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17-Oxo-16-(2-pyridylmethylene)-androst-5-en-3β-ol monohydrate

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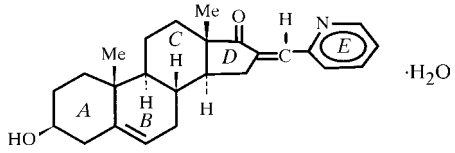
The title compound, $C_{25}H_{31}NO_2\cdot H_2O$, has the outer two six-membered rings in chair conformations, while the central ring is in an 8β,9α-half-chair conformation. The five-membered ring adopts a 13,14-half-chair conformation. The pyridylmethylene moiety has an *E* configuration with respect to the carbonyl group at position 17. The structure is stabilized by intermolecular O—H···N and O—H···O hydrogen bonds.

Comment

The structure determination of the title compound, (I), was undertaken to investigate the conformation of the fused-ring system and the configuration of the 16-(2-pyridylmethylene) functionality with respect to the carbonyl group at position 17.



(I)

Compound (I), an epiandrostene derivative, is a steroid in which rings *A*, *B* and *C* are essentially rigid, whereas ring *D* has a flexible conformation with respect to the side chain. The absolute configuration of (I) is based on the known configuration of the starting material, namely epiandrosterone (Weeks *et al.*, 1971). The torsion angles show that rings *A* and *C* adopt chair conformations. The short C2—C3 bond distance of 1.507 (4) Å in (I) is in agreement with other related steroids (Paixão *et al.*, 1998). Ring *B* has an 8β,9α-half-chair conformation. The C5—C6 distance of 1.338 (4) Å confirms the localization of a double bond at this position. Atoms C8 and C9 are displaced to opposite sides by 0.359 (5) and 0.389 (5) Å, respectively, from the mean C10/C5/C6/C7 plane (Cox *et al.*, 1981). Ring *D* has a 13,14-half-chair conformation. The five torsion angles of ring *D* [C13—C14—C15—C16 −32.4 (3), C14—C15—C16—C17 12.0 (3), C15—C16—C17—C13 12.8 (3), C16—C17—C13—C14 −32.3 (3) and C17—C13—C14—C15 40.1 (3)°] are comparable with the reported values of −37.6 (2), 16.3 (2), 11.3 (2), −33.7 (2) and 43.7 (2)°, respectively (Paixão *et al.*, 1998). The C17—C16—C20—C21 torsion angle of 173.2 (3)° indicates that the 2-pyridyl ring has an *E* configuration with respect to the carbonyl group at position 17; the C20 H atom is *Z* with respect to this carbonyl group. The O17 atom is equatorially substituted at C17, and O3 is equatorially substituted at C3. The dihedral angle between the pyridine ring and the androstene moiety is 8.71 (12)°. The geometry of the rings is *trans* at the *B*/*C* and *C*/*D* ring junctions.

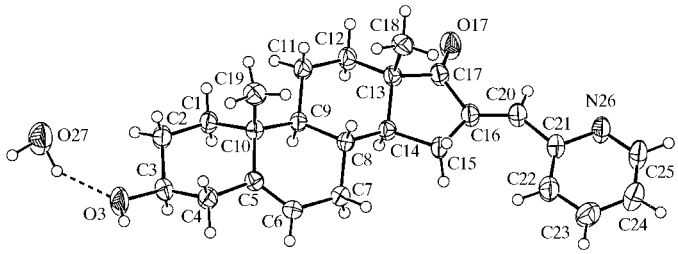


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

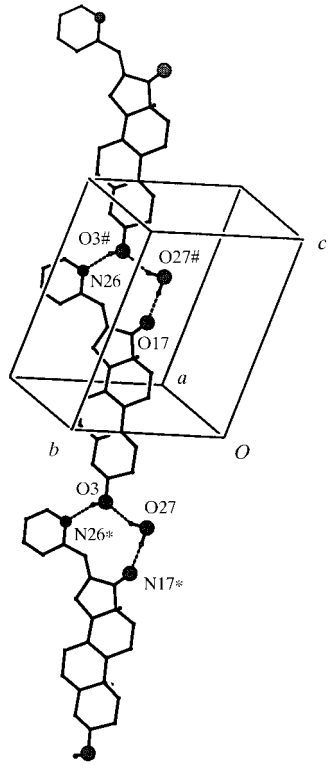


Figure 2
A view showing part of the infinite molecular hydrogen-bonded chain in (I). All H atoms, except those involved in hydrogen bonding, have been discarded. The hash (#) and asterisk (*) labels denote equivalent positions (1 + *x*, *y*, 1 + *z*) and (−1 + *x*, *y*, −1 + *z*), respectively.

