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Note

## The Crystal and Molecular Structure of 5 $\alpha$ -Cholestane-3,6-dione

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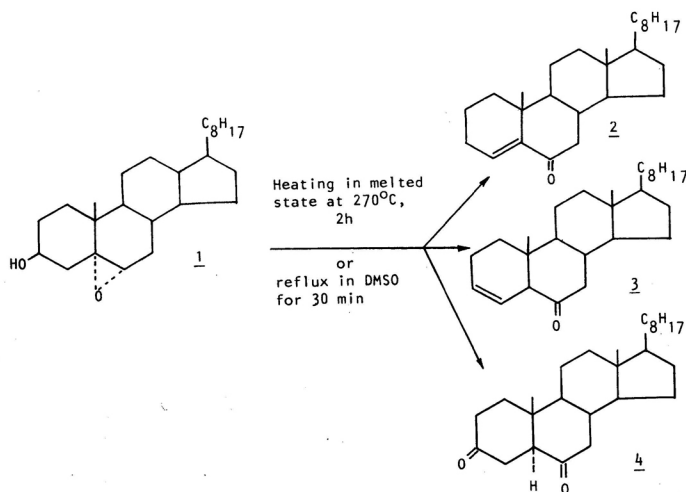
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The crystals of 5 $\alpha$ -cholestane-3,6-dione (C<sub>27</sub>H<sub>44</sub>O<sub>2</sub>) are monoclinic, space group *P*2<sub>1</sub> with *a* = 1.9695(3), *b* = 0.7593(3), *c* = 0.8176(6) nm,  $\beta$  = 92.78(3) $^\circ$ , *V* = 1.221(1) nm<sup>3</sup> and *Z* = 2. The structure was solved by the direct method and refined by the least squares technique to a conventional *R* = 0.097 for 2220 unique diffractometer observations. Ring D assumed an *envelope* shape. The side chain equatorially attached to C17 assumed open »zig-zag« conformation.

### INTRODUCTION

During our study,<sup>1</sup> pyrolysis of 3 $\beta$ -hydroxy-5 $\alpha$ ,6 $\alpha$ -epoxy-cholestane (1) was performed and the following products were isolated (Scheme 1): 4-cholestane-6-one (2), 3-cholestane-6-one (3) and compound 4 whose structure could not be determined unambiguously by spectroscopic means (NMR, IR, MS). However, using X-ray diffraction methods described in this paper, the structure of compound 4 was determined as 5 $\alpha$ -cholestane-3,6-dione, the compound whose synthesis was described previously.<sup>2-6</sup> Crystals suitable for X-ray diffraction analysis were obtained by recrystallization of 4 from methanol.



Scheme 1.

## EXPERIMENTAL

### Crystal Data

From rotation and Weissenberg photographs, using  $\text{CuK}\alpha$  radiation and from single crystal diffractometry with  $\text{MoK}\alpha$  radiation we have:  $\text{C}_{27}\text{H}_{44}\text{O}_2$ ,  $M = 400.65$ , monocyclic,  $a = 1.9695(3)$ ,  $b = 0.7593(3)$ ,  $c = 0.8176(6)$  nm,  $\beta = 92.78(3)^\circ$ ,  $V = 1.221(1)$  nm<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.089$  Mg m<sup>-3</sup>, space group  $P2_1$  (No 4),  $F(000) = 444$ ,  $\mu(\text{MoK}\alpha) = 0.62$  cm<sup>-1</sup>,  $\lambda = 0.07107$  nm, specimen size  $0.146 \times 0.102 \times 0.365$  mm.

### Intensity Data, Structure Determination and Refinement

2586 intensity data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromated  $\text{MoK}\alpha$  radiation using the  $\omega$ - $2\theta$  scanning technique in the range  $2\theta = 52^\circ$ , with  $h: -24$  to  $24$ ,  $k: 0$  to  $9$ ,  $l: 0$  to  $10$ . Systematic absences were:  $k = 2n + 1$  in  $0k0$ . The number of observed reflections with  $I > 1.5 \sigma(I)$  was 2220. Neither absorption nor extinction corrections were applied.

