

콜레스테릴 펜타노에이트의 결정 및 분자구조

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The Crystal and Molecular Structure of Cholesteryl Pentanoate

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요약. 콜레스테릴 펜타노에이트의 결정은 사방정계에 속하며 $a=21,930(3)$, $b=21,404(3)$, $c=6,419(5)$ Å이며 단위세포안에 4개의 분자가 있다. $1.0\sigma(I)$ 보다 큰 강도를 가진 1,502개의 회절 반점에 대한 최종 R 값은 0.086이다. 직접법에 의하여 구조를 풀었으며 C-H 결합길이와 메틸기는 길이를 고정시켜 이상적인 기하학적 구조에 맞춰 cascade diagonal least-squares refinement에 의하여 정밀화하였다. 테트라시클로 고리는 정상적인 구조를 하고 있으나 에스테르와 결사슬 부분은 열적효과에 의하여 정상적인 길이와 각도의 값에서 변화를 보이고 있으며 에스테르의 끝부분이 굽어져 치켜들고 있다. 분자는 비결합성 van der Waals 힘에 의하여 서로 쌓여져 있고 가장 짧은 분자간 거리는 3.529 Å이다.

ABSTRACT. Cholesteryl pentanoate ($C_{32}O_2H_{54}$) is orthorhombic, space group $P2_12_12_1$ with $a=21.930(3)$, $b=21.404(3)$, $c=6.419(5)$ Å, $Z=4$, $V=3012.8(5)$ Å³, $D_c=1.04$ g·cm⁻³, $\lambda(Mo K\alpha)=0.71069$ Å, $\mu=0.58$ cm⁻¹, $F(000)=1048$, $T=298$, $R=0.086$ for 1502 unique observed reflections with $I>1.0\sigma(I)$. The structure was solved by direct methods and refined by cascade diagonal least-squares refinement. The C-H bond lengths and the methyl groups are fixed and refined as their ideal geometry. A comparison with other cholesteryl esters gives normal structure for the tetracyclic ring, while the tail regions of the side chain and the ester group which stands on end, show a variation from their normal values, presumably due to thermal effects. The molecules are stacked together by non-bonded van der Waals forces with the shortest intermolecular distance of 3.529 Å.

INTRODUCTION

The crystal structure of cholesterol derivatives has been thoroughly investigated by using diffraction methods. Apart from cholesteryl iodide, all the crystal structures presently studied were determined since 1975, and much remain unknown.

It was known, by B.M. Craven¹, that the

portions of ester in cholesterol may have been described variously as three different types of crystal packing arrangement according to their molecular interactions, involving cholesteryl-cholesteryl (Type II monolayer), cholesteryl-fatty acid (Type I monolayer) and fatty acid-fatty acid (bilayers). For example, cholesteryl nonanoate,² decanoate,³ undecanoate,⁴ laurate,⁵ palmitole-

rate,⁶ all crystallized in space group $P2_1$ or $A2$ in Type I monolayer for which the crystal structure had been solved earlier. Similarly, cholesteryl chloroformate,⁷ hexanoate,⁸ octanoate,⁹ oleate,¹⁰ all crystallized in space group $P2_1$ in Type II monolayer, while cholesteryl myristate¹¹ and 17-bromoheptanoate¹² crystallized in bilayers. Cholesteryl acetate¹³ and formate,¹⁴ however, crystallized in an irrelevant type mentioned above.

The main object of this study for cholesteryl pentanoate is a comparison of packing mode, intermolecular interaction and molecular conformation, and its investigation of structural characteristics.

EXPERIMENTAL

Single crystals of title compound obtained from Sigma Chemical Company were grown from slow evaporation in acetone solvent at room temperature. Crystal sizes were $0.14 \times 0.26 \times 1.06$ mm with colorless needle-like shape.

Accurate lattice parameters were obtained by least-squares refinement of the diffractometer settings for the 25 reflections within $25^\circ < 2\theta < 35^\circ$ measured with graphite-monochromatized Mo K α radiation ($\lambda = 0.71069$ Å) on the Nicolet R3m/E diffractometer. The intensities were recorded by the θ - 2θ scan technique at variable rates 4.9 to 29.3 °/min. with $2\theta_{\max} = 45^\circ$ for the ranges $0 \leq h \leq 21$, $0 \leq k \leq 20$, $0 \leq l \leq 6$. Three standard reflections monitored every 97 reflections showed no decrease in intensity throughout the course of data collection. Of the 1699 measured reflections, the 1331 unique observed reflections gave $R_{\text{int}} = 0.0115$ and 1502 data with $I > 1.0 \sigma(I)$ were used for refinement. Corrections for Lorentz and polarization effects were applied to the intensity data, while no absorption or extinction correction was carried out. Table 1 gives the crystal data for cholesteryl pentanoate.

