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The Crystal and Molecular Structure of 4β,5β-Epoxycholestan-3-one

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The title steroid is orthorhombic, with a = 25·08 (1), b = 10·866 (5), c = 9·118 (5) Å, Z = 4, space group $P2_12_12_1$. The structure was determined from diffractometer data and refined by full-matrix least squares to a final R of 0·079 for 945 independent reflexions. Ring A is *cis*-fused to ring B whilst the remaining rings are *trans*-fused, the side chain being in an extended configuration.

Introduction

4β,5β-Epoxycholestan-3-one was prepared from cholestan-4-en-3-one (as an intermediate in the synthesis of 4-hydroxycholest-4-en-3-one, which is being studied as a metal-complexing agent) by reaction with alkaline hydrogen peroxide (Henbest & Jackson, 1967). Only the 4β,5β-epoxide was formed, in agreement with Henbest & Jackson who reported that Δ^4-3-ketosteroids not containing polar substituents yield exclusively the corresponding β-epoxide, whereas the presence of polar substituents at positions as remote from the site of reaction as C(17) results in the formation of mixtures containing varying amounts of the corresponding α-epoxides.

Experimental

The compound (m.p. 116–117°C) was recrystallized from ether–methanol. Microanalysis yielded the following results:

	C	H
Found	80·70%	11·30%
Calculated for $C_{27}H_{44}O_2$	80·87	11·07.

The crystals were colourless needles elongated along **b**.

Preliminary photographs (Cu $K\alpha$ radiation, λ = 1·542 Å) showed systematic absences $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$ and $00l$, $l = 2n + 1$, indicating space group $P2_12_12_1$. Crystal data are listed in Table 1.

The cell parameters of a crystal (0·68 × 0·16 × 0·12 mm) were obtained by least squares from the settings of 25 reflexions measured on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation (λ = 0·7107 Å, graphite-monochromated). The intensities of 1944 reflexions in the range $3° < \theta < 23°$ were recorded by the ω–2θ scan technique (scan width 0·9° θ, scan speed 0·03° θ s^{-1}). The background was counted on both sides of the peak for one half of the peak scan time. The intensities of three standard reflexions measured every hour remained constant to within 1·8% of their mean values. Lorentz–polarization corrections were applied. No absorption correction was made. With the criterion $I(\text{rel.}) > 2\sigma I(\text{rel.})$ for an observed reflexion, 999 were omitted leaving 945 unique reflexions for the analysis.

Table 1. *Crystal data*

Molecular formula: $C_{27}O_2H_{44}$
Space group $P2_12_12_1$
a = 25·08 (1) Å
b = 10·866 (5)
c = 9·118 (5)
V = 2484·53 Å^3
M_r = 400
D_m = 1·09 g cm^{-3}
D_c = 1·08 for Z = 4
μ = 0·34 cm^{-1}
$F(000)$ = 888

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Solution and refinement

The structure was solved with the *SHELX* program system. 128 permutations were generated from seven starting reflexions and after eight cycles of weighted tangent refinement for each phase permutation, eight E maps were calculated. The E maps were ranked by R_A (Sheldrick, 1976), and the first E map ($R_A = 0{\cdot}098$) yielded the positions of the 29 heavy atoms. Subsequent refinement with all these atoms isotropic yielded $R = 0{\cdot}255$. Further refinement with the heavy atoms anisotropic and a subsequent difference map yielded the positions of 26 of the H atoms.

In the final refinement the methyl H atoms were refined as rigid groups and the remaining H atoms were constrained at 1·08 Å from their respective C atoms,

Table 2. *Fractional atomic coordinates* (×10⁴) *of the heavy atoms*

	x	y	z
O(3)	8185 (3)	3453 (8)	3888 (8)
O(4)	7442 (3)	5111 (8)	6274 (7)
C(1)	6855 (4)	3023 (10)	5366 (13)
C(2)	7318 (5)	2698 (11)	4413 (15)
C(3)	7725 (5)	3647 (12)	4326 (12)
C(4)	7594 (4)	5008 (12)	4734 (9)
C(5)	7031 (4)	5278 (13)	5184 (10)
C(6)	6862 (4)	6591 (9)	4899 (12)
C(7)	6600 (3)	6651 (11)	3363 (11)
C(8)	6148 (4)	5706 (9)	3241 (12)
C(9)	6343 (4)	4394 (9)	3561 (12)
C(10)	6604 (4)	4301 (10)	5106 (12)
C(11)	5904 (4)	3433 (9)	3299 (11)
C(12)	5646 (4)	3531 (9)	1777 (11)
C(13)	5438 (4)	4844 (9)	1475 (11)
C(14)	5909 (4)	5714 (8)	1663 (11)
C(15)	5711 (4)	6939 (8)	1034 (12)
C(16)	5354 (4)	6545 (9)	−258 (11)
C(17)	5286 (4)	5120 (9)	−154 (10)
C(18)	4959 (4)	5148 (9)	2488 (10)
C(19)	6195 (4)	4534 (12)	6388 (10)
C(20)	4725 (4)	4682 (9)	−682 (10)
C(21)	4653 (4)	3289 (8)	−582 (12)
C(22)	4635 (4)	5103 (10)	−2299 (11)
C(23)	4043 (4)	4966 (11)	−2804 (12)
C(24)	3937 (5)	5451 (12)	−4256 (12)
C(25)	3377 (4)	5155 (13)	−4849 (12)
C(26)	3339 (5)	5519 (14)	−6408 (14)
C(27)	2951 (4)	5792 (12)	−3945 (16)

