N2—C2A—C2B	112.5 (5)	O11—C11—N1	121.3 (6)
N2—C2A—C2′	107.7 (5)	O11—C11—C12	122.2 (6)
C2B—C2A—C2′	112.1 (5)	N1—C11—C12	116.5 (6)

Table 3. *Hydrogen-bonding geometry (Å)*

N1···OW3^{i}	3.038 (7)	OW2···O1^{iii}	2.800 (7)
N2···OW4	2.948 (7)	OW2···O2	2.763 (6)
N2D···O′	2.733 (7)	OW3···OW5	2.751 (8)
N2E···O′^{ii}	2.701 (7)	OW3···OW1^{iv}	2.667 (7)
N3···OW3	2.878 (7)	OW4···OW2	3.056 (8)
OW1···O11	2.718 (7)	OW5···O′^{v}	2.710 (7)
OW1···OW2^{ii}	2.782 (8)	OW5···O1	2.947 (7)

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

A single crystal was sealed in a 1.00 mm quartz capillary tube along with mother liquor (McPherson, 1982). The crystal diffracted poorly, undoubtedly due to the inclusion of five water molecules per tripeptide in the structure. Data extended to 1.03 Å resolution; the resulting number of observed reflections was therefore limited, providing insufficient data to refine H-atom parameters and producing large agreement factors. A difference electron density synthesis following the initial structure solution revealed the locations of five water molecules. In order to estimate the validity of parameters introduced in the refinement process, every tenth reflection was set aside for calculation of an R_{free} value (Brunger, 1992). The H atoms involved in intermolecular and intramolecular interactions were placed in observed positions found in electron difference density maps and refined as riding atoms, maintaining the observed non-H-atom–H-atom separation. Inspection of the R_{free} value favored this approach over positions generated by standard geometry. Lifting of the initial restraints in the refinement process resulted in a slight deformation of the phenyl ring. The final difference electron density map showed a uniform distribution of residual electron density with some indication of disorder of the leucine methyl C atoms.

Data collection: *DATCOL* for *CAD*-4 (Enraf–Nonius, 1982). Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1993). Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1197). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Side-Chain Substituted Cholesterol Analog

ZSOLT BÖCSKEI,[a]* ZSUZSA SZENDI[b] AND FREDERICK SWEET[c]

[a]Department of Chemical Research, Chinoin Pharmaceuticals, POB 110, 1325 Budapest, Hungary, [b]Department of Organic Chemistry, József Attila University, Dóm tér 8, H-6720 Szeged, Hungary, and [c]Department of Obstetrics and Gynecology, Washington University, School of Medicine, 4911 Barnes Hospital Plaza, St. Louis, MO 63110, USA. E-mail: bocskei@ludens.elte.hu

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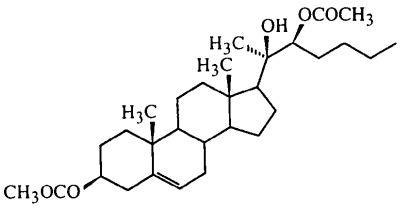
Abstract

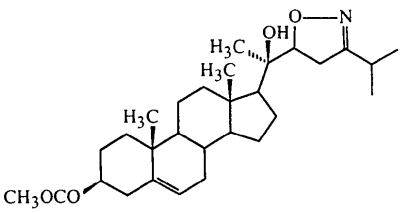
The crystal structure of (20*R*,22*RS*)-27-norcholest-5-en-3β,20,22-triol 3,22-diacetate, $C_{30}H_{48}O_5$, is reported.

Comment

A mixture of (20*R*,22*RS*)-27-norcholest-5-en-3β,20,22-triol 3,22-diacetate was fractionally crystallized and provided a single isomer, (1), for the present X-ray analysis. The 20*R*/*S* mixture was obtained by thermal decomposition of the hydrazone by the Wolff–Kishner reduction of (20*R*)-3β,20,26-trihydroxy-27-norcholest-5-en-22-one, which undergoes a base-catalyzed 1,5-



(1)



(2)

hydride shift during the reaction (Szendi, Tasi, Böcskei, Nyerges, Forgó & Sweet, 1996).

Analogs of cholestrol with an OH group in the side chain, like that of (1) (Fig. 1), have been described in the literature. The stereochemistry at the C20 and C22 positions has been investigated for many years by many different methods (Chaudhuri, Nickolson, Kimball & Gut, 1970; Morisaki, Sato & Ikekawa, 1977; Kyler & Watt, 1981; Kametani, Tsubuki, Furuyama & Honda, 1984), but it was reliably established only when the configuration of natural 20-hydroxyecdysone was determined in the crystalline state (Dammier & Hoppe, 1971). The present X-ray study confirms the 20*R* configuration proposed earlier by us for a 20-hydroxy analog of cholesterol (Szendi & Sweet, 1991).

