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15β,16β-Methylene-3-oxo-17α-pregn-4-ene-21,17-carbolactone

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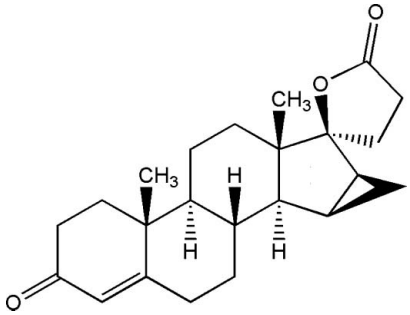
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.005 Å; R factor = 0.037; wR factor = 0.109; data-to-parameter ratio = 8.4.

In the title compound, $C_{23}H_{30}O_3$, ring A has a sofa conformation, rings B and C have regular chair conformations, and ring D and the carbolactone ring adopt envelope conformations. The crystal packing is stabilized by weak intermolecular C—H···O hydrogen bonding.

Related literature

For a related structure, see: Verma *et al.* (2006). For synthesis, see: Wlechert *et al.* (1978).



Experimental

Crystal data

$C_{23}H_{30}O_3$
M_r = 354.47
Orthorhombic, $P2_12_12_1$
a = 11.964 (8) Å
b = 12.647 (5) Å
c = 12.793 (4) Å
V = 1935.7 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 295 (2) K
0.40 × 0.35 × 0.15 mm

Data collection

Enraf–Nonius CAD4 diffractometer
Absorption correction: none
2175 measured reflections
1989 independent reflections
1183 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
3 standard reflections
frequency: 60 min
intensity decay: 0.1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.109
S = 1.03
1989 reflections
238 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C19—H19C···O3^{i}	0.96	2.58	3.540 (5)	177

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *CAD-4 EXPRESS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); 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: XU2349).

References

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Verma, R., Jasrotia, D., Sawhney, A. & Bhat, M. (2006). *J. Chem. Crystallogr.* **34**, 523–528.
Wlechert, R., Bittler, D., Kerb, U., Laurent, H., Casals, S. J. & Losert, W. (1978). US Patent No. 4 129 564.

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supplementary materials

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15β,16β-Methylene-3-oxo-17α-pregn-4-ene-21,17-carbolactone

W. Zhou, W.-X. Hu and C.-N. Xia

Comment

Drospirenone has been known as a new contraceptive drug with the special antimineralocorticoid and antiandrogenic properties, unlike any other progestin available in oral contraceptives. In our new process to synthesize drospirenone, the title compound, (1), has been obtained as an intermediate by the oxidation with cyclohexanone and aluminium isopropylate from the compound (2), 3β-hydroxy-15β,16β-methylene-5-androstene-[17(β-1')-spiro-5']- perhydrofuran-2'ξ-ol. We report here the crystal structure of (1).

The molecular structure of title molecule is illustrated in Fig. 1. The packing diagram is shown in Fig. 2. In the molecule, the Csp^3—Csp^3 bond lengths in the steroid nucleus are from 1.511 (6) to 1.557 (4) Å, in good agreement with the values found in the similar steroid (Verma *et al.*, 2006). The double bond length of 1.221 (5) Å for C3═O1 is in accordance with the expected value, while the length of 1.349 (5) Å for the C4═C5 double bond is somewhat longer than the typical value of 1.32 Å, indicating delocalization to some extent with C3═O1 double bond.

The C1-containing six-membered ring displays a 1α-envelope conformation. Atom C2–C5 and C10 form a plane within the deviation of 0.044 (3) and atom C1 lies under the plane by −0.587 (5) Å. The C6-containing six-membered rings and C11-containing ring show regular chair conformations. The C13-containing five-membered ring has a 13β-envelope conformation, the deviation of C13 from the plane of C14–C17 is 0.617 (5) Å. The three-membered ring makes a dihedral angle of 61.1 (3)° with the C14–C17 plane. In the C21-containing five-membered, the atom C23 deviates from the plane (C17/O2/C21/C22) by 0.438 (7) Å, showing a flater envelope conformation.

As shown in Fig. 2, there exists a weak C—H···O intermolecular hydrogen bond in the crystal structure (Table 1) and the molecules are linked by the hydrogen bonding.