Structure was solved by direct methods using

Table 1. Crystal data

Chemical formula:	$C_{25}H_{48}O_2$
Molecular weight:	470.86
Crystal system:	orthorhombic
Space group:	$P2_12_12_1$
systematic absences:	$h00 ; h = 2n + 1$ $0k0 ; k = 2n + 1$ $00l ; l = 2n + 1$
Unit cell parameters:	$a = 21.930(3)$ Å $b = 21.404(3)$ $c = 6.419(5)$ $V = 3012.8$ Å ³ $Z = 4$
$\mu(\text{Mo K}\alpha)$:	0.58 cm ⁻¹
Density: D_c :	1.04 g·cm ⁻³
F(000):	1048

200 reflections of which E values were greater than 1.22. All the non-hydrogen atoms except for three carbon atoms of the methyl group (one on the ester group and two on the side chain of cholesterol) were found in an asymmetric unit.

The further work by a difference Fourier map gave all the non-hydrogen atom positions. For refinement, all C-H bond lengths were fixed at 0.96 Å and the methyl groups refined rigid groups with ideal geometry. All the non-hydrogen atoms in the structure were refined anisotropically and the hydrogen atom was assigned by a common U_{eq} of 0.076 Å². The refinement was carried out by cascade block-diagonal least squares on F with the maximum $(\sin \theta) / \lambda = 0.59$ Å⁻¹, and with 307 least-squares parameters was converged to $R = 0.086$ and $wR = 0.113$, where $w = 1 / \{ \sigma^2(F) = 0.004 F^2 \}$; $\sigma^2(F)$ from statistics of counting; goodness of fit = 1.395. In final cycle $(\Delta / \sigma)_{\max}$ was -0.05 and a difference Fourier map contained the peaks, the highest peak 0.37 and the lowest hold -0.26 eÅ⁻³. All atomic scattering factors were from the International Tables for X-ray Crystallography¹⁵ and all calculations were performed on a Data General Eclipse S140 computer using the SHELXTL 5.1 program package (Nicolet Instrument Company¹⁶).

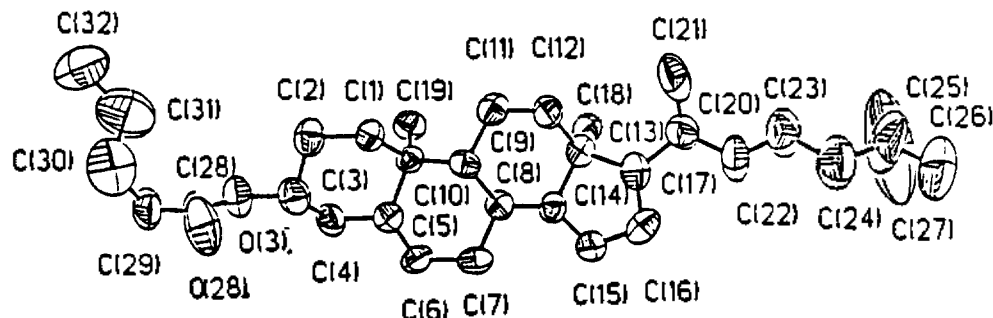


Fig. 1. Molecule of cholesteryl pentanoate showing the atomic numbering scheme and thermal ellipsoids.

Table 2. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms of cholesteryl pentanoate. The estimated standard deviations are in parentheses