The structure was solved by the direct method using the SHELX 86 program.<sup>7</sup> Positions of all 29 non-hydrogen atoms were found. The block-diagonal least-squares procedure with isotropic thermal parameters reduced  $R$  to 0.23. After their anisotropic refinement, positions of the hydrogen atoms were generated. Hydrogen atom positions were checked in the previously calculated difference Fourier map. Their common temperature factor ( $U = 634(32)$  pm<sup>2</sup>) was refined together with the anisotropic refinement of the parameters of non-hydrogen atoms (262 parameters). The final  $R = 0.097$  was obtained with unit weight function. The high value of the  $R$  factor reflects the poor quality of the crystal applied to the x-ray diffraction measurements. The maximum ratio of shift to error was 0.241. The difference Fourier map showed no significant peaks,  $(\Delta\rho)_{\text{max}} = 0.26$  e/Å<sup>3</sup>. Scattering factor were taken as in SHELX 76. All calculations\* were performed on an IBM PC/AT computer.

\* Lists of the observed and calculated structure factors and anisotropic thermal parameters are obtainable from the authors on request.

## DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The final fractional coordinates for non-hydrogen atoms and equivalent isotropic temperature factors are listed in Table I. Figure 1 shows a perspective view of the molecule with the atomic numbering. The relevant bond lengths and bond angles are given in Table II and the torsion angles in Table III. The corresponding values for the majority of bond angles and distances are similar. The strain inherent in the C/D ring junction is responsible for the bond angles  $C12-C13-C17=115.6(6)^\circ$  and  $C8-C14-C15=119.1(5)^\circ$  being greater than those normally observed for  $sp^3$ -hybridisation ( $109.5^\circ$ ) of C atoms. The sum of the torsion angles  $C12-C13-C14-C8=-60.1(8)^\circ$  and  $C17-C13-C14-C15=47.1(7)^\circ$  is  $107.2^\circ$ , which conforms with an empirical value of  $109(3)^\circ$  for *trans* C/D junctions.

TABLE I

Fractional coordinates for non-hydrogen atoms ( $\times 10^4$ ) and equivalent temperature factors ( $pm^2$ ) with e.s.d.' in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$$

Atom	$x/a$	$y/b$	$z/c$	$U_{eq}$
O1	687(2)	80(11)	8970(7)	621(15)
O2	-761(3)	4588(0)	5681(7)	802(17)
C1	841(3)	5945(13)	7140(10)	507(21)
C2	71(3)	6159(14)	7239(10)	533(20)
C3	-300(3)	4545(15)	6698(9)	518(19)
C4	-51(3)	2870(14)	7494(10)	512(20)
C5	726(3)	2695(13)	7335(8)	386(15)
C6	1004(3)	1046(13)	8129(9)	429(16)
C7	1747(3)	725(13)	7812(9)	470(19)
C8	2189(3)	2331(13)	8298(8)	368(14)
C9	1880(3)	4028(12)	7587(9)	382(15)
C10	1131(3)	4306(13)	8034(7)	338(12)
C11	2348(3)	5610(13)	8059(9)	427(17)
C12	3084(3)	5363(13)	7553(11)	518(22)
C13	3387(3)	3627(13)	8201(9)	416(16)
C14	2905(3)	2139(12)	7655(7)	307(12)
C15	3305(3)	443(13)	8017(10)	468(18)
C16	4049(3)	989(14)	7704(10)	542(20)
C17	4054(3)	3000(13)	7383(8)	385(15)
C18	3526(3)	3693(14)	10092(7)	443(14)
C19	1064(3)	4485(14)	9879(8)	504(17)
C20	4732(3)	3877(13)	7923(9)	426(15)
C21	4726(4)	5851(14)	7713(11)	620(25)
C22	5306(3)	3058(15)	6957(9)	553(20)
C23	6021(3)	3561(17)	7592(9)	606(22)
C24	6579(3)	2680(16)	6693(10)	650(24)
C25	7297(4)	3074(17)	7417(10)	650(24)
C26	7495(4)	4981(18)	7166(12)	848(30)
C27	7813(4)	1858(18)	6627(11)	827(30)