Experimental

The compound (2), 3β-hydroxy-15β,16β-methylene-5-androstene-[17(β-1')-spiro-5']- perhydrofuran-2'ξ-ol, was prepared *via* three steps from 5,15-androstdiene-3β-ol-17-one according to the literature method (Wlechert *et al.*, 1978).

The title compound (1) was prepared in the manner discribed below (Scheme 2): a toluene solution (200 ml) of compound (2) (12.5 g, 35 mmol) was mixed with cyclohexanone (28.4 g, 290 mmol) and a toluene solution (100 ml) of aluminium isopropylate (5 g, 25 mmol). The mixture was refluxed untill TLC test showing the reaction complete. The mixture was then diluted with ethyl acetate (50 ml), washed with 200 ml of 1 *M* sulfuric acid and 200 ml of water in turn. The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. To the residue was added 30 ml of isopropyl ether, then cooled overnight in a refrigerator to give crystalline compound (1) (8.0 g, yield 64.7%). Single crystals of the compound (1) were obtained by recrystallization from a toluene solution.

Refinement

H atoms bonded to C atoms were placed at calculated positions and refined using a riding model with C—H = 0.93–0.98 Å, and U_{iso}(H) = 1.2 times (or 1.5 times for methyl H) U_{eq}(C). In the absence of significant anomalous dispersion effects, Friedel pairs were merged.

Figures

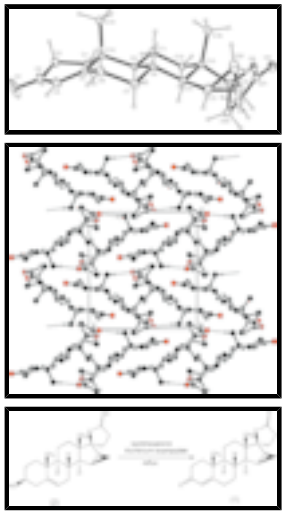


Fig. 1. The structure of (1) with 30% probability displacement ellipsoids.
Fig. 2. Packing diagram of (1), viewed along the *b* axis, showing hydrogen bonds as dashed lines. For clarity, H atoms have been omitted except for those involved in hydrogen bonding.

15β,16β-Methylene-3-oxo-17α-pregna-4-ene-21,17-carbolactone

Crystal data

$C_{23}H_{30}O_3$	D_x = 1.216 Mg m^{-3}
M_r = 354.47	Melting point = 427–429 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 25 reflections
a = 11.964 (8) Å	θ = 10.8–12.0º
b = 12.647 (5) Å	μ = 0.08 mm^{-1}
c = 12.793 (4) Å	*T* = 295 (2) K
V = 1935.7 (16) Å^3	Prismatic, colourless
Z = 4	0.40 × 0.35 × 0.15 mm
F_{000} = 768	

Data collection

Enraf–Nonius CAD4 diffractometer	R_{int} = 0.028
Radiation source: fine-focus sealed tube	θ_{max} = 25.2º
Monochromator: graphite	θ_{min} = 2.3º

T = 295(2) K	h = 0→14
ω/2θ scans	k = −1→15
Absorption correction: none	l = 0→15
2175 measured reflections	3 standard reflections
1989 independent reflections	every 60 min
1183 reflections with $I > 2\sigma(I)$	intensity decay: 0.1%

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.1311P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{max} < 0.001$
S = 1.03	$\Delta\rho_{max} = 0.19$ e Å^{-3}
1989 reflections	$\Delta\rho_{min} = -0.12$ e Å^{-3}
238 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.038 (3)
Secondary atom site location: difference Fourier map	

Special details

Experimental. IR (KBr, cm^{-1}) 3514, 2945, 1770, 1670, 1612, 1190, 1016, 923, 901, 864, 680, 516. ^{1}H NMR ($CDCl_3$) 5.76 (s, 1H, C=CH), 1.03–2.63 (m, 21H), 1.21 (s, 3H, –CH_3), 1.03 (s, 3H, –CH_3), 0.47 (q, 2H, methylene).

