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3,8α-Dihydroxyestra-1,3,5(10),6-tetraen-17-one

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Abstract

The molecular parameters of the title compound, $C_{18}H_{20}O_3$, are all within normal limits. The A/B ring junction is planar and the C/D junction is *trans*, as expected. However, the B/C junction is *cis* with an interplanar angle of 65.1 (2)°. There are only two intermolecular contacts involving the 8α-hydroxyl of one molecule and the 3-hydroxyl and 17-keto O atoms on two symmetry related molecules.

Comment

The title compound (I) was synthesized as described by Cao & Liehr (1993). The crystal structure study was undertaken to ascertain the conformation of the

(I)
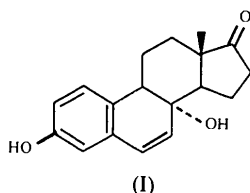
compound and to determine on which face of the steroid skeleton the 8-hydroxyl group was located. Fig. 1 shows the structure of the molecule in the asymmetric unit with the thermal vibration ellipsoids of the non-H atoms. Bond lengths, bond angles and torsion angles of the non-H atoms are given in Table 2 and are within the range of expected values (Duax & Norton, 1975; Griffin, Duax & Weeks, 1984). The packing of the molecules is shown in Fig. 2. All intermolecular distances correspond to normal van der Waals interactions. The only intermolecular contacts involve O8 with $O3(-x, y - \frac{1}{2}, \frac{1}{2} - z)$ [2.715 (5) Å] and $O17(\frac{1}{2} - x, 2 - y, z - \frac{1}{2})$ [2.804 (5) Å] resulting in an O3···O8···O17 angle of 92.3 (2)°. Steroid ring A (C1, C2, C3, C4, C5, C10) possesses bond parameters consistent with a benzene ring and is planar to within experimental error. The O3 hydroxyl group is coplanar with ring A. The asymmetry parameters defined by Duax & Norton (1975) for ring A range from 0.6 to 2.8° with $\langle \tau \rangle = 1.2°$. Ring B (C5, C6, C7, C8, C9, C10) adopts a distorted sofa conformation largely due to the unsaturated C5—C10 and C6—C7 bonds. C9 is nearly coplanar with the plane formed by the atoms of ring A and O3. C7 and C8 deviate from this plane towards the α face of the molecule. The asymmetry parameters are $\Delta C_2^{5,6} = 7.2°$, $\Delta C_s^6 = 14.9°$ and $\Delta C_s^7 = 39.9°$, with $\langle \tau \rangle = 22.8°$. These data indicate that ring B is distorted from the C9α,C10β-half-chair conformation ($\Delta C_2 = 0°$) towards a C8α-sofa conformation. Ring C (C8, C9, C11, C12, C13, C14) does not have any unusual substituents and assumes the commonly found chair conformation ($\Delta C_2^{9,11} = 2.5°$, $\Delta C_s^{11} = 3.0°$, $\langle \tau \rangle = 55.4°$).
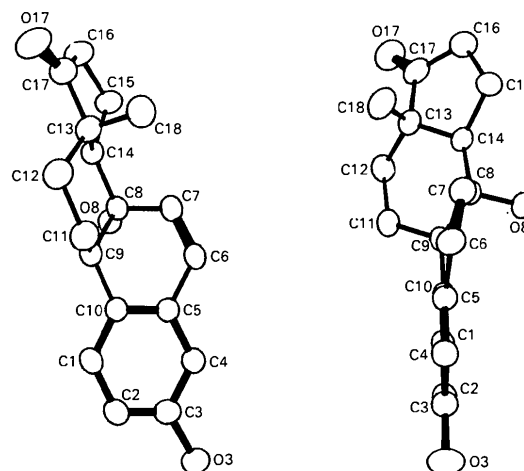

