16)
C6—C5—C10	110.76 (19)	O3—C18—C13	123.1 (2)
C6—C5—C4	113.66 (17)	O3—C18—C17	119.1 (2)
C10—C5—C4	117.46 (18)	C13—C18—C17	117.7 (2)
C6—C5—H5	104.5	O4—C22—O5	124.3 (2)
C10—C5—H5	104.5	O4—C22—C17	120.6 (2)
C4—C5—H5	104.5	O5—C22—C17	115.0 (2)
C7—C6—C5	110.10 (18)	C4—C23—H23A	109.5
C7—C6—H6A	109.6	C4—C23—H23B	109.5
C5—C6—H6A	109.6	H23A—C23—H23B	109.5
C7—C6—H6B	109.6	C4—C23—H23C	109.5
C5—C6—H6B	109.6	H23A—C23—H23C	109.5
H6A—C6—H6B	108.2	H23B—C23—H23C	109.5
C6—C7—C8	113.9 (2)	C4—C24—H24A	109.5
C6—C7—H7A	108.8	C4—C24—H24B	109.5
C8—C7—H7A	108.8	H24A—C24—H24B	109.5
C6—C7—H7B	108.8	C4—C24—H24C	109.5
C8—C7—H7B	108.8	H24A—C24—H24C	109.5
H7A—C7—H7B	107.7	H24B—C24—H24C	109.5
C7—C8—C26	107.7 (2)	C10—C25—H25A	109.5
C7—C8—C9	109.31 (18)	C10—C25—H25B	109.5
C26—C8—C9	111.75 (19)	H25A—C25—H25B	109.5
C7—C8—C14	109.66 (18)	C10—C25—H25C	109.5
C26—C8—C14	109.55 (18)	H25A—C25—H25C	109.5
C9—C8—C14	108.87 (17)	H25B—C25—H25C	109.5
C11—C9—C8	111.18 (18)	C8—C26—H26A	109.5
C11—C9—C10	113.93 (18)	C8—C26—H26B	109.5
C8—C9—C10	116.33 (17)	H26A—C26—H26B	109.5
C11—C9—H9	104.7	C8—C26—H26C	109.5
C8—C9—H9	104.7	H26A—C26—H26C	109.5
C10—C9—H9	104.7	H26B—C26—H26C	109.5
C25—C10—C1	107.38 (19)	C14—C27—H27A	109.5
C25—C10—C5	114.52 (18)	C14—C27—H27B	109.5

C1—C10—C5	107.82 (18)	H27A—C27—H27B	109.5
C25—C10—C9	112.74 (19)	C14—C27—H27C	109.5
C1—C10—C9	108.09 (17)	H27A—C27—H27C	109.5
C5—C10—C9	106.03 (17)	H27B—C27—H27C	109.5
C12—C11—C9	111.76 (19)	O2—C28—O1	123.7 (2)
C12—C11—H11A	109.3	O2—C28—C29	124.6 (2)
C9—C11—H11A	109.3	O1—C28—C29	111.7 (2)
C12—C11—H11B	109.3	C28—C29—H29A	109.5
C9—C11—H11B	109.3	C28—C29—H29B	109.5
H11A—C11—H11B	107.9	H29A—C29—H29B	109.5
C13—C12—C11	111.81 (18)	C28—C29—H29C	109.5
C13—C12—H12A	109.3	H29A—C29—H29C	109.5
C11—C12—H12A	109.3	H29B—C29—H29C	109.5
C13—C12—H12B	109.3	O5—C30—H30A	109.5
C11—C12—H12B	109.3	O5—C30—H30B	109.5
H12A—C12—H12B	107.9	H30A—C30—H30B	109.5
C18—C13—C12	111.67 (18)	O5—C30—H30C	109.5
C18—C13—C14	111.25 (18)	H30A—C30—H30C	109.5
C12—C13—C14	112.51 (18)	H30B—C30—H30C	109.5
C18—C13—H13	107.0	C28—O1—C3	117.74 (19)
C12—C13—H13	107.0	C22—O5—C30	115.4 (2)
C14—C13—H13	107.0		
C10—C1—C2—C3	−58.5 (3)	C11—C12—C13—C14	55.6 (3)
C1—C2—C3—O1	−178.6 (2)	C18—C13—C14—C15	55.4 (2)
C1—C2—C3—C4	60.5 (3)	C12—C13—C14—C15	−178.43 (18)
O1—C3—C4—C23	−52.4 (3)	C18—C13—C14—C27	−61.2 (2)
C2—C3—C4—C23	70.1 (2)	C12—C13—C14—C27	65.0 (2)
O1—C3—C4—C24	66.4 (2)	C18—C13—C14—C8	176.50 (17)
C2—C3—C4—C24	−171.20 (19)	C12—C13—C14—C8	−57.3 (2)
O1—C3—C4—C5	−177.48 (19)	C7—C8—C14—C15	−64.0 (2)
C2—C3—C4—C5	−55.1 (3)	C26—C8—C14—C15	54.0 (3)
C23—C4—C5—C6	60.1 (3)	C9—C8—C14—C15	176.47 (19)
C3—C4—C5—C6	−176.5 (2)	C7—C8—C14—C27	57.2 (3)
C24—C4—C5—C6	−61.6 (3)	C26—C8—C14—C27	175.2 (2)
C23—C4—C5—C10	−71.4 (3)	C9—C8—C14—C27	−62.3 (3)
C3—C4—C5—C10	51.9 (3)	C7—C8—C14—C13	177.42 (19)
C24—C4—C5—C10	166.8 (2)	C26—C8—C14—C13	−64.6 (2)
C10—C5—C6—C7	−63.3 (2)	C9—C8—C14—C13	57.9 (2)
C4—C5—C6—C7	161.9 (2)	C27—C14—C15—C16	55.6 (3)
C5—C6—C7—C8	57.3 (3)	C13—C14—C15—C16	−61.7 (3)
C6—C7—C8—C26	72.8 (2)	C8—C14—C15—C16	179.35 (18)
C6—C7—C8—C9	−48.8 (3)	C14—C15—C16—C17	56.4 (3)
C6—C7—C8—C14	−168.11 (19)	C15—C16—C17—C22	−163.6 (2)
C7—C8—C9—C11	−178.25 (18)	C15—C16—C17—C18	−43.1 (3)
C26—C8—C9—C11	62.7 (2)	C15—C16—C17—Cl1	72.8 (2)
C14—C8—C9—C11	−58.5 (2)	C12—C13—C18—O3	8.8 (3)
C7—C8—C9—C10	49.1 (3)	C14—C13—C18—O3	135.5 (2)
C26—C8—C9—C10	−70.0 (2)	C12—C13—C18—C17	−173.91 (19)
C14—C8—C9—C10	168.91 (18)	C14—C13—C18—C17	−47.3 (3)