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	−0.2159 (3)	0.9187 (3)	0.1112 (5)	0.196 (3)
O2	0.5682 (2)	0.6374 (2)	0.43323 (19)	0.0708 (8)
O3	0.5940 (3)	0.4708 (3)	0.4846 (2)	0.0979 (11)
C1	0.0138 (3)	0.7426 (3)	0.1572 (3)	0.0579 (9)
H1A	0.0356	0.6732	0.1323	0.070*
H1B	−0.0053	0.7359	0.2305	0.070*
C2	−0.0889 (3)	0.7778 (3)	0.0978 (3)	0.0731 (12)

H2A	−0.0748	0.7719	0.0233	0.088*
H2B	−0.1508	0.7314	0.1149	0.088*
C3	−0.1200 (4)	0.8877 (4)	0.1227 (4)	0.0961 (16)
C4	−0.0318 (3)	0.9583 (3)	0.1544 (3)	0.0738 (12)
H4	−0.0511	1.0275	0.1711	0.089*
C5	0.0768 (3)	0.9308 (3)	0.1615 (3)	0.0535 (9)
C6	0.1659 (3)	1.0119 (3)	0.1788 (3)	0.0634 (10)
H6A	0.1311	1.0792	0.1949	0.076*
H6B	0.2085	1.0205	0.1148	0.076*
C7	0.2457 (3)	0.9819 (3)	0.2677 (3)	0.0598 (10)
H7A	0.3060	1.0329	0.2712	0.072*
H7B	0.2058	0.9839	0.3337	0.072*
C8	0.2943 (3)	0.8713 (2)	0.2511 (2)	0.0449 (8)
H8	0.3425	0.8719	0.1892	0.054*
C9	0.1999 (3)	0.7905 (2)	0.2348 (2)	0.0444 (8)
H9	0.1567	0.7916	0.2999	0.053*
C10	0.1143 (3)	0.8175 (2)	0.1471 (2)	0.0467 (8)
C11	0.2461 (3)	0.6768 (3)	0.2263 (3)	0.0546 (9)
H11A	0.1841	0.6278	0.2199	0.066*
H11B	0.2911	0.6710	0.1635	0.066*
C12	0.3170 (3)	0.6461 (3)	0.3208 (3)	0.0548 (9)
H12A	0.3463	0.5753	0.3112	0.066*
H12B	0.2708	0.6462	0.3832	0.066*
C13	0.4138 (3)	0.7240 (2)	0.3346 (2)	0.0482 (8)
C14	0.3620 (3)	0.8358 (2)	0.3451 (2)	0.0507 (9)
H14	0.3057	0.8272	0.4001	0.061*
C15	0.4509 (3)	0.9039 (3)	0.3963 (3)	0.0713 (12)
H15	0.4268	0.9675	0.4337	0.086*
C16	0.5281 (3)	0.8279 (3)	0.4522 (3)	0.0800 (13)
H16	0.5509	0.8473	0.5232	0.096*
C17	0.4799 (3)	0.7185 (3)	0.4376 (3)	0.0615 (10)
C18	0.4921 (3)	0.7078 (3)	0.2392 (3)	0.0645 (11)
H18A	0.4801	0.6387	0.2103	0.097*
H18B	0.5685	0.7144	0.2612	0.097*
H18C	0.4760	0.7604	0.1872	0.097*
C19	0.1670 (3)	0.8072 (3)	0.0371 (2)	0.0623 (10)
H19A	0.1143	0.8306	−0.0146	0.093*
H19B	0.1863	0.7347	0.0242	0.093*
H19C	0.2331	0.8501	0.0333	0.093*
C20	0.5711 (3)	0.8954 (4)	0.3656 (4)	0.0929 (15)
H20A	0.5883	0.8613	0.2997	0.111*
H20B	0.6201	0.9536	0.3839	0.111*
C21	0.5375 (4)	0.5488 (4)	0.4848 (3)	0.0721 (12)
C22	0.4292 (4)	0.5656 (3)	0.5394 (3)	0.0802 (13)