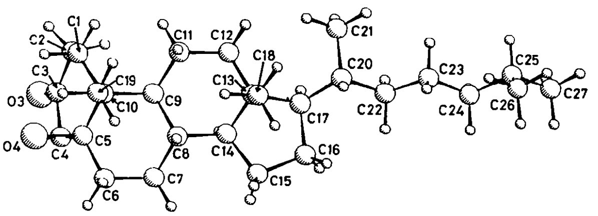
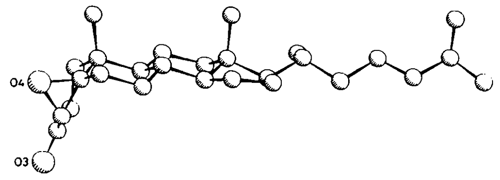


Fig. 1. Perspective view of the molecule with atomic nomenclature.

Table 3. *Fractional coordinates of the hydrogen atoms* (×10³)

	x	y	z
H(11)	654	233	522
H(12)	699	300	648
H(21)	716	252	332
H(22)	749	186	483
H(4)	789	485	389
H(61)	657	688	572
H(62)	720	718	492
H(71)	689	645	253
H(72)	644	756	318
H(8)	585	596	404
H(9)	665	418	277
H(111)	607	252	340
H(112)	559	355	412
H(121)	593	329	95
H(122)	531	289	172
H(14)	626	543	107
H(151)	548	744	184
H(152)	604	749	66
H(161)	497	699	−17
H(162)	554	678	−127
H(17)	553	459	−87
H(181)	481	606	226
H(182)	508	508	361
H(183)	464	450	228
H(191)	588	384	635
H(192)	601	543	626
H(193)	639	448	742
H(20)	443	509	3
H(211)	471	300	53
H(212)	494	284	−127
H(213)	425	303	−91
H(221)	474	606	−237
H(222)	488	455	−299
H(231)	378	543	−201
H(232)	394	399	−280
H(241)	397	643	−419
H(242)	422	508	−499
H(25)	331	417	−475
H(261)	364	505	−703
H(262)	339	650	−648
H(263)	295	526	−681
H(271)	298	551	−280
H(272)	256	554	−434
H(273)	300	677	−402

4β,5β-EPOXYCHOLESTAN-3-ONE



CHOLEST-4-EN-3-ONE

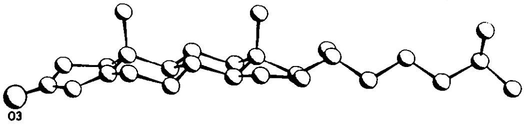


Fig. 2. Comparative views of the molecule under study and the parent compound (cholest-4-en-3-one).

their positions being dictated by the geometry of the molecule. The isotropic temperature factor for the methyl H refined to 0·164 Å^2, whereas that for the remaining H atoms refined to 0·134 Å^2.

The refinement converged to $R_w = \Sigma w^{1/2}|F_o - F_c|/\Sigma w^{1/2}|F_o| = 0\cdot060$ and $R = 0\cdot079$, with $w = 1/\sigma^2$. A final difference map had no peaks $> 0\cdot2$ e Å^{-3}. Tables 2 and 3 show the atomic coordinates.*

Description of the structure and discussion

Perspective views of the molecule are shown in Figs. 1 and 2, the former showing the atomic nomenclature. Fig. 2 also shows a similar view of cholest-4-en-3-one (Sheldrick, Oeser, Caira, Nassimbeni & Pauptit, 1976), the parent compound of that under study. Only ring *A* differs substantially; this is because of the oxidation of the double bond in cholest-4-en-3-one to give the β-epoxide, in which rings *A* and *B* are *cis*-fused; such *cis*-fusion causes ring *A* to dip sharply away from the plane of the remainder of the molecule. Ring *A* has a 1β-envelope conformation somewhat distorted towards

Table 6. *Torsion angles* (°)

