Brown & Shannon (1973). Selon Pauling (1929), la somme des forces de liaison autour d'un cation ou d'un anion est approximativement égale à la valence. Les résultats de ce calcul sont rassemblés dans le Tableau 6. Nous trouvons sur les oxygènes une valence très proche de deux, sur le calcium une valence proche aussi de deux et sur le chrome de l'ordre de six.

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The Crystal and Molecular Structure of Cholest-4-en-6-one

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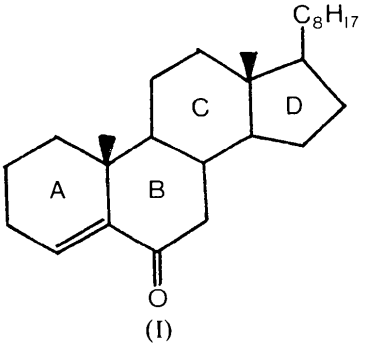
Crystals of the title steroid are monoclinic with $a = 14{\cdot}125\ (5)$, $b = 8{\cdot}117\ (5)$, $c = 10{\cdot}765\ (5)$ Å, $\beta = 104{\cdot}4\ (2)°$, $Z = 2$, space group $P2_1$. The structure is isomorphous with that of the isomeric steroid cholest-4-en-3-one. Ring *A* is quasi *trans*-fused to ring *B*; rings *B*, *C* and *D* are *trans*-fused and the side chain is in the extended configuration.

Introduction

Cholest-4-en-6-one (I) has been synthesized from cholest-5-ene as an intermediate in the preparation of 4-hydroxycholest-4-en-6-one. The synthesis of the latter compound is being undertaken with a view to investigating its complexing ability with various metals.



(I)

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Experimental

Cholest-4-en-6-one was prepared from cholest-5-ene by the following route: epoxidation of cholest-5-ene with *m*-chloroperbenzoic acid gave the 5α,6α-epoxide which was cleaved with perchloric acid to yield 5α-cholestane-5,6β-diol. Oxidation of the diol with Jones reagent, and treatment of the resultant 5-hydroxy-5α-cholestan-6-one with thionyl chloride in pyridine gave the desired compound (m.p. 102–104°C) (Jones, Lewis, Shoppee & Summers, 1955).

Microanalysis yielded the following results:

	C(%)	H(%)
Found	83·8	11·45
Calculated for $C_{27}H_{44}O$	84·35	11·45.

The crystals were colourless needles elongated along **b**. From preliminary oscillation and Weissenberg photographs (Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å), the monoclinic space group $P2_1$ was indicated by the systematic absences $0k0$, $k = 2n + 1$. The crystal density was measured in aqueous sodium chloride

Table 1. *Crystal data*

	Cholest-4-en-6-one	Cholest-4-en-3-one
Molecular formula	$C_{27}H_{44}O$	$C_{27}H_{44}O$
M_r	384·3	384·3
Space group	$P2_1$	$P2_1$
a	14·125 (5) Å	14·634 (5) Å
b	8·117 (5)	7·862 (5)
c	10·765 (5)	10·674 (5)
β	104·4 (2)°	105·1 (2)°
V	1195·3 Å^3	1185·2 Å^3
D_m	1·08 g cm^{-3}	1·08 g cm^{-3}
D_c for $Z = 2$	1·08	1·08
μ	0·32 cm^{-1}	0·32 cm^{-1}
$F(000)$	428	428

solution. Crystal data of the title compound and of the isomorphous cholest-4-en-3-one are listed in Table 1.

The unit-cell parameters were obtained by a least-squares analysis of the settings of 25 reflexions measured on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å, graphite-monochromated) and a crystal 0·5 × 0·25 × 0·1 mm. The intensities of 1064 reflexions in the range $3° < \theta < 20°$ were recorded by the ω–2θ scan technique [scan width $1{\cdot}2°(\theta)$, scan speed $0{\cdot}04°(\theta)$ 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 ±1·9% of their mean values. Lorentz–polarization corrections were applied. No absorption correction was made. 712 reflexions, considered observed when $I_{rel} > 3\sigma I_{rel}$, were used in the analysis.

