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9α-Chloro-16α-methyl-3,11-dioxo-androsta-1,4,6-triene-17β-carboxylic acid pinacolone solvate: catemeric hydrogen bonding and pinacolone solvation in a steroidal diketo acid derived from a commercial glucocorticoid

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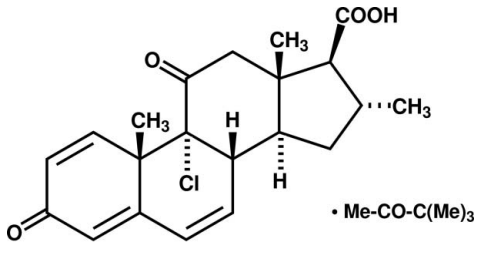
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.046; wR factor = 0.121; data-to-parameter ratio = 11.4.

The title ketocarboxylic acid, synthesized from the anti-inflammatory clocortolone pivalate, crystallizes as $C_{21}H_{23}ClO_4\cdot C_6H_{12}O$, with one molecule of steroid and one of 3,3-dimethylbutanone per asymmetric unit. The carboxyl group is highly ordered and the steroid molecules form translational carboxyl-to-ketone hydrogen-bonding catemers [O···O = 2.682 (3) Å and O—H···O = 158°] that utilize the 3-ketone group, with one chain proceeding in the [110] direction and the other in the [$\bar{1}$10] direction. One close intermolecular C—H···O=C contact is present, which involves the solvent O atom, but neither it nor the Cl atom nor the 11-ketone group play any role in the classical hydrogen bonding.

Related literature

For the *A*-ring geometry of a related steroid dienone, see: Thompson *et al.* (1999).



Experimental

Crystal data

$C_{21}H_{23}ClO_4\cdot C_6H_{12}O$
M_r = 475.00
Monoclinic, $P2_1$
a = 6.5000 (4) Å
b = 11.3153 (5) Å
c = 16.4559 (8) Å
β = 90.716 (4)°
V = 1210.23 (11) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 1.69 mm^{-1}
T = 100 (2) K
0.51 × 0.46 × 0.13 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.480, T_{max} = 0.811
6187 measured reflections
3494 independent reflections
3358 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.121
S = 1.08
3494 reflections
306 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Absolute structure: Flack (1983), 1425 Friedel pairs
Flack parameter: 0.026 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1^{i}	0.84	1.88	2.682 (3)	158
C2—H2···O5^{ii}	0.95	2.52	3.331 (4)	143

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS* (Sheldrick, 2004); program(s) used to refine structure: *SHELXL* (Sheldrick, 2004); molecular graphics: *SHELXTL* (Sheldrick, 2004); 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: LH2378).

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supplementary materials

Acta Cryst. (2007). E**63**, o2853 [**doi:10.1107/S1600536807021435**]

9α-Chloro-16α-methyl-3,11-dioxoandrosta-1,4,6-triene-17β-carboxylic acid pinacolone solvate: catemeric hydrogen bonding and pinacolone solvation in a steroidal diketo acid derived from a commercial glucocorticoid

I. Azim, M. Davison, M. D. V. Dufort, R. A. Lalancette and H. W. Thompson

Comment

Our study of hydrogen-bonding modes in ketocarboxylic acids often employs terpenoids as subjects, and we now report the structure and aggregation mode of the title steroid, (I), derived from a commercial topical anti-inflammatory glucocorticoid.

Fig. 1 shows the asymmetric unit. The only significant conformational option involves the carboxyl, whose plane lies near the C16—C17 bond, with the C=O bond turned toward C16; the C16—C17—C20—O3 torsion angle = 2.55 (4)°. The A-ring is highly planar (Thompson *et al.*, 1999), with C10 only 0.095 (2) Å out of the average plane for all six ring atoms. The C6—C7 double bond plane (C5—C6—C7—C8) lies at a 13.27 (2)° dihedral angle to this average A-ring plane.

Complete or partial averaging of C—O bond lengths and C—C—O angles, frequent in carboxyl dimers, cannot occur in acid-to-ketone catemers, whose geometry precludes the disordering processes required. In (I), which is catemeric, these values are ones typical of highly ordered dimeric carboxyls.

