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3β-Hydroxy-14β-androsta-5,15-dien-17-one

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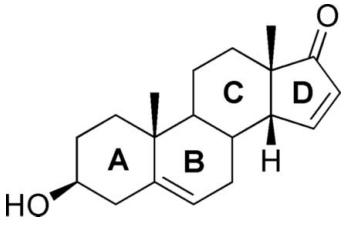
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.067; data-to-parameter ratio = 7.5.

The steric structure of the title compound, $C_{19}H_{26}O_2$, has been reported previously [Sondheimer *et al.* (1960). *J. Am. Chem. Soc.* **82**, 3209–3214] as 14-isoandrosten by optical rotatory dispersion data. The X-ray data of the single crystal shows that ring *A* has a chair conformation and ring *C* has a boat conformation. An O—H···O hydrogen bond between the hydroxyl group and the carbonyl O atom of an adjacent molecule helps to establish infinite chains along the body diagonal of the unit cell.

Related literature

The corresponding steroid without a double bond at C15═C16 was described by Quader *et al.* (2006), with layers of molecules linked by O—H···O hydrogen bonds.

For related literature, see: Bernstein *et al.* (1995); Pataki & Siade (1972); Sondheimer *et al.* (1960).



Experimental

Crystal data

$C_{19}H_{26}O_2$
M_r = 286.40
Monoclinic, $P2_1$
a = 5.9984 (8) Å
b = 11.4923 (14) Å
c = 11.5350 (14) Å
β = 98.413 (1)°
V = 786.61 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 273 (2) K
0.30 × 0.30 × 0.25 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.978, T_{max} = 0.981
4092 measured reflections
1460 independent reflections
1384 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.067
S = 1.12
1460 reflections
194 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.11 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—C17	1.223 (3)	C17—C16	1.446 (3)
O1—C3	1.429 (3)	C15—C16	1.320 (3)
C5—C6	1.330 (3)		
C15—C14—C8	114.72 (17)	C6—C5—C10	122.44 (18)
C15—C14—C13	103.69 (17)	O1—C3—C4	111.22 (19)
C8—C14—C13	113.99 (15)	O2—C17—C16	126.4 (2)
C6—C5—C4	120.82 (18)	C15—C16—C17	110.1 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.82	2.19	2.958 (3)	156

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); 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: AT2272).

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supplementary materials

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3β-Hydroxy-14β-androsta-5,15-dien-17-one

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Comment

The title compound, (I) (Fig 1), a steroid derivative used as an intermediate in the synthesis of steroid hormones, was prepared from dehydroepiandrosterone (Sondheimer *et al.*, 1960, Pataki & Siade, 1972). A Cotton effect positive for the title compound was reported to identify it as 14β isomer. It is a C14 epimer of 3-hydroxyandrosta-5, 15-dien-17- one. The only difference between them lies in that the former is C14β-H, while the latter is C14α-H.

In the solid state of (I), ring A has a chair conformation (Fig. 1), ring C has a boat conformation. The C5═C6 bond length of 1.330 (3)Å confirms the presence of the double bond in this position and imposes an 8β, 9α-half-chair conformation on ring B. Differing from the normal steroid compounds, its C/D ring junction shows *cis* fusion. The five-membered ring D is essentially planar, mainly due to conjugation of the C15═ C16 and C17═ O2 bonds. The C16—C17 bond length of 1.446 (3) Å suggests partial double-bond character.

In (I), the hydroxyl group forms an intermolecular (Bernstein *et al.*, 1995) O—H···O hydrogen bond with the carbonyl atom O2 of an adjacent molecule (Table 2), forming infinite chains along the body diagonal of the unit cell.

