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17-Allyl-16,17a-dioxo-17-aza-D-homoestra-1,3,5(10)-trien-3-ol

R. Hema,[a] V. Parthasarathi,[a]* Ranju Bansal,[b] K. Ravikumar[c] and B. Sridhar[c]

[a]School of Physics, Bharathidasan University, Tiruchirappalli 620 024, India, [b]University Institute of Pharmaceutical Sciences, Panjab University, Chandigarh 160 014, India, and [c]Laboratory of X-ray Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Correspondence e-mail: vpsarati@yahoo.com

Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.004 Å
R factor = 0.042
wR factor = 0.109
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.

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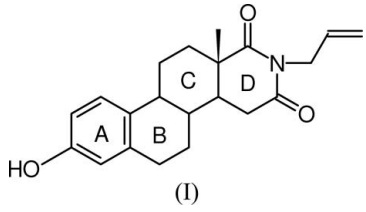
In the title compound, $C_{21}H_{25}NO_3$, a modified synthetic D-homo steroid, the cyclohexene ring adjacent to the aromatic ring adopts a half-chair conformation, while the cyclohexane ring has an ideal chair conformation. The heterocyclic ring adopts a 14β-sofa conformation. In the crystal structure, intermolecular O—H···O hydrogen bonds link the molecules into extended chains with graph-set motif *C*(12). The compound also exhibits some weak intermolecular C—H···O interactions.

Comment

It is very well known that the activity of steroid derivatives is dependent upon a number of factors including solubility, motility, transport, metabolism and complementarity of fit between hormone and receptor. Since the functional differences caused by structural modifications may be due to an influence of the modification upon any or all of these factors, we have undertaken an X-ray crystallographic study of the title compound, (I), a D-homo-steroid derivative, to investigate the influence of structural modification upon overall geometry and conformation. Compound (I) possesses a bulky substituent at the N atom of the heterocyclic ring and a hydroxy substituent at C3.



(I)

A view of the molecule of (I) with the atom-labelling scheme is shown in Fig. 1. The bond lengths and angles are comparable with those of related structures, *viz*. (8*R*,9*S*,13*S*,14*S*)-17-butyl-16,17*a*-dioxo-17-aza-D-homoestra-1,3,5(10)-trien-3-ol, (II) (Hema *et al.*, 2005*b*), and 17-allyl-16,17*a*-17-aza-D-homaestra-1,3,5-trien-3yl acetate, (III) (Hema *et al.*, 2005*a*). The cyclohexene ring, *B*, adopts a 7β,8α-half-chair conformation [puckering parameters (Cremer & Pople, 1975): Q = 0.508 (3) Å, θ = 46.7 (3)° and φ = 155.5 (4)°] as a result of the fusion with the planar aromatic ring, *A*. The cyclohexane ring, *C*, has an ideal chair conformation [Q = 0.568 (3) Å, θ = 0.9 (3)° and φ = 68 (20)°]. With the substitution by the allyl group at N17, heterocyclic ring *D* adopts a flattened 14β-sofa conformation [Q = 0.500 (3) Å, θ = 56.9 (3)° and φ = 197.2 (4)°].