Fig. 2 illustrates the chains created by the acid-to-ketone H bonding among translationally related steroid molecules (Table 2). This arrangement closely resembles those found in other steroid keto acids that share important structural features with (I). We have now examined a half-dozen 3-ketosteroids with additional ketones in various positions but have yet to observe any involvement of those additional functions in the H-bonding schemes.

Neither the solvate nor the Cl atom nor the C11 ketone plays any direct role in the H bonding. However, in the stacking of adjacent steroid molecules there is an intermolecular contact of 3.044 Å between the Cl and O2 atoms, and within the 2.6 Å range surveyed for non-bonded intermolecular C—H···O packing interactions, one close contact was found involving the solvent oxygen; the solvent occupancy is 100%.

Three-dimensionally, strings of screw-related solvate molecules, associating with each other only *via* van der Waals' contacts, extend along the *b* axis, forming sheets in the *ab* plane. Each solvate sheet is sandwiched between a sheet of [110] catemers and one of [−110] catemers, where it is stabilized by the close C—H···O=C steroid contacts.

We characterize the geometry of H bonding to carbonyls using a combination of H···O=C angle and H···O=C—C torsional angle. These describe the approach of the acid H atom to the O in terms of its deviation from, respectively, C=O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). In (I) the values for these two angles are 130 and −23°.

Experimental

Compound (I), previously unreported, was synthesized from (+)-9α-chloro-6α-fluoro-11β,21-dihydroxy-16α-methylpregna-1,4-diene-3,20-dione 21-pivalate (clocortolone pivalate), of known rotation and absolute stereochemistry, a synthetic topical anti-inflammatory glucocorticoid obtained from DFB Pharmaceuticals, Fort Worth, Texas, USA. Preparatory to C20—C21

bond cleavage, the ester function was removed reductively with diisobutylaluminum hydride; this was successful but failed to avoid dehydrofluorination. Following oxidation with pyridinium dichromate in CH_2Cl_2, $NaIO_4$ cleavage provided a low yield of (I), which was crystallized from pinacolone, to give material of X-ray quality, mp *ca* 512 K. The ^{1}H NMR spectrum showed five vinyl peaks (δ 5.8–7.8), confirming the loss of fluorine. The solid-state (KBr) IR spectrum of (I) displays C=O absorptions at 1716, 1654 and 1648 cm^{-1}, with an alkene absorption at 1595 cm^{-1}. In $CDCl_3$ solution, where dimers predominate, these peaks appear at 1704, 1656 & 1607 cm^{-1}.

Refinement

All H atoms for (I) were found in electron density difference maps. The O—H was constrained to an idealized position with its distance fixed at 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O). The methyl H atoms were put in ideally staggered positions with C—H distances of 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C). The methylene and methine Hs were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C—H distances of 0.99 and 1.00 Å, respectively, and U_{iso}(H) = 1.2U_{eq}(C).

Figures

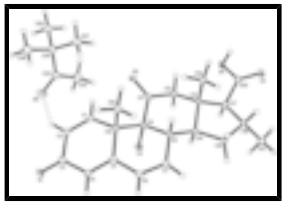

Fig. 1. A view of compound (I) with its steroid numbering. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates a hydrogen bond.

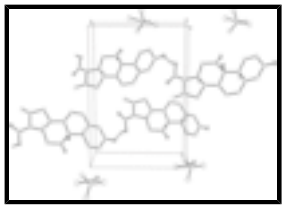

Fig. 2. A packing diagram with extracellular molecules included to illustrate the two translational catemers passing through the cell, the first in the [110] direction, and the second in the [−110] direction. All C-bound H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

9α-Chloro-16α-methyl-3,11-dioxoandrosta-1,4,6-triene-17β-carboxylic acid

Crystal data

$C_{21}H_{23}ClO_4 \cdot C_6H_{12}O$	F_{000} = 508
M_r = 475.00	D_x = 1.303 Mg m^{-3}
Monoclinic, $P2_1$	Melting point: 512 K
Hall symbol: P 2yb	Cu $K\alpha$ radiation λ = 1.54178 Å
a = 6.5000 (4) Å	Cell parameters from 6186 reflections
b = 11.3153 (5) Å	θ = 6.8–66.4º
c = 16.4559 (8) Å	μ = 1.69 mm^{-1}
β = 90.716 (4)º	T = 100 (2) K
V = 1210.23 (11) Å^3	Triangular plate, colourless
Z = 2	0.51 × 0.46 × 0.13 mm

