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3β,17β-Diacetoxy-16-(3-pyridylmethylene)-androst-5-ene monohydrate

G. Vasuki,[a] V. Parthasarathi,[a]* K. Ramamurthi,[a] S. Dubey[b] and D. P. Jindal[b]†

[a]Department of Physics, Bharathidasan University, Tiruchirappalli 620 024, India, and [b]University Institute of Pharmaceutical Sciences, Panjab University, Chandigarh 160 014, India

† Deceased.

Correspondence e-mail: sarati@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
H-atom completeness 95%
Disorder in main residue
R factor = 0.062
wR factor = 0.181
Data-to-parameter ratio = 8.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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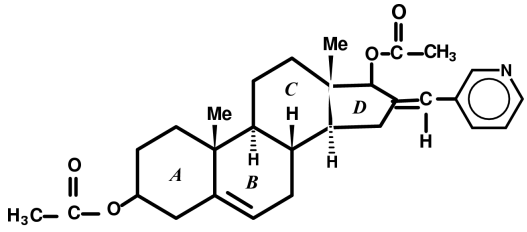
In the title compound, $C_{29}H_{37}NO_4\cdot H_2O$, an androst-5-ene steroid, rings *A* and *C* adopt chair conformations, while ring *B* is in a half-chair conformation. The five-membered ring *D* adopts an envelope conformation. The molecular packing is probably stabilized by intermolecular O—H···N and O—H···O hydrogen bonds involving the disordered water molecules.

Comment

The X-ray investigation of the title compound, (I), was undertaken as part of our study on the structure and conformation of new synthetic steroid derivatives (Hema *et al.*, 2002; Vasuki *et al.*, 2001; Vasuki, Parthasarathi, Ramamurthi, Dubey & Jindal, 2002*a*,*b*; Vasuki, Parthasarathi, Ramamurthi, Jindal & Dubey, 2002*a*,*b*; Vasuki, Thamotharan, Parthasarathi, Ramamurthi, Jindal & Dubey, 2002; Vasuki, Thamotharan, Parthasarathi, Ramamurthi, Dubey & Jindal, 2002). We are particularly interested in the study of the possible influence of various substituents at the C3, C16 and C17 positions (Fig. 1) on the conformation of the steroid nucleus, as it is well known that steroid receptors are able to modify the mode of binding at ring *D* to accommodate several different types of C17 substitution (Duax & Norton, 1975).



(I)

In (I), rings *A* and *C* adopt chair conformations. The C5—C6 (Csp^2—Csp^2) distance of 1.306 (6) Å confirms the localization of a double bond at this position. As a result of this double bond, the geometry around atom C5 is planar and hence ring *B* adopts an 8β,9α-half-chair conformation, with Q = 0.503 (5) Å, θ = 50.1 (6)° and φ = 210.0 (7)° (Cremer & Pople, 1975). Similar observations have been reported for related structures (Hema *et al.*, 2002; Vasuki *et al.*, 2001; Vasuki, Parthasarathi, Ramamurthi, Dubey & Jindal, 2002*a*; Vasuki, Thamotharan, Parthasarathi, Ramamurthi, Jindal & Dubey, 2002). Ring *D* has a 13β-envelope conformation, with ΔCs (C13) = 2.9 (5)° and the pseudo-rotational parameters Δ = 41.6° and φ_m = 47.3 (3)° (Altona *et al.*, 1968). The *B*/*C* and *C*/*D* ring junctions show *trans* fusion. The usual chair conformation adopted by ring *A* is not disturbed by the

