Absorption correction:
empirical *via* ψ-scan
(*XSCANS*; Siemens, 1994)
$T_{\min} = 0.720$, $T_{\max} = 0.811$
7919 measured reflections
6927 independent reflections
5257 reflections with
$I > 2\sigma(I)$

$h = -1 \rightarrow 11$
$k = -14 \rightarrow 15$
$l = -19 \rightarrow 19$
3 standard reflections
every 297 reflections
intensity decay: random
5.1%

Refinement

Refinement on F^2
$R(F)[F > 4\sigma(F)] = 0.044$
$wR(F^2)[F^2 > 2\sigma(F^2)] = 0.114$
$S(F^2)[F^2 > 2\sigma(F^2)] = 1.068$
6927 reflections
397 parameters
All H-atom positions were refined using a riding model

$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.438$ e Å^{-3}
$\Delta\rho_{\min} = -0.303$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C1	1.669 (2)	S3—C2	1.672 (3)
S2—C1	1.640 (2)	S4—C2	1.637 (3)
P1—C11	1.829 (2)	P2—C41	1.832 (2)
P1—C21	1.833 (2)	P2—C51	1.837 (2)
P1—C31	1.838 (2)	P2—C61	1.842 (2)
P1—C1	1.863 (2)	P2—C2	1.862 (2)
C11—P1—C21	112.95 (10)	C41—P2—C51	113.33 (10)
C11—P1—C31	106.33 (9)	C41—P2—C61	106.49 (9)
C21—P1—C31	110.38 (9)	C51—P2—C61	109.90 (9)
C11—P1—C1	110.18 (10)	C41—P2—C2	109.89 (11)
C21—P1—C1	109.74 (10)	C51—P2—C2	109.82 (10)
C31—P1—C1	107.06 (9)	C61—P2—C2	107.18 (9)
S2—C1—S1	130.24 (14)	S4—C2—S3	130.46 (14)
S2—C1—P1	116.31 (13)	S4—C2—P2	116.78 (14)
S1—C1—P1	113.35 (12)	S3—C2—P2	112.69 (13)
C12—C11—P1	115.63 (14)	C42—C41—P2	115.35 (14)
C16—C11—P1	113.83 (15)	C46—C41—P2	113.6 (2)
C22—C21—P1	113.43 (15)	C52—C51—P2	112.93 (15)
C26—C21—P1	113.6 (2)	C56—C51—P2	114.36 (15)
C32—C31—P1	110.31 (14)	C62—C61—P2	110.42 (14)
C36—C31—P1	113.76 (15)	C66—C61—P2	114.26 (15)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1026). Services for accessing these data are described at the back of the journal.

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Methyl 3β-Bromine-7α-hydroxy-5β-cholan-24-oate

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Abstract

In the title compound, $C_{25}H_{41}BrO_3$, the Br atom bonded to C3 is β-axially oriented and is (−)-synclinal to the C4—C5 bond. The six-membered rings (*A*, *B* and *C*) have chair conformations as expected. The five-membered ring (*D*) adopts a distorted 13β-envelope conformation. The *A*/*B* ring junction is *cis* and the *B*/*C* and *C*/*D* ring junctions are both *trans*.

Comment

Elimination reactions of 3-halogenated steroids yield steroidal alkenes, key intermediates in the synthesis of biologically active steroids such as ecdysteroids and brassinosteroids. We report here the crystal structure

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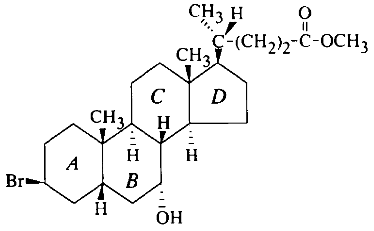
of methyl 3β-bromine-7α-hydroxy-5β-cholan-24-oate, (I), used to introduce a double bond into the steroidal nucleus of quenodeoxycholic acid, the starting material used in the synthesis of analogs of brassinosteroids.