atom	x	y	z
C(1)	2756(3)	8804(4)	-4582(11)
C(2)	3428(3)	8818(4)	-5218(12)
C(3)	3747(3)	8267(4)	-4273(13)
C(4)	3690(3)	8249(4)	-1949(12)
C(5)	3026(3)	8248(3)	-1328(11)
C(6)	2833(3)	7842(3)	-50(12)
C(7)	2179(3)	7806(3)	677(12)
C(8)	1826(3)	8404(3)	364(11)
C(9)	1959(3)	8656(3)	-1883(11)
C(10)	2629(3)	8797(3)	-2216(10)
C(11)	1531(3)	9197(3)	-2389(12)
C(12)	870(3)	9098(4)	-1971(11)
C(13)	735(3)	8885(3)	217(11)
C(14)	1148(3)	8289(3)	589(12)
C(15)	915(3)	8025(4)	2657(13)
C(16)	237(3)	8149(4)	2566(13)
C(17)	106(3)	8584(3)	737(13)
C(18)	865(3)	9403(3)	1788(12)
C(19)	2829(3)	9407(3)	-1243(12)
C(20)	-440(3)	9025(3)	1088(14)
C(21)	-560(4)	9427(5)	-745(17)
C(22)	-1017(3)	8670(4)	1644(17)
C(23)	-1512(4)	9027(4)	2608(22)
C(24)	-2031(5)	8678(5)	3465(24)
C(25)	-2550(7)	8972(7)	4443(25)
C(26)	-3071(5)	8578(7)	4675(33)
C(27)	-2434(7)	9202(12)	6420(34)
C(28)	4608(4)	7950(4)	-6356(15)
C(29)	5281(4)	8065(5)	-6707(14)
C(30)	5385(5)	8346(6)	-8677(22)
C(31)	5244(7)	8977(6)	-8829(33)
C(32)	5431(7)	9285(7)	-10953(26)
O(3)	4404(2)	8312(3)	-4775(10)
O(28)	4295(3)	7612(4)	-7319(11)

RESULTS AND DISCUSSION

Fig. 1 depicts a thermal-ellipsoid plot of the molecule showing the atomic numbering scheme. Final fractional atomic coordinates and anisotropic temperature factors for non-hydrogen atoms of cholesteryl pentanoate are listed in Table 2 and 3. Table 4 gives the fractional hydrogen coordinates with equivalent isotropic thermal parameters.

Bond lengths and angles involving non-hydrogen atoms are given in Table 5 and 6. In the tetracyclic ring of cholesteryl pentanoate, the average single C-C bond length gives 1.520(9) Å and the double C(5)-C(6) bond is 1.269(10) Å. These are similar to the distances observed in other cholesterol derivatives. On the other hand, in Table 5 the C-C bond lengths for the side chain of cholesterol show a variation ranging 1.385(27)–1.540(10) Å with relatively large standard deviations, as can often be seen from other cholesterol derivatives. Even in the ester group, the variations of the bond length between carbon atoms are observed in the ranges of 1.398(18)–1.569(25) Å. It is noticed that all these variations in the hydrocarbon chain of cholesterol might be due to the torsional and the thermal motion¹⁷ for the molecules in these regions. The carbonyl C(28)-O(28) bond length is 1.173(11) Å similar to that of cholesteryl hexanoate (1.167 Å).⁸ In the side chain and the ester group, the hydrocarbon chain angles between carbon atoms range

Table 3. Anisotropic temperature factors ($\times 10^3$) for the non-hydrogen atoms of cholesteryl pentanoate. The temperature factor expression used is $\exp \{-2\pi^2(u_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + \dots + 2u_{12}hka^*b^*)\}$. The *c.s.d.*'s are in parentheses