Data collection

Bruker SMART CCD APEXII area-detector diffractometer	3494 independent reflections
Radiation source: fine-focus sealed tube	3358 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.026$
$T = 100(2)$ K	$\theta_{max} = 66.4^{o}$
φ and ω scans	$\theta_{min} = 6.8^{o}$
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$h = -7\rightarrow6$
$T_{min} = 0.480$, $T_{max} = 0.811$	$k = -13\rightarrow13$
6187 measured reflections	$l = -19\rightarrow18$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0924P)^2 + 0.1345P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.121$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
3494 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}
306 parameters	Extinction coefficient: ?
1 restraint	Absolute structure: Flack (1983), 1425 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.026 (15)
Secondary atom site location: difference Fourier map	

Special details

Experimental. Crystal mounted on cryoloop using Paratone-N

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}
Cl1	0.84202 (9)	0.70938 (6)	0.22592 (3)	0.02168 (18)
O1	0.9050 (4)	0.2425 (2)	0.20777 (14)	0.0348 (6)

C1	0.5626 (5)	0.4870 (3)	0.19898 (18)	0.0226 (6)
H1	0.4746	0.5245	0.1603	0.027*
O2	0.3017 (3)	0.69661 (19)	0.19372 (12)	0.0256 (4)
C2	0.6607 (5)	0.3887 (3)	0.17632 (18)	0.0245 (6)
H2	0.6285	0.3541	0.1251	0.029*
O3	0.2612 (3)	1.2072 (2)	0.37098 (11)	0.0265 (4)
C3	0.8170 (5)	0.3330 (3)	0.22881 (19)	0.0249 (6)
O4	0.2583 (4)	1.1318 (2)	0.24547 (13)	0.0326 (6)
H4	0.1654	1.1824	0.2380	0.049*
C4	0.8666 (4)	0.3938 (3)	0.30430 (18)	0.0210 (6)
H4A	0.9724	0.3624	0.3383	0.025*
C5	0.7692 (4)	0.4927 (2)	0.32825 (17)	0.0184 (6)
O5	0.5009 (4)	0.3998 (2)	0.98335 (15)	0.0389 (6)
C6	0.8388 (5)	0.5560 (3)	0.40089 (18)	0.0246 (6)
H6	0.9289	0.5169	0.4380	0.029*
C7	0.7810 (5)	0.6669 (3)	0.41736 (17)	0.0223 (6)
H7	0.8429	0.7070	0.4621	0.027*
C8	0.6205 (4)	0.7297 (2)	0.36684 (15)	0.0167 (6)
H8	0.4855	0.7124	0.3928	0.020*
C9	0.6052 (4)	0.6794 (2)	0.27984 (16)	0.0179 (6)
C10	0.5831 (4)	0.5415 (2)	0.28173 (17)	0.0190 (6)
C11	0.4376 (4)	0.7476 (2)	0.23028 (16)	0.0181 (6)
C12	0.4479 (5)	0.8818 (3)	0.23319 (17)	0.0210 (6)
H12A	0.3261	0.9158	0.2050	0.025*
H12B	0.5727	0.9096	0.2052	0.025*
C13	0.4534 (4)	0.9227 (2)	0.32201 (17)	0.0166 (6)
C14	0.6402 (4)	0.8645 (2)	0.36483 (17)	0.0180 (6)
H14	0.7643	0.8837	0.3320	0.022*
C15	0.6619 (4)	0.9307 (2)	0.44546 (17)	0.0206 (6)
H15A	0.8070	0.9311	0.4645	0.025*
H15B	0.5760	0.8936	0.4877	0.025*
C16	0.5865 (4)	1.0584 (2)	0.42656 (17)	0.0189 (6)
H16	0.4672	1.0758	0.4624	0.023*
C17	0.5061 (4)	1.0545 (2)	0.33729 (16)	0.0191 (6)
H17	0.6222	1.0766	0.3010	0.023*
C18	0.2481 (4)	0.8926 (3)	0.36221 (18)	0.0224 (6)
H18A	0.1399	0.9444	0.3405	0.034*
H18B	0.2609	0.9040	0.4211	0.034*
H18C	0.2125	0.8100	0.3507	0.034*
C19	0.3888 (5)	0.5055 (3)	0.32943 (19)	0.0237 (6)
H19A	0.2673	0.5430	0.3047	0.036*
H19B	0.4034	0.5313	0.3860	0.036*
H19C	0.3728	0.4194	0.3277	0.036*
C20	0.3295 (5)	1.1397 (2)	0.32129 (17)	0.0208 (6)
C21	0.7482 (5)	1.1537 (3)	0.44052 (19)	0.0267 (7)
H21A	0.7892	1.1547	0.4980	0.040*
H21B	0.6909	1.2308	0.4254	0.040*
H21C	0.8686	1.1369	0.4072	0.040*
C22	0.4332 (6)	0.6001 (3)	0.9566 (3)	0.0463 (10)