Experimental

16α-Brornoandrost-5-en-3β-ol-l7-one (5.04 g, 17.6 mmol) was dissolved in 100 ml of dimethylacetamide, and 7.38 g of lithium bromide and 6.38 g of lithium carbonate were added. The mixture was refluxed for 4 hrs under nitrogen. To the cooled mixture 20% acetic acid was added until no bubble emerged and the mixture was extracted with a 1: 1 mixture of toluene-ether. The organic layer was washed with a 5% $NaHCO_3$ solution and with H_2O. After evaporation of the solvent, the dried solution was recrystallized from acetone to give colorless crystals suitable for X-ray diffraction (yield 23%). Analytical data: m.p. 216.1—216.7º; $[\alpha]_D$= (+)307º (c=2.3, $CHCl_3$); ^{1}HNMR (500 MHz, $CDCl_3$): 0.99 (s, 3H, CH_3-19), 1.09 (s, 3H, CH_3-18), 3.46–3.52(m, 1H, H-3), 5.41–5.42 (m, 1H, H-6), 6.26–6.28(m, 1H, H-16), 7.80(dd, J=2.6 Hz, 1H, H-15); ^{13}C-NMR (126 MHz, $CDCl_3$): 17.71, 19.11, 22.84, 29.75, 30.27, 31.18, 33.52, 36.43, 38.54, 41.94, 42.38, 47.63, 53.69, 71.64, 120.87, 134.59, 141.36, 165.43, 216.49.

Refinement

All the H atoms were placed in geometrically idealized positions and constrained to ride their parent atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Figures

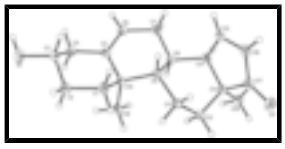

Fig. 1. View of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

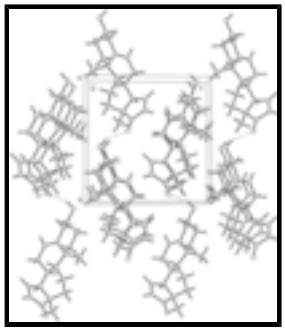

Fig. 2. Packing diagram. Hydrogen bonds are shown as dashed lines.

3β-Hydroxy-14β-androsta-5,15-dien-17-one

Crystal data

$C_{19}H_{26}O_2$	F_{000} = 312
M_r = 286.40	D_x = 1.209 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 5.9984 (8) Å	Cell parameters from 2564 reflections
b = 11.4923 (14) Å	θ = 2.5–27.5º
c = 11.5350 (14) Å	μ = 0.08 mm^{-1}
β = 98.4130 (10)º	T = 273 (2) K
V = 786.61 (17) Å^3	Block, colorless
Z = 2	0.30 × 0.30 × 0.25 mm

Data collection

Bruker SMART CCD area-detector diffractometer	1460 independent reflections
Radiation source: fine-focus sealed tube	1384 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.015
T = 273(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.5º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −7→6
T_{min} = 0.978, T_{max} = 0.981	k = −9→13
4092 measured reflections	l = −13→13

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H-atom parameters constrained
$wR(F^2) = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.0991P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{max} < 0.001$
1460 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
194 parameters	$\Delta\rho_{min} = -0.11$ e Å^{-3}
1 restraint	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.026 (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}
O2	0.0766 (3)	0.92718 (15)	0.65893 (15)	0.0641 (5)
O1	0.0741 (4)	0.05263 (15)	0.88264 (17)	0.0693 (5)
H1	0.0881	0.0018	0.8343	0.104*
C8	0.4141 (3)	0.54983 (17)	0.69129 (16)	0.0332 (4)
H8	0.5373	0.5563	0.7569	0.040*
C9	0.1990 (3)	0.52163 (16)	0.74278 (15)	0.0310 (4)
H9	0.0854	0.4996	0.6765	0.037*
C14	0.3967 (3)	0.66663 (18)	0.62660 (16)	0.0373 (5)
H14	0.5392	0.6802	0.5967	0.045*
C5	0.3398 (3)	0.31637 (17)	0.76381 (16)	0.0345 (4)
C7	0.4703 (3)	0.44943 (19)	0.61473 (17)	0.0418 (5)
H7A	0.3727	0.4529	0.5399	0.050*
H7B	0.6247	0.4573	0.6000	0.050*
C3	0.0842 (4)	0.16448 (19)	0.82944 (19)	0.0466 (5)
H3	−0.0094	0.1632	0.7523	0.056*
C10	0.2314 (3)	0.41454 (16)	0.82460 (15)	0.0313 (4)
C19	0.3807 (4)	0.4429 (2)	0.94150 (16)	0.0434 (5)
H19A	0.4125	0.3726	0.9858	0.065*
H19B	0.3032	0.4965	0.9854	0.065*
H19C	0.5193	0.4772	0.9261	0.065*

