DAEHAN HWAHAK HWOEJEE
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Cholesteryl Hexanoate의 실온 및 저온에서의 분자 및 결정구조*

朴英子† · B. M. Craven**
숙명여자대학교 이과대학 화학과
**미국 핏츠버그대학교 결정학과

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The Crystal and Molecular Structure of Cholesteryl Hexanoate at Room and Low Tempreature

Young Ja Park† and **B. M. Craven****
Department of Chemistry, Sook Myung Women's University, Seoul 140, Korea
***Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15260, U. S. A.*

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요 약. Cholesteryl hexanoate의 결정 및 분자구조를 실온과 −75 °C에서 X-ray 회절방법으로 결정하였다. 이 화합물의 결정은 단사형계에 속하며 a=12.162(3), b=9.314(3), c=13.643(5) Å, β=93.55°(3)이며 단위세포안에 두개의 분자가 있다. 분자구조는 cholesteryl octanoate의 원자좌표를 trial 구조로 하여 Fourier 방법으로 결정하여 정밀화하였다. 최종 R값은 실온과 저온에서 얻은 X-ray 회절강도들에 대하여 각각 0.129와 0.105이다. 분자들은 서로 반대로 나란히 길게 놓여 있으며 이들이 monolayer를 만들면서 모여져 있다. Monolayer들 안에서는 cholesteryl군들이 서로 촘촘히 쌓인 구조를 가지고 있다. 결정구조는 cholesteryl octanoate와 cholesteryl oleate와 매우 비슷하다.

ABSTRACT. Cholesteryl hexanoate ($C_{33}H_{56}O_2$) is monoclinic, space group $P2_1$, with a=12.162(3), b=9.314(3), c=13.643(5) Å, β=93.55°(3) and two molecules per unit cell. The atomic coordinates from cholesteryl octanoate were used in an initial trial structure using X-ray intensities(Mo Kα radiation) measured by a diffractometer at room temperature and −75 °C. Structure refinement by block-diagonal least squares gave R=0.129 and 0.105 for room and low temperature experiments respectively. The molecules are arranged in monolayers with their long axes antiparallel and severely tilted. There is a close packing of cholesteryl groups within the monolayers. The crystal structure is very similar to those of cholesteryl octanoate and cholesteryl oleate.

INTRODUCTION

We have undertaken a series of crystal structure determinations[1~7] of fatty acid esters of cholestrol to obtain structural information relevant to the liquid crystalline phases of cholesteryl esters and the possible modes of association of cholesterol and cholesteryl esters with themselves and other substances in biological systems.

Barnard and Lydon[8] have conducted a crystallographic study on fourteen straight chain cholesteryl esters. Examination of the unit cell parameters they obtained in addition to other crystallographic data, suggestes that majority of esters may have one of the three common

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crystal packing arrangements. The crystal structures of cholesteryl nonanoate[5], hexanoate, myristate[1] have been served as the prototype for a classification of packing arrangements, which are called structures with Type I monolayers, Type II monolayers and Bilayers respectively.

Other crystal structure determinations in this series have been carried out at room temperature except for cholesteryl acetate[6]. Because of the weak intermolecular forces in nonpolar lipid structures, atomic details tend to be obscured by large apparent thermal-vibrational averaging. These effects are particularly severe in the chain at C(17) and sometimes also in the fatty acid chain. In several crystal structures, there appeared to be conformational disorder at the ends of the molecules. The crystal structure of cholesteryl hexanoate was also determined at low temperature in order to minimize thermal effects and hence obtain greater detail and accuracy.

The crystal of cholesteryl hexanoate has enantiotropic phase transitions suggesting possible structural similarity between the crystalline solid and cholesteric mesophases.

$$\text{Crystal} \overset{91.2\sim99.5^\circ}{\longleftrightarrow} \text{Cholesteric} \overset{100.1\sim101.5^\circ}{\longleftrightarrow} \text{Isotropic liquid}$$

(The temperatures shown are the range of values reported for independent measurements.[9])

EXPERIMENTAL

A cholesteryl hexanoate sample was obtained from Sigma Chemical Company and single crystals of excellent quality were obtained directly from this sample as well as by recrystallization from *n*-pentanol. Preliminary crystal data obtained from X-ray Weissenberg photographs were in agreement with those reported by Barnard and Lydon.

Subsequent X-ray data collections were carried out at room and low temperatures using a Nonius CAD-4 diffractometer and graphite-monochromated Mo Kα radiation.