H22A	0.4548	0.6448	1.0070	0.069*
H22B	0.3242	0.6378	0.9240	0.069*
H22C	0.5610	0.5990	0.9256	0.069*
C23	0.3712 (5)	0.4758 (3)	0.97662 (18)	0.0273 (7)
C24	0.1458 (5)	0.4496 (3)	0.98863 (19)	0.0292 (7)
C25	0.0240 (6)	0.4828 (4)	0.9108 (2)	0.0414 (9)
H25A	0.0370	0.5679	0.9008	0.062*
H25B	−0.1214	0.4626	0.9176	0.062*
H25C	0.0791	0.4391	0.8645	0.062*
C26	0.1127 (7)	0.3193 (3)	1.0063 (3)	0.0482 (10)
H26A	0.1727	0.2718	0.9628	0.072*
H26B	−0.0351	0.3030	1.0094	0.072*
H26C	0.1792	0.2989	1.0582	0.072*
C27	0.0596 (5)	0.5230 (4)	1.0594 (2)	0.0364 (8)
H27A	0.1228	0.4966	1.1107	0.055*
H27B	−0.0899	0.5123	1.0618	0.055*
H27C	0.0909	0.6067	1.0508	0.055*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0178 (3)	0.0224 (3)	0.0250 (3)	0.0013 (3)	0.0035 (2)	0.0021 (3)
O1	0.0356 (13)	0.0275 (13)	0.0412 (13)	0.0152 (9)	−0.0107 (10)	−0.0111 (9)
C1	0.0178 (16)	0.0226 (15)	0.0272 (15)	0.0005 (10)	−0.0044 (11)	−0.0007 (11)
O2	0.0185 (10)	0.0239 (11)	0.0342 (10)	0.0045 (8)	−0.0073 (8)	−0.0058 (9)
C2	0.0223 (16)	0.0245 (15)	0.0265 (15)	0.0027 (12)	−0.0043 (12)	−0.0038 (12)
O3	0.0261 (11)	0.0235 (10)	0.0299 (10)	0.0068 (10)	−0.0011 (8)	−0.0025 (10)
C3	0.0218 (17)	0.0200 (15)	0.0328 (16)	0.0021 (12)	0.0003 (12)	−0.0003 (12)
O4	0.0359 (14)	0.0296 (12)	0.0319 (12)	0.0191 (10)	−0.0089 (10)	−0.0068 (10)
C4	0.0163 (15)	0.0186 (13)	0.0278 (14)	−0.0020 (10)	−0.0042 (11)	0.0050 (11)
C5	0.0166 (15)	0.0173 (14)	0.0214 (14)	−0.0009 (10)	0.0015 (10)	0.0048 (11)
O5	0.0308 (14)	0.0413 (14)	0.0446 (15)	0.0055 (11)	0.0005 (11)	0.0051 (11)
C6	0.0231 (16)	0.0263 (16)	0.0242 (15)	0.0057 (11)	−0.0034 (12)	0.0035 (12)
C7	0.0224 (16)	0.0223 (14)	0.0221 (14)	0.0003 (11)	−0.0027 (11)	−0.0002 (11)
C8	0.0130 (13)	0.0171 (15)	0.0198 (12)	0.0002 (10)	0.0012 (9)	0.0014 (10)
C9	0.0089 (13)	0.0207 (16)	0.0240 (13)	0.0026 (9)	0.0015 (9)	0.0030 (10)
C10	0.0145 (15)	0.0170 (15)	0.0255 (14)	0.0006 (10)	0.0016 (11)	−0.0003 (11)
C11	0.0158 (15)	0.0224 (14)	0.0162 (12)	0.0042 (10)	0.0007 (10)	−0.0019 (10)
C12	0.0212 (16)	0.0207 (15)	0.0210 (14)	0.0050 (11)	−0.0029 (11)	0.0015 (11)
C13	0.0148 (15)	0.0138 (14)	0.0211 (14)	0.0031 (10)	−0.0010 (10)	0.0005 (11)
C14	0.0099 (14)	0.0198 (14)	0.0242 (14)	0.0011 (10)	−0.0005 (10)	0.0036 (11)
C15	0.0186 (16)	0.0183 (14)	0.0248 (15)	0.0013 (11)	−0.0027 (11)	0.0014 (11)
C16	0.0155 (15)	0.0161 (14)	0.0249 (15)	0.0010 (10)	0.0008 (11)	−0.0018 (11)
C17	0.0174 (16)	0.0185 (15)	0.0215 (14)	−0.0002 (10)	0.0014 (11)	0.0000 (11)
C18	0.0149 (16)	0.0213 (14)	0.0311 (16)	0.0007 (11)	0.0010 (12)	−0.0024 (12)
C19	0.0194 (16)	0.0185 (15)	0.0334 (16)	−0.0036 (11)	0.0034 (12)	0.0009 (12)
C20	0.0205 (16)	0.0135 (14)	0.0285 (15)	−0.0003 (10)	0.0004 (11)	−0.0004 (11)
C21	0.0236 (17)	0.0224 (15)	0.0340 (16)	−0.0009 (12)	−0.0040 (12)	0.0011 (13)