Fig. 1. Two orthogonal views of the molecular structure of the estratetraene in the asymmetric unit showing the numbering scheme and the thermal vibration ellipsoids of the non-H atoms. The thickest lines denote the double bonds.
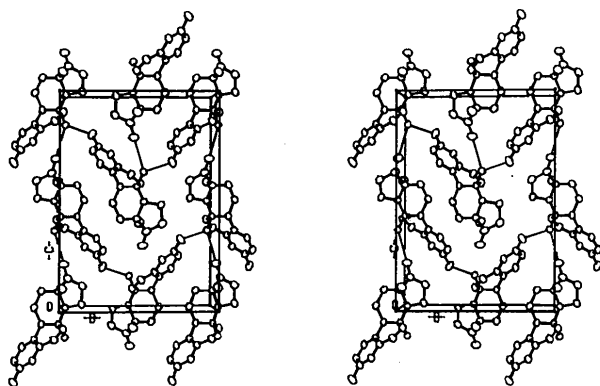
$C_{18}H_{20}O_3$

Fig. 2. Stereoview along the a axis showing the molecular packing. Thin lines depict the hydrogen bonds between O8 and O3$(-x, y-\frac{1}{2}, \frac{1}{2}-z)$ and O17$(\frac{1}{2}-x, 2-y, z-\frac{1}{2})$.

The D-ring (C13, C14, C15, C16, C17) pseudo-rotation parameters, $\Delta = -23.6°$ and $\varphi_m = 44.0°$, are near those of a 14α-envelope conformation ($\Delta = -36.0°$, $\varphi_m = 46.7°$) (Altona, Geise & Romers, 1968). This is consistent with the finding by Duax, Weeks & Rohrer (1976) that the other steroid D rings that have an sp^2-hybrid C17 atom have a 14α-envelope conformation.

The A/B ring junction is planar and the C/D junction is *trans* (Fig. 1, Table 2). However, the B/C junction is *cis*. The angle between the least-squares mean plane of rings B and C is 65.1 (2)°.

The overall conformation of rings A, B and C of the title compound is very nearly identical with the conformation of estra-1,3,5(10),6-tetraene-3-methoxy-8α-methyl-17β-bromoacetoxy (Weber & Galantay, 1972). The O8 hydroxyl group of the title compound is orientated on the α face of the molecule, as is the respective 8α-methyl group of the related estratetraene compound. The D-ring conformation is as found in a 9(11)-estratetraene compound which has a keto O atom on C17 (Pitt, Rector, White, Wani, McPhail & Onan, 1977).

Experimental

Crystal data

$C_{18}H_{20}O_3$
$M_r = 284.4$
Orthorhombic
$P2_12_12_1$
$a = 6.192$ (1) Å
$b = 13.990$ (1) Å
$c = 16.883$ (2) Å
$V = 1462.6$ (5) Å^3
$Z = 4$
$D_x = 1.291$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 24 reflections
$\theta = 10-35°$
$\mu = 0.658$ mm^{-1}
$T = 292$ K
Irregular
$0.5 \times 0.4 \times 0.3$ mm
Colorless
Crystal source: diethyl ether

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DI-FABS*; Walker & Stuart, 1983)
$T_{min} = 0.81$, $T_{max} = 1.51$
1627 measured reflections
1627 independent reflections

1607 observed reflections
$[I > 3\sigma(I)]$
$\theta_{max} = 70°$
$h = -7 \to 0$
$k = -17 \to 0$
$l = -20 \to 0$
3 standard reflections frequency: 60 min intensity variation: none

Refinement

Refinement on F
$R = 0.067$
$wR = 0.066$
$S = 1.006$
1607 reflections
267 parameters
All H-atom parameters refined

Unit weights applied
$(\Delta/\sigma)_{max} = 0.03$
$\Delta\rho_{max} = 0.25$ (1) e Å^{-3}
$\Delta\rho_{min} = -0.33$ (1) e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for non-H atoms; B_{iso} for H. Coordinates of HO3 were restrained in the last cycles of refinement.

