

3 α ,7 α ,12 α -Triformyloxy-24-nor-5 β -chol-22-eneL. C. R. Andrade,^a J. A. Paixão,^a
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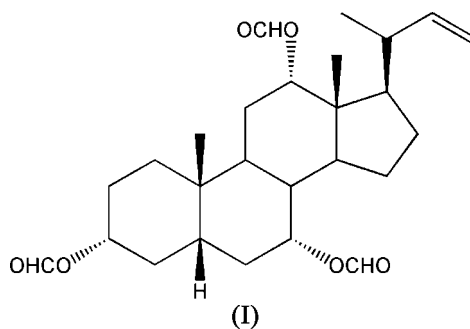
Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.036
 wR factor = 0.110
Data-to-parameter ratio = 8.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{26}\text{H}_{38}\text{O}_6$, has a *cis* junction between two of the six-membered rings (*A* and *B*). All three of the six-membered rings have chair conformations that are slightly flattened and the five-membered ring has an unusual 13 β -envelope conformation. The 7 α and 12 α ring substituents are both axial and the 3 α and 17 β groups are equatorial and pseudo-equatorial, respectively. The 3 α -formyloxy group is involved in one weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ bond, which links the molecules into dimers in a head-to-head fashion.

Comment

Bile acids, such as cholic acid, have many uses in supramolecular chemistry (Davis, 1993). The crystallographic study of these receptors and their synthetic intermediates improves the understanding of molecular-recognition principles. In this context, the 3 β isomer of the title compound, (I), has already been studied (Andrade *et al.*, 2004). In an attempt to construct a cholic acid-based synthetic receptor, (I) has been synthesized as an intermediate according to the method reported by Davis & Walsh (1996).



An *ORTEP* (Johnson, 1976) plot of (I) is shown in Fig. 1. The three formyloxy groups have 3 α , 7 α and 12 α configurations. Average values for bond lengths are in good agreement with reported values (Allen *et al.*, 1987).

The distance between the terminal atoms O31A and C23 is 13.841 (8) Å, and the C19–C10 \cdots C13–C18 pseudo-torsion angle [-1.6 (2) $^\circ$] indicates that the molecule is not twisted. Rings *A* (C1–C5/C10), *B* (C5–C10) and *C* (C8/C9/C11–C14) have slightly distorted chair conformations, with average torsion angles of 56 (2), 53 (2) and 53 (2) $^\circ$, respectively, as shown by the values of the θ puckering parameter (Cremer & Pople, 1975) of 174.7 (3), 7.5 (2) and 4.5 (2) $^\circ$ for rings *A*, *B* and *C*, respectively. A *cis* *A/B* ring junction characteristic of the 5 β configuration is evidenced by the bowing angle between ring *A* and the least-squares plane of the remaining rings [56.57 (9) $^\circ$]. The five-membered ring *D* (C13–C17) assumes a

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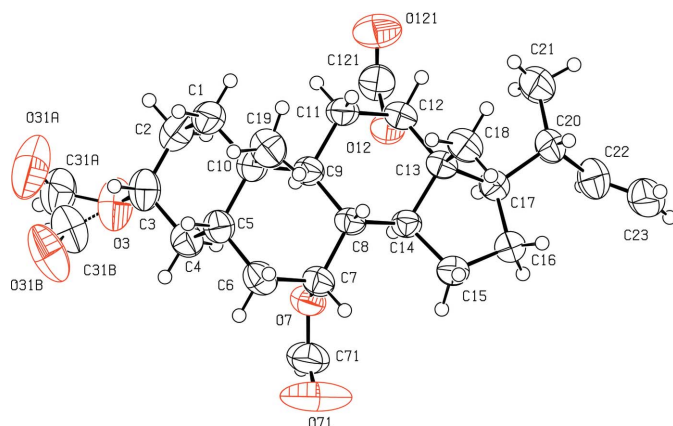


Figure 1

A drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

13 β -envelope conformation [puckering parameters $q_2 = 0.480$ (3) Å and $\varphi_2 = -175.7$ (4) $^\circ$; pseudo-rotation (Altona *et al.*, 1968) and asymmetry parameters (Duax & Norton, 1975): $\Delta = 26.2$ (4), $\varphi_m = 48.6$ (2), $\Delta C_s(14) = 30.4$ (3), $\Delta C_2(13,14) = 17.5$ (3), $\Delta C_s(13) = 5.4$ (3) $^\circ$]. This unusual ring conformation is different from that found in the 3 β isomer (Andrade *et al.*, 2004).