C22	0.034 (2)	0.033 (2)	0.072 (3)	−0.0071 (15)	0.0062 (18)	0.0003 (18)
C23	0.0264 (17)	0.0324 (17)	0.0231 (15)	0.0025 (13)	−0.0024 (12)	0.0001 (12)
C24	0.0266 (18)	0.0301 (18)	0.0308 (17)	−0.0005 (13)	0.0006 (13)	−0.0052 (13)
C25	0.028 (2)	0.061 (2)	0.0349 (19)	0.0022 (16)	−0.0027 (15)	−0.0053 (17)
C26	0.046 (2)	0.028 (2)	0.071 (3)	−0.0023 (17)	0.0167 (19)	0.0008 (19)
C27	0.033 (2)	0.0396 (19)	0.0369 (18)	−0.0018 (16)	0.0031 (14)	−0.0051 (16)

Geometric parameters (Å, °)

Cl1—C9	1.818 (3)	C14—H14	1.0000
O1—C3	1.226 (4)	C15—C16	1.556 (4)
C1—C2	1.338 (4)	C15—H15A	0.9900
C1—C10	1.500 (4)	C15—H15B	0.9900
C1—H1	0.9500	C16—C21	1.521 (4)
O2—C11	1.209 (4)	C16—C17	1.554 (4)
C2—C3	1.467 (4)	C16—H16	1.0000
C2—H2	0.9500	C17—C20	1.520 (4)
O3—C20	1.208 (4)	C17—H17	1.0000
C3—C4	1.453 (4)	C18—H18A	0.9800
O4—C20	1.328 (4)	C18—H18B	0.9800
O4—H4	0.8400	C18—H18C	0.9800
C4—C5	1.347 (4)	C19—H19A	0.9800
C4—H4A	0.9500	C19—H19B	0.9800
C5—C6	1.461 (4)	C19—H19C	0.9800
C5—C10	1.527 (4)	C21—H21A	0.9800
O5—C23	1.209 (4)	C21—H21B	0.9800
C6—C7	1.338 (4)	C21—H21C	0.9800
C6—H6	0.9500	C22—C23	1.501 (5)
C7—C8	1.504 (4)	C22—H22A	0.9800
C7—H7	0.9500	C22—H22B	0.9800
C8—C14	1.532 (4)	C22—H22C	0.9800
C8—C9	1.543 (3)	C23—C24	1.510 (5)
C8—H8	1.0000	C24—C26	1.519 (5)
C9—C11	1.557 (3)	C24—C27	1.542 (5)
C9—C10	1.567 (4)	C24—C25	1.544 (5)
C10—C19	1.550 (4)	C25—H25A	0.9800
C11—C12	1.521 (4)	C25—H25B	0.9800
C12—C13	1.533 (4)	C25—H25C	0.9800
C12—H12A	0.9900	C26—H26A	0.9800
C12—H12B	0.9900	C26—H26B	0.9800
C13—C18	1.535 (4)	C26—H26C	0.9800
C13—C14	1.544 (3)	C27—H27A	0.9800
C13—C17	1.550 (4)	C27—H27B	0.9800
C14—C15	1.528 (4)	C27—H27C	0.9800
C2—C1—C10	123.9 (3)	C21—C16—C17	112.7 (2)
C2—C1—H1	118.0	C21—C16—C15	114.4 (2)
C10—C1—H1	118.0	C17—C16—C15	105.3 (2)
C1—C2—C3	121.4 (3)	C21—C16—H16	108.1
C1—C2—H2	119.3	C17—C16—H16	108.1