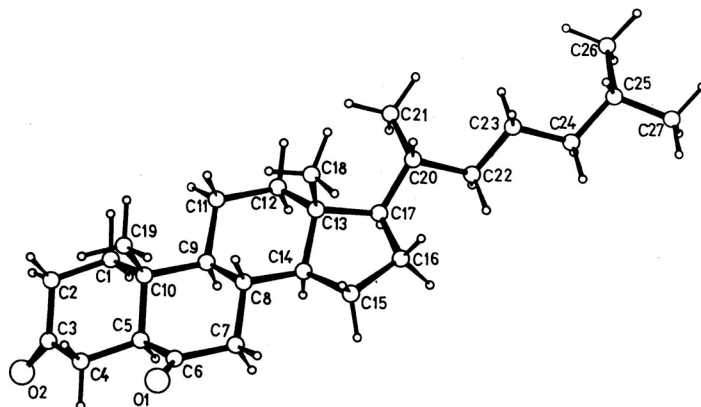


Figure 1. A perspective view of the molecule showing atomic numbering. The Hydrogen atoms are shown but not labelled.

The conformation of the cyclopentane ring D can be described by phase-angle parameter  $\Delta = 47.1(2)^\circ$  and maximum torsion angle  $\varphi_m = 33.3^\circ$ <sup>8,9</sup> showing envelope conformation. The side chain, attached to C17 equatorially, as shown by the relevant torsion angles ( $\pm ap$ ),<sup>10</sup> has open »zig-zag« conformation similar to those appearing in the related compounds.<sup>11</sup> Methyl groups C(21) and C(26) lie on the same side chain and form bonds C20–C21 and C25–C26 which are approximately perpendicular to the C–methyl bonds (C10–C19 and C13–C18) that are mutually parallel (Figure 2).

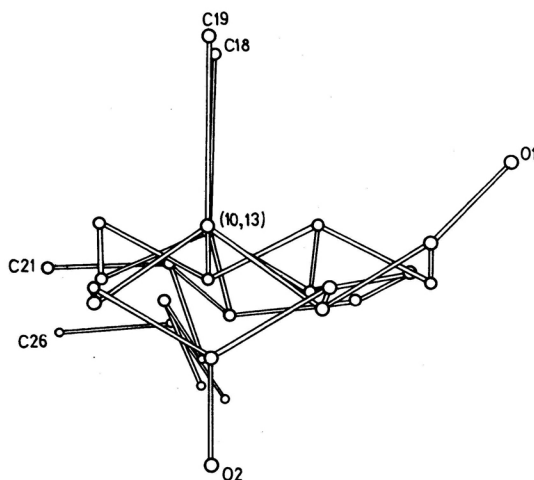


Figure 2. The molecule viewed in a projection from C10 to C13.