Solution and refinement

Inspection of the unit-cell parameters (Table 1) and of the corresponding reflexion intensities showed that the title compound was probably isomorphous with its isomer cholest-4-en-3-one. We therefore used the C coordinates of the latter structure (Sheldrick, Oeser, Caira, Nassimbeni & Pauptit, 1976), omitting the O at C(3), and carried out three cycles of least-squares refinement with the C atoms treated isotropically. This yielded an R value of 0·175 and a subsequent difference Fourier map clearly showed the position of the O atom bonded to C(6). Further least-squares refinement treating all the heavy atoms anisotropically yielded $R = 0{\cdot}100$, 24 of the H atoms then being located in the difference map. In the final refinement the methyl H atoms were refined as rigid groups and all the remaining H atoms were confined at 1·08 Å from their respective C atoms, their positions being dictated by the geometry of the molecule (Sheldrick, 1977). The isotropic temperature factor for the methyl H atoms refined to 0·136 Å^2 and that for the remaining H atoms to 0·115 Å^2.

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *of the heavy atoms*

	x	y	z
O(6)	210 (6)	−1277 (11)	7636 (8)
C(1)	53 (9)	4648 (14)	7931 (12)
C(2)	−565 (9)	4409 (16)	8917 (11)
C(3)	−1290 (9)	2930 (14)	8674 (13)
C(4)	−798 (8)	1519 (17)	8190 (9)
C(5)	56 (10)	1596 (13)	7815 (10)
C(6)	430 (9)	116 (16)	7307 (13)
C(7)	1009 (8)	247 (15)	6298 (10)
C(8)	1674 (8)	1766 (14)	6440 (11)
C(9)	1088 (7)	3289	6651 (9)
C(10)	688 (8)	3152 (14)	7865 (10)
C(11)	1648 (8)	4899 (13)	6594 (11)
C(12)	2060 (7)	4989 (14)	5395 (10)
C(13)	2675 (7)	3487 (16)	5266 (9)
C(14)	2036 (7)	1958 (14)	5238 (9)
C(15)	2626 (8)	544 (14)	4841 (10)
C(16)	3117 (9)	1364 (15)	3881 (11)
C(17)	2952 (8)	3257 (14)	3981 (10)
C(18)	3620 (7)	3443 (15)	6392 (8)
C(19)	1530 (7)	3107 (16)	9112 (8)
C(20)	3804 (8)	4218 (16)	3691 (10)
C(21)	3751 (10)	6098 (15)	3862 (12)
C(22)	3899 (8)	3837 (16)	2331 (10)
C(23)	4901 (8)	4198 (16)	2148 (9)
C(24)	4972 (7)	3832 (16)	786 (9)
C(25)	5974 (9)	4172 (16)	555 (10)
C(26)	6782 (8)	3044 (16)	1314 (10)
C(27)	5982 (9)	4101 (16)	−861 (9)

The refinement converged to $R_w = \Sigma w^{1/2}||F_o| - |F_c||/\Sigma w^{1/2}|F_o| = 0{\cdot}052$ and $R = 0{\cdot}058$ with $w = 1/\sigma^2$. As a check for the correctness of the structure a difference map was computed. This had no peaks >0·13 e Å^{-3}. Table 2 shows the final atomic coordinates of the non-hydrogen atoms.*

Description of the structure and discussion

A perspective view of the molecule with the atomic nomenclature is shown in Fig. 1. Fig. 2 shows perspective views of the title compound and its isomer cholest-4-en-3-one. The conformations of the two compounds differ, particularly in rings A and B, because of the change in position of the carbonyl group. These differences can be seen in Table 3 which compares their asymmetry parameters (Duax &

* Lists of structure factors, anisotropic thermal parameters and H atomic coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32811 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

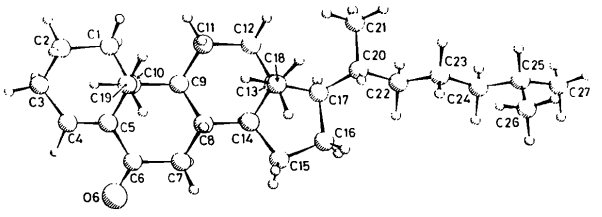

Fig. 1. Perspective view of the molecule with the atomic nomenclature.

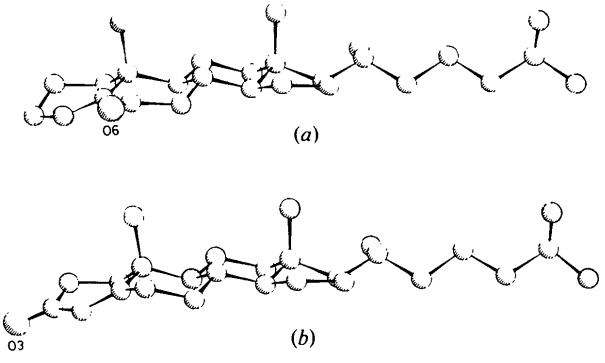

Fig. 2. Comparative views of (*a*) the molecule under study and (*b*) its isomer cholest-4-en-3-one.