	x	y	z	B_{iso}/B_{eq}
C1	0.0831 (9)	1.2421 (3)	0.3230 (3)	3.17 (9)
C2	-0.0297 (9)	1.2862 (3)	0.2621 (3)	3.4 (1)
C3	-0.2295 (9)	1.2498 (3)	0.2398 (3)	3.5 (1)
O3	-0.3548 (7)	1.2889 (3)	0.1799 (2)	4.85 (8)
C4	-0.3130 (9)	1.1682 (3)	0.2764 (3)	3.22 (9)
C5	-0.1948 (8)	1.1238 (3)	0.3360 (3)	2.88 (9)
C6	-0.2713 (8)	1.0328 (3)	0.3694 (3)	3.33 (9)
C7	-0.1430 (8)	0.9774 (3)	0.4131 (3)	3.16 (9)
C8	0.0898 (8)	1.0046 (3)	0.4277 (2)	2.51 (8)
O8	0.2149 (6)	0.9658 (2)	0.3617 (2)	3.07 (6)
C9	0.1200 (8)	1.1147 (3)	0.4288 (3)	2.87 (9)
C10	0.0052 (8)	1.1606 (3)	0.3601 (3)	2.78 (8)
C11	0.0427 (9)	1.1594 (3)	0.5076 (3)	3.6 (1)
C12	0.147 (1)	1.1141 (4)	0.5810 (3)	4.01 (1)
C13	0.1076 (9)	1.0056 (3)	0.5799 (3)	3.21 (9)
C14	0.1929 (8)	0.9635 (3)	0.5018 (2)	2.80 (8)
C15	0.200 (1)	0.8547 (3)	0.5165 (3)	3.8 (1)
C16	0.287 (1)	0.8494 (4)	0.6024 (3)	4.2 (1)
C17	0.237 (1)	0.9469 (4)	0.6386 (3)	3.9 (1)
O17	0.2948 (9)	0.9726 (3)	0.7037 (2)	5.7 (1)
C18	-0.132 (1)	0.9835 (4)	0.5996 (3)	4.4 (1)
HO3	-0.293	1.346	0.168	7 (2)
HO8	0.183 (8)	0.992 (3)	0.319 (3)	1 (1)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.388 (7)	C8—C14	1.518 (6)
C1—C10	1.387 (7)	C9—C10	1.505 (7)
C2—C3	1.389 (8)	C9—C11	1.545 (7)
C3—O3	1.387 (6)	C11—C12	1.535 (8)
C3—C4	1.398 (7)	C12—C13	1.538 (7)
C4—C5	1.391 (7)	C13—C14	1.538 (7)
C5—C6	1.470 (6)	C13—C17	1.517 (7)
C5—C10	1.402 (7)	C13—C18	1.553 (9)
C6—C7	1.333 (7)	C14—C15	1.542 (7)
C7—C8	1.511 (7)	C15—C16	1.548 (7)
C8—O8	1.461 (6)	C16—C17	1.527 (8)
C8—C9	1.552 (6)	C17—O17	1.210 (6)
C2—C1—C10	121.7 (5)	C1—C10—C5	118.6 (5)
C1—C2—C3	119.1 (5)	C1—C10—C9	122.3 (5)
C2—C3—O3	123.5 (5)	C5—C10—C9	118.9 (4)