C3—C2—H2	119.3	C15—C16—H16	108.1
O1—C3—C4	122.5 (3)	C20—C17—C13	114.7 (2)
O1—C3—C2	121.0 (3)	C20—C17—C16	112.9 (2)
C4—C3—C2	116.4 (3)	C13—C17—C16	104.6 (2)
C20—O4—H4	109.5	C20—C17—H17	108.1
C5—C4—C3	122.9 (3)	C13—C17—H17	108.1
C5—C4—H4A	118.5	C16—C17—H17	108.1
C3—C4—H4A	118.5	C13—C18—H18A	109.5
C4—C5—C6	120.4 (3)	C13—C18—H18B	109.5
C4—C5—C10	121.7 (3)	H18A—C18—H18B	109.5
C6—C5—C10	117.9 (2)	C13—C18—H18C	109.5
C7—C6—C5	122.7 (3)	H18A—C18—H18C	109.5
C7—C6—H6	118.6	H18B—C18—H18C	109.5
C5—C6—H6	118.6	C10—C19—H19A	109.5
C6—C7—C8	121.7 (3)	C10—C19—H19B	109.5
C6—C7—H7	119.2	H19A—C19—H19B	109.5
C8—C7—H7	119.2	C10—C19—H19C	109.5
C7—C8—C14	115.1 (2)	H19A—C19—H19C	109.5
C7—C8—C9	112.0 (2)	H19B—C19—H19C	109.5
C14—C8—C9	110.6 (2)	O3—C20—O4	123.5 (3)
C7—C8—H8	106.1	O3—C20—C17	124.6 (3)
C14—C8—H8	106.1	O4—C20—C17	111.9 (2)
C9—C8—H8	106.1	C16—C21—H21A	109.5
C8—C9—C11	109.9 (2)	C16—C21—H21B	109.5
C8—C9—C10	110.7 (2)	H21A—C21—H21B	109.5
C11—C9—C10	116.1 (2)	C16—C21—H21C	109.5
C8—C9—Cl1	109.82 (17)	H21A—C21—H21C	109.5
C11—C9—Cl1	104.06 (18)	H21B—C21—H21C	109.5
C10—C9—Cl1	105.89 (18)	C23—C22—H22A	109.5
C1—C10—C5	111.5 (2)	C23—C22—H22B	109.5
C1—C10—C19	106.7 (2)	H22A—C22—H22B	109.5
C5—C10—C19	107.2 (2)	C23—C22—H22C	109.5
C1—C10—C9	113.5 (2)	H22A—C22—H22C	109.5
C5—C10—C9	107.3 (2)	H22B—C22—H22C	109.5
C19—C10—C9	110.3 (2)	O5—C23—C22	119.9 (3)
O2—C11—C12	121.6 (3)	O5—C23—C24	121.6 (3)
O2—C11—C9	121.7 (3)	C22—C23—C24	118.5 (3)
C12—C11—C9	116.6 (2)	C23—C24—C26	110.9 (3)
C11—C12—C13	109.4 (2)	C23—C24—C27	110.8 (3)
C11—C12—H12A	109.8	C26—C24—C27	108.9 (3)
C13—C12—H12A	109.8	C23—C24—C25	109.4 (3)
C11—C12—H12B	109.8	C26—C24—C25	108.9 (3)
C13—C12—H12B	109.8	C27—C24—C25	107.9 (3)
H12A—C12—H12B	108.2	C24—C25—H25A	109.5
C12—C13—C18	109.5 (2)	C24—C25—H25B	109.5
C12—C13—C14	108.4 (2)	H25A—C25—H25B	109.5
C18—C13—C14	113.1 (2)	C24—C25—H25C	109.5
C12—C13—C17	116.6 (2)	H25A—C25—H25C	109.5
C18—C13—C17	109.6 (2)	H25B—C25—H25C	109.5