atom	u_{11}	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}
C(1)	75(5)	70(5)	57(5)	9(5)	16(4)	9(4)
C(2)	59(4)	97(5)	50(5)	1(5)	0(4)	-1(5)
C(3)	65(5)	74(5)	75(6)	-17(5)	4(4)	-1(5)
C(4)	67(5)	70(5)	63(6)	-5(5)	11(4)	13(4)
C(5)	66(4)	53(4)	52(5)	-7(4)	-1(4)	-5(4)
C(6)	78(5)	51(4)	60(5)	10(4)	11(4)	-8(4)
C(7)	84(5)	53(4)	55(5)	11(4)	-15(4)	-2(4)
C(8)	59(4)	62(4)	35(4)	1(4)	-4(4)	3(4)
C(9)	66(4)	48(4)	54(5)	-3(4)	-6(4)	5(4)
C(10)	50(4)	53(4)	39(4)	8(4)	-2(3)	-2(3)
C(11)	62(4)	83(5)	49(4)	14(5)	-13(4)	-7(4)
C(12)	69(5)	78(5)	53(5)	5(4)	4(4)	8(4)
C(13)	56(4)	59(4)	41(4)	-10(4)	-9(3)	-12(3)
C(14)	64(4)	60(4)	52(5)	1(4)	9(4)	-1(4)
C(15)	76(5)	68(5)	77(6)	14(5)	13(5)	9(4)
C(16)	88(6)	71(5)	72(6)	4(5)	7(5)	-28(4)
C(17)	54(4)	84(5)	64(5)	-11(5)	-6(4)	-5(4)
C(18)	73(5)	62(4)	72(5)	6(5)	11(5)	-6(4)
C(19)	69(5)	46(4)	73(5)	-7(4)	-5(4)	-9(4)
C(20)	75(5)	66(5)	95(7)	-3(5)	5(5)	3(4)
C(21)	57(5)	173(10)	156(10)	24(10)	2(6)	27(6)
C(22)	59(5)	107(6)	128(8)	-21(7)	26(6)	-10(5)
C(23)	73(6)	121(7)	168(11)	-14(8)	7(7)	-17(6)
C(24)	113(8)	133(9)	214(15)	-22(11)	61(10)	-4(7)
C(25)	181(12)	178(12)	235(17)	-27(13)	153(13)	-28(11)
C(26)	143(11)	246(17)	419(32)	70(22)	150(17)	9(12)
C(27)	195(17)	757(53)	368(29)	-269(37)	96(20)	70(26)
C(28)	66(5)	107(7)	77(6)	-5(6)	4(5)	17(5)
C(29)	89(6)	147(8)	73(6)	25(7)	26(5)	40(6)
C(30)	140(9)	180(11)	151(12)	-30(11)	-13(9)	-14(8)
C(31)	242(16)	111(9)	245(21)	-19(13)	-1(15)	5(10)
C(32)	222(15)	155(12)	190(16)	71(13)	15(12)	-9(11)
O(3)	65(3)	98(4)	95(4)	-16(4)	15(3)	1(3)
O(28)	100(4)	179(6)	101(5)	-54(5)	-2(4)	23(4)

112.0(6)-123.6(11)° and 110.0(7)-116.7(6)°, respectively.

Selected torsion angles for the tetracyclic ring, the ester group and the side chain are given in Table 7. In the steroid skeleton, the ring A and C form chair conformations, whereas the B seems to be somewhat twisted with the half chair conformation, presumably owing to the ethylenic double bond C(5)-C(6). The five membered ring D is expected

near a C(13)-C(14) twisted conformation with a torsion angle C(17)-C(13)-C(14)-C(15) = -46.1(6)°.

The angle C(19)-C(10)...C(13)-C(18), known as a pseudo-torsion angle which involves a measure of the twisting ring systems on the long axis of the steroid skeleton is 14.0(5)°, slightly larger than expected for those of cholesteryl isobutyrate¹⁸ 5.8 and 7.3°, and 10.9° for cholesteryl hexanoate.⁹ The bond C(3)-O(3) is almost a *trans*-form either

Table 4. Fractional hydrogen coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$)

atom	x	y	z	U_{eq}^*
H(1a)	2562	9167	-5157	76
H(1b)	2577	8435	-5172	76
H(2a)	3612	9197	-4726	85
H(2b)	3460	8799	-6709	85
H(3)	3562	7897	-4830	74
H(4a)	3882	7878	-1427	79
H(4b)	3886	8610	-1367	79
H(6)	2778	7501	907	77
H(7a)	2178	7707	2136	73
H(7b)	1978	7479	-82	73
H(8)	1950	8703	1398	58
H(9)	1873	8334	-2880	61
H(11a)	1575	9290	-3844	71
H(11b)	1659	9551	-1579	71
H(12a)	659	9485	-2211	73
H(12b)	721	8787	-2921	73
H(14)	1109	7980	-484	65
H(15a)	1099	8236	3818	78
H(15b)	996	7585	2755	78
H(16a)	22	7763	2379	85
H(16b)	107	8343	3839	85
H(17)	-43	8368	-473	69
H(18a)	786	9252	3171	78
H(18b)	606	9754	1503	78
H(18c)	1284	9528	1681	78
H(19a)	2585	9742	-1789	75
H(19b)	3250	9482	-1564	75
H(19c)	2777	9386	241	75
H(20)	-328	9286	2243	82
H(21a)	-198	9657	-1087	131
H(21b)	-884	9713	-427	131
H(21c)	-676	9171	-1909	131
H(22a)	-905	8343	2597	107
H(22b)	-1173	8488	385	107
H(23a)	-1670	9306	1566	130
H(23b)	-1338	9266	3726	130
H(24a)	-1862	8403	4496	167
H(24b)	-2191	8436	2330	167
H(25)	-2635	9302	3474	253
H(26a)	-3255	8508	3337	207
H(26b)	-3361	8776	5580	207
H(26c)	-2949	8185	5264	207
H(27a)	-2089	9477	6371	230
H(27b)	-2347	8859	7338	230
H(27c)	-2784	9426	6924	230
H(29a)	5494	7674	-6650	119
H(29b)	5432	8337	-5633	119
H(30a)	5144	8126	-9686	175