H22A	0.4332	0.5416	0.6113	0.096*
H22B	0.3691	0.5284	0.5042	0.096*
C23	0.4118 (4)	0.6842 (3)	0.5342 (3)	0.0742 (12)
H23A	0.4394	0.7184	0.5969	0.089*
H23B	0.3333	0.7012	0.5255	0.089*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.078 (2)	0.142 (4)	0.370 (8)	0.052 (2)	−0.080 (4)	−0.108 (4)
O2	0.0616 (15)	0.0783 (18)	0.0723 (16)	0.0173 (15)	−0.0096 (14)	0.0074 (15)
O3	0.108 (2)	0.091 (2)	0.095 (2)	0.047 (2)	−0.0054 (19)	0.0140 (18)
C1	0.048 (2)	0.066 (2)	0.060 (2)	0.0054 (19)	−0.0064 (19)	−0.0075 (19)
C2	0.059 (2)	0.082 (3)	0.079 (3)	0.010 (2)	−0.014 (2)	−0.016 (2)
C3	0.059 (2)	0.099 (4)	0.130 (4)	0.031 (3)	−0.025 (3)	−0.033 (3)
C4	0.070 (3)	0.065 (2)	0.087 (3)	0.026 (2)	−0.011 (2)	−0.019 (2)
C5	0.055 (2)	0.056 (2)	0.049 (2)	0.0097 (18)	−0.0015 (19)	0.0020 (17)
C6	0.071 (2)	0.051 (2)	0.068 (2)	0.015 (2)	−0.002 (2)	0.003 (2)
C7	0.064 (2)	0.0417 (19)	0.073 (2)	0.0032 (19)	−0.006 (2)	−0.0055 (18)
C8	0.0448 (17)	0.0428 (18)	0.0472 (18)	0.0042 (16)	0.0000 (16)	−0.0013 (16)
C9	0.0508 (19)	0.0405 (19)	0.0418 (17)	0.0030 (17)	0.0034 (16)	−0.0039 (14)
C10	0.0447 (18)	0.0488 (19)	0.0467 (18)	0.0099 (17)	−0.0009 (16)	−0.0063 (16)
C11	0.055 (2)	0.0464 (19)	0.062 (2)	0.0003 (18)	−0.0076 (19)	−0.0027 (17)
C12	0.061 (2)	0.0485 (19)	0.055 (2)	0.0083 (19)	−0.0062 (18)	0.0003 (18)
C13	0.049 (2)	0.0505 (19)	0.0454 (18)	0.0027 (17)	−0.0033 (18)	−0.0024 (17)
C14	0.0540 (19)	0.0471 (19)	0.0512 (18)	−0.0006 (17)	−0.0006 (17)	−0.0043 (17)
C15	0.076 (3)	0.056 (2)	0.082 (3)	0.003 (2)	−0.025 (2)	−0.013 (2)
C16	0.081 (3)	0.073 (3)	0.086 (3)	−0.003 (3)	−0.038 (3)	−0.010 (2)
C17	0.063 (2)	0.063 (2)	0.058 (2)	0.014 (2)	−0.007 (2)	−0.0036 (19)
C18	0.060 (2)	0.074 (3)	0.060 (2)	0.012 (2)	−0.001 (2)	0.0005 (19)
C19	0.066 (2)	0.070 (3)	0.0507 (18)	0.016 (2)	−0.002 (2)	−0.0015 (18)
C20	0.067 (3)	0.080 (3)	0.132 (4)	−0.018 (2)	−0.021 (3)	0.007 (3)
C21	0.082 (3)	0.079 (3)	0.056 (2)	0.021 (3)	−0.011 (2)	0.009 (2)
C22	0.100 (3)	0.084 (3)	0.057 (2)	0.023 (3)	−0.001 (3)	0.015 (2)
C23	0.087 (3)	0.086 (3)	0.049 (2)	0.022 (3)	−0.006 (2)	0.000 (2)

Geometric parameters (Å, °)

