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3β-Acetoxy-5α,6β-dihydroxybisnorcholanic acid 22→16 lactone

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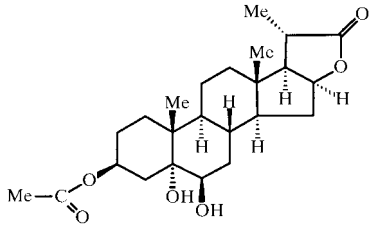
In the title compound, $C_{24}H_{36}O_6$, the ester linkage in ring *A* is equatorial. The six-membered rings *A*, *B* and *C* have chair conformations. The five-membered ring *D* adopts a 13β,14α-half-chair conformation and the *E* ring adopts an envelope conformation. The *A*/*B*, *B*/*C* and *C*/*D* ring junctions are *trans*, whereas the *D*/*E* junction is *cis*.

Comment

In connection with our studies on the synthesis and characterization of bioactive steroids, we determined the molecular structure of 3β-acetoxy-5α,6β-dihydroxybisnorcholanic acid 22→16 lactone, (I), an intermediate compound in the synthesis of the 3β,5α,6β-triol and 3β,5α-diol-6-keto compounds. The starting material was the steroidal alkaloid solasodine, isolated from *Solanum globiferum* Dunae, a plant that grows in the fields of Cuba. These products will be tested as plant growth promoters. The absolute configuration was assumed to be the same as that of previous related structures (Novoa de Armas *et al.*, 1999), and confirmed the one predicted beforehand from the synthetic route.

Fig. 1 shows the molecular structure of the title compound, (I), with the corresponding numbering scheme. The C3—O31 bond of the acetoxy group is equatorially oriented and (−)-antiperiplanar to the C3—C4 bond. The presence of the acetoxy group bonded to C3 does not disturb the chair conformation of the ring *A* of the steroidal nucleus. Ring *A* has a highly symmetrical chair conformation with all asymmetry parameters below 6.4 (3)° (Duax *et al.*, 1976). Rotational symmetry is dominant, a pseudo-C_2 axis intercepts the C3—C4 bond with asymmetry parameters ΔC_2(C3—C4) = 3.2 (3), ΔC_S(C1) = 4.4 (2) and ΔC_S(C3) = 0.7 (2)°. The average magnitude of the torsion angles is 55.37 (12)°. Rings *B*



(I)

and *C* have chair conformations, as expected (Pfeiffer *et al.*, 1985). The five-membered ring *D* adopts a 13β,14α-half-chair conformation (Altona *et al.*, 1968) and the *E* ring, which has a carbonyl group instead of an additional spiro ring, adopts an envelope conformation with the flap at C17 on the opposite side of the mean plane of ring *E* to the methyl substituent C21. In related steroids reported in the Cambridge Structural Database (Allen & Kennard, 1993) that have a spirostan *F* ring (Novoa de Armas *et al.*, 1999), the *E* ring has a half-chair conformation. The *A*/*B*, *B*/*C* and *C*/*D* ring junctions are *trans*, whereas the *D*/*E* junction is *cis*. The bond distances and valence angles are close to the expected values (Honda *et al.*, 1996). The packing of the molecules is assumed to be dictated mainly by intermolecular O—H···O hydrogen bonds, and by intermolecular C—H···O interactions (Taylor & Kennard, 1982). The molecules are linked into an infinite two-dimensional network, with base vectors [100] and [010], by means of the O—H···O hydrogen bonds (Table 2).

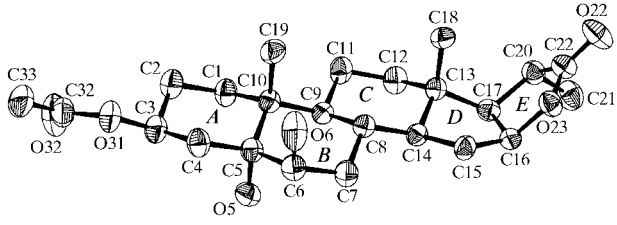


Figure 1
Plot showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms; H atoms have been omitted for clarity.