atom	x	y	z	U_{eq}^*
H(30b)	5809	8298	-9006	175
H(31a)	4811	9023	-8661	206
H(31b)	5450	9194	-7726	206
H(32a)	5334	9722	-10918	185
H(32b)	5211	9089	-12070	185
H(32c)	5861	9232	-11170	185

*Equivalent isotropic U defined as one of the trace of the orthogonalized U_{ij} tensor.

Table 5. Bond lengths (\AA) for non-hydrogen atoms of cholesteryl pentanoate. The e.s.d.'s are in parentheses

C(1)-C(2)	1.529(9)	C(1)-C(10)	1.544(10)
C(2)-C(3)	1.500(11)	C(3)-C(4)	1.497(11)
C(3)-C(3)	1.478(9)	C(4)-C(5)	1.510(9)
C(5)-C(6)	1.269(10)	C(5)-C(10)	1.569(9)
C(6)-C(7)	1.509(9)	C(7)-C(8)	1.510(9)
C(8)-C(9)	1.567(10)	C(8)-C(14)	1.515(9)
C(9)-C(10)	1.514(8)	C(9)-C(11)	1.526(9)
C(10)-C(19)	1.514(9)	C(11)-C(12)	1.489(19)
C(12)-C(13)	1.506(11)	C(13)-C(14)	1.581(9)
C(13)-C(17)	1.559(9)	C(13)-C(18)	1.525(10)
C(14)-C(15)	1.531(11)	C(15)-C(16)	1.512(10)
C(16)-C(17)	1.526(11)	C(17)-C(20)	1.540(10)
C(20)-C(21)	1.482(14)	C(20)-C(22)	1.519(10)
C(22)-C(23)	1.465(13)	C(23)-C(24)	1.468(15)
C(24)-C(25)	1.443(19)	C(25)-C(26)	1.429(19)
C(25)-C(27)	1.385(27)	C(28)-C(29)	1.514(11)
C(28)-O(3)	1.352(11)	C(28)-O(28)	1.173(11)
C(29)-C(30)	1.418(16)	C(30)-C(31)	1.389(18)
C(31)-C(32)	1.569(25)		

to the bond C(3)-C(2) or to the bond C(3)-C(4), having the ester linkage torsion angles C(28)-O(3)-C(3)-C(2) = $-100.8(8)^\circ$ and C(28)-O(3)-C(3)-C(4) = $137.2(7)^\circ$, respectively. The angle C(2)-C(3)-C(4) resulted from above two torsion angles is 122° similar to that of cholesteryl octanoate 121° .⁹ In the ester group, the atom C(31) is almost in vertical direction with the torsion angle C(28)-C(29)-C(30)-C(31) = $75.8(1.4)^\circ$ against the triangular plane included atoms O(3), C(28), O(28) and C(29), while the angle C(29)-C(30)-C(31)-C(32) is $173.8(1.1)^\circ$, so that the resultant terminal carbon atoms stand on end.

Table 6. Bond angles ($^{\circ}$) for cholesteryl pentanoate. The e.s.d.'s are in parentheses