O1—C3	1.221 (5)	C11—H11B	0.9700
O2—C21	1.351 (5)	C12—C13	1.531 (5)
O2—C17	1.473 (4)	C12—H12A	0.9700
O3—C21	1.195 (5)	C12—H12B	0.9700
C1—C2	1.512 (5)	C13—C17	1.538 (5)
C1—C10	1.536 (5)	C13—C14	1.550 (4)
C1—H1A	0.9700	C13—C18	1.551 (5)
C1—H1B	0.9700	C14—C15	1.517 (5)
C2—C3	1.474 (6)	C14—H14	0.9800
C2—H2A	0.9700	C15—C20	1.493 (6)
C2—H2B	0.9700	C15—C16	1.512 (6)
C3—C4	1.441 (6)	C15—H15	0.9800
C4—C5	1.349 (5)	C16—C20	1.489 (6)
C4—H4	0.9300	C16—C17	1.511 (5)
C5—C6	1.496 (5)	C16—H16	0.9800
C5—C10	1.513 (5)	C17—C23	1.543 (5)

C6—C7	1.533 (5)	C18—H18A	0.9599
C6—H6A	0.9700	C18—H18B	0.9599
C6—H6B	0.9700	C18—H18C	0.9599
C7—C8	1.530 (5)	C19—H19A	0.9599
C7—H7A	0.9700	C19—H19B	0.9599
C7—H7B	0.9700	C19—H19C	0.9599
C8—C14	1.518 (4)	C20—H20A	0.9700
C8—C9	1.537 (4)	C20—H20B	0.9700
C8—H8	0.9800	C21—C22	1.487 (6)
C9—C11	1.544 (4)	C22—C23	1.516 (6)
C9—C10	1.557 (4)	C22—H22A	0.9700
C9—H9	0.9800	C22—H22B	0.9700
C10—C19	1.548 (4)	C23—H23A	0.9700
C11—C12	1.527 (4)	C23—H23B	0.9700
C11—H11A	0.9700		
C21—O2—C17	111.4 (3)	C12—C13—C17	117.3 (3)
C2—C1—C10	114.4 (3)	C12—C13—C14	107.1 (3)
C2—C1—H1A	108.7	C17—C13—C14	99.9 (3)
C10—C1—H1A	108.7	C12—C13—C18	106.4 (3)
C2—C1—H1B	108.7	C17—C13—C18	110.9 (3)
C10—C1—H1B	108.7	C14—C13—C18	115.5 (3)
H1A—C1—H1B	107.6	C15—C14—C8	123.3 (3)
C3—C2—C1	112.0 (4)	C15—C14—C13	105.9 (3)
C3—C2—H2A	109.2	C8—C14—C13	114.4 (3)
C1—C2—H2A	109.2	C15—C14—H14	103.6
C3—C2—H2B	109.2	C8—C14—H14	103.6
C1—C2—H2B	109.2	C13—C14—H14	103.6
H2A—C2—H2B	107.9	C20—C15—C16	59.4 (3)
O1—C3—C4	121.5 (4)	C20—C15—C14	121.4 (4)
O1—C3—C2	120.9 (5)	C16—C15—C14	105.8 (3)
C4—C3—C2	117.4 (4)	C20—C15—H15	118.1
C5—C4—C3	124.3 (4)	C16—C15—H15	118.1
C5—C4—H4	117.8	C14—C15—H15	118.1
C3—C4—H4	117.8	C20—C16—C15	59.7 (3)
C4—C5—C6	121.3 (3)	C20—C16—C17	124.4 (4)
C4—C5—C10	121.5 (3)	C15—C16—C17	106.9 (3)
C6—C5—C10	117.1 (3)	C20—C16—H16	116.7
C5—C6—C7	112.6 (3)	C15—C16—H16	116.7
C5—C6—H6A	109.1	C17—C16—H16	116.7
C7—C6—H6A	109.1	O2—C17—C16	111.7 (3)
C5—C6—H6B	109.1	O2—C17—C13	111.6 (3)
C7—C6—H6B	109.1	C16—C17—C13	105.1 (3)
H6A—C6—H6B	107.8	O2—C17—C23	102.3 (3)
C8—C7—C6	111.1 (3)	C16—C17—C23	111.1 (3)
C8—C7—H7A	109.4	C13—C17—C23	115.3 (3)
C6—C7—H7A	109.4	C13—C18—H18A	109.5
C8—C7—H7B	109.4	C13—C18—H18B	109.5
C6—C7—H7B	109.4	H18A—C18—H18B	109.5
H7A—C7—H7B	108.0	C13—C18—H18C	109.5