C2	−0.0080 (4)	0.2544 (2)	0.90441 (19)	0.0470 (5)
H2B	0.0813	0.2553	0.9816	0.056*
H2A	−0.1618	0.2346	0.9133	0.056*
C6	0.4423 (3)	0.33427 (18)	0.67060 (17)	0.0382 (5)
H6	0.5015	0.2696	0.6375	0.046*
C1	−0.0033 (3)	0.37422 (19)	0.84925 (19)	0.0412 (5)
H1A	−0.0591	0.4304	0.9008	0.049*
H1B	−0.1059	0.3743	0.7760	0.049*
C11	0.1058 (4)	0.63047 (17)	0.79864 (19)	0.0400 (5)
H11A	−0.0271	0.6578	0.7478	0.048*
H11B	0.0604	0.6087	0.8730	0.048*
C17	0.1567 (4)	0.8350 (2)	0.63157 (19)	0.0453 (5)
C13	0.3531 (3)	0.77164 (18)	0.70425 (17)	0.0381 (5)
C4	0.3239 (4)	0.1954 (2)	0.8138 (2)	0.0473 (5)
H4A	0.4198	0.1908	0.8890	0.057*
H4B	0.3785	0.1393	0.7618	0.057*
C15	0.2089 (4)	0.6739 (2)	0.52509 (17)	0.0473 (5)
H15	0.1843	0.6178	0.4665	0.057*
C12	0.2756 (4)	0.72926 (18)	0.81897 (17)	0.0422 (5)
H12A	0.4059	0.7032	0.8725	0.051*
H12B	0.2085	0.7939	0.8555	0.051*
C16	0.0822 (4)	0.7676 (2)	0.52722 (19)	0.0515 (6)
H16	−0.0374	0.7874	0.4699	0.062*
C18	0.5541 (4)	0.8536 (2)	0.7317 (2)	0.0513 (6)
H18A	0.6015	0.8790	0.6599	0.077*
H18B	0.6759	0.8134	0.7784	0.077*
H18C	0.5114	0.9198	0.7741	0.077*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0709 (11)	0.0462 (11)	0.0742 (11)	0.0139 (9)	0.0077 (9)	0.0010 (9)
O1	0.0964 (14)	0.0402 (10)	0.0754 (12)	−0.0073 (10)	0.0256 (11)	0.0106 (9)
C8	0.0339 (10)	0.0377 (11)	0.0284 (9)	0.0004 (8)	0.0059 (8)	−0.0005 (8)
C9	0.0313 (9)	0.0341 (10)	0.0277 (9)	0.0008 (8)	0.0049 (7)	−0.0004 (8)
C14	0.0401 (11)	0.0419 (12)	0.0316 (9)	−0.0037 (9)	0.0105 (8)	0.0034 (9)
C5	0.0327 (10)	0.0338 (11)	0.0362 (10)	0.0015 (8)	0.0019 (8)	−0.0008 (9)
C7	0.0440 (11)	0.0475 (12)	0.0363 (10)	0.0032 (10)	0.0140 (9)	−0.0024 (10)
C3	0.0601 (14)	0.0348 (12)	0.0446 (12)	−0.0052 (10)	0.0069 (10)	0.0056 (10)
C10	0.0311 (9)	0.0332 (10)	0.0298 (9)	0.0003 (8)	0.0054 (7)	−0.0001 (8)
C19	0.0517 (12)	0.0470 (13)	0.0303 (9)	−0.0013 (11)	0.0019 (9)	0.0018 (10)
C2	0.0457 (12)	0.0468 (13)	0.0507 (12)	−0.0056 (11)	0.0148 (10)	0.0074 (11)
C6	0.0390 (11)	0.0366 (12)	0.0401 (10)	0.0048 (9)	0.0094 (8)	−0.0067 (9)
C1	0.0375 (11)	0.0406 (12)	0.0478 (12)	0.0012 (9)	0.0140 (9)	0.0057 (10)
C11	0.0470 (12)	0.0347 (11)	0.0419 (11)	0.0050 (9)	0.0190 (9)	0.0027 (9)
C17	0.0482 (12)	0.0405 (13)	0.0482 (12)	−0.0002 (11)	0.0109 (10)	0.0079 (10)
C13	0.0437 (11)	0.0351 (11)	0.0357 (10)	−0.0017 (9)	0.0070 (9)	0.0023 (9)
C4	0.0552 (13)	0.0372 (12)	0.0503 (12)	0.0078 (10)	0.0110 (10)	0.0019 (10)