Experimental

The starting material was the steroidal alkaloid solasodine. The alkaloid was transformed to 3β,16β-dihydroxy-5-bisnorcholenic acid 22→16 lactone, dissolved in dry pyridine with Ac_2O, and converted to the 3β-acetate. The acetate was treated with *m*-chloroperoxybenzoic acid in CH_2Cl_2 to give a mixture of the α and β epoxides, with about 30% of the β component. Upon treatment with 60% $HClO_4$ in aqueous acetone, the mixture yielded (I) with a melting point of 536–538 K. Crystals were grown by slow evaporation from ethanol.

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Crystal data

$C_{24}H_{36}O_6$
M_r = 420.53
Orthorhombic, $P2_12_12_1$
a = 6.3980 (4) Å
b = 9.7142 (5) Å
c = 35.119 (4) Å
V = 2182.7 (3) Å^3
Z = 4
D_x = 1.280 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 42 reflections
θ = 5.03–28.80°
μ = 0.730 mm^{-1}
T = 293 K
Prism, colourless
0.38 × 0.22 × 0.18 mm

Data collection

Siemens $P4$ four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.679, T_{max} = 0.877
3136 measured reflections
2865 independent reflections
2668 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.0243
θ_{max} = 69.13°
$h = -1 \rightarrow 6$
$k = -1 \rightarrow 11$
$l = -1 \rightarrow 42$
3 standard reflections
every 100 reflections
intensity decay: 4.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0457
$wR(F^2)$ = 0.1329
S = 1.051
2865 reflections
278 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0791P)^2 + 0.6321P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0037 (5)

H atoms were calculated geometrically and included in the refinement, but were constrained to ride on their parent atoms. The isotropic displacement parameters of the H atoms were fixed to 1.3 times U_{eq} of their parent atoms. The number of unique reflections is 2291. The number of Friedel related pairs is 574.

Table 1
Selected geometric parameters (Å, °).

O5—C5	1.456 (3)	O23—C22	1.348 (3)
O6—C6	1.431 (4)	O31—C3	1.470 (3)
O22—C22	1.204 (4)	O31—C32	1.328 (5)
O23—C16	1.463 (3)	O32—C32	1.191 (5)
C16—O23—C22	110.9 (2)	O23—C16—C17	105.39 (16)
C3—O31—C32	119.6 (3)	O23—C16—C15	111.7 (2)
O31—C3—C2	111.4 (2)	O22—C22—C20	128.6 (3)
O31—C3—C4	103.4 (2)	O23—C22—C20	110.8 (2)
O5—C5—C10	107.14 (19)	O22—C22—O23	120.6 (3)
O5—C5—C4	107.7 (2)	O32—C32—C33	123.0 (4)
O5—C5—C6	104.4 (2)	O31—C32—O32	124.6 (3)
O6—C6—C7	111.9 (2)	O31—C32—C33	112.4 (4)
O6—C6—C5	109.4 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O32^{i}	0.82	2.26	3.071 (4)	173
O6—H6···O5^{ii}	0.82	2.25	2.986 (3)	150
C3—H3···O6^{iii}	0.98	2.44	3.352 (4)	155
C16—H16···O23^{iv}	0.98	2.42	3.146 (3)	131

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $1+x, y, z$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON* (Spek, 1990) and *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1086). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.
Bergerhoff, G. (1996). *DIAMOND*. Gerhard-Domagk-Strasse 1, Bonn, Germany.
Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. Eliel & N. Allinger, pp. 271–283. New York: John Wiley.
Honda, T., Fujii, I., Hirayama, N., Ishikawa, D., Kawagishi, H., Song, K.-S. & Yoo, I.-D. (1996). *Acta Cryst.* C**52**, 1550–1552.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Novoa de Armas, H., Blaton, N. M., Peeters, O. M., De Ranter, C. J., Pomés Hernández, R., Iglesias Arteagas, M., Pérez Gil, R. & Coll Manchado, F. (1999). *Acta Cryst.* C**55**, 601–603.
Pfeiffer, D., Kutschabsky, L., Kretschmer, R. G., Collect, F. & Adam, G. (1985). *Z. Chem.* **25**, 183–184.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1996). *XSCANS*. *X-ray Single Crystal Analysis System*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.