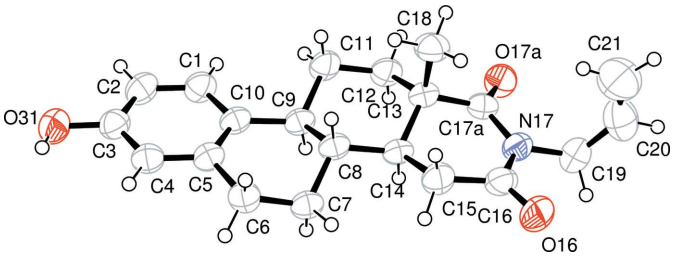


Figure 1
View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

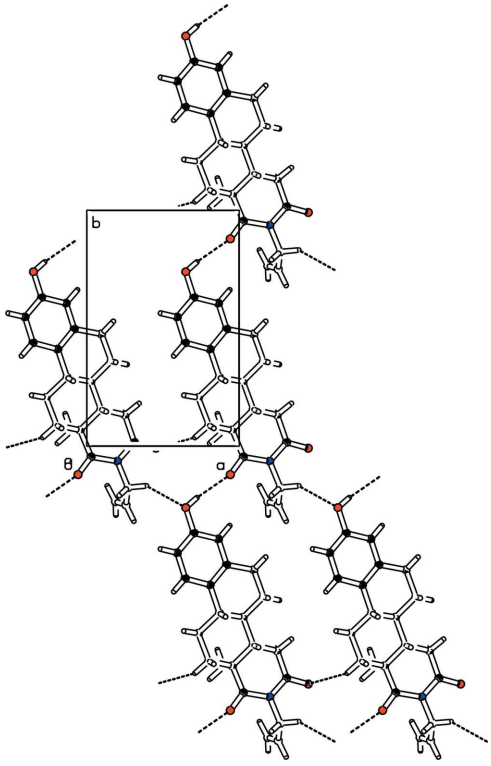


Figure 2
Packing diagram showing O—H···O and weak C—H···O hydrogen bonds (dashed lines) linking the molecules into two-dimensional sheets perpendicular to the *c* axis

The flattening of ring *D* is indicated by the torsion angles C13—C17a—N17—C16 [2.8 (4)°] and C17a—N17—C16—C15 [8.0 (4)°]. The flattening is associated with the constraints to the ring conformation introduced by the normal planar arrangement about the amide N—C bond (sum of the angle at N17 = 360.0°). The *B*/*C* and *C*/*D* rings are *trans*-fused.

In (I), atom O31 of the hydroxyl group forms an intermolecular O—H···O hydrogen bond with carbonyl atom O17*A* of an adjacent molecule (Table 1). This interaction links the molecules into extended chains, which run parallel to the [010] direction and have a graph-set motif of *C*(12) (Bernstein *et al.*, 1995). Atom C12 acts as a donor for a weak intermolecular C—H···O interaction with carbonyl atom O16 of a different neighbouring molecule and thereby links the molecules into continuous chains, which run parallel to the [100] direction and can be described by the graph-set motif *C*(7). Finally, atom C19 is involved in a weak intermolecular C—H···O interaction with carbonyl atom O31 of yet another adjacent molecule, which produces continuous chains that also run parallel to the [100] direction and have a graph-set motif *C*(13). The combination of the O—H···O and weak C—H···O hydrogen bonds forms a two-dimensional framework perpendicular to the *c* axis.

Experimental

A mixture of 17-allyl-16,17*a*-dioxo-17-aza-D-homo-1,3,5(10)-estratrien-3-yl acetate (0.4 g), potassium carbonate (1.5 g) and aqueous methanol (50 ml) was stirred at room temperature for 1 h. The slurry obtained was poured into water. The precipitated material was crystallized from methanol to afford the title compound (0.325 g, 91.54%; m.p. 511–513 K).

Crystal data

$C_{21}H_{25}NO_3$
M_r = 339.42
Orthorhombic, $P2_12_12_1$
a = 7.8071 (8) Å
b = 12.0975 (12) Å
c = 18.3120 (19) Å
V = 1729.5 (3) Å^3
Z = 4
D_x = 1.304 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4707 reflections
θ = 2.2–26.4°
μ = 0.09 mm^{-1}
T = 273 (2) K
Block, colourless
0.21 × 0.11 × 0.08 mm

Data collection

Bruker SMART CCD area-dDetector diffractometer
ω scans
Absorption correction: none
12531 measured reflections
1769 independent reflections
1632 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25.0°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.109
S = 1.17
1769 reflections
228 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.2367P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O31—H31···O17A^{i}	0.82	2.12	2.930 (3)	168
C19—H191···O31^{ii}	0.97	2.52	3.371 (4)	146
C12—H121···O16^{iii}	0.97	2.58	3.440 (4)	147

Symmetry codes: (i) $x, y+1, z$; (ii) $x+1, y-1, z$; (iii) $x-1, y, z$.

The methyl H atoms were constrained to an ideal geometry [C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C)] but were allowed to rotate freely about the C—C bonds. The hydroxy H atom was positioned geometrically [O—H = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O)]. All other H atoms in the structure were placed in geometrically idealized positions (C—H = 0.93–0.98 Å) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C). In the absence of any significant anomalous scatterers, Friedel pairs were merged before the final refinement and the absolute configuration was assigned to corre-

spond with that of the known chiral centres in a precursor molecule, which remained unchanged during the synthesis of the title compound.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Version 1.64.05; Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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