TABLE II

*Bond lengths (pm) and bond angles (°) with e.s.d.'s in parentheses*

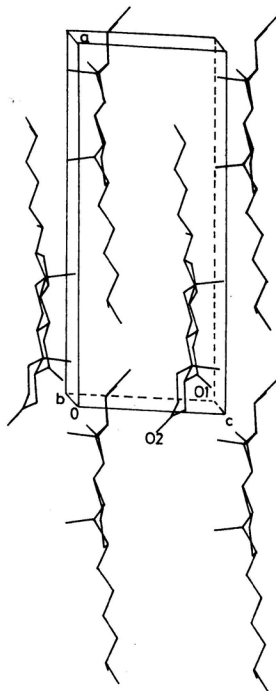
O1-C6	120.2(8)	C11-C12	153.9(8)
O2-C3	120.2(8)	C12-C13	153.1(9)
C1-C2	153.2(9)	C13-C14	152.8(8)
C1-C10	153.9(9)	C13-C17	157.6(8)
C2-C3	148.3(11)	C13-C18	155.8(9)
C3-C4	150.0(11)	C14-C15	153.1(9)
C4-C5	154.7(9)	C15-C16	155.7(9)
C5-C6	150.2(9)	C16-C17	155.0(10)
C5-C10	155.4(8)	C17-C20	153.6(8)
C6-C7	151.7(9)	C20-C21	150.9(10)
C7-C8	154.0(9)	C20-C22	154.1(9)
C8-C9	152.8(8)	C22-C23	152.6(9)
C8-C14	153.5(8)	C23-C24	150.8(10)
C9-C10	155.2(8)	C24-C25	153.5(10)
C9-C11	155.1(8)	C25-C26	151.7(15)
C10-C19	152.7(8)	C25-C27	153.8(12)
C2-C1-C10	114.0(6)	C9-C11-C12	113.3(5)
C1-C2-C3	111.8(6)	C11-C12-C13	111.6(6)
C2-C3-C4	115.1(6)	C12-C13-C14	108.0(5)
C2-C3-O2	121.9(8)	C12-C13-C17	115.6(6)
C4-C3-O2	122.9(7)	C12-C13-C18	111.3(6)
C3-C4-C5	109.9(7)	C14-C13-C18	113.0(6)
C4-C5-C10	113.2(5)	C14-C13-C17	99.9(5)
C4-C5-C6	112.1(6)	C17-C13-C18	108.7(5)
C10-C-C6	109.1(5)	C8-C14-C13	113.4(5)
C5-C6-C7	113.2(6)	C8-C14-C15	119.1(5)
C5-C6-O1	124.6(6)	C13-C14-C15	105.0(5)
C7-C6-O1	122.2(6)	C14-C15-C16	102.9(6)
C6-C7-C8	111.5(6)	C15-C16-C17	107.7(6)
C7-C8-C9	111.1(5)	C16-C17-C13	102.3(6)
C7-C8-C14	110.7(5)	C16-C17-C20	113.0(6)
C9-C8-C14	107.8(5)	C13-C17-C20	118.5(5)
C8-C9-C10	113.0(5)	C17-C20-C22	109.0(6)
C8-C9-C11	109.7(5)	C17-C20-C21	113.4(6)
C10-C9-C11	113.4(5)	C21-C20-C22	110.1(7)
C5-C10-C9	106.5(5)	C20-C22-C23	114.4(6)
C5-C10-C1	106.9(5)	C22-C23-C24	113.9(7)
C5-C10-C19	111.5(5)	C23-C24-C25	113.9(7)
C1-C10-C19	110.5(5)	C24-C25-C26	111.8(8)
C1-C10-C9	109.4(5)	C24-C25-C27	109.7(8)
C9-C10-C19	111.9(5)	C26-C25-C27	109.6(7)

In the crystal structure, the quasi planar molecules are packed approximately parallel to the (001) plane (Figure 3). The molecules related by the two fold screw-axis parallel to b axis are held together by weak Van der Waals contact with the neighboring molecules lying in parallel planes.

TABLE III

*Torsion angles (°) with e.s.d.'s in parentheses*

O1 C6 C5 C4	-8.9(11)	C8 C9 C10 C19	62.4(8)	C13 C17 C20 C21	-56.7(9)
O1 C6 C7 C8	-124.3(8)	C8 C14 C13 C17	178.7(6)	C13 C17 C20 C22	-179.8(6)
O2 C3 C4 C5	127.1(8)	C8 C14 C13 C18	63.4(8)	C14 C8 C9 C11	-57.0(8)
O2 C3 C2 C1	-128.2(8)	C8 C14 C15 C16	-162.0(6)	C14 C13 C12 C11	53.5(8)
C3 C2 C1 C10	-52.9(9)	C9 C8 C14 C15	-173.2(6)	C14 C13 C17 C16	-41.2(7)
C3 C4 C5 C6	179.4(7)	C9 C10 C1 C2	169.5(6)	C14 C15 C16 C17	6.5(8)
C3 C4 C5 C10	55.4(9)	C9 C10 C5 C4	-173.1(6)	C16 C17 C13 C18	77.4(7)
C4 C3 C2 C1	51.0(10)	C10 C5 C6 O1	117.2(9)	C16 C17 C20 C21	-176.4(7)
C4 C5 C10 C1	-56.2(8)	C10 C5 C6 C7	-60.9(8)	C16 C17 C20 C22	60.6(8)
C4 C5 C10 C19	64.5(8)	C10 C9 C8 C7	54.0(8)	C17 C13 C12 C11	164.4(6)
C5 C4 C3 C2	-52.1(9)	C10 C9 C8 C14	175.5(6)	C17 C13 C14 C15	47.1(7)
C5 C10 C1 C2	54.6(8)	C10 C9 C11 C12	-177.7(6)	C17 C20 C22 C23	-169.2(7)
C5 C10 C9 C11	174.8(6)	C11 C9 C10 C1	59.6(8)	C18 C13 C14 C15	-68.2(8)
C6 C5 C10 C1	178.2(6)	C11 C9 C10 C19	-63.2(8)	C19 C10 C1 C2	-66.8(8)
C6 C5 C10 C9	61.3(8)	C11 C12 C13 C18	-71.0(8)	C20 C17 C13 C12	78.3(9)
C6 C5 C10 C19	-61.0(8)	C12 C11 C9 C8	54.9(8)	C20 C17 C13 C14	-166.2(6)
C6 C7 C8 C9	-48.8(8)	C12 C13 C14 C8	-60.1(8)	C20 C17 C13 C18	-47.7(9)
C6 C7 C8 C14	-168.5(6)	C12 C13 C14 C15	168.3(6)	C20 C17 C16 C15	150.2(7)
C7 C6 C5 C4	172.9(6)	C12 C13 C17 C16	-156.7(7)	C20 C22 C23 C24	177.1(7)
C7 C8 C9 C11	-178.4(6)	C13 C12 C11 C9	-53.4(9)	C22 C23 C24 C25	-175.5(8)
C7 C8 C14 C15	-51.5(9)	C13 C14 C8 C7	-175.8(6)	C23 C24 C25 C26	-68.6(10)
C8 C7 C6 C5	53.9(9)	C13 C14 C8 C9	62.5(8)	C23 C24 C25 C27	169.5(8)
C8 C9 C10 C1	-174.7(6)	C13 C14 C15 C16	-33.7(7)	C23 C22 C20 C21	65.8(9)
C8 C9 C10 C5	-59.6(8)	C13 C17 C16 C15	21.6(8)		