C15	0.0640 (14)	0.0477 (13)	0.0289 (10)	−0.0011 (11)	0.0023 (9)	0.0016 (10)
C12	0.0589 (13)	0.0342 (11)	0.0353 (10)	0.0027 (10)	0.0133 (9)	−0.0030 (9)
C16	0.0543 (13)	0.0542 (14)	0.0429 (12)	0.0028 (12)	−0.0031 (10)	0.0090 (11)
C18	0.0554 (13)	0.0476 (13)	0.0502 (12)	−0.0094 (11)	0.0056 (10)	−0.0001 (11)

Geometric parameters (Å, °)

O2—C17	1.223 (3)	C19—H19B	0.9600
O1—C3	1.429 (3)	C19—H19C	0.9600
O1—H1	0.8200	C2—C1	1.518 (3)
C8—C7	1.520 (3)	C2—H2B	0.9700
C8—C14	1.532 (3)	C2—H2A	0.9700
C8—C9	1.532 (3)	C6—H6	0.9300
C8—H8	0.9800	C1—H1A	0.9700
C9—C10	1.546 (2)	C1—H1B	0.9700
C9—C11	1.549 (3)	C11—C12	1.520 (3)
C9—H9	0.9800	C11—H11A	0.9700
C14—C15	1.504 (3)	C11—H11B	0.9700
C14—C13	1.548 (3)	C17—C16	1.446 (3)
C14—H14	0.9800	C17—C13	1.527 (3)
C5—C6	1.330 (3)	C13—C18	1.526 (3)
C5—C4	1.513 (3)	C13—C12	1.544 (3)
C5—C10	1.523 (3)	C4—H4A	0.9700
C7—C6	1.492 (3)	C4—H4B	0.9700
C7—H7A	0.9700	C15—C16	1.320 (3)
C7—H7B	0.9700	C15—H15	0.9300
C3—C2	1.504 (3)	C12—H12A	0.9700
C3—C4	1.518 (3)	C12—H12B	0.9700
C3—H3	0.9800	C16—H16	0.9300
C10—C19	1.540 (3)	C18—H18A	0.9600
C10—C1	1.547 (3)	C18—H18B	0.9600
C19—H19A	0.9600	C18—H18C	0.9600
C3—O1—H1	109.5	C1—C2—H2A	109.5
C7—C8—C14	112.78 (15)	H2B—C2—H2A	108.1
C7—C8—C9	109.60 (16)	C5—C6—C7	125.50 (19)
C14—C8—C9	111.88 (16)	C5—C6—H6	117.3
C7—C8—H8	107.4	C7—C6—H6	117.3
C14—C8—H8	107.4	C2—C1—C10	114.95 (17)
C9—C8—H8	107.4	C2—C1—H1A	108.5
C8—C9—C10	111.56 (15)	C10—C1—H1A	108.5
C8—C9—C11	111.49 (15)	C2—C1—H1B	108.5
C10—C9—C11	114.19 (14)	C10—C1—H1B	108.5
C8—C9—H9	106.3	H1A—C1—H1B	107.5
C10—C9—H9	106.3	C12—C11—C9	113.13 (16)
C11—C9—H9	106.3	C12—C11—H11A	109.0
C15—C14—C8	114.72 (17)	C9—C11—H11A	109.0
C15—C14—C13	103.69 (17)	C12—C11—H11B	109.0
C8—C14—C13	113.99 (15)	C9—C11—H11B	109.0
C15—C14—H14	108.0	H11A—C11—H11B	107.8