C14—C8—C7	111.2 (3)	H18A—C18—H18C	109.5
C14—C8—C9	107.6 (3)	H18B—C18—H18C	109.5
C7—C8—C9	110.3 (3)	C10—C19—H19A	109.5
C14—C8—H8	109.2	C10—C19—H19B	109.5
C7—C8—H8	109.2	H19A—C19—H19B	109.5
C9—C8—H8	109.2	C10—C19—H19C	109.5
C8—C9—C11	111.4 (3)	H19A—C19—H19C	109.5
C8—C9—C10	115.8 (3)	H19B—C19—H19C	109.5
C11—C9—C10	112.9 (3)	C16—C20—C15	60.9 (3)
C8—C9—H9	105.2	C16—C20—H20A	117.7
C11—C9—H9	105.2	C15—C20—H20A	117.7
C10—C9—H9	105.2	C16—C20—H20B	117.7
C5—C10—C1	109.9 (3)	C15—C20—H20B	117.7
C5—C10—C19	108.1 (3)	H20A—C20—H20B	114.8
C1—C10—C19	110.1 (3)	O3—C21—O2	121.9 (4)
C5—C10—C9	108.4 (3)	O3—C21—C22	127.7 (4)
C1—C10—C9	108.6 (3)	O2—C21—C22	110.3 (4)
C19—C10—C9	111.7 (2)	C21—C22—C23	103.9 (4)
C12—C11—C9	112.3 (3)	C21—C22—H22A	111.0
C12—C11—H11A	109.1	C23—C22—H22A	111.0
C9—C11—H11A	109.1	C21—C22—H22B	111.0
C12—C11—H11B	109.1	C23—C22—H22B	111.0
C9—C11—H11B	109.1	H22A—C22—H22B	109.0
H11A—C11—H11B	107.9	C22—C23—C17	103.9 (3)
C11—C12—C13	110.3 (3)	C22—C23—H23A	111.0
C11—C12—H12A	109.6	C17—C23—H23A	111.0
C13—C12—H12A	109.6	C22—C23—H23B	111.0
C11—C12—H12B	109.6	C17—C23—H23B	111.0
C13—C12—H12B	109.6	H23A—C23—H23B	109.0
H12A—C12—H12B	108.1		
C10—C1—C2—C3	−52.0 (5)	C12—C13—C14—C15	160.2 (3)
C1—C2—C3—O1	−155.9 (6)	C17—C13—C14—C15	37.5 (3)
C1—C2—C3—C4	28.0 (6)	C18—C13—C14—C15	−81.5 (4)
O1—C3—C4—C5	−175.3 (6)	C12—C13—C14—C8	−60.6 (3)
C2—C3—C4—C5	0.8 (7)	C17—C13—C14—C8	176.6 (3)
C3—C4—C5—C6	170.4 (4)	C18—C13—C14—C8	57.6 (4)
C3—C4—C5—C10	−6.5 (7)	C8—C14—C15—C20	−93.2 (5)
C4—C5—C6—C7	130.7 (4)	C13—C14—C15—C20	41.3 (5)
C10—C5—C6—C7	−52.2 (4)	C8—C14—C15—C16	−156.7 (3)
C5—C6—C7—C8	53.3 (4)	C13—C14—C15—C16	−22.1 (4)
C6—C7—C8—C14	−173.1 (3)	C14—C15—C16—C20	117.5 (4)
C6—C7—C8—C9	−53.7 (4)	C20—C15—C16—C17	−120.4 (4)
C14—C8—C9—C11	−54.1 (3)	C14—C15—C16—C17	−2.9 (4)
C7—C8—C9—C11	−175.6 (3)	C21—O2—C17—C16	140.6 (3)
C14—C8—C9—C10	175.1 (2)	C21—O2—C17—C13	−102.1 (3)
C7—C8—C9—C10	53.6 (3)	C21—O2—C17—C23	21.7 (4)
C4—C5—C10—C1	−16.6 (5)	C20—C16—C17—O2	83.6 (4)
C6—C5—C10—C1	166.3 (3)	C15—C16—C17—O2	148.1 (3)
C4—C5—C10—C19	103.5 (4)	C20—C16—C17—C13	−37.5 (5)