C2—C1—C10—C25	−71.1 (3)	C22—C17—C18—O3	−20.2 (3)
C2—C1—C10—C5	52.8 (3)	C16—C17—C18—O3	−142.1 (2)
C2—C1—C10—C9	167.0 (2)	Cl1—C17—C18—O3	99.4 (2)
C6—C5—C10—C25	−65.2 (2)	C22—C17—C18—C13	162.45 (19)
C4—C5—C10—C25	67.7 (3)	C16—C17—C18—C13	40.5 (3)
C6—C5—C10—C1	175.40 (18)	Cl1—C17—C18—C13	−78.0 (2)
C4—C5—C10—C1	−51.7 (3)	C16—C17—C22—O4	44.6 (4)
C6—C5—C10—C9	59.8 (2)	C18—C17—C22—O4	−78.9 (3)
C4—C5—C10—C9	−167.29 (19)	Cl1—C17—C22—O4	166.4 (2)
C11—C9—C10—C25	−59.8 (2)	C16—C17—C22—O5	−137.7 (2)
C8—C9—C10—C25	71.6 (2)	C18—C17—C22—O5	98.8 (2)
C11—C9—C10—C1	58.8 (2)	Cl1—C17—C22—O5	−15.9 (3)
C8—C9—C10—C1	−169.87 (19)	O2—C28—O1—C3	−4.3 (4)
C11—C9—C10—C5	174.18 (18)	C29—C28—O1—C3	176.7 (2)
C8—C9—C10—C5	−54.5 (2)	C2—C3—O1—C28	89.2 (3)
C8—C9—C11—C12	56.5 (2)	C4—C3—O1—C28	−145.9 (2)
C10—C9—C11—C12	−169.71 (19)	O4—C22—O5—C30	−2.7 (4)
C9—C11—C12—C13	−54.1 (3)	C17—C22—O5—C30	179.7 (2)
C11—C12—C13—C18	−178.44 (18)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25C···O2^{i}	0.96	2.55	3.407 (3)	148
C11—H11B···O3^{ii}	0.97	2.58	3.290 (3)	130