equatorial substitution of an acetoxy group at C3. The acetoxy group at C17 is also equatorially substituted. The C17—C16—C20—C21 torsion angle of 177.6 (5)° indicates that the 3-pyridyl ring has an *E* configuration with respect to atom C17. The widening of the exocyclic angle C15—C16—C20 [130.0 (4)°] compared with C17—C16—C20 [122.4 (4)°] might be a consequence of the steric repulsion between atoms H15*B* and H22 (H15*B*···H22 = 2.27 Å). The pseudo-torsion angle C19—C10···C13—C18 is 10.8 (3)°. The acetoxy groups substituted at C3 and C17 form dihedral angles of 51.6 (3) and 57.7 (2)°, respectively, with the mean plane through the steroid nucleus (C1–C17). A similar observation has been reported recently for an isomorphous compound (Vasuki, Parthasarathi, Ramamurthi, Dubey & Jindal, 2002*a*). The dihedral angle between the pyridine ring and the average molecular plane comprising rings *A*, *B*, *C* and *D* is 25.4 (2)°. A short intramolecular C—H···O contact is observed between C20 and O27, with an H20···O27 distance of 2.39 Å. Possible hydrogen bonds involving the disordered solvent water O atom are observed, with O1*WA*···N25^{i} = 3.054 (8) Å, O1*WB*···N25^{i} = 2.762 (8) Å, O1*WA*···O29^{ii} = 3.049 (7) Å and O1*WB*···O29^{ii} = 3.279 (7) Å [symmetry codes: (i) x, y, $1 + z$; (ii) $\frac{3}{2} - x$, $2 - y$, $\frac{1}{2} + z$].

Experimental

The title compound was prepared by reacting 16-(3-pyridylmethylene)androst-5-en-3β,17β-diol (0.5 g, 1.32 m*M*) with acetic anhydride (1 ml, 9.8 m*M*), using dried pyridine (1 ml, 12.66 m*M*) as catalyst, in a boiling water bath for 2 h. The reaction mixture was poured on to crushed ice and the precipitate was filtered off, washed with cold distilled water and dried under vacuum. The solid residue was crystallized from methanol to afford crystals of (I) (0.42 g, 68.5%; m.p. 411–415 K).

Crystal data

$C_{29}H_{37}NO_4\cdot H_2O$
M_r = 481.61
Orthorhombic, $P2_12_12_1$
a = 11.523 (2) Å
b = 15.279 (4) Å
c = 15.409 (6) Å
V = 2712.9 (14) Å^3
Z = 4
D_x = 1.179 Mg m^{-3}
Mo Kα radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.08 mm^{-1}
T = 293 (2) K
Plate, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.984, T_{max} = 0.992
2783 measured reflections
2697 independent reflections
1783 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 25.0°
$h = 0 \rightarrow 13$
$k = -8 \rightarrow 18$
$l = -17 \rightarrow 18$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.181
S = 1.06
2697 reflections
308 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1135P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

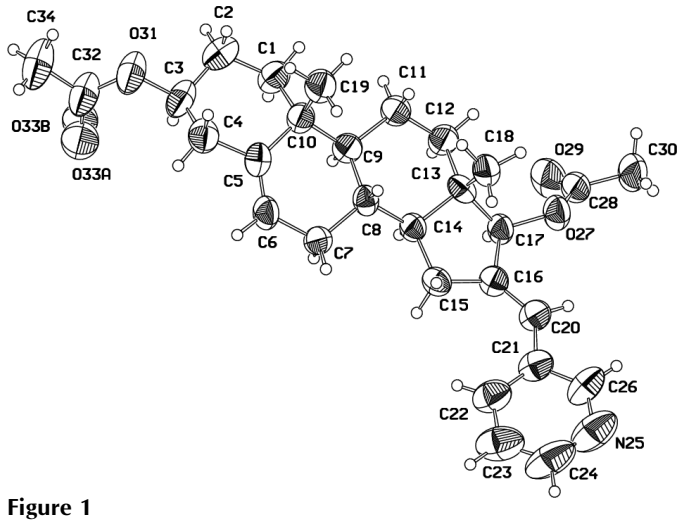


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

All H atoms were fixed geometrically and allowed to ride on the parent non-H atoms, with C—H = 0.93–0.98 Å and U_{iso}(H) = 1.5U_{eq} for methyl H and 1.2U_{eq} for all other H atoms. The solvent water O atom was found to be disordered over two sites with partial occupancies of 0.68 (O1*WA*) and 0.32 (O1*WB*). The H atoms of the solvent water molecule were not located. One of the O atoms (O33) of the acetoxy group showed very high displacement parameters, indicating positional disorder. The occupancies of the disordered positions, O33*A* and O33*B*, were initially refined along with isotropic displacement parameters and later fixed at 55 and 45%, respectively. The absolute configuration was assigned to correspond with that of a known chiral centre in a starting molecule, namely 16-(3-pyridylmethylene)androst-5-ene-3β,17β-diol. The Friedel pairs were merged during the refinement.

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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