Ring *A*	
C(2)–C(1)–C(10)–C(5)	−53·29
C(10)–C(1)–C(2)–C(3)	48·63
C(1)–C(2)–C(3)–C(4)	−19·87
C(2)–C(3)–C(4)–C(5)	−1·11
C(3)–C(4)–C(5)–C(10)	−5·58
C(4)–C(5)–C(10)–C(1)	30·82
Ring *B*	
C(6)–C(5)–C(10)–C(9)	56·38
C(10)–C(5)–C(6)–C(7)	−57·14
C(5)–C(6)–C(7)–C(8)	53·96
C(7)–C(8)–C(9)–C(10)	57·07
C(6)–C(7)–C(8)–C(9)	−56·73
C(8)–C(9)–C(10)–C(5)	−53·67
Ring *C*	
C(14)–C(8)–C(9)–C(11)	−53·31
C(8)–C(9)–C(11)–C(12)	52·54
C(9)–C(11)–C(12)–C(13)	−53·87
C(11)–C(12)–C(13)–C(14)	56·35
C(9)–C(8)–C(14)–C(13)	60·65
C(12)–C(13)–C(14)–C(8)	−61·72
Ring *D*	
C(17)–C(13)–C(14)–C(15)	47·44
C(13)–C(14)–C(15)–C(16)	−35·57
C(14)–C(15)–C(16)–C(17)	9·37
C(15)–C(16)–C(17)–C(13)	19·14
C(14)–C(13)–C(17)–C(16)	−40·14

Table 4. *Bond lengths* (Å)

O(3)–C(3)	1·241 (11)	C(14)–C(8)	1·558 (13)
O(4)–C(5)	1·444 (10)	C(14)–C(13)	1·522 (11)
C(1)–C(10)	1·543 (12)	C(15)–C(14)	1·533 (11)
C(2)–C(1)	1·492 (14)	C(16)–C(15)	1·540 (12)
C(2)–C(3)	1·453 (13)	C(16)–C(17)	1·561 (11)
C(4)–C(3)	1·560 (13)	C(17)–C(13)	1·563 (11)
C(4)–C(5)	1·499 (13)	C(18)–C(13)	1·551 (11)
C(4)–O(4)	1·459 (10)	C(19)–C(10)	1·575 (12)
C(6)–C(5)	1·511 (13)	C(20)–C(17)	1·562 (12)
C(7)–C(6)	1·548 (12)	C(21)–C(20)	1·527 (10)
C(7)–C(8)	1·533 (11)	C(22)–C(20)	1·559 (12)
C(9)–C(8)	1·535 (12)	C(23)–C(22)	1·561 (11)
C(9)–C(10)	1·557 (13)	C(24)–C(23)	1·449 (12)
C(10)–C(5)	1·509 (13)	C(24)–C(25)	1·539 (12)
C(11)–C(9)	1·535 (11)	C(26)–C(25)	1·479 (13)
C(12)–C(11)	1·535 (12)	C(27)–C(25)	1·516 (13)
C(12)–C(13)	1·544 (11)		

Table 5. *Bond angles* (°)

C(4)–O(4)–C(5)	62·2 (6)	C(7)–C(8)–C(14)	110·3 (8)	C(18)–C(13)–C(17)	109·6 (7)
C(2)–C(1)–C(10)	116·2 (10)	C(14)–C(8)–C(9)	107·6 (9)	C(8)–C(14)–C(13)	113·5 (8)
C(1)–C(2)–C(3)	114·1 (11)	C(8)–C(9)–C(10)	111·5 (9)	C(15)–C(14)–C(8)	118·3 (8)
C(2)–C(3)–C(4)	120·8 (10)	C(11)–C(9)–C(8)	111·9 (7)	C(15)–C(14)–C(13)	104·2 (7)
C(2)–C(3)–O(3)	123·4 (12)	C(11)–C(9)–C(10)	113·4 (9)	C(16)–C(15)–C(14)	103·5 (8)
C(4)–C(3)–O(3)	115·7 (12)	C(1)–C(10)–C(5)	109·7 (8)	C(15)–C(16)–C(17)	107·1 (8)
C(5)–C(4)–C(3)	116·7 (11)	C(1)–C(10)–C(9)	111·7 (9)	C(16)–C(17)–C(13)	102·8 (8)
O(4)–C(4)–C(3)	110·9 (9)	C(9)–C(10)–C(5)	107·2 (9)	C(16)–C(17)–C(20)	112·5 (9)
O(4)–C(4)–C(5)	58·4 (5)	C(19)–C(10)–C(1)	107·2 (10)	C(20)–C(17)–C(13)	117·1 (8)
C(4)–C(5)–C(10)	121·1 (10)	C(19)–C(10)–C(5)	108·3 (9)	C(21)–C(20)–C(17)	112·9 (8)
C(4)–C(5)–O(4)	59·4 (6)	C(19)–C(10)–C(9)	112·8 (7)	C(21)–C(20)–C(22)	109·3 (9)
C(6)–C(5)–C(4)	113·7 (11)	C(12)–C(11)–C(9)	113·3 (8)	C(22)–C(20)–C(17)	109·4 (8)
C(6)–C(5)–C(10)	117·2 (9)	C(11)–C(12)–C(13)	111·6 (8)	C(23)–C(22)–C(20)	112·8 (9)
C(6)–C(5)–O(4)	116·0 (10)	C(12)–C(13)–C(14)	106·9 (7)	C(24)–C(23)–C(22)	114·1 (10)
O(4)–C(5)–C(10)	116·8 (10)	C(12)–C(13)–C(17)	115·4 (9)	C(23)–C(24)–C(25)	114·3 (11)
C(7)–C(6)–C(5)	108·3 (9)	C(17)–C(13)–C(14)	100·3 (8)	C(26)–C(25)–C(24)	109·9 (10)
C(6)–C(7)–C(8)	110·6 (9)	C(18)–C(13)–C(12)	110·6 (8)	C(27)–C(25)–C(24)	110·9 (10)
C(7)–C(8)–C(9)	111·9 (8)	C(18)–C(13)–C(14)	113·7 (8)	C(27)–C(25)–C(26)	110·8 (11)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32419 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 7. *Least-squares planes calculations*