C(2)-C(1)-C(10)	115.9(6)	C(1)-C(2)-C(3)	109.0(6)
C(2)-C(3)-C(4)	112.6(7)	C(22)-C(3)-O(3)	108.4(6)
C(4)-C(3)-O(3)	107.5(6)	C(3)-C(4)-C(5)	110.1(6)
C(4)-C(5)-C(6)	119.6(6)	C(4)-C(5)-C(10)	116.0(6)
C(6)-C(5)-C(10)	124.2(6)	C(5)-C(6)-C(7)	123.5(6)
C(6)-C(7)-C(8)	113.8(5)	C(7)-C(8)-C(9)	108.0(5)
C(7)-C(8)-C(14)	110.7(5)	C(9)-C(8)-C(14)	109.0(5)
C(8)-C(9)-C(10)	112.3(5)	C(8)-C(9)-C(11)	110.0(5)
C(10)-C(9)-C(11)	114.6(5)	C(1)-C(10)-C(5)	105.3(5)
C(1)-C(10)-C(9)	108.4(5)	C(5)-C(10)-C(9)	109.8(5)
C(1)-C(10)-C(19)	110.2(6)	C(5)-C(10)-C(19)	109.6(5)
C(9)-C(10)-C(19)	113.2(5)	C(9)-C(11)-C(1)	116.9(6)
C(11)-C(12)-C(13)	113.7(6)	C(12)-C(13)-C(14)	105.8(5)
C(12)-C(13)-C(17)	119.9(6)	C(14)-C(13)-C(17)	98.1(5)
C(12)-C(13)-C(18)	111.1(6)	C(14)-C(13)-C(18)	112.3(5)
C(17)-C(13)-C(18)	108.9(6)	C(8)-C(14)-C(13)	114.6(5)
C(8)-C(14)-C(15)	118.0(6)	C(13)-C(14)-C(15)	103.8(5)
C(14)-C(15)-C(16)	103.2(6)	C(15)-C(16)-C(17)	108.8(6)
C(13)-C(17)-C(16)	104.5(5)	C(13)-C(17)-C(20)	117.8(6)
C(16)-C(17)-C(20)	114.0(6)	C(17)-C(20)-C(21)	112.2(7)
C(17)-C(20)-C(22)	112.0(6)	C(21)-C(20)-C(22)	109.2(7)
C(20)-C(22)-C(23)	117.1(7)	C(22)-C(23)-C(24)	117.8(8)
C(23)-C(24)-C(25)	123.6(11)	C(24)-C(25)-C(26)	114.8(12)
C(24)-C(25)-C(27)	114.2(13)	C(26)-C(25)-C(27)	105.1(15)
C(29)-C(28)-O(3)	110.0(7)	C(29)-C(28)-O(28)	126.3(9)
C(3)-C(28)-O(28)	123.7(8)	C(28)-C(29)-C(30)	111.0(8)
C(29)-C(30)-C(31)	116.0(13)	C(30)-C(31)-C(32)	114.3(14)
C(3)-O(3)-C(28)	116.7(6)		

Table 7. Selected torsion angles ($^{\circ}$) in cholesteryl pentanoate. The e.s.d.'s are in parentheses

(1) Steroid skeleton

ring A

C(10)-C(1)-C(2)-C(3)	57.0(8)
C(1)-C(2)-C(3)-C(4)	-57.2(8)
C(2)-C(3)-C(4)-C(5)	56.8(8)
C(3)-C(4)-C(5)-C(10)	-54.9(8)
C(4)-C(5)-C(10)-C(1)	50.6(7)
C(2)-C(1)-C(10)-C(5)	-51.7(7)

ring B

C(10)-C(5)-C(6)-C(7)	4.3(1.1)
C(5)-C(6)-C(7)-C(8)	-19.7(1.0)
C(6)-C(7)-C(8)-C(9)	45.6(8)
C(7)-C(8)-C(9)-C(10)	-60.6(7)
C(8)-C(9)-C(10)-C(5)	44.9(7)
C(6)-C(5)-C(10)-C(9)	-17.5(9)

ring C

C(14)-C(8)-C(9)-C(11)	49.8(7)
C(8)-C(9)-C(11)-C(12)	-48.9(8)