C14—C13—C17	99.5 (2)	C24—C26—H26A	109.5
C15—C14—C8	118.4 (2)	C24—C26—H26B	109.5
C15—C14—C13	104.5 (2)	H26A—C26—H26B	109.5
C8—C14—C13	111.7 (2)	C24—C26—H26C	109.5
C15—C14—H14	107.2	H26A—C26—H26C	109.5
C8—C14—H14	107.2	H26B—C26—H26C	109.5
C13—C14—H14	107.2	C24—C27—H27A	109.5
C14—C15—C16	104.8 (2)	C24—C27—H27B	109.5
C14—C15—H15A	110.8	H27A—C27—H27B	109.5
C16—C15—H15A	110.8	C24—C27—H27C	109.5
C14—C15—H15B	110.8	H27A—C27—H27C	109.5
C16—C15—H15B	110.8	H27B—C27—H27C	109.5
H15A—C15—H15B	108.9		
C10—C1—C2—C3	−7.1 (5)	Cl1—C9—C11—C12	−68.6 (3)
C1—C2—C3—O1	179.5 (3)	O2—C11—C12—C13	124.3 (3)
C1—C2—C3—C4	−3.2 (5)	C9—C11—C12—C13	−53.1 (3)
O1—C3—C4—C5	−179.3 (3)	C11—C12—C13—C18	−66.3 (3)
C2—C3—C4—C5	3.3 (4)	C11—C12—C13—C14	57.4 (3)
C3—C4—C5—C6	−174.2 (3)	C11—C12—C13—C17	168.6 (2)
C3—C4—C5—C10	6.5 (4)	C7—C8—C14—C15	−50.5 (3)
C4—C5—C6—C7	164.4 (3)	C9—C8—C14—C15	−178.7 (2)
C10—C5—C6—C7	−16.3 (4)	C7—C8—C14—C13	−172.0 (2)
C5—C6—C7—C8	7.1 (5)	C9—C8—C14—C13	59.8 (3)
C6—C7—C8—C14	−152.4 (3)	C12—C13—C14—C15	167.6 (2)
C6—C7—C8—C9	−24.9 (4)	C18—C13—C14—C15	−70.8 (3)
C7—C8—C9—C11	−179.9 (2)	C17—C13—C14—C15	45.3 (3)
C14—C8—C9—C11	−50.0 (3)	C12—C13—C14—C8	−63.2 (3)
C7—C8—C9—C10	50.6 (3)	C18—C13—C14—C8	58.4 (3)
C14—C8—C9—C10	−179.5 (2)	C17—C13—C14—C8	174.5 (2)
C7—C8—C9—Cl1	−66.0 (3)	C8—C14—C15—C16	−156.8 (2)
C14—C8—C9—Cl1	63.9 (2)	C13—C14—C15—C16	−31.8 (3)
C2—C1—C10—C5	15.5 (4)	C14—C15—C16—C21	−119.1 (3)
C2—C1—C10—C19	−101.3 (3)	C14—C15—C16—C17	5.2 (3)
C2—C1—C10—C9	136.9 (3)	C12—C13—C17—C20	78.0 (3)
C4—C5—C10—C1	−15.0 (4)	C18—C13—C17—C20	−47.1 (3)
C6—C5—C10—C1	165.7 (2)	C14—C13—C17—C20	−165.8 (2)
C4—C5—C10—C19	101.5 (3)	C12—C13—C17—C16	−157.8 (2)
C6—C5—C10—C19	−77.8 (3)	C18—C13—C17—C16	77.2 (3)
C4—C5—C10—C9	−139.9 (3)	C14—C13—C17—C16	−41.6 (3)
C6—C5—C10—C9	40.7 (3)	C21—C16—C17—C20	−86.3 (3)
C8—C9—C10—C1	178.7 (2)	C15—C16—C17—C20	148.4 (2)
C11—C9—C10—C1	52.5 (3)	C21—C16—C17—C13	148.4 (2)
Cl1—C9—C10—C1	−62.3 (3)	C15—C16—C17—C13	23.1 (3)
C8—C9—C10—C5	−57.6 (3)	C13—C17—C20—O3	122.2 (3)
C11—C9—C10—C5	176.3 (2)	C16—C17—C20—O3	2.5 (4)
Cl1—C9—C10—C5	61.4 (2)	C13—C17—C20—O4	−58.0 (3)
C8—C9—C10—C19	58.9 (3)	C16—C17—C20—O4	−177.7 (2)
C11—C9—C10—C19	−67.2 (3)	O5—C23—C24—C26	−1.9 (4)
Cl1—C9—C10—C19	177.93 (18)	C22—C23—C24—C26	178.6 (4)