The equations of the planes are expressed in orthogonalized space as $lX + mY + nZ = P$. d is the perpendicular distance (Å) from the plane. Atoms marked with an asterisk were included in the least-squares plane calculation.

Ring *A*

$$0\cdot2459X - 0\cdot1778Y + 0\cdot9528Z = 7\cdot8222$$

	d		*d*
C(1)	0·483	O(3)	−0·064
C(2)*	0·003	O(4)	1·231
C(3)*	−0·005	C(6)	−0·609
C(4)*	0·005	C(9)	−1·666
C(5)*	−0·003	C(19)	0·671
C(10)	−0·145		

Ring *B*

$$0\cdot8694X - 0\cdot2584Y - 0\cdot4211Z = 11\cdot2293$$

	d		*d*
C(5)	0·626	O(4)	1·153
C(6)*	−0·001	C(1)	0·808
C(7)*	0·001	C(4)	2·103
C(8)	−0·672	C(11)	−0·587
C(9)*	−0·001	C(14)	−0·589
C(10)*	0·001		

Ring *C*

$$-0\cdot6504X - 0\cdot0807Y + 0\cdot7553Z = -8\cdot2875$$

	d		*d*
C(8)*	−0·008	C(7)	−0·744
C(9)*	0·009	C(10)	0·655
C(11)	0·628	C(15)	−0·924
C(12)*	−0·008	C(17)	−0·889
C(13)*	0·008	C(18)	1·461
C(14)	−0·706		

Ring *D*

$$0\cdot8118X - 0\cdot1252Y - 0\cdot5704Z = 10\cdot1441$$

	d		*d*
C(13)	−0·500	C(8)	−0·091
C(14)	0·243	C(12)	−0·054
C(15)*	0·000	C(18)	−2·044
C(16)*	0·000	C(20)	−0·808
C(17)*	0·000		

a 1β,10α-half-chair conformation. Mirror symmetry dominates about the plane through C(1) and C(4), with asymmetry parameters (Duax & Norton, 1975) $\Delta C_s^1 = 7\cdot9$ and $\Delta C_2^{1,10} = 16\cdot2$. Ring *B* has a highly symmetrical chair conformation with all six asymmetry parameters below 3·3. Mirror symmetry is slightly favoured to rotational symmetry as is shown by the following asymmetry parameters: $\Delta C_s^5 = 0\cdot5$, $\Delta C_2^{6,7} = 0\cdot6$. Ring *C* which is *trans*-fused to ring *B* also has a symmetrical chair conformation, mirror symmetry again being dominant. The plane is through C(11) and C(14) with $\Delta C_s^{11} = 2\cdot0$ and $\Delta C_2^{9,11} = 3\cdot1$. The five-membered ring *D* which is *trans*-fused to ring *C* has a conformation mid-way between a 13β-envelope and a 13β,14α-half-chair conformation, common for many steroids. The pseudorotational parameters (Altona, Geise & Romers, 1968) are $\Delta = 11\cdot2°$ and $\varphi_m = 47\cdot7°$. Deviations from least-squares planes for each ring system are shown in Table 7. The side chain has an extended configuration and lies in approximately the same plane as rings *B*, *C* and *D*. Bond lengths, bond angles and torsion angles are listed in Tables 4, 5 and 6 respectively. There are no significant short intermolecular contacts.

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