Data collections at -75°C were carried out with the Enraf-Nonius Universal Low Temperature Device with liquid nitrogen as the coolant. Icing on the crystal was prevented by enclosing the difffractometer in a plastic bag together with containers of phosphorus pentaoxide.

The intensities were collected by an $\omega/2\theta$ scan. The reflections with $I<2\sigma(I)$ were assumed to be unobserved. The variance in an integrated intensity was assumed to be $\sigma^2(I)=\sigma^2+(0.02I)^2$ where σ^2 is the variance due to counting statistics.

Unit cell volume at low temperature is decreased by 2.7% compared with that of room temperature. The crystal data at both temperatures are listed in *Table* 1.

Since the cell dimensions and X-ray intensity data for cholesteryl hexanoate were similar to those of cholesteryl octanoate[2], the atomic positional parameters of tetracyclic ring part of latter molecule were used as a starting model in Fourier refinement with room temperature data. The initial *R*-factor for the model from

Table 1. Crystal data for cholesteryl hexanoate.

$C_{33}H_{56}O_2$		M. W. =484.8
Space Group : $P2_1$		$F(000)=540.0$
Z : 2		$\mu(MoK\alpha)=0.32\ cm^{-1}$
at -75°C		at room temperature
a=12.162 (3) Å		12.247 (5)
b=9.314 (3)		9.372 (5)
c=13.643 (5)		13.817 (9)
β=93.55° (3)		91.89 (6)
D_c=1.044 g/cm^3		1.016
Number of total reflections	2716	1797
Number of observed reflections	1740	1145
$2\theta_{max}$	50°	40°

Table 2. Fractional atomic coordinates for cholesteryl hexanoate. The key to the atomic numbering is given in *Fig.* 2. The estimated standard deviations given in parentheses refer to the last decimal positions of the corresponding parameters. For each atom, the low temperature result is given on the first line and the the room temperature result on the second line.

