Data collection

Rigaku R-AXIS II*C* IP diffractometer
Oscillation frame scans
Absorption correction: none
2158 measured reflections
1186 independent reflections
1104 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.064$
$\theta_{\rm max} = 25.62°$
$h = -10 \rightarrow 0$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 13$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.175$
$S = 1.115$
1186 reflections
124 parameters
Only positional coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0948P)^2 + 0.2199P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.394$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.648$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C3	1.485 (5)	C2—C3	1.504 (5)
N2—C1	1.328 (4)	Cl1—O12	1.415 (3)
N2—C2	1.449 (5)	Cl1—O11	1.417 (3)
O1—C1	1.234 (4)	Cl1—O13	1.439 (3)
C1—C1$^{\rm i}$	1.536 (6)	Cl1—O14	1.445 (3)
C1—N2—C2	122.4 (3)	O12—Cl1—O11	110.0 (3)
O1—C1—N2	125.0 (3)	O12—Cl1—O13	109.5 (2)
O1—C1—C1$^{\rm i}$	121.3 (4)	O11—Cl1—O13	108.9 (2)
N2—C1—C1$^{\rm i}$	113.7 (4)	O12—Cl1—O14	108.8 (2)
N2—C2—C3	114.0 (3)	O11—Cl1—O14	110.4 (2)
N1—C3—C2	112.0 (3)	O13—Cl1—O14	109.2 (2)

Symmetry code: (i) $3 - x, 1 - y, 1 - z$.

Diffraction intensities were collected on a Rigaku R-AXIS II*C* image-plate diffractometer by taking oscillation photographs (total oscillation range ϕ = 0–180°, 20 frames in total; oscillation angle $\Delta\phi$ = 9° per frame; exposure time = 8 min per frame). The data set is complete only to 82% due to a blind region in the experimental set-up. H atoms were located in a difference map and the positional coordinates were refined.

Cell refinement: *BIOTEX* (Pflugrath *et al.*, 1996). Data reduction: *BIOTEX*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXS*86. Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1034). Services for accessing these data are described at the back of the journal.

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3,17-Dioxo-4-oxaandrostane-5α-carbaldehyde

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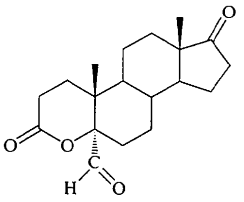
Abstract

The title compound, $C_{19}H_{26}O_4$, has a C5 atom with an unusual environment, which leads to a molecular 5α configuration. Ring *A* is highly flattened. The carbaldehyde group is slightly disordered, with interchange of the H and O positions.

Comment

This work is part of an ongoing project of the structure determination of steroids with clinical interest and their precursors (Ramos Silva *et al.*, 1996; Andrade *et al.*, 1997; Paixão *et al.*, 1997; Paixão, Andrade, de Almeida, Costa *et al.*, 1998; Paixão, Andrade, de Almeida, Tavares da Silva *et al.*, 1998). During former studies leading to an improved synthesis of formestane (Tavares da Silva *et al.*, 1996), an aromatase inhibitor used to treat breast cancer, the title compound, (I), has been isolated as one of the products obtained through oxidation of androst-4-ene-3,17-dione with potassium permanganate. Knowing that *trans*-fused aldehydo lactones of this type can be important intermediates in preparing 4-cyclooctenone derivatives, *e.g.* in steroids to increase a biological response (Philippo *et al.*, 1991), we have successfully increased the amount of the title compound in the product distribution by changing the reaction conditions.