The structure of (I) is stabilized by a network of hydrogen bonds involving the hydroxyl O, carbonyl O and pyridyl N atoms of the steroid moiety, and the O atom of the water molecule (Table 2). The hydroxyl O3 atom at C3 takes part in two intermolecular hydrogen bonds, one as a donor towards the pyridyl nitrogen (N26) and the other as an acceptor from the water molecule (O27). In addition to this, the water molecule also has another intermolecular hydrogen bond involving the carbonyl oxygen (O17). In this way, an infinite one-dimensional chain of molecules is assembled (Fig. 2).

Experimental

The title compound was prepared by condensing dehydroepiandrosterone (1 g, 3.47 m*M*) with 2-pyridinecarboxaldehyde (1.75 g, 16.34 m*M*) in the presence of sodium hydroxide (1.75 g, 43.75 m*M*) in methanol (20 ml). The absolute configuration of the epiandrosterone is already known (Weeks *et al.*, 1971). The reaction mixture was shaken at room temperature for 1 h, and then poured into ice-cold water and allowed to stand overnight. The precipitate was filtered off, washed with distilled water and dried under vacuum. The solid residue was crystallized from methanol to afford crystals of (I) (1.0 g, 72.9%; m.p. 478–483 K).

Crystal data

$C_{25}H_{31}NO_2\cdot H_2O$
$M_r = 395.52$
Monoclinic, $P2_1$
$a = 6.5376\ (3)$ Å
$b = 11.8766\ (10)$ Å
$c = 13.5312\ (15)$ Å
$\beta = 91.197\ (12)^\circ$
$V = 1050.39\ (15)$ Å^3
$Z = 2$
$D_x = 1.251$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20$–30°
$\mu = 0.64$ mm^{-1}
$T = 293\ (2)$ K
Rectangular, colourless
0.3 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.800$, $T_{max} = 0.988$
2187 measured reflections
2003 independent reflections
1888 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 67.9^\circ$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 14$
$l = -16 \rightarrow 16$
2 standard reflections
frequency: 120 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

O17—C17	1.206 (3)	C10—C19	1.549 (4)
C1—C2	1.523 (3)	C13—C18	1.547 (4)
C2—C1—C10	114.2 (2)	C17—C13—C18	104.7 (2)
O3—C3—C2	108.1 (2)	O17—C17—C13	126.8 (3)
C5—C10—C19	108.5 (2)		
C10—C1—C2—C3	−57.1 (3)	C7—C8—C9—C10	60.6 (3)
C10—C5—C6—C7	0.1 (4)	C6—C5—C10—C9	15.4 (3)
C5—C6—C7—C8	14.8 (4)	C8—C9—C10—C5	−45.5 (3)
C6—C7—C8—C9	−43.6 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···N26^{i}	0.82	2.04	2.833 (3)	162
O27—H27A···O3	1.01	2.05	2.886 (3)	139
O27—H27B···O17^{i}	1.01	1.90	2.907 (3)	176

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.117$
$S = 1.14$
2003 reflections
267 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0724P)^2 + 0.1862P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0044 (10)

All H atoms of the steroid were located from difference Fourier maps and were then included in the structure-factor calculations as riding atoms, with C—H distances in the range 0.93–0.98 Å. The H atoms of the water molecule were also obtained from a difference map and were initially refined subject to a free-variable *DFIX* O—H restraint with a common U_{iso} free variable. In the final cycles, the water H atoms were then not adjusted (*AFIX* 1) from the O—H distance (1.01 Å) so obtained. The analysis does not allow the absolute configuration of (I) to be determined, but this was known from the synthesis.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); 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: VJ1136). Services for accessing these data are described at the back of the journal.

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