

16-(3-Pyridylmethylene)androst-4-ene-3,17-dione

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.041

wR factor = 0.108

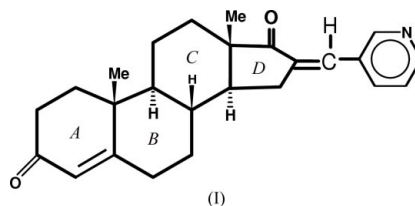
Data-to-parameter ratio = 8.6

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

In the title compound, $\text{C}_{25}\text{H}_{29}\text{NO}_2$, ring *A* adopts a slightly distorted half-chair conformation, while rings *B* and *C* are in chair conformations. The five-membered ring *D* adopts a $13\beta,14\alpha$ -half-chair conformation. The 3-pyridyl ring has an *E* configuration with respect to the carbonyl group at position 17. The crystal structure is stabilized by weak intra- and intermolecular $\text{C}-\text{H}\cdots\text{O}$ 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 steroid derivatives (Hema *et al.*, 2002; Vasuki *et al.*, 2001; Vasuki, Parthasarathi, Ramamurthi, Dubey & Jindal, 2002*a,b*; Vasuki, Parthasarathi, Ramamurthi, Jindal & Dubey, 2002; Vasuki, Thamotharan *et al.*, 2002*a,b*). We are particularly interested in studying the conformational flexibilities of steroids resulting from various substitutions at the C3, C16 and C17 positions, since it is well known that steroid receptors are able to modify the mode of binding at ring *D* to accommodate several different types of substitution at C17 (Duax & Norton, 1975).



In (I), ring *A* has a slightly distorted half-chair conformation, with asymmetry parameters (Duax & Norton, 1975) $\Delta C_2(\text{C}1-\text{C}2) = 9.26^\circ$ and $\Delta C_s(\text{C}1) = 13.83^\circ$, as observed in a similar androstene derivative (Galdecki *et al.*, 1990). Rings *B* and *C* adopt chair conformations, while ring *D* adopts a $13\beta,14\alpha$ -half-chair conformation, with pseudo-rotational parameters $\Delta = 1.2^\circ$ and $\varphi_m = 41.5(3)^\circ$ (Altona *et al.*, 1968). The geometry of the rings is *trans* at the *B/C* and *C/D* ring junctions. The $\text{C}17-\text{C}16-\text{C}20-\text{C}21$ torsion angle of $172.5(3)^\circ$ indicates that the 3-pyridyl ring has an *E* configuration with respect to the carbonyl group at position 17. The larger exocyclic angle $\text{C}15-\text{C}16-\text{C}20$ [$132.1(3)^\circ$] compared with $\text{C}17-\text{C}16-\text{C}20$ [$119.2(3)^\circ$] might be a consequence of steric repulsion between $\text{H}15\text{B}$ and $\text{H}22$ ($\text{H}15\text{B}\cdots\text{H}22 = 2.23\text{ \AA}$). The dihedral angle between the plane of the pyridine ring and the average molecular plane comprising rings *A*, *B*, *C* and *D* is $5.27(1)^\circ$. The values of the $\text{C}8-\text{C}14-\text{C}15$ [$120.4(2)^\circ$] and $\text{C}14-\text{C}13-\text{C}17$ [$100.6(2)^\circ$] angles are close to the expected values of 119.3 and 99.2° , respectively (Duax

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& Norton, 1975). The pseudo-torsion angle C19—C10···C13—C18 is observed to be 6.3 (3)°. The C4—C5 ($C_{sp^2}-C_{sp^2}$) distance of 1.343 (4) Å confirms the localization of a double bond at this position (Vasuki, Parthasarathi, Ramamurthi, Jindal & Dubey, 2002; Vasuki, Thamocharan *et al.*, 2002a). A short intramolecular C—H···O contact is observed between C20 and O17, with an H20···O17 distance of 2.54 Å. An intermolecular C—H···O contact is observed between C26 and O3ⁱ, with an H26···O3ⁱ distance of 2.53 Å [symmetry code: (i) $x, y, z - 1$]. The structure is stabilized by van der Waals interactions.

Experimental

The title compound was prepared by dissolving 17-oxo-16-(3-pyridylmethylene)androst-5-en-3 β -ol (1 g, 2.66 mmol) in dry toluene (150 ml) under reflux, and then adding cyclohexanone (10 ml) to it. Traces of moisture were removed by azeotropic distillation. The distillation was continued at a slow rate during dropwise addition of a solution of aluminium isopropoxide (1 g) in dry toluene (15 ml). The reaction mixture was refluxed for 4 h and left overnight at room temperature. The slurry was filtered and the residue washed thoroughly with dry toluene. The combined filtrate and washing were steam distilled until the organic solvent was completely removed. The solid residue was allowed to stand overnight and then filtered, washed, dried and crystallized from methanol to afford crystals of (I) (yield 0.6 g, 59.68%, m.p. 475–481 K).

Crystal data

$C_{25}H_{29}NO_2$	Mo $K\alpha$ radiation
$M_r = 375.49$	Cell parameters from 25 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 10-15^\circ$
$a = 11.4545$ (12) Å	$\mu = 0.08$ mm ⁻¹
$b = 12.207$ (2) Å	$T = 293$ (2) K
$c = 14.784$ (3) Å	Plate, white
$V = 2067.2$ (6) Å ³	0.20 × 0.15 × 0.10 mm
$Z = 4$	
$D_x = 1.207$ Mg m ⁻³	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.008$
$\omega-2\theta$ scans	$\theta_{max} = 25.0^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -2 \rightarrow 13$
$T_{min} = 0.993$, $T_{max} = 1.000$	$k = -5 \rightarrow 14$
2222 measured reflections	$l = -10 \rightarrow 17$
2172 independent reflections	2 standard reflections
1671 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.4599P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.12$	$\Delta\rho_{max} = 0.26$ e Å ⁻³
2172 reflections	$\Delta\rho_{min} = -0.18$ e Å ⁻³
253 parameters	
H-atom parameters constrained	

All H atoms were placed geometrically and refined using a riding model, with C—H = 0.93–0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl

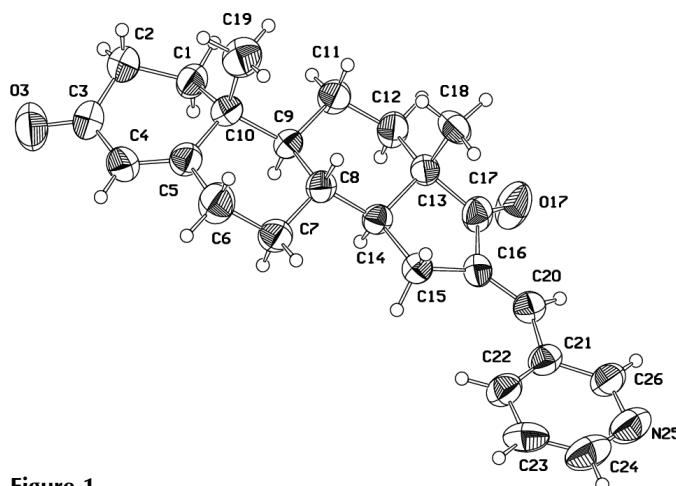


Figure 1

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

H and $1.2U_{eq}(C)$ for all others. The absolute configuration was assigned to correspond with that of the known chiral centres in the starting molecules, namely 17-oxo-16-(3-pyridylmethylene)androst-5-en-3 β -ol. Friedel pairs were not merged.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP97* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL97*.

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