	x	y	z		x	y	z
C(1)	0.5770(7)	0.3529(13)	0.2066(7)	C(22)	0.0350(5)	0.3529(11)	0.6537(4)
	0.5769(8)	0.3518(15)	0.2126(7)		0.0339(6)	0.3476(13)	0.6509(7)
C(2)	0.6671(11)	0.3195(14)	0.1427(10)	C(23)	−0.0821(5)	0.2963(11)	0.6774(6)
	0.6742(14)	0.3251(16)	0.1564(11)		−0.0857(7)	0.2892(14)	0.6739(7)
C(3)	0.7749(9)	0.3037(16)	0.2064(7)	C(24)	−0.1209(6)	0.3583(13)	0.7685(6)
	0.7746(9)	0.3069(18)	0.2053(8)		−0.1197(8)	0.3426(15)	0.7764(7)
C(4)	0.7713(7)	0.1990(15)	0.2843(8)	C(25)	−0.2452(13)	0.3242(19)	0.7976(10)
	0.7714(8)	0.2076(16)	0.2859(9)		−0.2519(16)	0.3268(28)	0.7976(14)
C(5)	0.6705(8)	0.2166(10)	0.3488(9)	C(26)	−0.2684(7)	0.4135(15)	0.8782(5)
	0.6695(9)	0.2158(13)	0.3525(11)		−0.2698(8)	0.4056(18)	0.8863(6)
C(6)	0.6839(8)	0.2234(13)	0.4422(7)	C(27)	−0.2677(10)	0.1683(16)	0.7997(10)
	0.6809(9)	0.2346(15)	0.4381(8)		−0.2677(17)	0.1771(23)	0.8055(17)
C(7)	0.5923(6)	0.2365(10)	0.5124(6)	C(28)	0.9443(3)	0.3470(16)	0.1297(10)
	0.5894(6)	0.2354(13)	0.5089(6)		0.9419(11)	0.3464(29)	0.1327(12)
C(8)	0.4767(5)	0.2174(11)	0.4583(6)	C(29)	1.0245(6)	0.2857(17)	0.0614(7)
	0.4767(6)	0.2199(12)	0.4618(6)		1.0258(9)	0.2804(21)	0.0593(9)
C(9)	0.4742(5)	0.2918(11)	0.3589(6)	C(30)	1.1071(9)	0.3601(18)	0.0357(7)
	0.4733(6)	0.2952(12)	0.3611(6)		1.1084(13)	0.3564(22)	0.0398(9)
C(10)	0.5595(7)	0.2415(13)	0.2891(5)	C(31)	1.2075(9)	0.2901(16)	−0.0217(9)
	0.5600(8)	0.2391(15)	0.2893(6)		1.2098(11)	0.3040(28)	−0.0192(10)
C(11)	0.3523(5)	0.2969(11)	0.3118(5)	C(32)	1.3095(11)	0.3438(17)	−0.0264(11)
	0.3559(6)	0.2978(12)	0.3122(6)		1.3038(15)	0.3317(28)	−0.0221(14)
C(12)	0.2683(5)	0.3469(10)	0.3806(7)	C(33)	1.3947(9)	0.2560(17)	−0.0722(7)
	0.2715(6)	0.3499(11)	0.3859(7)		1.3889(11)	0.2515(21)	−0.0700(9)
C(13)	0.2706(5)	0.2540(11)	0.4776(5)	O(3)	0.8625(7)	0.2645(10)	0.1438(5)
	0.2659(6)	0.2514(13)	0.4776(6)		0.8637(8)	0.2754(12)	0.1438(6)
C(14)	0.3877(4)	0.2717(9)	0.5247(5)	O	0.9523(9)	0.4604(13)	0.1658(9)
	0.3856(5)	0.2725(9)	0.5247(6)		0.9576(11)	0.4573(20)	0.1659(12)
C(15)	0.3832(6)	0.2069(9)	0.6254(5)	H(C1)	0.502	0.346	0.171
	0.3788(7)	0.2072(10)	0.6254(6)	H′(C1)	0.582	0.439	0.244
C(16)	0.2657(6)	0.2527(11)	0.6535(5)	H(C2)	0.679	0.382	0.095
	0.2601(7)	0.2537(12)	0.6530(6)	H′(C2)	0.663	0.212	0.116
C(17)	0.2041(6)	0.3160(9)	0.5600(6)	H(C3)	0.790	0.402	0.239
	0.2017(7)	0.3155(11)	0.5554(7)	H(C4)	0.764	0.079	0.259
C(18)	0.2397(7)	0.0977(10)	0.4566(4)	H′(C4)	0.837	0.178	0.336
	0.2393(7)	0.0975(12)	0.4589(6)	H(C6)	0.760	0.198	0.474
C(19)	0.5265(8)	0.0963(12)	0.2463(7)	H(C7)	0.592	0.339	0.538
	0.5259(9)	0.0961(14)	0.2469(7)	H′(C7)	0.601	0.171	0.571
C(20)	0.0789(4)	0.2923(11)	0.5593(6)	H(C8)	0.465	0.099	0.441
	0.0755(6)	0.2923(12)	0.5569(8)	H(C9)	0.486	0.387	0.384
C(21)	0.0197(6)	0.3522(12)	0.4688(4)	H(C11)	0.339	0.187	0.296
	0.0186(7)	0.3486(16)	0.4658(6)	H′(C11)	0.359	0.349	0.259

H(C12)	0.199	0.332	0.350	H′(C22)	0.089	0.336	0.702
H′(C12)	0.288	0.441	0.400	H(C23)	−0.071	0.177	0.689
H(C14)	0.395	0.371	0.538	H′(C23)	−0.135	0.299	0.627
H(C15)	0.378	0.089	0.617	H(C24)	−0.113	0.453	0.759
H′(C15)	0.437	0.228	0.669	H′(C24)	−0.061	0.322	0.821
H(C16)	0.271	0.329	0.706	H(C25)	−0.285	0.356	0.757
H′(C16)	0.218	0.169	0.684	H(C26)	−0.240	0.350	0.940
H(C17)	0.217	0.413	0.557	H′(C26)	−0.340	0.425	0.920
H(C18)	0.160	0.125	0.420	H″(C26)	−0.220	0.500	0.920
H′(C18)	0.240	0.075	0.540	H(C29)	0.997	0.236	0.002
H(C19)	0.580	0.025	0.220	H′(C29)	1.063	0.181	0.099
H′(C19)	0.480	0.000	0.280	H(C30)	1.170	0.406	0.107
H″(C19)	0.460	0.125	0.220	H′(C30)	1.098	0.471	0.014
H(C20)	0.065	0.167	0.566	H(C31)	1.161	0.298	−0.090
H(C21)	−0.080	0.350	0.460	H′(C31)	1.189	0.187	−0.002
H′C21)	0.040	0.325	0.420	H(C32)	1.296	0.332	0.049
H(C22)	0.025	0.446	0.629	H′(C32)	1.273	0.422	−0.047

the cholesteryl octanoate was 0.42. The atomic parameters of tail and fatty acid chain of the molecule were located in a difference Fourier map. There is no evidence of conformational disorder at fatty acid chain unlike the structure of cholesteryl octanoate.