(I)

The assignment of the stereochemistry for the stereogenic centre at the C5 position is one of the purposes of this work. The X-ray analysis clearly establishes a 5α configuration for the molecular structure. All rings are fused *trans*. A shorter than usually reported C═O bond in the carbaldehyde group was observed, and there is evidence that this group is slightly disordered, with interchange of the H and O positions. Due to the highly planar environment of the C3 atom, as evidenced by the sum of the valence angles around this atom of 359.9 (5)°, ring *A* is highly distorted, assuming a 2α,3β-half-chair conformation [asymmetry parameters (Duax & Norton, 1975) are $\Delta C_2(2,3)$ = 3.6 (4), $\Delta C_s(2)$ = 33.8 (3) and $\Delta C_s(1)$ = 63.4 (3)°]. Rings *B* and *C* are slightly flattened, the mean values of their torsion angles being 55 (1) and 56 (2)°, respectively. The five-membered *D* ring assumes a conformation intermediate between a 14α-envelope and a 13β,14α-half-chair conformation [pseudorotation (Altona *et al.*, 1968) and asymmetry parameters (Duax & Norton, 1975) being Δ = −18.0 (6), φ_m = 43.8 (2), $\Delta C_s(14)$ = 8.3 (3) and $\Delta C_2(13,14)$ = 10.8 (3)°]. As normally found in similar structures, the four atoms C13, C16, C17 and O17 are coplanar, as can be seen from the sum of the valence angles around C17 of 360.1 (5)°. The distance between the terminal O atoms, O3 and O17, is 10.639 (5) Å. The pseudotorsion angle C19—C10···C13—C18 is 0.3 (2)°, indicating that the molecule is practically untwisted.

Cohesion of the structure is achieved mainly by van der Waals interactions. However, three weak C—H···O hydrogen-bond interactions might be considered: intramolecular C9···O51*A* [3.136 (5) Å], C6···O17^{i} [3.387 (4) Å] and C51···O17^{ii} [3.110 (4) Å] [symmetry codes: (i) $1-x$, $\frac{1}{2}+y$, $-z$; (ii) $-x$, $\frac{1}{2}+y$, $-z$].

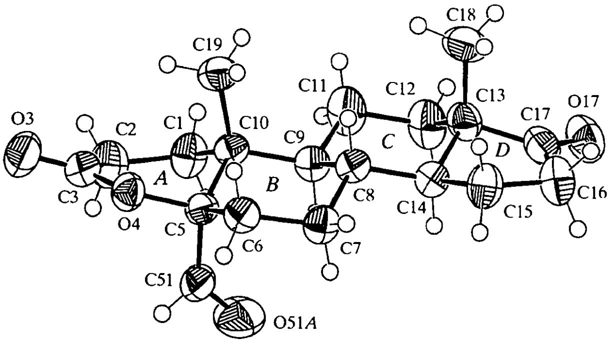


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

To prepare the title compound, a 2.5% solution of potassium permanganate in aqueous KOH 0.05 *N* (130 ml, 20.6 mmol) was added dropwise to a cold (268 K) stirred solution of androst-4-ene-3,17-dione (3.0 g, 10.5 mmol) in methanol (200 ml). The temperature was then raised to 288 K and after 5–10 min the excess oxidant was destroyed with saturated aqueous $Na_2S_2O_5$ (20 ml). After separation of the formed MnO_2 by centrifugation, the methanol was evaporated and the solution diluted with water (200 ml), neutralized with aqueous 1 *N* H_2SO_4, and extracted with dichloromethane (3 × 100 ml). The organic extract was washed with 10% aqueous $Na_2S_2O_5$ (100 ml) and then water (2 × 100 ml), dried ($MgSO_4$) and evaporated to dryness to give 1.36 g (41%) of a crude product from which the title compound was isolated by crystallization (m.p. 447–448 K). Analysis found: C 71.60, H 8.56%; $C_{19}H_{26}O_4$ requires: C 71.67, H 8.23%); IR (KBr disc) ν_{max}: 2750 (C—H), 1720–1760 (C3═O, C17═O, C51═O), 1245, 1050 cm^{-1} (C—O); ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si): δ_H 0.91 (3H, *s*, 18H-3), 1.22 (3H, *s*, 19H-3), 2.13 (1H, *ddd*, $J_{16\alpha,16\beta}$ = 19.5, $J_{16\alpha,15\beta}$ = 9.0, $J_{16\alpha,15\alpha}$ = 9.0 Hz, 16α-H), 2.50 (1H, *ddd*, $J_{16\beta,16\alpha}$ = 19.5, $J_{16\beta,15\beta}$ = 9.0, $J_{16\beta,15\alpha}$ = 1.0 Hz, 16β-H), 2.57 (1H, *ddd*, $J_{2\alpha,2\beta}$ = 19.5, $J_{2\alpha,1\alpha}$ = 10.0, $J_{2\alpha,1\beta}$ = 2.5 Hz, 2α-H), 2.68 (1H, *ddd*, $J_{2\beta,2\alpha}$ = 19.5, $J_{2\beta,1\alpha}$ = 9.5, $J_{2\beta,1\beta}$ = 7.5 Hz, 2β-H), 10.0 p.p.m. (1H, *s*, 51-H); ^{13}C NMR (50.3 MHz, $CDCl_3$, Me_4Si): δ_C 13.7 (C18), 14.3 (C19), 20.5, 21.5, 25.5, 26.9, 27.0, 28.8, 30.9, 33.8, 35.5, 38.9, 47.5, 47.6, 50.5, 88.0 (C5), 170.5 (C3), 200.1 (C51), 219.7 p.p.m. (C17). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the steroid in absolute ethanol.