C6—C5—C10—C19	−73.5 (4)	C15—C16—C17—C13	26.9 (4)
C4—C5—C10—C9	−135.2 (4)	C20—C16—C17—C23	−162.8 (4)
C6—C5—C10—C9	47.7 (4)	C15—C16—C17—C23	−98.4 (4)
C2—C1—C10—C5	45.5 (4)	C12—C13—C17—O2	84.5 (4)
C2—C1—C10—C19	−73.5 (4)	C14—C13—C17—O2	−160.2 (3)
C2—C1—C10—C9	164.0 (3)	C18—C13—C17—O2	−37.9 (4)
C8—C9—C10—C5	−48.6 (3)	C12—C13—C17—C16	−154.2 (3)
C11—C9—C10—C5	−178.7 (3)	C14—C13—C17—C16	−39.0 (3)
C8—C9—C10—C1	−168.0 (3)	C18—C13—C17—C16	83.3 (3)
C11—C9—C10—C1	61.9 (3)	C12—C13—C17—C23	−31.6 (4)
C8—C9—C10—C19	70.4 (3)	C14—C13—C17—C23	83.7 (3)
C11—C9—C10—C19	−59.7 (4)	C18—C13—C17—C23	−154.0 (3)
C8—C9—C11—C12	55.7 (4)	C17—C16—C20—C15	90.5 (4)
C10—C9—C11—C12	−172.0 (3)	C14—C15—C20—C16	−90.5 (4)
C9—C11—C12—C13	−57.3 (4)	C17—O2—C21—O3	174.8 (4)
C11—C12—C13—C17	168.3 (3)	C17—O2—C21—C22	−6.1 (4)
C11—C12—C13—C14	57.1 (3)	O3—C21—C22—C23	166.5 (4)
C11—C12—C13—C18	−67.0 (3)	O2—C21—C22—C23	−12.5 (4)
C7—C8—C14—C15	−49.0 (4)	C21—C22—C23—C17	24.9 (4)
C9—C8—C14—C15	−170.0 (3)	O2—C17—C23—C22	−28.0 (4)
C7—C8—C14—C13	179.7 (3)	C16—C17—C23—C22	−147.3 (3)
C9—C8—C14—C13	58.8 (3)	C13—C17—C23—C22	93.3 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19—H19C···O3^{i}	0.96	2.58	3.540 (5)	177