After several cycles of block diagonal least squares refinements, R-factor dropped to 0.18, where $R=\sum|\Delta|/\sum|F_{obs}|$ and $\Delta=|F_{obs}|-|F_{cal}|$. The function minimized was $\sum w\Delta^2$, where $w=1/\sigma^2(F_{obs})$. A difference map computed at this stage revealed some hydrogen atoms. Hydrogen atomic positions were also calculated from the carbon framework assuming standard geometry. (C-H distance is 1.0 Å.) Hydrogen atoms excepting those bonded to the methyl groups were included in the refinement with isotropic temperature factors of 3.5 Å^2. The parameters of hydrogen atoms were not refined. After final cycles of refinement, R-value for the room temperature experiment was 0.129.

The refinement procedure with low temperature data, is very similar to that of room temperature study. A difference map computed with carbon and oxygen atoms revealed all the hydrogen atoms except those bonded to methyl groups of C(18), C(21), C(27) and (33). The positional parameters of hydrogen atoms were also refined. The isotropic temperature factors of 3.5 Å^2 were assigned to hydrogen atoms and were not refined. The refinement converged with $R=0.105$ for 1740 observed reflections. Atomic form factors were those of Cromer and Waber[10] for carbon and oxygen and Stewart, Davidson and Simpson[11] for hydrogen. Final positional parameters for non-hydrogen atoms at both temperatures are listed in *Table* 2* along with those for hydrogen atoms at −75 °C. Since positional parameters for low temperature study are more accurate than those for room temperature study, we will only discussed bond lengths and angles observed at −75 °C.

RESULTS AND DISCUSSION

The Molecular Structure. The molecular conformation (ORTEP diagram) is depicted in *Fig.* 1. As can be seen in *Fig.* 1, the thermal motion of the molecule increases as the temperature increases. The bond distances and

* Observed and calculated structure factor amplitudes and anisotropic thermal parameters of the non-hydrogen atoms can be obtained from the authors

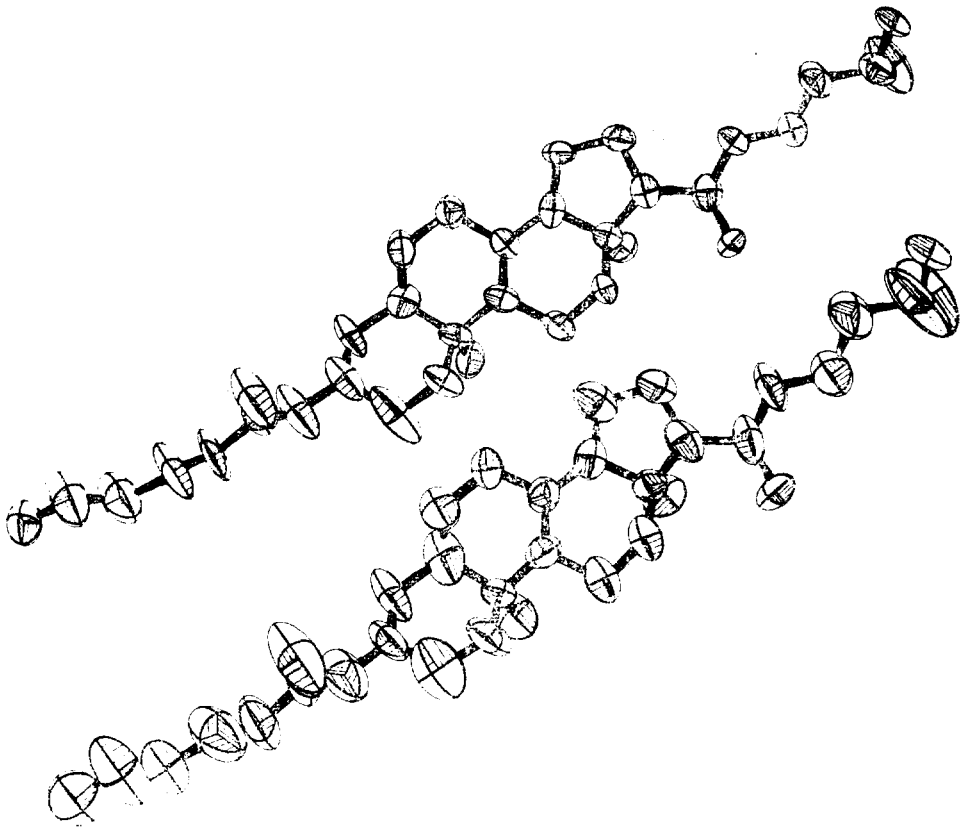

Fig. 1. Cholesteryl hexanoate molecule in its observed configuration. above: at −75°C, below: at room temperature.