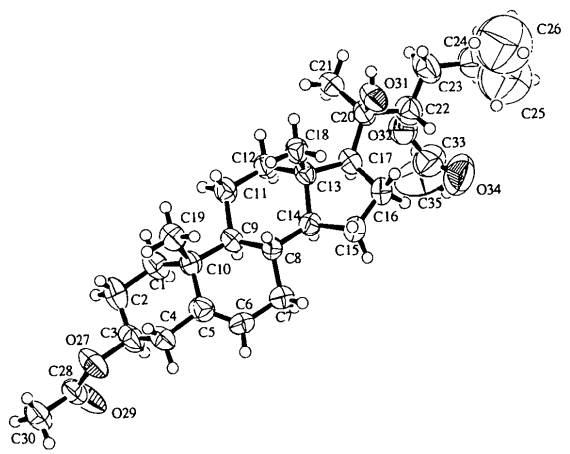


Fig. 1. The molecular structure and atomic numbering for compound (1). Displacement ellipsoids are plotted at the 50% probability level.

The crystal structure determination of (1) reveals that a single medium–strong intermolecular hydrogen bond exists between the carbonyl O29 atom and the O31—H31 group. Literature data suggest that compound (2) ($C_{29}H_{45}NO_4$; Verenich *et al.*, 1992) is isostructural with compound (1) (Figs. 2 and 3). Although other structures (Weber, Craven, Sawzik & McMullan, 1991; Sawzik & Craven, 1979; Barner, Hubscher, Daly & Schonholzer, 1981) are seemingly closely similar analogs of (1), their crystal structures are not isostructural with this steroid, apparently because they do not contain an OH group at the C20 position. These results illustrate the role that hydrogen bonds play in maintaining structures within a family of isostructural crystals (Kálmán, Párkányi & Argay, 1993).

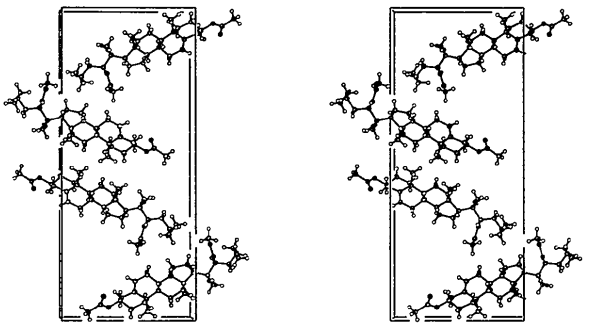


Fig. 2. Packing diagram of the title compound (1), with the *a* axis horizontal and the *b* axis vertical.

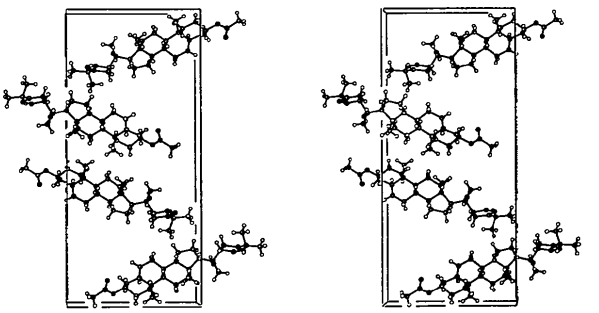


Fig. 3. Packing diagram of (2), with the *c* axis vertical and the *a* axis horizontal.

Experimental

The title compound, (1) (m.p. 423–426 K) was synthesized according to Szendi, Tasi, Böcskei, Nyerges, Forgó & Sweet (1996).

Crystal data

$C_{30}H_{48}O_5$
M_r = 488.68
Orthorhombic
$P2_12_12_1$
a = 13.926 (2) Å
b = 32.800 (4) Å
c = 6.283 (4) Å
V = 2870.0 (18) Å^3
Z = 4
D_x = 1.131 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 16 reflections
θ = 27.61–48.65°
μ = 0.592 mm^{-1}
T = 293 (2) K
Plate
0.40 × 0.30 × 0.10 mm
White

Data collection

Rigaku AFC-6*S* diffractometer	θ_{max} = 75.18°
$\omega/2\theta$ scans	$h = 0 \rightarrow 17$
Absorption correction: none	$k = 0 \rightarrow 41$
3356 measured reflections	$l = 0 \rightarrow 7$
3356 independent reflections	3 standard reflections monitored every 150 reflections
1214 observed reflections $[I > 2\sigma(I)]$	intensity decay: 0.67%

