Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

$3\beta,17\beta$-Diacetoxy-16-(2-pyridylmethylene)-androst-5-ene hydrate (1/0.46)

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

Correspondence e-mail: vpsarati@yahoo.com

Received 10 December 2001
Accepted 25 February 2002
Online 8 March 2002

Key indicators

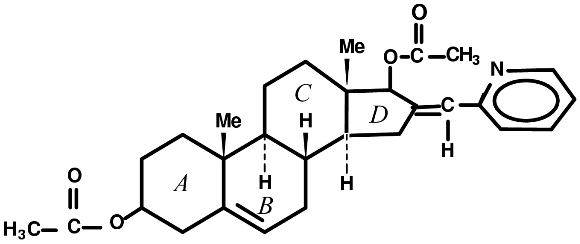
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
H-atom completeness 98%
Disorder in solvent or counterion
R factor = 0.040
wR factor = 0.113
Data-to-parameter ratio = 7.8

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

In the title compound, $C_{29}H_{37}NO_4 \cdot 0.46H_2O$, rings *A* and *C* adopt chair conformations and ring *B* is in a half-chair conformation. The five-membered ring *D* adopts an envelope conformation. The crystal structure is stabilized by weak intermolecular C—H···O interactions and van der Waals forces.

Comment

The X-ray investigation of the title compound, (I), was undertaken as a part of our study on the structure and conformation of new synthetic steroids. Steroids are known for their biological importance and are active hormones essential to life. It is well known that minor changes in the composition of steroid hormones result in significant variation in their chemical and biological activities. In addition to having a direct influence on membrane transport and protein binding, structural changes affect activity by changing the overall conformation of the molecule (Duax & Norton, 1975). Hence, 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. The absolute configuration of (I) is based on the known configuration of the starting material, an epiandrosterone derivative (Vasuki *et al.*, 2001).



(I)

Rings *A* and *C* adopt chair conformations. Ring *B* adopts a half-chair conformation with $Q = 0.485$ (3) Å, $\theta = 50.7$ (4)° and $\varphi = 208.9$ (5)° (Cremer & Pople, 1975). Ring *D* has a 13β-envelope conformation with ΔCs(C13) = 2.5 (3)°. The *B/C* and *C/D* ring junctions show *trans* fusion. The acetoxy groups at C3 and C17 are in equatorial positions. The usual chair conformation adopted by ring *A* of the steroidal nucleus is not disturbed by the substitution of an acetoxy group at C3. The C17—C16—C20—C21 torsion angle of 179.8 (3)° indicates that the 2-pyridyl ring has an *E* configuration with respect to atom C17. The deviation of the exocyclic angle C15—C16—C20 [129.7 (3)°] from the normal value might be a consequence of repulsion between the lone pair of electrons on

DOI: 10.1107/S1600536802003550

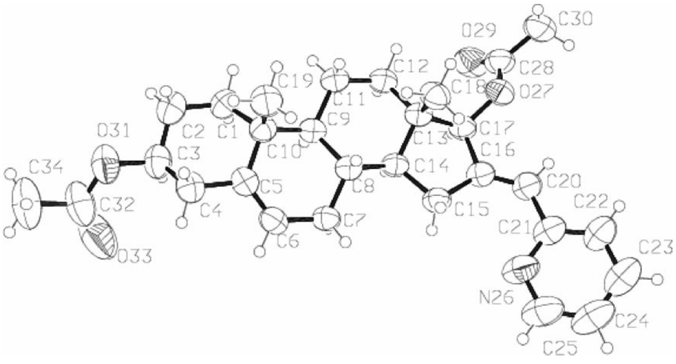


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. For clarity, the disordered solvent water molecules have been omitted.

N26 and H15*B* attached to C15 (N26···H15*B* 2.77 Å). The pseudo-torsion angle C19—C10···C13—C18 in (I) is 10.5 (2)°. The acetoxy groups substituted at C3 and C17 form dihedral angles of 46.4 (2) and 56.6 (1)°, respectively, with the mean plane through the androstene moiety. Similar observations have been reported by Andrade *et al.* (2001) for a related compound. A short intramolecular C—H···O contact is observed between C20 and O27 with an H20···O27 distance of 2.43 Å. The structure is stabilized by van der Waals interactions.

Experimental

The title compound was prepared by reacting 17-oxo-16-(2-pyridylmethylene)androst-5en-3β-ol (1 g, 2.65 m*M*) with acetic anhydride (2 ml, 21.18 m*M*), using dried pyridine (1 ml, 13.29 m*M*) as catalyst, on 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) (1.0 g, 81.86%; m.p. 409–413 K).

Crystal data

$C_{29}H_{37}NO_4 \cdot 0.46H_2O$
$M_r = 471.88$
Orthorhombic, $P2_12_12_1$
$a = 11.493$ (2) Å
$b = 15.285$ (2) Å
$c = 15.293$ (3) Å
$V = 2686.5$ (8) Å^3
$Z = 4$
$D_x = 1.167$ Mg m^{-3}

Cu *Kα* radiation
Cell parameters from 25 reflections
$\theta = 20$–$30°$
$\mu = 0.62$ mm^{-1}
$T = 293$ (2) K
Rectangular block, colourless
0.35 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.818$, $T_{\max} = 0.890$
2530 measured reflections
2472 independent reflections
2064 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\max} = 67.9°$
$h = 0 \rightarrow 13$
$k = -4 \rightarrow 18$
$l = 0 \rightarrow 18$
2 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.113$
$S = 1.06$
2472 reflections
316 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.3741P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0023 (3)

All H atoms were fixed geometrically and allowed to ride on their parent atoms. At this stage, the maximum difference density of 0.72 e Å^{-3} indicated the presence of a possible atom site. Also a check for the solvent-accessible volume using *PLATON* (Spek, 2001) showed a void of 236.2 Å^3. This peak was found near O29, at a distance of 2.98 (1) Å. Attempts to refine this peak as a water oxygen (O1*W*) with full occupancy resulted in a high $U_{\rm iso}$ value and hence it was refined with partial occupancy. At this stage, the maximum density (0.26 e Å^{-3}) in the difference Fourier map was found to be twice the absolute value of the deepest trough. Also a void of 69.7 Å^3 was identified. This peak was found at a hydrogen bonding distance of 2.75 (3) Å from N26. Hence, this peak (O2*W*) was also refined as a solvent water oxygen (O2*W*) with partial occupancy. The occupancies of O1*W* and O2*W* were found to be 0.35 (1) and 0.11 (1), respectively. These values were fixed during the final cycles of refinement. The H atoms of these solvent water molecules were not located. One of the O atoms (O33) has some slightly unusual displacement parameters. However, a satisfactory disorder model for this atom was not found.

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: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97.

SD thanks CSIR, India, for financial assistance and DPJ thanks Cipla Ltd, Mumbai, for providing the steroid. GV thanks the UGC, India, for the award of an FIP fellowship (1999–2001).

References

Andrade, L. C. R., Paixao, J. A., De Almeida, M. J. M., Martins, R. M. L. M., Soares, H. I. M., Morais, G. J. R., Moreno, M. J. S. M., Sa e Melo, M. L. & Campos Neves, A. S. (2001). *Acta Cryst.* C**57**, 587–589.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structures*. New York: Plenum.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN.* Enraf–Nonius, Delft, The Netherlands.
North, A. C. T., Phillips, D. C & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2001). *PLATON* for Windows. Utrecht University, The Netherlands.
Vasuki, G., Parthasarathi, V., Ramamurthi, K., Jindal, D. P. & Dubey, S. (2001). *Acta Cryst.* C**57**, 1062–1063.