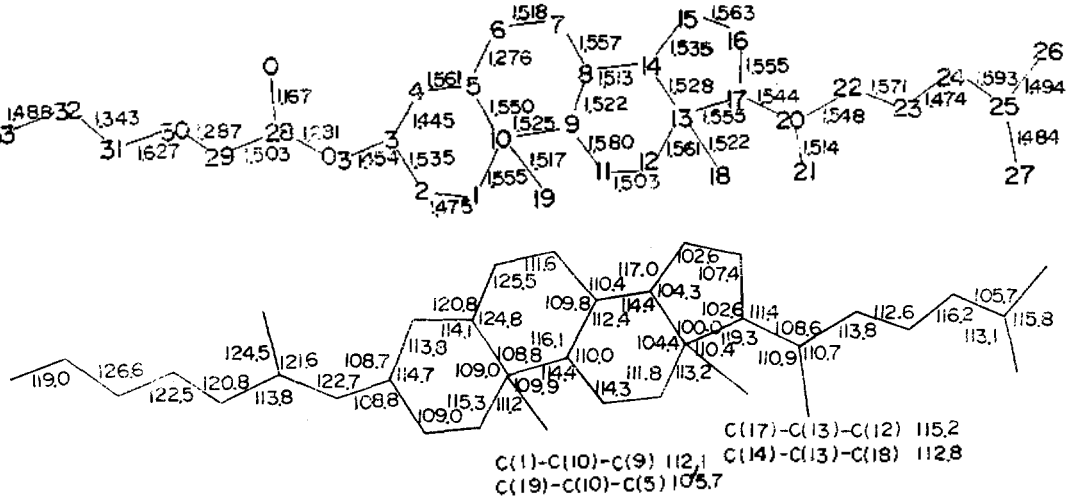

Fig. 2. Atomic numbering system and interatomic distances(Å) and angles (°). The average estimated standard deviations for these values are 0.06 Å and 0.7° respectively.

angles are in agreement within experimental error with those found in other cholesteryl esters[6] (see *Fig.* 2.). The C-dC distances range from 1.445 to 1.580 Å within the tetracyclic systems. The double bond distance C(5)=C(6) is 1.276 Å The torsion angle C(19)-C(10)-C(13)-C(18) which is a measure of the twist within the tetracyclic system, is 10.9°. This angle ranges between 7.9 to 12.0° in other related structures. The intramolecular distance C(3)-C(16) which is useful for comparing the length of the tetracyclic system has a value of 8.970 Å which is close to the limits of range (8.86 to 9.01 Å) observed in other related molecules. Within experimental error, atoms are coplanar in the ethylene group C(4) through C(7) and C(10) and also in the ester linkage C(28), C(29), O and O(3) (See *Table* 3).

The torsion angle C(2)-C(3)-O(3)-C(28) which is important for determining the overall shape of the molecule is 114.3°, so that the carbonyl bond is parallel to the C(3)-C(3)H bond. The corresponding torsion angles are 121° in cholesteryl octanoate and 137° in cholesteryl oleate.

The hexanoate chain is almost fully extended. The C(17) side chain is also almost fully extended. The interesting torsion angles along the chains are listed in *Table* 4.

The Molecular Packing. The crystal structure shown in *Fig.* 3 consists of antiparallel molecules arranged to form monolayers which are parallel to the crystal planes(001) and have a thickness of d_{001}=13.64 Å. The molecular long axes are parallel to the [20$\bar{1}$] axis.

All the crystal structures of cholesteryl hexanoate, octanoate and oleate have a common packing arrangement containing closely stacked

Table 3. Selected torsion angles in cholesteryl hexanoate.