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

Fig. 1

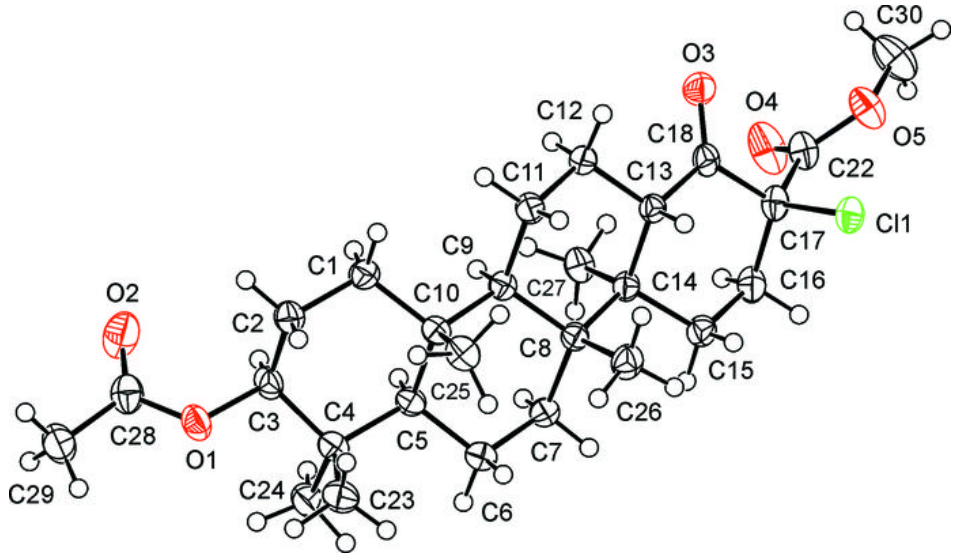

C30
O3
O4
O5
C12
C18
C22
C11
C13
Cl1
C17
C9
C1
C14
C16
O2
C10
C27
C2
C8
C15
C25
C26
C3
C4
C5
C7
C28
O1
C29
C24
C23
C6

Fig. 2

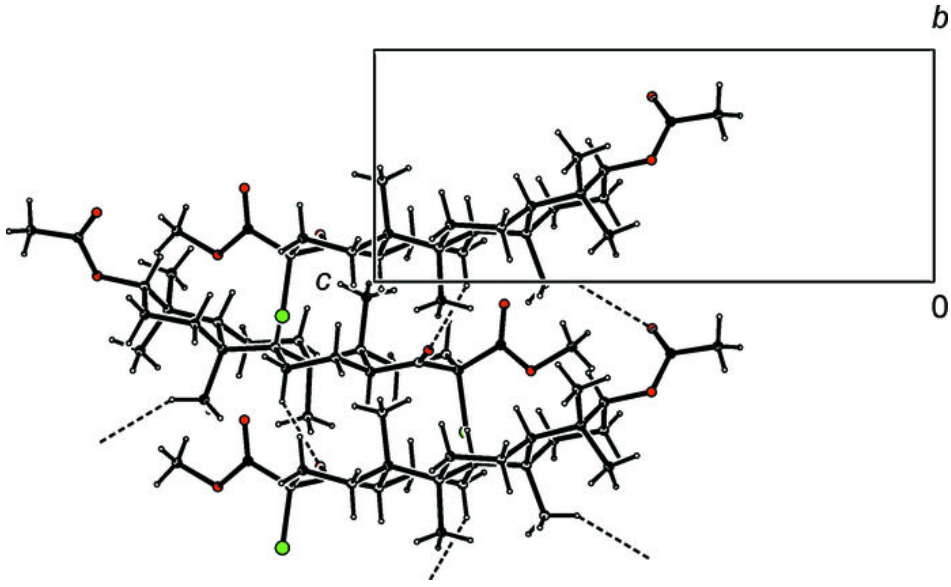
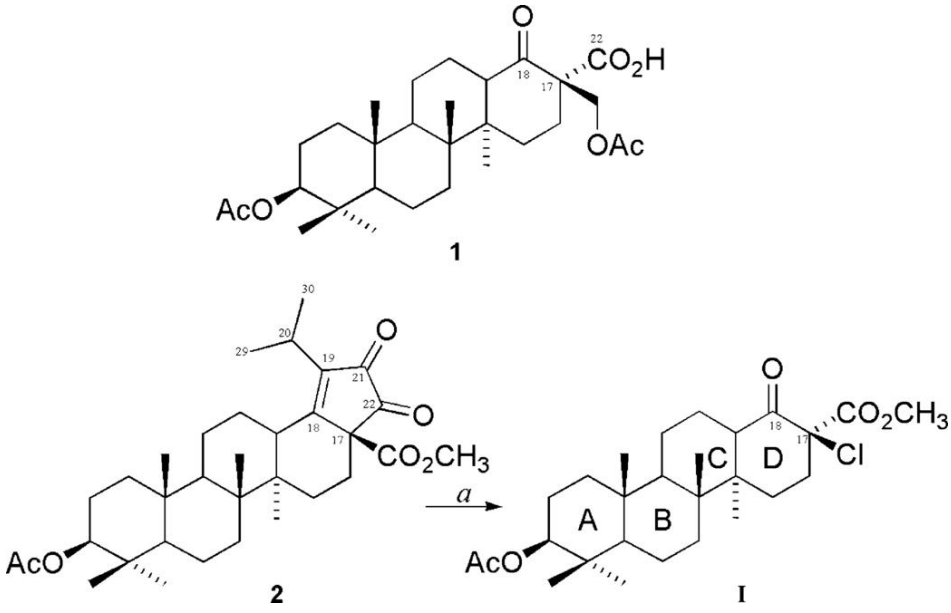


Fig. 3


O
22
CO2H
18
17
OAc
AcO
1
30
20
29
19
21
O
22
O
18
17
CO2CH3
AcO
2
a
O
18
CO2CH3
17
Cl
C
D
A
B
AcO
I