C8—C14—H14	108.0	O2—C17—C16	126.4 (2)
C13—C14—H14	108.0	O2—C17—C13	124.9 (2)
C6—C5—C4	120.82 (18)	C16—C17—C13	108.71 (19)
C6—C5—C10	122.44 (18)	C18—C13—C17	110.03 (18)
C4—C5—C10	116.74 (16)	C18—C13—C12	110.16 (17)
C6—C7—C8	111.94 (15)	C17—C13—C12	108.41 (17)
C6—C7—H7A	109.2	C18—C13—C14	113.96 (17)
C8—C7—H7A	109.2	C17—C13—C14	103.66 (16)
C6—C7—H7B	109.2	C12—C13—C14	110.33 (16)
C8—C7—H7B	109.2	C5—C4—C3	111.97 (18)
H7A—C7—H7B	107.9	C5—C4—H4A	109.2
O1—C3—C2	109.22 (18)	C3—C4—H4A	109.2
O1—C3—C4	111.22 (19)	C5—C4—H4B	109.2
C2—C3—C4	109.98 (18)	C3—C4—H4B	109.2
O1—C3—H3	108.8	H4A—C4—H4B	107.9
C2—C3—H3	108.8	C16—C15—C14	113.5 (2)
C4—C3—H3	108.8	C16—C15—H15	123.3
C5—C10—C19	109.08 (16)	C14—C15—H15	123.3
C5—C10—C9	109.42 (14)	C11—C12—C13	112.48 (17)
C19—C10—C9	111.79 (15)	C11—C12—H12A	109.1
C5—C10—C1	108.90 (16)	C13—C12—H12A	109.1
C19—C10—C1	109.29 (16)	C11—C12—H12B	109.1
C9—C10—C1	108.31 (15)	C13—C12—H12B	109.1
C10—C19—H19A	109.5	H12A—C12—H12B	107.8
C10—C19—H19B	109.5	C15—C16—C17	110.1 (2)
H19A—C19—H19B	109.5	C15—C16—H16	124.9
C10—C19—H19C	109.5	C17—C16—H16	124.9
H19A—C19—H19C	109.5	C13—C18—H18A	109.5
H19B—C19—H19C	109.5	C13—C18—H18B	109.5
C3—C2—C1	110.56 (17)	H18A—C18—H18B	109.5
C3—C2—H2B	109.5	C13—C18—H18C	109.5
C1—C2—H2B	109.5	H18A—C18—H18C	109.5
C3—C2—H2A	109.5	H18B—C18—H18C	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.82	2.19	2.958 (3)	156

Symmetry codes: (i) *x*, *y*−1, *z*.

Fig. 1

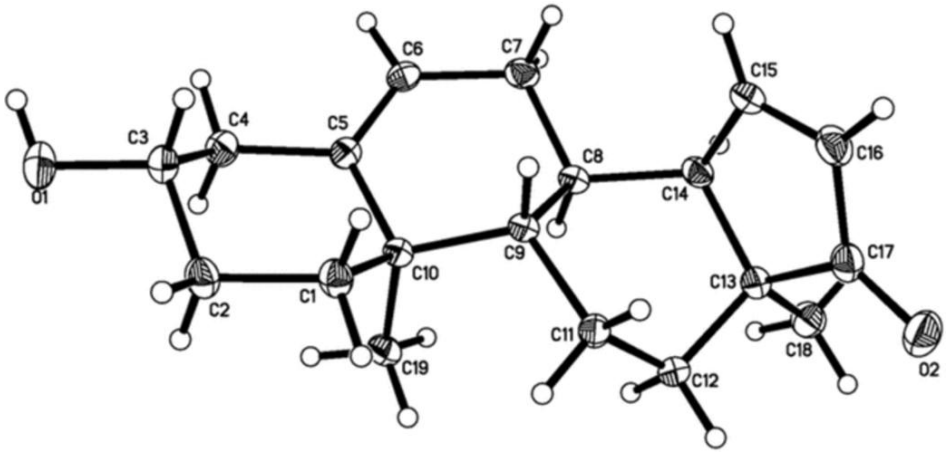
C6
C7
C15
C4
C5
C3
C16
C8
O1
C14
C9
C17
C10
C13
C1
C2
C11
C18
O2
C19
C12

Fig. 2