Figure 3. The molecular packing in the unit cell viewed down the *b* axis.

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## REFERENCES

1. D. Miljković, Z. Sakač, K. Gaši, S. Stanković, and B. Ribár, *J. Serb. Chem. Soc.* (1990), submitted to publication.
2. W. Szczepek, J. Gumulka, and J. Jagodzinski, *Bull. Acad. Pol. Sci. Ser. Chim.* **28** (1980) 165.
3. J. Jagodzinski, J. Gumulka, and W. Szczepek, *Tetrahedron* **37** (1981) 1015.
4. D. Barton, S. Motherwell, and S. Zard, *Tetrahedron Lett.* **24** (1983) 5227.
5. M. Ahmad, S. Ahmad, and I. Ansari, *Ind. J. Chem. Sect B* **25B** (1986) 1161.
6. D. Barton, J. Baivin, and Ch. Hill, *J. Chem. Soc. Perkin Trans.* **10** (1986) 1797.
7. G. M. Sheldrick, (1976–1988) *The SHELX System of Crystallographic Computer Program*, University of Cambridge, England.
8. C. Altona, H. J. Geise, and S. Romers, *Tetrahedron* **24** (1968) 13.
9. W. L. Duax and D. A. Norton, *Atlas of Steroid Structure*, Plenum, New York, 1975.
10. W. Klyne and V. Prelog, *Experientia*, **16** (1960) 521.
11. T. Ishida, M. Inoue, S. Harusawa, J. Hamada, and T. Shioiri, *Acta Cryst.* **B37** (1981) 1881.

## SAŽETAK

Kristalna i molekularna struktura 5 $\alpha$ -holestan-3,6-diona

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Kristali 5 $\alpha$ -holestan-3,6-diona (C<sub>27</sub>H<sub>44</sub>O<sub>2</sub>) jesu monoklinski prostorne grupe P2<sub>1</sub>, s parametrima elementarne ćelije  $a = 1.9695(3)$ ,  $b = 0.7593(3)$ ,  $c = 0.8174(6)$  nm,  $\beta = 92.78(3)^\circ$  i  $V = 1.221(1)$  nm<sup>3</sup>,  $Z = 2$ . Struktura je riješena direktnom metodom i utačnjena metodom najmanjih kvadrata do  $R = 0.097$  za 2220 opaženih refleksa. Konformacija D-prstena najbliža je *envelope* formi. Bočni lanac vezan je za atom C17 *ekvatorijalno*, čineći otvorenu »cik-cak« konformaciju.