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

Fig. 1

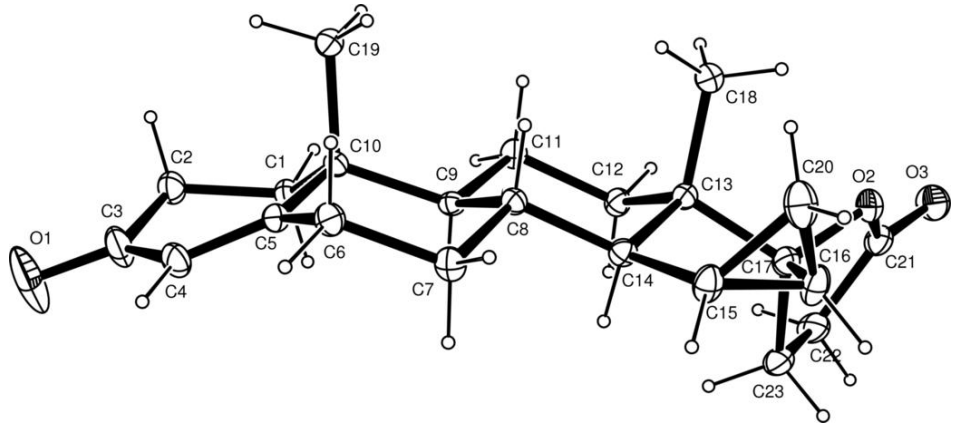

C19
C18
C10
C11
C2
C1
C9
C12
C13
C20
O2
O3
C3
C8
O1
C5
C6
C16
C21
C17
C4
C7
C14
C15
C22
C23

Fig. 2

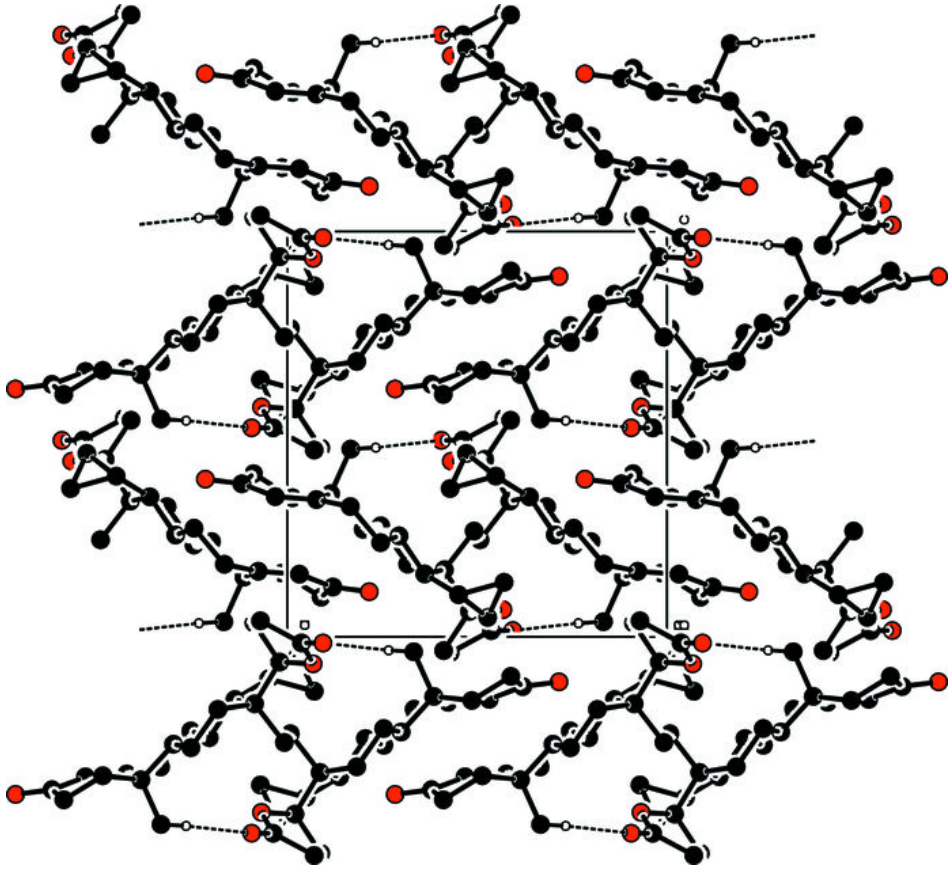
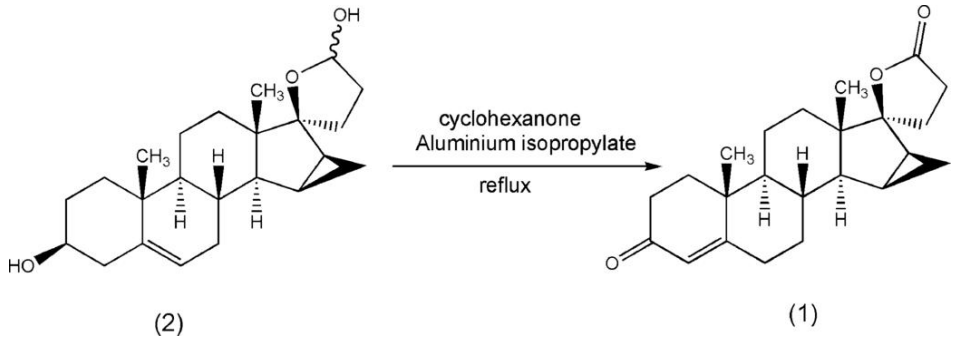


Fig. 3


OH
O
CH3
CH3
H
H
H
HO
cyclohexanone
Aluminium isopropylate
reflux
O
O
CH3
CH3
H
H
H
O

(2) (1)