C(9)-C(11)-C(12)-C(13)	53.2(9)
C(11)-C(12)-C(13)-C(14)	-53.5(7)
C(12)-C(13)-C(14)-C(8)	59.5(7)
C(9)-C(8)-C(14)-C(13)	-58.8(7)
ring D	
C(17)-C(13)-C(14)-C(15)	-46.1(6)
C(13)-C(14)-C(15)-C(16)	36.0(7)
C(14)-C(15)-C(16)-C(17)	-11.1(8)
C(15)-C(16)-C(17)-C(13)	-18.3(8)
C(14)-C(13)-C(17)-C(16)	38.4(7)
(2) Ester	
C(1)-C(2)-C(3)-O(3)	-176.0(6)
C(5)-C(4)-C(3)-O(3)	176.1(6)
C(4)-C(3)-O(3)-C(28)	137.2(7)
C(2)-C(3)-O(3)-C(28)	-100.8(8)
O(28)-C(28)-O(3)-C(3)	0.0(1.3)
C(29)-C(28)-O(3)-C(3)	178.4(7)
O(3)-C(28)-C(29)-C(30)	-114.0(1.0)
O(28)-C(28)-C(29)-C(30)	64.2(1.4)
C(28)-C(29)-C(30)-C(31)	75.8(1.4)
C(29)-C(30)-C(31)-C(32)	173.8(1.1)
(3) Side chain	
C(13)-C(17)-C(20)-C(21)	58.5(9)
C(13)-C(17)-C(20)-C(22)	-178.3(7)
C(16)-C(17)-C(20)-C(22)	-55.3(9)
C(17)-C(20)-C(22)-C(23)	162.3(9)
C(21)-C(20)-C(22)-C(23)	-72.7(1.1)
C(20)-C(22)-C(23)-C(24)	-170.2(1.0)
C(22)-C(23)-C(24)-C(25)	179.6(1.3)
C(23)-C(24)-C(25)-C(26)	164.2(1.5)
C(23)-C(24)-C(25)-C(27)	-74.3(2.1)
C(23)-C(24)-C(25)-C(27)	-74.3(2.1)
C(16)-C(17)-C(20)-C(21)	-178.6(7)

The least squares planes and deviations of neighboring atoms from each plane are listed in Table 8. The atoms for the ethylenic group are coplanar with the maximum deviation 0.025 Å in the C(5). The atoms C(17), C(20), C(22) through C(26) are in zigzag planar chain. The branched atoms C(21) and C(27) lie above 1.296 Å and below -1.442 Å from the plane, respectively. In the ester group, the C(28), C(29), O(3) and O(28) atoms are nearly coplanar with the maximum deviation of 0.009 Å in the C(28).

The steroid length calculated between C(3)-C(16) is 8.865(10) Å similar to those reported in other cholesterol esters, ranged from 8.85 to

Table 8. Least-squares planes and deviations (\AA) of individual atoms from these planes in cholesteryl pentanoate. The equation of plane is expressed in the form $Ax + By + Cz = D$, where x, y and z are in \AA and with respect to orthogonal axes

(1) Cholesteryl ring system, C(1) through C(17)	$6.357x + 15.782y + 3.916z = 14.220$
(2) Ethylenic group, C(4) through C(7) and C(10)	$-0.234x - 0.580y + 0.781z = -11.144$ C(4) -0.006 ; C(5) 0.025 ; C(6) -0.013 ; C(7) 0.002 ; C(10) -0.008
(3) Ester linkage, C(28), C(29), O(3) and O(28)	$0.213x - 0.735y - 0.644z = -12.988$ C(28) 0.009 ; C(29) -0.003 ; O(3) -0.003 ; O(28) -0.004
(4) Side chain, C(17) through C(26)	$-0.375x + 0.030y + 0.927z = 0.209$ C(17) -0.187 ; C(20) 0.081 ; C(22) 0.202 ; C(23) 0.058 ; C(24) -0.048 ; C(25) -0.185 ; C(26) 0.080 ; C(21)* 1.296 ; C(27)* -1.442
(5) Pentanoate chain, C(29) through C(32)	$0.910x + 0.238y - 0.339z = 13.148$ C(29) 0.039 ; C(30) -0.040 ; C(31) -0.033 ; C(32) 0.034 ; C(28)* -1.287

*Atom not included in derivation of the plane.

9.02 \AA . The length of the side chain C(17)–C(25), which is taken as a measure of the extension of the tail, is $6.346(17) \text{ \AA}$. This is slightly longer than 6.27 and 6.28 \AA for those of cholesteryl isobutyrate.¹⁸

The packing diagrams are shown in Fig. 2a and 2b. The plane of the cholesteryl group is almost parallel to the ac plane with the entire molecule oriented parallel to the (101) direction. The unit cells of the cholesteryl pentanoate are four molecules thick, one molecule wide and one molecule long, where, as given by Duax and Norton,¹⁹ the length of the steroid is the dimension parallel to the C(10)–C(13) direction, the width is the dimension parallel to the C(14)–C(12) direction and the thickness is the dimension orthogonal to the length and the width. Therefore, the modified Hodgkin notation is $O411(thw)$. In this $O411$ subgroup, the molecular arrangement relative to screw operators is such that the molecules of any layer are stacked with respect to one adjacent

