X-ray crystal structure of 3β,22-dihydroxy-23,24-dinorchol-4-ene

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The crystal structure of 3β,22-dihydroxy-23,24-dinorchol-4-ene, previously synthesised from 3-oxo-23,24-dinorchol-4-ene-22-al, has been determined by X-ray crystallography.

Keywords: steroids, X-ray crystallography.

Introduction

The title compound (I) was synthesised as part of a study on 23-oxocholestane conjugates.[1]

We undertook an X-ray crystallographic analysis to confirm the molecular structure and to establish the crystal structure. Of particular interest was the potential hydrogen bonding between hydroxy groups at positions 3 and 22.[2] Previously, the helical arrangement of steroid molecules in the solid state formed by a combination of the crystallographic screw axis and intermolecular hydrogen bonding has been reported .[3]

X-ray crystallography

All crystallographic measurements were performed with a Bruker-KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation. A rotating anode source, an area detector and ϕ and ω scans were used with a detector-to-crystal distance of 35 mm. The programs DENZO[4] and COLLECT[5] were used in data collection and cell refinement. $C_{22}H_{36}O_2$, M = 332.5, T = 120(2) K, λ = 0.71073Å, Monoclinic, $P2_1$, a = 10.4690(7), b = 7.1864(6), c = 13.3318(11) Å, β = 104.142(3)°, U = 972.61(13)Å^3, Z = 2, Density (calculated) = 1.135 Mg/m^3, μ = 0.070 mm^{-1}, F(000) = 368, Crystal size = 0.35 × 0.10 × 0.02 mm, θ range for data collection = 3.15 to 27.50°, Index ranges: –13<=*h*<=13, –7<=*k*<=9, –17<=*l*<=17, reflections collected = 7745, independent reflections = 2329 [R(int) = 0.0936], observed reflections [(I>2σ(I)] = 1209, number of parameters= 223, Goodness-of-fit on F^2 (S) = 0.947 , final R_1 [I>2σ(I)] = 0.0596, R_2 (all data) = 0.1502. The structure was solved with SIR-97[6] and refined with SHELX-97.[7]

All non-hydrogen atoms were allowed to refine with anisotropic displacement parameters. The hydrogen atoms were located geometrically and allowed to ride with isotropic temperature factors constrained to be 1.1 U_{eq} (non-methyl hydrogens) or 1.4 U_{eq} (methyl hydrogens) of the attached atom. Plots and molecular geometries were obtained with PLATON.[8] Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 239661).

Discussion

The bond lengths and angles are normal for this type of molecule. As no heavy atom is present the absolute stereochemistry of the molecule has not been determined by the X-ray study and is assumed to correspond to that of pregnane. The chiral centres in the molecule (Fig.1) then become R at C8, C10, and C17 and S at C3, C9, C13, C14 and C20.

Ring conformations are: A (C1α, C2β half-chair), B (chair), C (chair), D (C13 envelope).

The bond lengths and angles are as expected with C4–C5 = 1.325(5)Å; the non-bonded intramolecular separation O2...O3 = 11.995(4)Å and the pseudo-torsion angle C19–C10...C13–C18 = –0.1(3)°.

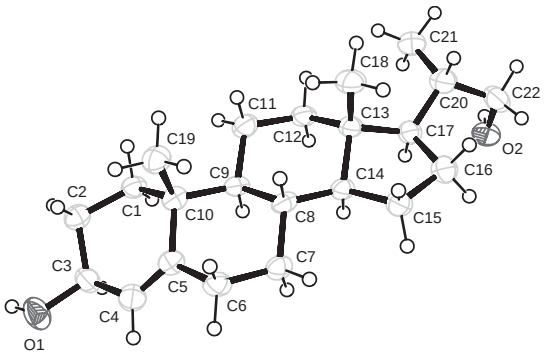

Fig.1 The atomic arrangement in the molecule

Head-to-tail intermolecular hydrogen bonds between the hydroxy groups attached to positions 3 and 22 are present. Here O1–H1...O2^{i} = 161(3)° (symmetry code (i) = 2–*x*, –0.5+*y*,1–*z*), O1–H1 = 0.98(4)Å, O1...O2^{i} = 2.677(4)Å and H1...O2^{i} = 1.73(4)Å. This results in chains of hydrogen-bonded molecules that form into a helix or corkscrew arrangement along the b axis of the unit cell as dictated by the crystallographic screw axis. Another hydrogen bond is present: O2–H2...O1^{ii} = 175(4)° (symmetry code (ii) = *x*,*y*, –1+*z*), O2-H2 = 0.97(3)Å, O2...O1^{ii} = 2.665(4)Å and H2...O1^{ii} = 1.70(4)Å. This links molecules into chains along the c axis on the unit cell.

Figure 2 shows the molecules linked by hydrogen bonding. The combination of the two hydrogen bonds results in an infinite helical arrangement of ...O2–H2...O1–H1...O2–H2... atoms along the b axis at each corner of the unit cell. Here O1 and O2 oxygens of the hydroxy groups act as both donors and acceptors in the hydrogen bonding scheme. A similar hydrogen bonding motif between hydoxy groups in positions 3 and 17 has been found in 2-(hydroxymethyl)androstene derivatives.[9]

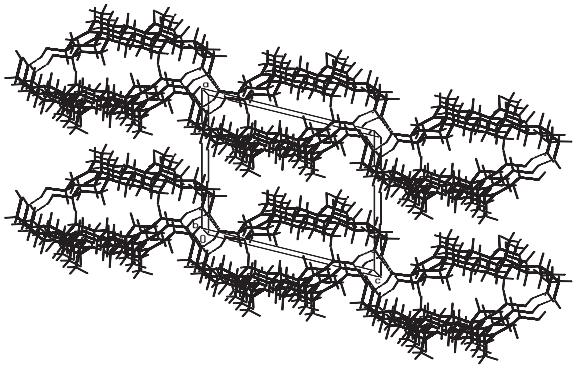

Fig.2 A crystal packing diagram

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