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.388 e Å^{-3}
$R[F^2 > 2\sigma(F^2)]$ = 0.0705	$\Delta\rho_{min}$ = −0.276 e Å^{-3}
$wR(F^2)$ = 0.3207	Extinction correction: *SHELXL*93 (Sheldrick, 1993)
S = 1.051	Extinction coefficient: 0.0007 (4)
3347 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
316 parameters	
Only H-atom U's refined	
$w = 1/[\sigma^2(F_o^2) + (0.1237P)^2 + 1.9639P]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max}$ = 0.350	

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O27	0.8467 (5)	1.0440 (2)	1.5471 (14)	0.091 (3)
O29	0.8029 (5)	1.0811 (3)	1.8198 (15)	0.114 (3)
O31	1.6260 (5)	1.1219 (2)	0.9107 (12)	0.082 (2)
O32	1.6433 (5)	1.2040 (2)	1.2979 (14)	0.091 (2)
O34	1.6073 (9)	1.2594 (3)	1.1087 (21)	0.145 (4)
C1	1.1149 (6)	1.0598 (3)	1.5800 (16)	0.071 (3)
C2	1.0159 (7)	1.0396 (3)	1.6215 (18)	0.081 (3)
C3	0.9392 (7)	1.0658 (3)	1.5257 (20)	0.075 (3)
C4	0.9525 (6)	1.0719 (3)	1.2936 (18)	0.074 (3)
C5	1.0515 (6)	1.0900 (3)	1.2440 (17)	0.064 (3)
C6	1.0600 (7)	1.1225 (3)	1.1213 (19)	0.076 (3)
C7	1.1531 (6)	1.1427 (3)	1.0664 (19)	0.070 (3)
C8	1.2390 (6)	1.1153 (2)	1.1113 (15)	0.050 (2)
C9	1.2284 (6)	1.0949 (2)	1.3277 (14)	0.049 (2)
C10	1.1358 (6)	1.0680 (2)	1.3427 (13)	0.050 (2)
C11	1.3201 (6)	1.0724 (3)	1.3948 (16)	0.064 (2)
C12	1.4120 (6)	1.0977 (3)	1.3706 (15)	0.059 (2)
C13	1.4236 (5)	1.1155 (2)	1.1458 (14)	0.049 (2)
C14	1.3310 (5)	1.1396 (2)	1.1037 (15)	0.049 (2)
C15	1.3548 (6)	1.1639 (2)	0.9015 (16)	0.064 (2)
C16	1.4612 (7)	1.1742 (3)	0.9210 (17)	0.069 (3)
C17	1.4985 (5)	1.1506 (2)	1.1188 (16)	0.054 (2)
C18	1.4385 (6)	1.0810 (2)	0.9859 (15)	0.059 (2)
C19	1.1496 (7)	1.0268 (3)	1.2239 (16)	0.069 (3)
C20	1.6063 (5)	1.1408 (2)	1.1136 (17)	0.060 (2)
C21	1.6406 (7)	1.1144 (3)	1.2950 (18)	0.080 (3)
C22	1.6652 (6)	1.1814 (3)	1.1053 (21)	0.079 (3)
C23	1.7698 (7)	1.1766 (3)	1.095 (3)	0.103 (4)
C24	1.8299 (9)	1.2123 (3)	1.037 (3)	0.136 (6)
C25	1.8151 (20)	1.2273 (7)	0.812 (3)	0.288 (15)
C26	1.8620 (19)	1.1957 (7)	0.669 (4)	0.332 (18)
C28	0.7854 (7)	1.0546 (3)	1.6937 (19)	0.069 (3)
C30	0.6944 (7)	1.0303 (3)	1.6819 (22)	0.099 (4)
C33	1.6157 (11)	1.2429 (4)	1.288 (3)	0.112 (5)
C35	1.5983 (15)	1.2631 (5)	1.486 (4)	0.185 (10)

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

O27—C3	1.478 (11)	O32—C22	1.453 (13)
O31—C20	1.445 (11)	C5—C6	1.321 (13)
O32—C33	1.334 (14)		
C6—C5—C10	123.8 (8)	C10—C5—C4	115.5 (8)
C6—C5—C4	120.7 (9)		
C28—O27—C3—C2	102.7 (11)	O31—C20—C22—C23	−64.5 (13)
C16—C17—C20—O31	−50.7 (9)	C21—C20—C22—C23	54.4 (14)
C16—C17—C20—C21	−174.2 (8)	C17—C20—C22—C23	−178.7 (11)
C13—C17—C20—C22	−175.1 (9)	C20—C22—C23—C24	166.1 (11)
C33—O32—C22—C20	−128.6 (11)	C23—C24—C25—C26	−72.5 (23)

D—H···A	D···A	D—H···A
O31—H31···O29^i	2.861 (11)	157 (7)

Symmetry code: (i) $1 + x, y, z - 1$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1164). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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