(I)

The absolute stereochemistry was known prior to the X-ray analysis and the results of the Friedel refinement are in complete agreement with it. A view of the molecule with the atomic atom-numbering scheme is shown in Fig. 1. The Br atom bonded to C3 is β-axially oriented and is (−)-synclinal to the C4—C5 bond. The presence of the Br atom does not disturb the chair conformation in ring *A* of the steroidal nucleus. Ring *A* has a symmetrical chair conformation with all asymmetric parameters below 4.2° (Duax, Weeks & Rohrer, 1976). Rotational symmetry is dominant; a C_2 axis intercepts the C2—C3 bond with asymmetric parameters ΔC_2(C2—C3) = 1.3 (8), ΔC_s(C3) = 1.5 (8) and ΔC_s(C1) = 3.5 (8)°. The modulus of the ring *A* torsion angles is in the range 48.3 (7)–53.7 (8)°. Rings *B* and *C* adopt chair conformations, as usual. Ring *D* has a distorted 13β-envelope conformation (Altona, Geise & Romers, 1968). The *A*/*B* junction is *cis* and the *B*/*C* and *C*/*D* junctions are both *trans*. The packing of the molecules is assumed to be dictated by van der Waals interactions. The closest intermolecular contact between non-H atom is 3.529 (8) Å for Br···C24.

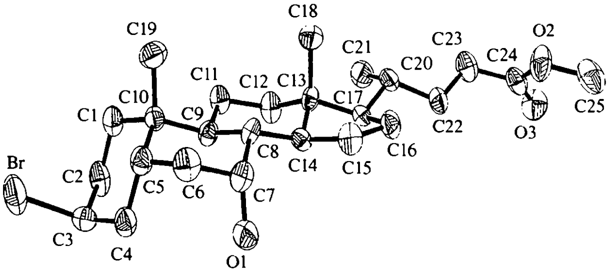


Fig. 1. Plot showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms; H atoms have been omitted for clarity.

Experimental

The title compound was synthesized from 3α,7α-dihydroxy-5β-cholanoic acid by esterification, tosylation and bromo-substitution procedures. The methyl ester was obtained by reaction with methanol and sulfuric acid (Iida *et al.*, 1991), then treated with tosyl chloride and pyridine (Iida & Chan, 1983) to afford methyl 3α-tosyl-7α-hydroxy-5β-cholan-24-oate. Treatment of the tosylate with LiBr, Li_2CO_3 and dimethylformamide yielded a mixture of methyl 3α-bromine-7α-hydroxy-5β-cholan-24-oate and methyl 3β-bromine-7α-hydroxy-5β-cholan-24-oate. The compounds were separated by column chromatography. Crystals of the 3β form suitable for X-ray analysis were obtained by slow evaporation of an *n*-heptane–ethyl acetate solution.

Crystal data

$C_{25}H_{41}BrO_3$
M_r = 469.49
Orthorhombic
$P2_12_12_1$
a = 7.641 (3) Å
b = 16.534 (1) Å
c = 18.569 (2) Å
V = 2345.9 (10) Å^3
Z = 4
D_x = 1.329 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 8–36°
μ = 1.775 mm^{-1}
T = 293 (2) K
Prismatic
0.4 × 0.2 × 0.2 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
4100 measured reflections
3873 independent reflections
1583 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.033

$\theta_{\rm max}$ = 27.97°
$h = -10 \rightarrow 10$
$k = -1 \rightarrow 21$
$l = -1 \rightarrow 24$
2 standard reflections every 200 reflections frequency: 60 min intensity decay: 2.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.127$
$S = 1.169$
3872 reflections
263 parameters
All H-atom parameters were refined as riding atoms with a common isotropic displacement parameter
$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 2.0363P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.005$
$\Delta\rho_{\rm max}$ = 0.415 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.764 e Å^{-3}

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: known prior to the X-ray analysis and the results of the Friedel refinement are in complete agreement with it; 35 Friedel pairs were used in the refinement (Flack, 1983)
Flack parameter = 0.00 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br	0.14733 (13)	0.63445 (5)	0.65591 (6)	0.0691 (3)
C1	0.0448 (10)	0.8285 (4)	0.6788 (4)	0.044 (2)
C2	0.0198 (9)	0.7882 (4)	0.6063 (5)	0.046 (2)
C3	0.1657 (12)	0.7291 (4)	0.5901 (4)	0.048 (2)