Table 3. *A comparison of the asymmetry and pseudo-rotation parameters* (°) *for cholest-4-en-6-one and cholest-4-en-3-one*

	Cholest-4-en-6-one	Cholest-4-en 3 one
Ring *A*		
ΔC_s^1	14·48	6·69
$\Delta C_2^{1,2}$	8·22	19·95
$\Delta C_2^{2,3}$	34·18	54·05
ΔC_s^3	39·94	41·56
Ring *B*		
ΔC_s^5	15·04	1·08
ΔC_s^6	4·97	8·11
$\Delta C_2^{5,10}$	24·66	5·02
$\Delta C_2^{5,6}$	7·43	6·10
$\Delta C_2^{6,7}$	17·69	11·05
Ring *C*		
$\Delta C_2^{9,11}$	1·66	3·17
ΔC_s^9	3·50	3·49
ΔC_s^8	7·62	7·36
Ring *D*		
Δ	3·35	12·20
φ_m	46·96	46·16

Norton, 1975). In cholest-4-en-3-one sp^2 hybridization of C(3), C(4) and C(5) requires planarity in this portion of ring *A*, mirror symmetry about the plane through C(1) and C(4) being dominant. However, in cholest-4-en-6-one only C(4) and C(5) are sp^2 hybridized and ring *A* is somewhat distorted, rotational symmetry whereby the C_2 axis intersects the C(4)–C(5) and C(1)–C(2) bonds being pre-eminent. Ring *A* is quasi *trans*-fused to ring *B* in both compounds.

Ring *B* in cholest-4-en-3-one has a fairly symmetrical chair conformation despite the sp^2 hybridization of C(5), mirror symmetry about the plane through C(5) and C(8) being dominant. The chair conformation in

Table 4. *Bond lengths* (Å)

O(6)–C(6)	1·25 (1)	C(14)–C(13)	1·53 (1)
C(1)–C(10)	1·52 (1)	C(15)–C(14)	1·54 (1)
C(2)–C(1)	1·55 (1)	C(16)–C(15)	1·53 (1)
C(3)–C(2)	1·56 (1)	C(16)–C(17)	1·56 (1)
C(3)–C(4)	1·50 (1)	C(17)–C(13)	1·54 (1)
C(4)–C(5)	1·37 (1)	C(18)–C(13)	1·56 (1)
C(6)–C(5)	1·47 (1)	C(19)–C(10)	1·56 (1)
C(7)–C(6)	1·52 (1)	C(20)–C(17)	1·53 (1)
C(7)–C(8)	1·53 (1)	C(21)–C(20)	1·54 (1)
C(9)–C(8)	1·54 (1)	C(22)–C(20)	1·54 (1)
C(9)–C(10)	1·55 (1)	C(23)–C(22)	1·51 (1)
C(10)–C(5)	1·54 (1)	C(24)–C(23)	1·52 (1)
C(11)–C(9)	1·54 (1)	C(24)–C(25)	1·52 (1)
C(12)–C(11)	1·55 (1)	C(26)–C(25)	1·53 (1)
C(12)–C(13)	1·52 (1)	C(27)–C(25)	1·53 (1)
C(14)–C(8)	1·51 (1)		

Table 5. *Bond angles* (°)