C8—C9—C11—O2	−128.4 (3)	O5—C23—C24—C27	119.2 (3)
C10—C9—C11—O2	−1.9 (4)	C22—C23—C24—C27	−60.3 (4)
Cl1—C9—C11—O2	114.0 (3)	O5—C23—C24—C25	−122.0 (3)
C8—C9—C11—C12	49.0 (3)	C22—C23—C24—C25	58.6 (4)
C10—C9—C11—C12	175.5 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O1^{i}	0.84	1.88	2.682 (3)	158
C2—H2···O5^{ii}	0.95	2.52	3.331 (4)	143

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

Fig. 1

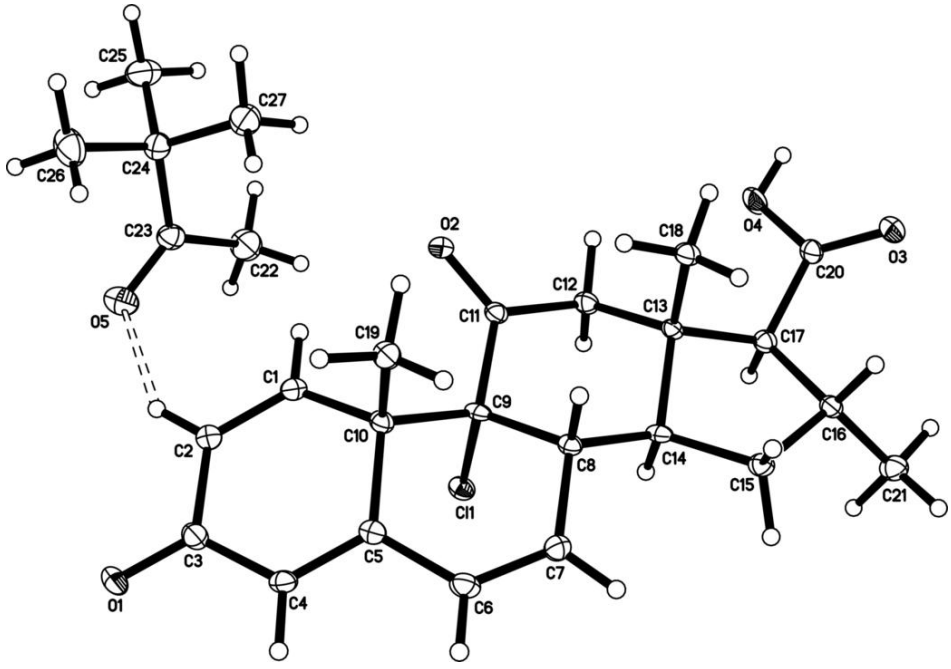
C25
C27
C26
C24
C23
C22
O5
O2
C18
O4
C20
O3
C12
C11
C13
C19
C17
C1
C9
C16
C10
C2
C8
C14
C15
C21
Cl1
C3
C5
C7
O1
C4
C6

Fig. 2