C4	0.3402 (11)	0.7681 (4)	0.5973 (4)	0.043 (2)
C5	0.3692 (10)	0.8099 (4)	0.6703 (4)	0.039 (2)
C6	0.5525 (9)	0.8486 (4)	0.6755 (4)	0.047 (2)
C7	0.5704 (10)	0.9275 (4)	0.6344 (4)	0.039 (2)
C8	0.4260 (8)	0.9860 (4)	0.6568 (4)	0.033 (2)
C9	0.2438 (9)	0.9489 (4)	0.6450 (4)	0.034 (2)
C10	0.2225 (9)	0.8694 (4)	0.6900 (4)	0.034 (2)
C11	0.0938 (8)	1.0089 (3)	0.6562 (4)	0.040 (2)
C12	0.1232 (10)	1.0917 (4)	0.6207 (4)	0.043 (2)
C13	0.2983 (8)	1.1281 (4)	0.6412 (3)	0.031 (2)
C14	0.4389 (9)	1.0672 (4)	0.6193 (4)	0.031 (2)
C15	0.6122 (9)	1.1128 (4)	0.6268 (4)	0.044 (2)
C16	0.5611 (10)	1.2019 (4)	0.6098 (4)	0.042 (2)
C17	0.3611 (10)	1.2031 (4)	0.5987 (4)	0.033 (2)
C18	0.3033 (10)	1.1468 (4)	0.7229 (3)	0.049 (2)
C19	0.2311 (10)	0.8881 (4)	0.7720 (3)	0.050 (2)
C20	0.2786 (11)	1.2869 (4)	0.6154 (4)	0.040 (2)
C21	0.0806 (10)	1.2873 (4)	0.6023 (5)	0.052 (2)
C22	0.3696 (11)	1.3523 (3)	0.5721 (4)	0.044 (2)
C23	0.3055 (10)	1.4383 (4)	0.5887 (4)	0.051 (2)
C24	0.4218 (11)	1.5018 (4)	0.5590 (5)	0.046 (2)
C25	0.6982 (11)	1.5633 (5)	0.5753 (4)	0.072 (3)
O1	0.5659 (7)	0.9138 (3)	0.5588 (3)	0.0533 (15)
O2	0.5676 (8)	1.5074 (3)	0.5986 (3)	0.062 (2)
O3	0.3988 (7)	1.5419 (3)	0.5067 (3)	0.059 (2)

Table 2. *Selected geometric parameters (Å, °)*

Br—C3	1.990 (7)	C3—C4	1.487 (11)
C1—C2	1.513 (10)	C4—C5	1.538 (9)
C1—C10	1.531 (9)	C5—C10	1.535 (9)
C2—C3	1.513 (10)		
C2—C1—C10	115.2 (6)	C3—C4—C5	113.8 (7)
C3—C2—C1	111.6 (7)	C10—C5—C4	113.1 (7)
C4—C3—C2	111.3 (6)	C10—C5—C6	112.5 (5)
C4—C3—Br	110.4 (6)	C4—C5—C6	111.9 (7)
C2—C3—Br	109.5 (5)		
C10—C1—C2—C3	53.7 (8)	C3—C4—C5—C10	−52.4 (8)
C1—C2—C3—C4	−53.3 (8)	C2—C1—C10—C5	−50.5 (8)
C2—C3—C4—C5	53.6 (9)	C4—C5—C10—C1	48.3 (7)
Br—C3—C4—C5	−68.2 (7)		

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1983).

The X-ray diffraction experiments were carried out at the Diffraction National Laboratory (LANADI), La Plata, Argentina.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1305). Services for accessing these data are described at the back of the journal.

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1,12-Dodecanediol

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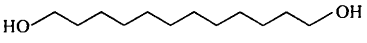
Abstract

The crystal structure analysis of 1,12-dodecanediol, $C_{12}H_{26}O_2$, has been carried out by X-ray diffraction. Both hydroxyl groups show a *trans* conformation with respect to the hydrocarbon skeleton. The structure, which adopts a herring-bone motif, appears to be common to α,ω-disubstituted long-chain alkanes with even numbers of C atoms. These structures could be regarded as model structures of the smectic C liquid crystals.

Comment

There are a few reports of the crystal structures of α,ω-alkanediols. Recently, one of the present authors analyzed the crystal structure of two long-chain α,ω-alkanediols. The structural feature of the compounds with an even number of C atoms (1,16-hexadecanediol) was a herring-bone motif with both hydroxyl groups located at the ends of the molecular skeleton having a *trans* conformation (Nakamura & Yamamoto, 1994). The homolog with an odd number of C atoms (1,13-tridecanediol) showed a parallel arrangement of the molecules similar to that of the smectic A liquid crystals, with one of the hydroxyl groups *gauche* with respect to the hydrocarbon skeleton, the other being *trans* (Nakamura, Tanihara & Takayama, 1997). These compounds have been of great interest recently as liquid crystalline model materials. In the present work, the crystal structure of the title compound, 1,12-dodecanediol, (I), has been determined.



(I)