The 3 α substituent is equatorial, with an angle of 70.86 (19) $^\circ$, and the two 7 α and 12 α substituents are axial (Luger & Bülow, 1983), with angles of 7.91 (19) and 4.71 (18) $^\circ$, respectively (the angles are between the substituent bond to the ring and the normal to the mean plane of the ring atoms). The 17 β chain is pseudo-equatorial. The orientation of the C5–C17 reference plane relative to the C17/C20/C21 and C20/C22/C23 least-squares planes is characterized by angles of 26.1 (4) and 86.8 (3) $^\circ$, respectively, with the angle between these two planes being 89.4 (3) $^\circ$. The C17–C20–C22–C23 [–116.1 (4) $^\circ$] and C21–C20–C22–C23 [119.6 (5) $^\circ$] torsion angles are similar to those found for the 3 β isomer [–109.7 (3) and 126.7 (3) $^\circ$; Andrade *et al.*, 2004].

The intra- and intermolecular C–H \cdots O hydrogen-bonding network of (I) (Table 1) is also similar to that of the β -epimer.

Experimental

The title compound was prepared according to previously described procedures, starting from the formylation of cholic acid (Tserng & Klein, 1977) with formic and perchloric acids, followed by oxidative decarboxylation (Concepción *et al.*, 1986) with iodosobenzene diacetate. Crystals of (I) suitable for X-ray analysis were obtained from an ethyl acetate solution by slow evaporation.

Crystal data

C₂₆H₃₈O₆
 $M_r = 446.56$
 Monoclinic, $P2_1$
 $a = 10.8379$ (11) Å
 $b = 8.3682$ (11) Å
 $c = 13.621$ (8) Å
 $\beta = 95.92$ (3) $^\circ$
 $V = 1228.7$ (8) Å³

$Z = 2$
 $D_x = 1.207$ Mg m^{–3}
 Cu $K\alpha$ radiation
 $\mu = 0.68$ mm^{–1}
 $T = 298$ (2) K
 Prism, colourless
 0.24 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius MACH-3
 diffractometer
 Profile data from $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.774$, $T_{\max} = 0.873$
 5138 measured reflections

2614 independent reflections
 1905 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$
 $\theta_{\text{max}} = 72.5^\circ$
 3 standard reflections
 frequency: 300 min
 intensity decay: 9.6%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.110$
 $S = 1.01$
 2614 reflections
 312 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.1662P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.13$ e Å^{–3}
 $\Delta\rho_{\text{min}} = -0.11$ e Å^{–3}
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.0046 (7)

Table 1

Hydrogen-bond geometry (Å, $^\circ$).

D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
C2–H2B \cdots O31A ⁱ	0.97	2.59	3.5331	164
C4–H4A \cdots O7	0.97	2.43	3.0662	122
C14–H14 \cdots O12	0.98	2.54	2.9286	104
C17–H17 \cdots O12	0.98	2.48	2.8947	105
C22–H22 \cdots O31B ⁱⁱ	0.93	2.57	3.3366	140
C31A–H31B \cdots O121 ⁱⁱⁱ	1.13	2.59	3.6611	158
C121–H121 \cdots O31B ⁱ	0.93	2.42	3.2211	144

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

H atoms were positioned geometrically, with C–H = 0.93 and 0.98 (for methine H), 0.93 and 0.97 (for methylene H) and 0.96 Å (for methyl H), and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H. Friedel pairs were merged because the anomalous dispersion of the light atoms at the Cu $K\alpha$ wavelength was negligible, and thus the absolute configuration was not determined from the X-ray data. However, the configuration was known from the synthetic route. In the 3 α branch, one O atom, one C atom and one H atom were refined with statistical disorder over two positions, with site occupancies of 0.613 (8) (for O31A, C31A and H31A) and 0.387 (8) (for O31B, C31B and H31B).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *PLATON* (Spek, 2003); 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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