In the title compound, C_{23}H_{27}NO_{4}, 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 and the heterocyclic ring has a sofa conformation. The plane of the allyl substituent lies almost perpendicular to the least-squares plane of the heterocyclic ring. The crystal structure contains a series of weak C–H⋯O intermolecular interactions.

Comment

Recently, synthetic steroids have been proposed as potential drug delivery systems targeting estrogen receptor positive breast cancer and other diseases associated with the estrogen receptor Erα (Yamamoto et al., 2004, and references therein). Because of the common phenolic ring, A, the estradiol structures analogous to the title compound, (I), are expected to bind to the estrogen receptor (Roszak et al., 1991). The title compound, however, does not possess a 17α-hydroxy function, which is important for high-affinity binding. When the 17α-hydroxy substituent is replaced with a 17-carbonyl group as, for example, in estrone, the binding affinity may be decreased (see, for example, Roszak et al., 1991). It has also been suggested that the absence of an oxygen substituent, comparable to the estradiol 17-O, accounts for the inactivity or antagonistic properties observed for some ligands (Duax et al., 1985). Recently, we have reported a related structure which was also a modified steroid (Hema et al., 2004). As a continuation of our studies on modified steroids containing alkylating and other functional groups, the synthesis and crystal structure determination of the title compound, (I), has been undertaken.

Compound (I) is pseudo-isostructural with the related 17-buty1-16,17a-dioxo-17-aza-D-homoestra-1,3,5(10)-trien-3-yl acetate (Hema et al., 2004), which possesses a 17-butyl group instead of the 17-allyl group of (I). The unit-cell dimensions for the two structures are very similar and the space groups are the same.

A view of the molecule of (I) with the atomic labeling scheme is shown in Fig. 1. In (I), the cyclohexene ring B, adjacent to the aromatic ring has a 7α,8β-half-chair
to the structures of (I) and the 17-butyl analog (Hema et al., 2004), gives an r.m.s. deviation of 0.06 Å, which shows that replacement of the butyl substituent at N17 by an allyl group has a negligible effect on the conformation of the steroid nucleus.

Atom C4 acts as a donor for a weak C–H⋯O intermolecular interaction (via H4) with carbonyl atom O17a of a symmetry-related molecule. This interaction links the molecules into chains which run in the [010] direction and can be described by a graph-set motif of C(10) (Bernstein et al., 1995; Table 1). Atom C8 is involved in a weak C–H⋯O interaction with carbonyl atom O16 of another adjacent molecule and thereby produces a continuous chain which runs in the [100] direction and has a graph-set motif C(6). Atom C15 interacts via H151 and H152 with atom O32 in two other neighboring molecules, giving chains which run in the [001] and [010] directions, respectively. Each of these chains has a graph-set motif of C(12). A weak C–H⋯π interaction is also present between atom C14 and the centroid, Cg1, of aromatic ring A of a neighboring molecule [H14⋯Cg1iv = 2.99 Å, C14⋯Cg1iv = 3.951 (3) Å and C14–H14⋯Cg1iv = 162°; symmetry code: (iv) –x, y – 1/2, z].

**Experimental**

To a solution of 16,17a-dioxo-17-aza-d-homoestra-1,3,5(10)-tri-en-3-yl acetate (0.5 g, 1.46 mmol) in ethyl methyl ketone was added allyl bromide (2 ml) and the mixture was heated for 10 min. Anhydrous potassium carbonate (1.5 g) was then added and reaction mixture was refluxed with stirring for 3.5 h. The slurry obtained was filtered and the residue obtained after removal of solvent was crystallized from methanol to afford crystals of the title compound (yield: 0.47 g, 84%; m.p. 453–455 K).
Crystal data

C₂₃H₂₇NO₄
Mᵣ = 381.46
Orthorhombic, P2₁₂₁₂₁
a = 9.3546 (2) Å
b = 10.7074 (2) Å
c = 19.9204 (5) Å
V = 1995.30 (8) Å³
Z = 4
Dₓ = 1.270 Mg m⁻³

Mo Kα radiation
Cell parameters from 2614 reflections
θ = 2.0–27.5°
μ = 0.09 mm⁻¹
T = 160 (2) K
Tablet, colourless
0.25 × 0.18 × 0.10 mm

Data collection
Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
Absorption correction: none
30780 measured reflections
2596 independent reflections
R(int) = 0.068

Refinement
Refinement on F²
wR(F²) = 0.128
S = 1.06
2591 reflections
256 parameters
H-atom parameters constrained

w = 1/[σ²(Fo)² + (0.0731P)² + 0.1695P]
where P = (Fo)² + 2F²c/3

D–H · · · A
D–H
H · · · A
D–A
D–H · · · A

C4–H₄ · · · O17A⁺ 0.95 2.32 3.204 (3) 155
C8–H₈ · · · O16⁻ 1.00 2.45 3.404 (3) 159
C15–H151 · · · O32w 0.99 2.53 3.428 (3) 151
C15–H152 · · · O32w 0.99 2.44 3.181 (3) 131
C14–H14 · · · Cg1w 1.00 2.99 3.591 (3) 162

Symmetry codes: (i) x, 1+y, z; (ii) ½+x, ½−y, ½−z; (iii) ½−x, 1−y, ½+z; (iv) −x, −y, −½−z. Cg1 is the centroid of the aromatic ring.

The structure of (I) was solved successfully by using the atomic coordinates from the structure of the pseudo-isostuctural compound 17-buty-16,17a-dioxo-17-aza-d-homoestra-1,3,5(10)-tri-en-3-yl acetate (Hema et al., 2004), minus the atoms of the butyl group, as a starting model in the structure refinement. The methyl H atoms were constrained to an ideal geometry (C–H = 0.98 Å), with Ueq(H) = 1.5Ueq(C), but were allowed to rotate freely about the C–C bonds. All remaining H atoms were placed in geometrically idealized positions (C–H = 0.95–1.00 Å) and constrained to ride on their parent atoms, with Ueq(H) = 1.2Ueq(C). Due to the absence of any significant anomalous scatterers in the molecule, attempts to confirm the absolute configuration by refinement of the Flack (1983) parameter in the presence of 1958 Friedel pairs led to an inconclusive value (Flack & Bernardinelli, 2000) of 0.0 (12). Therefore, the Friedel pairs were merged before the final refinement and the absolute configuration was assigned to correspond with that of the known chiral centers in a precursor molecule, which remained unchanged during the synthesis of the title compound. Five low-angle reflections (012, 011, 002, 102 and 100) were partially obscured by the beam stop and were omitted.

Data collection: COLLECT (Nonius, 2000); cell refinement: DENZOSMN (Otwinowski & Minor, 1997); data reduction: DENZOSMN and SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: coordinates taken from pseudo-isostuctural compound; program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1999); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2003).

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References