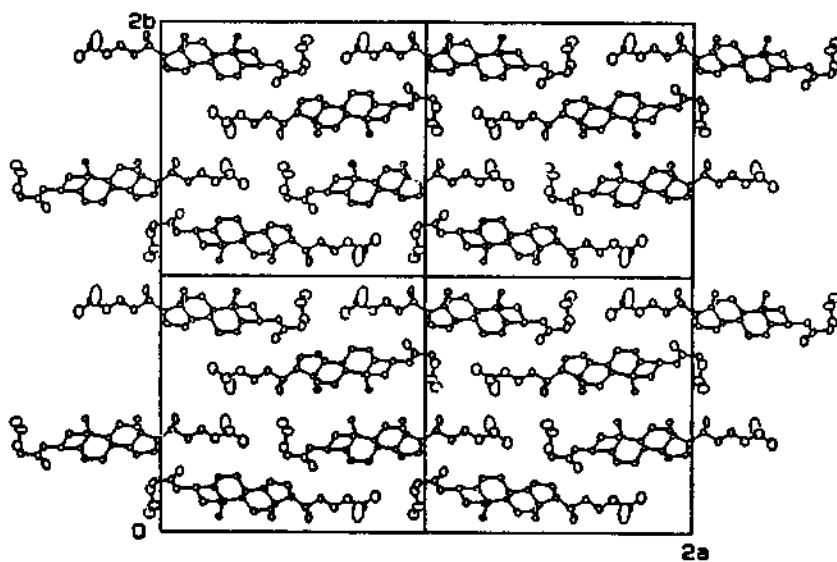


Fig. 2a. The crystal structure of cholesteryl pentanoate in projection down the c axis.

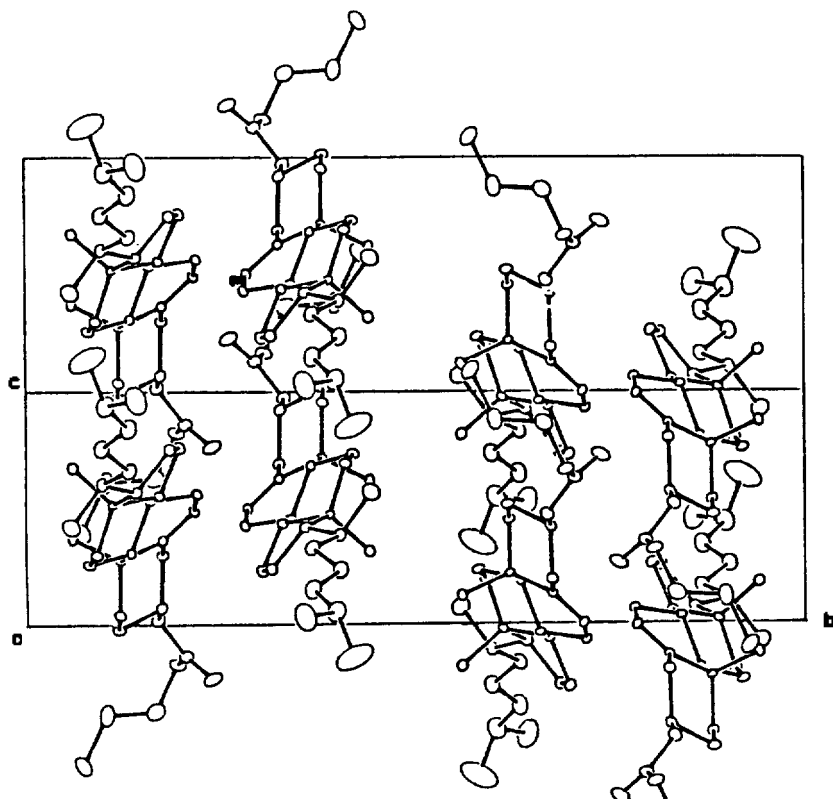


Fig. 2b. The crystal structure of cholesteryl pentanoate in projection down the *a* axis.

layer and staggered with respect to the other adjacent layer. Hence the adjacent layers are alternately stacked and staggered. The molecules within the layers are translationally equivalent. Similar packing arrangements are frequently observed in steroid structure, but rather unique among the crystals of cholesterol related compounds.

In cholesteryl pentanoate, the three dimensional structure is stabilized by non-bonded van der Waal's forces. There are 14 intermolecular contacts less than 4.0 Å, of which the shortest is 3.529(11) Å of C(4)···O(28) (*x*, *y*, *z*-1).

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