Crystal data

$C_{19}H_{26}O_4$
M_r = 318.40
Monoclinic
$P2_1$
a = 6.893 (4) Å
b = 18.222 (8) Å
c = 6.981 (3) Å
β = 108.05 (5)°
V = 833.8 (7) Å^3
Z = 2
D_x = 1.268 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.03–15.63°
μ = 0.087 mm^{-1}
T = 293 (2) K
Prism
0.49 × 0.24 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: none
3648 measured reflections
1955 independent reflections
1385 reflections with $I > 2\sigma(I)$

R_{int} = 0.033
θ_{max} = 27.40°
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 23$
$l = -9 \rightarrow 8$
3 standard reflections
frequency: 180 min
intensity decay: 3.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.113$
$S = 1.056$
1955 reflections
221 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.1143P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.171$ e Å^{-3}
$\Delta\rho_{\min} = -0.166$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O3—C3	1.199 (4)	C5—C51	1.485 (4)
O4—C3	1.349 (4)	C13—C17	1.516 (4)
O4—C5	1.454 (3)	C16—C17	1.513 (5)
O17—C17	1.209 (4)	C51—O51*A*	1.190 (2)
C2—C3	1.501 (5)	C51—O51*B*	1.198 (2)
O3—C3—O4	118.1 (3)	O17—C17—C16	125.2 (3)
O3—C3—C2	122.8 (3)	O17—C17—C13	126.4 (3)
O4—C3—C2	119.0 (3)	C16—C17—C13	108.5 (3)

It should be noted that because none of the atoms are strong enough anomalous scatterers at the Mo $K\alpha$ wavelength, the absolute configuration was not determined by the X-ray data, and the assumed chirality of the molecule is that determined from the synthesis route. The H atoms of the organic moiety were placed at calculated positions and refined as riding using *SHELXL*97 (Sheldrick, 1997) defaults. During the refinement, the C=O bond length refined to an unusually short 1.14 Å, while the electron density at the carbaldehyde H-atom position was found to be higher than expected. Considering the possibility of disorder, the carbaldehyde group was split into two groups with the O- and H-atom positions interchanged. The occupancy of the two alternate fragments were constrained to unity and the C=O and C—H bond lengths restrained to 1.20 and 0.98 Å, respectively. The refinement gave a more satisfactory fit than the original refinement. The refined occupancy of the two groups was 0.842 (7)/0.158 (7). Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice. All calculations were performed on a Pentium 150 MHz PC running LINUX.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1231). Services for accessing these data are described at the back of the journal.

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2-(*N*,*N*-Dimethylamino)-6-hydroxy-1,4-naphthoquinone

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Abstract

The title compound, $C_{12}H_{11}NO_3$, is an intermediate in the synthesis of furonaphthoquinones. There are two molecules in the asymmetric unit. In one of them all the