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(20*R*)-Methyl-3-oxochola-1,4,22-trien-24-oate

Manuela Linker, Markus Schürmann, Hans Preut* and Wolfgang Kreiser

Fachbereich Chemie, Universität Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany

Correspondence e-mail:
uch002@uxp1.hrz.uni-dortmund.de

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Methyl-3-oxochola-1,4,22-trien-24-oate, $C_{25}H_{34}O_3$, is a naturally occurring steroid, the configuration at C20 of which has not yet been determined. Here we report the synthesis and the crystal structure analysis *via* X-ray diffraction of the 20*R*-epimer. Comparison with data reported for the natural product indicates a different configuration.

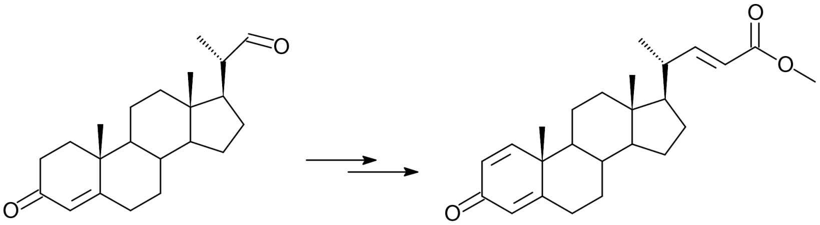
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.047
wR factor = 0.114
Data-to-parameter ratio = 10.1

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

Comment

Tomono *et al.* (1999) isolated an unknown steroid from an octocoral *Dendronephthya sp*. of the order Alcyonacea and they characterized it as methyl 3-oxochola-1,4,22-trien-24-oate without specifying the configuration at C20. In order to determine its structure unequivocally, an X-ray analysis has been undertaken. Starting from 3-keto-bisnor-4-cholen-22-al, the title compound, (I), has been synthesized in a three-step procedure and crystals were grown from cyclohexane.


(II) (I)

The structure shown in Fig. 1 discloses the expected all-*trans* stereochemistry at the ring junctions. All bond lengths and angles of the steroidal skeleton are within normal range (Duax & Norton, 1975). Selected torsion angles of the side chain and ring *D* are given in Table 1. The calculated values of Δ = 20.15° and ψ_m = 45.2° indicate a *D* ring conformation midway between a 13β-envelope and a 13β,14α-half-chair (Altona *et al.*, 1968). To us, the most valuable piece of information that can be deduced from Fig. 1 is the relative configuration at C20. Since the stereochemistry in the cholan-type ring system is established, one can easily determine the C20 configuration to be *R*. The substituents at C20 are staggered with respect to those at C17, with the methyl C21 *anti* to C16. The remainder of the side chain extends away from the steroid rings. The shortest intermolecular H···O contact is 2.641 (3) Å. A comparison of the title compound with the natural product shows great differences mainly in the ^{1}H NMR chemical shifts of the side chain. This observation indicates a different configuration at C20. To obtain a reliable proof, the corresponding (20*S*)-methyl ester has been synthesized. Its crystal structure is described by Linker *et al.* (2001).

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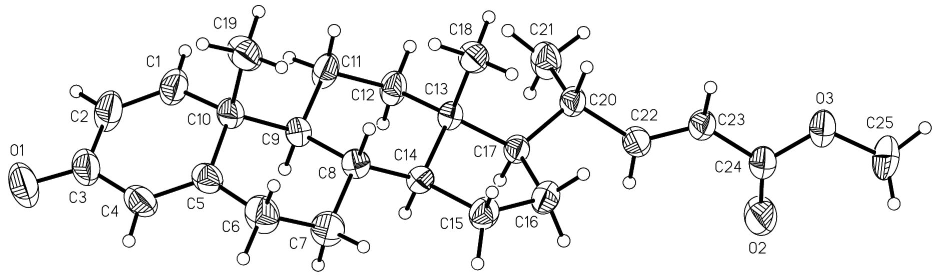

Figure 1

View (*SHELXTL-Plus*; Sheldrick, 1991) of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 30% probability levels. H atoms are drawn as circles of arbitrary radii.

Experimental

The title compound, (I), was synthesized from 3-keto-bisnor-4-cholen-22-al by Horner–Wittig reaction, re-esterification and DDQ-dehydration. The resulting ester was purified by column chromatography (cyclohexane–ethyl acetate = 2:1, R_F = 0.30) and then crystallized from cyclohexane with the addition of active charcoal. After filtration of the hot solution, crystals (m.p. 440.5–441.5 K) began to grow immediately on cooling to room temperature.

Table 1

Selected torsion angles (°).

C17—C13—C14—C15	45.9 (2)	C16—C17—C20—C21	172.8 (2)
C13—C14—C15—C16	−32.3 (3)	C13—C17—C20—C21	−66.0 (3)
C14—C15—C16—C17	5.7 (3)	C17—C20—C22—C23	−132.3 (3)
C15—C16—C17—C13	22.1 (3)	C21—C20—C22—C23	103.0 (3)
C14—C13—C17—C16	−41.0 (2)		

Crystal data

$C_{25}H_{34}O_3$
M_r = 382.52
Monoclinic, $P2_1$
a = 10.4164 (2) Å
b = 7.5425 (2) Å
c = 14.4209 (3) Å
β = 107.7621 (11)°
V = 1078.98 (4) Å^3
Z = 2
D_x = 1.177 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9365 reflections
θ = 3.0–27.5°
μ = 0.08 mm^{-1}
T = 293 (1) K
Block, colourless
0.50 × 0.50 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
316 frames *via* ω-rotation ($\Delta\omega$ = 1°) with three sets at different κ-angles and two times 30 s per frame
9365 measured reflections
2593 independent reflections
1545 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.032
$\theta_{\rm max}$ = 27.5°
$h = -13 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -18 \rightarrow 17$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.114
S = 1.01
2593 reflections
257 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.13 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.13 e Å^{-3}

H atoms were placed in calculated positions with $U_{\rm iso}$ constrained to be 1.5 times $U_{\rm eq}$ of the carrier atom for the methyl–H and 1.2 times $U_{\rm eq}$ for the remaining H atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97 and *PARST*95 (Nardelli, 1995).

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