C(2)–C(1)–C(10)	111·9 (9)	C(11)–C(9)–C(10)	113·2 (7)	C(15)–C(14)–C(8)	118·8 (9)
C(3)–C(2)–C(1)	116·3 (9)	C(1)–C(10)–C(5)	108·3 (8)	C(15)–C(14)–C(13)	104·6 (8)
C(2)–C(3)–C(4)	107·7 (9)	C(1)–C(10)–C(9)	109·0 (8)	C(16)–C(15)–C(14)	103·3 (8)
C(3)–C(4)–C(5)	126·1 (11)	C(9)–C(10)–C(5)	111·0 (8)	C(15)–C(16)–C(17)	106·3 (8)
C(4)–C(5)–C(6)	119·9 (10)	C(19)–C(10)–C(1)	108·1 (9)	C(16)–C(17)–C(13)	104·9 (9)
C(4)–C(5)–C(10)	125·0 (10)	C(19)–C(10)–C(5)	108·8 (8)	C(16)–C(17)–C(20)	110·4 (8)
C(10)–C(5)–C(6)	115·1 (11)	C(19)–C(10)–C(9)	111·6 (8)	C(20)–C(17)–C(13)	120·6 (8)
C(7)–C(6)–C(5)	121·1 (10)	C(12)–C(11)–C(9)	112·3 (8)	C(21)–C(20)–C(17)	114·6 (10)
C(7)–C(6)–O(6)	119·0 (12)	C(11)–C(12)–C(13)	112·4 (9)	C(21)–C(20)–C(22)	109·4 (10)
O(6)–C(6)–C(5)	119·7 (13)	C(12)–C(13)–C(14)	107·7 (8)	C(22)–C(20)–C(17)	110·6 (8)
C(8)–C(7)–C(6)	114·3 (9)	C(12)–C(13)–C(17)	117·2 (9)	C(23)–C(22)–C(20)	113·2 (8)
C(7)–C(8)–C(9)	108·7 (8)	C(17)–C(13)–C(14)	99·5 (8)	C(24)–C(23)–C(22)	112·2 (8)
C(7)–C(8)–C(14)	109·1 (8)	C(18)–C(13)–C(12)	110·1 (8)	C(23)–C(24)–C(25)	114·1 (9)
C(14)–C(8)–C(9)	110·7 (8)	C(18)–C(13)–C(14)	112·5 (8)	C(26)–C(25)–C(24)	113·9 (9)
C(8)–C(9)–C(10)	113·0 (7)	C(18)–C(13)–C(17)	109·6 (8)	C(27)–C(25)–C(26)	108·7 (9)
C(11)–C(9)–C(8)	112·1 (8)	C(8)–C(14)–C(13)	112·9 (8)	C(27)–C(25)–C(24)	113·3 (9)

Table 6. *Torsion angles* (°) (*atomic coordinates to four significant figures*)

Ring *A*	
C(2)–C(1)–C(10)–C(5)	45·58
C(10)–C(1)–C(2)–C(3)	−59·97
C(1)–C(2)–C(3)–C(4)	38·61
C(2)–C(3)–C(4)–C(5)	−10·50
C(3)–C(4)–C(5)–C(10)	2·10
C(4)–C(5)–C(10)–C(1)	−19·86
Ring *B*	
C(6)–C(5)–C(10)–C(9)	40·13
C(10)–C(5)–C(6)–C(7)	−31·36
C(5)–C(6)–C(7)–C(8)	35·28
C(7)–C(8)–C(9)–C(10)	59·58
C(6)–C(7)–C(8)–C(9)	−47·04
C(8)–C(9)–C(10)–C(5)	−56·38
Ring *C*	
C(14)–C(8)–C(9)–C(11)	−51·33
C(8)–C(9)–C(11)–C(12)	49·46
C(9)–C(11)–C(12)–C(13)	−53·43
C(11)–C(12)–C(13)–C(14)	56·94
C(9)–C(8)–C(14)–C(13)	58·03
C(12)–C(13)–C(14)–C(8)	−60·23
Ring *D*	
C(17)–C(13)–C(14)–C(15)	46·48
C(13)–C(14)–C(15)–C(16)	−36·11
C(14)–C(15)–C(16)–C(17)	10·87
C(15)–C(16)–C(17)–C(13)	17·65
C(14)–C(13)–C(17)–C(16)	−38·70

ring *B* of the title compound is distorted owing to the additional sp^2 hybridization of C(6), mirror symmetry about the plane through C(6) and C(9) now prevailing. All the remaining rings are *trans*-fused to each other.

Ring *C* has a symmetrical chair conformation in both compounds, all the asymmetry parameters falling below 8·5°. Rotational symmetry is dominant, the C_2 axis intersecting the C(9)–C(11) and C(13)–C(14) bonds.

Both *D* rings have the common conformation intermediate between a 13β,14α-half-chair and a 13β-envelope. Their pseudorotation parameters (Altona, Geise & Romers, 1968) are shown in Table 3. Both side chains are in extended conformations approximately in the same plane as the remainder of the molecules.

Cholest-4-en-6-one and cholest-4-en-3-one are isomorphous. The structures are packed two molecules thick, one molecule wide and one molecule long in the unit cell. The molecule width [molecular dimension parallel to the C(14)–C(12) direction (Bernal, Crowfoot & Fankuchen, 1940)] lies approximately parallel to the *b* axis but the thickness and length are parallel to the diagonals in the *ac* face. This type of molecular packing may be described as (2)1 in the modified Hodgkin notation (Duax & Norton, 1975).

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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