C2—C3—C4	120.6 (5)	C9—C11—C12	113.4 (4)
O3—C3—C4	115.9 (5)	C11—C12—C13	109.3 (5)
C3—C4—C5	119.4 (5)	C12—C13—C14	109.5 (4)
C4—C5—C6	119.7 (5)	C12—C13—C17	116.2 (5)
C4—C5—C10	120.7 (4)	C12—C13—C18	110.2 (5)
C6—C5—C10	119.5 (4)	C14—C13—C17	99.8 (4)
C5—C6—C7	121.6 (5)	C14—C13—C18	115.8 (5)
C6—C7—C8	120.8 (5)	C17—C13—C18	105.1 (5)
C7—C8—O8	106.7 (4)	C8—C14—C13	114.7 (4)
C7—C8—C9	111.5 (4)	C8—C14—C15	121.2 (4)
C7—C8—C14	116.1 (4)	C13—C14—C15	104.5 (4)
O8—C8—C9	108.4 (4)	C14—C15—C16	102.0 (4)
O8—C8—C14	105.4 (4)	C15—C16—C17	105.2 (5)
C9—C8—C14	108.3 (4)	C13—C17—C16	109.2 (4)
C8—C9—C10	110.9 (4)	C13—C17—O17	126.0 (6)
C8—C9—C11	112.1 (4)	C16—C17—O17	124.8 (6)
C10—C9—C11	110.1 (4)		
C10—C1—C2—C3	2.5 (7)	C9—C8—C14—C13	56.1 (5)
C2—C1—C10—C5	−1.4 (7)	C9—C8—C14—C15	−177.0 (4)
C2—C1—C10—C9	−176.9 (4)	C8—C9—C10—C1	−146.8 (4)
C1—C2—C3—O3	179.8 (4)	C8—C9—C10—C5	37.6 (6)
C1—C2—C3—C4	−2.0 (7)	C11—C9—C10—C1	88.5 (6)
C2—C3—C4—C5	0.4 (7)	C11—C9—C10—C5	−87.1 (5)
O3—C3—C4—C5	178.8 (4)	C8—C9—C11—C12	54.2 (6)
C3—C4—C5—C6	−174.0 (4)	C10—C9—C11—C12	178.1 (4)
C3—C4—C5—C10	0.7 (7)	C9—C11—C12—C13	−55.3 (6)
C4—C5—C6—C7	164.9 (5)	C11—C12—C13—C14	55.7 (6)
C10—C5—C6—C7	−9.9 (7)	C11—C12—C13—C17	167.9 (4)
C4—C5—C10—C1	−0.3 (7)	C11—C12—C13—C18	−72.8 (5)
C4—C5—C10—C9	175.5 (4)	C12—C13—C14—C8	−59.3 (5)
C6—C5—C10—C1	174.5 (4)	C12—C13—C14—C15	165.6 (4)
C6—C5—C10—C9	−9.7 (6)	C17—C13—C14—C8	178.2 (4)
C5—C6—C7—C8	−2.1 (7)	C17—C13—C14—C15	43.1 (5)
C6—C7—C8—O8	−87.4 (5)	C18—C13—C14—C8	66.0 (5)
C6—C7—C8—C9	30.8 (6)	C18—C13—C14—C15	−69.1 (5)
C6—C7—C8—C14	155.5 (4)	C12—C13—C17—C16	−147.0 (5)
C7—C8—C9—C10	−46.4 (5)	C12—C13—C17—O17	32.6 (8)
C7—C8—C9—C11	77.2 (5)	C14—C13—C17—C16	−29.4 (5)
O8—C8—C9—C10	70.8 (5)	C14—C13—C17—O17	150.2 (6)
O8—C8—C9—C11	−165.6 (4)	C18—C13—C17—C16	90.9 (5)
C14—C8—C9—C10	−175.3 (4)	C18—C13—C17—O17	−89.5 (7)
C14—C8—C9—C11	−51.8 (5)	C8—C14—C15—C16	−172.1 (4)
C7—C8—C14—C13	70.3 (5)	C13—C14—C15—C16	−40.7 (5)
C7—C8—C14—C15	56.6 (6)	C14—C15—C16—C17	21.5 (6)
O8—C8—C14—C13	171.9 (4)	C15—C16—C17—C13	5.1 (6)
O8—C8—C14—C15	−61.2 (5)	C15—C16—C17—O17	−174.5 (6)

The crystal structure was solved by the direct-methods program *SHELXS*86 (Sheldrick, 1985). All H atoms were located from difference Fourier maps and refined isotropically. A secondary extinction correction, $g = 1.0 \times 10^{-6}$ (Stout & Jensen, 1991), was included but not refined in the least-squares refinement process. There were no significant features in the final difference Fourier map. All refinement calculations were performed on a DEC VAXstation 3100 Model 76 computer using the Enraf-Nonius *SDP-Plus* package (Frenz, 1985).

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5- and 7-Dicyanomethylene-1,2-ethylenedithiocycloheptatrienes

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Abstract

The exocyclic double-bond lengths in 2,3-ethylenedithio-2,4,6-cycloheptatrien-1-ylidenemalononitrile, (1), $C_{12}H_8N_2S_2$, and 4,5-ethylenedithio-2,4,6-cycloheptatrien-1-ylidenemalononitrile, (2), $C_{12}H_8N_2S_2$, are 1.389 (3) and 1.392 (5) Å, respectively. The planarity of (2) is fairly good, whereas the shape of the seven-membered ring of (1) is puckered.