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5α,6β-Dihydroxycholestan-3β-yl acetate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.051
wR factor = 0.153
Data-to-parameter ratio = 10.0

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

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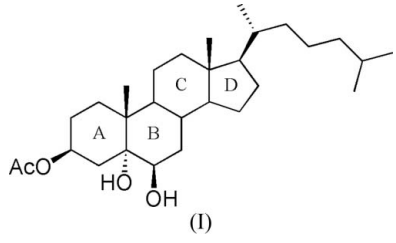
In the title compound, $C_{29}H_{50}O_4$, the six-membered rings adopt slightly flattened chair conformations. The five-membered ring has an envelope conformation. The molecules are linked into chains running along the *b* axis by O—H···O hydrogen bonds.

Comment

As a result of the relatively non-toxic character of bismuth, bismuth(III) salts are considered ecofriendly catalysts suitable for green chemistry (Gaspard-Iloughmane & Le Roux, 2004). The title compound, (I) (Fig. 1), isolated as part of our continuing study on the ring opening of epoxysteroids (Pinto *et al.*, 2006), is an important oxysteroid which can be converted by hydrolysis to the corresponding 3β,5α,6β-triol, one of the cytotoxic oxysteroids that have remarkable influence on cell-membrane composition and function, apoptosis, signal transduction, and immunomodulation (Schroepfer, 2000; Wielkoszynski *et al.*, 2006), as well as having genotoxic effects that have been detected *in vivo* (Cheng *et al.*, 2005).



(I)

The formation of a 5α,6β-disubstituted derivative is clearly demonstrated in this study, thus confirming the *trans*-diaxial nature of the nucleophilic ring opening. All ring junctions are *trans*. The six-membered rings have slightly flattened chair conformations, as shown by the Cremer & Pople (1975) puckering parameters [ring *A*: Q = 0.577 (5) Å, θ = 4.9 (5) and φ = 276 (6)°; ring *B*: Q = 0.564 (4) Å, θ = 3.0 (5) and φ = 269 (8)°; ring *C*: Q = 0.568 (5) Å, θ = 6.6 (5) and φ = 274 (4)°]. The five-membered ring *D* has an envelope conformation with

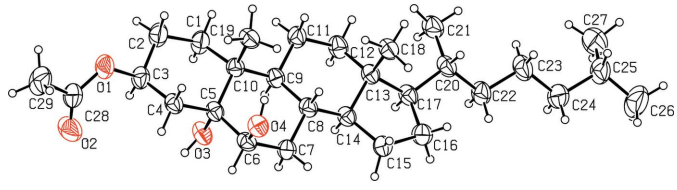


Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

C13 as the flap atom; the puckering parameters are q_2 = 0.464 (5) Å and φ_2 = 185.6 (6)°. The substituent hydroxy groups are axial to the ring system while the substituents at C3 and C17 are equatorial. The molecules assemble in chains along the *b* axis *via* O—H···O hydrogen bonds (Fig. 2 and Table 1).

Experimental

The treatment of 5α,6α-epoxycholestan-3β-yl acetate (0.222 g, 0.50 mmol) (prepared by epoxidation with *m*-chloroperbenzoic acid) in non-purified benzonitrile (15 ml) with a catalytic amount of $BiBr_3$ (0.044 g, 0.10 mmol) afforded the title compound (yield 0.092 g, 40%) which was isolated by column chromotography. Colorless single crystals of (I) [m.p. 479–480 K; literature m.p. 479.6–481.6 K (Yates & Stiver, 1987)] suitable for X-ray diffraction were obtained from acetone at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.67 (*s*, 3H, 18-H_3), 1.18 (*s*, 3H, 19-H_3), 2.02 (*s*, 3H, CH_3CO), 3.54 (*br s*, 1H, 6α-H), 5.15 (*m*, 1H, 3α-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 71.2 (C3), 75.6 (C5), 76.1 (C6), 170.9 (COO).

Crystal data

$C_{29}H_{50}O_4$
M_r = 462.69
Monoclinic, $P2_1$
a = 12.5293 (13) Å
b = 8.6751 (5) Å
c = 14.0660 (16) Å
β = 112.578 (12)°
V = 1411.7 (2) Å^3
Z = 2
Cu *Kα* radiation
μ = 0.55 mm^{-1}
T = 293 (2) K
0.37 × 0.29 × 0.22 mm

Data collection

Enraf–Nonius MACH3 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.768, T_{max} = 0.882
9973 measured reflections
3074 independent reflections
1490 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
3 standard reflections
frequency: 180 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.153
S = 0.99
3074 reflections
306 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H31···O4^{i}	0.82	2.05	2.850 (4)	164

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+2$.

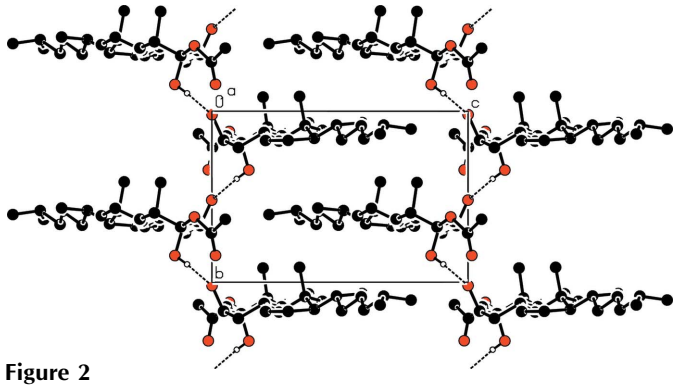


Figure 2
Hydrogen-bonding pattern, viewed along *a*. H atoms not involved in hydrogen bonds (dashed lines) have been omitted for clarity.

All H atoms were refined as riding on their parent atoms [C—H = 0.93–0.98, O—H = 0.82 Å and U_{iso}(H) = 1.2U_{eq}(C,O) or 1.5U_{eq}(methyl C)]. The absolute configuration was not determined from the X-ray data but was known from the synthetic route. In the absence of significant anomalous scattering, Friedel-equivalent reflections were merged prior to the final refinement.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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