C(19)-C(10)-C(13)-C(18)	10.9°
C(17)-C(20)-C(22)-C(23)	163.8
C(20)-C(22)-C(23)-C(24)	−179.1
C(22)-C(23)-C(24)-C(25)	171.9
C(23)-C(24)-C(25)-C(26)	172.7
C(23)-C(24)-C(25)-C(27)	−59.6
C(2)-C(3)-O(3)-C(28)	114.3
C(3)-O(3)-C(28)-C(29)	179.4
O(3)-C(28)-C(29)-C(30)	175.7
C(28)-C(29)-C(30)-C(31)	−168.9
C(29)-C(30)-C(31)-C(32)	−159.1
C(30)-C(31)-C(32)-C(33)	172.6

Table 4. Best least squares planes calculated for selected groups of atoms in cholesteryl hexanoate. The planes are : (1) tetracyclic ring system, C(1) through C(17) ; (2) ethylenic group, C(4) through C(7) and C(10) ; (3) ester linkage, O(3), C(28), C(29), O ; (4) C(17) side chain, C(17), C(20), C(22) through C(26) : (5) hexanoate chain, C(28) through C(33). Equations are of the form $ax+by+cz=d$, referred to the crystallographic axes. The plane constants are in Å.

(a) Plane constant

Plane	*a*	*b*	*c*	*d*
(1)	0.179	0.957	0.218	4.642
(2)	0.145	0.989	−0.014	3.144
(3)	0.470	−0.407	0.753	5.407
(4)	−0.292	0.798	−0.508	−2.146
(5)	0.364	−0.338	0.844	4.374

(b) Distances in Å of atoms from the plane.

(2) : C(4) −0.003 ; C(5) −0.031 ; C(6) 0.037 ; C(7) −0.017 ; C(10) 0.014

(3) : C(28) 0.009 ; C(29) −0.002 ; O −0.003 ; O(3) −0.003

(4) : C(17) −0.114 ; C(20) 0.127 ; C(22) 0.111 ; C(23) −0.058 ; C(24) −0.091 ; C(25) −0.058 ; C(26) 0.083

(5) : C(28) 0.208 ; C(29) −0.030 ; C(30) −0.194 ; C(31) −0.189 ; C(32) 0.039 ; C(33) 0.166

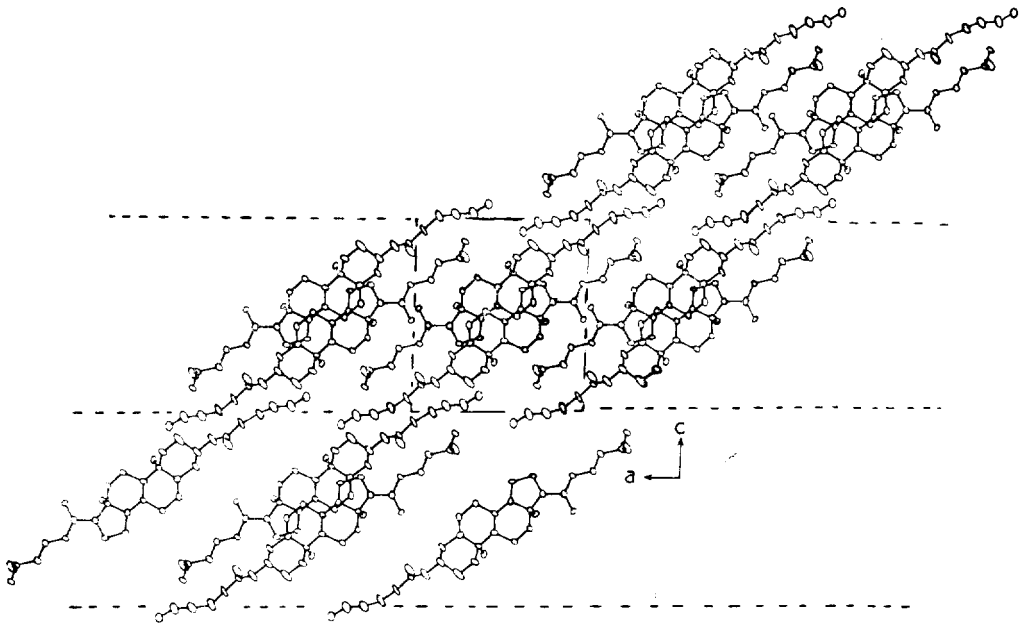

Fig. 3. The crystal structure of cholesteryl hexanoate in projection down the *b*-axis. Dashed lines separate the monolayers.

cholesterol moieties along a two-fold screw axis. The arrangement of tetracyclic ring systems is nearly identical in each case as shown in *Fig* 4. As a result of this packing mode, unit cell dimension along the symmetry axis is about 9.2 Å in the above crystals. In the directions more or less parallel to the crystal *b*-axis there are multiple intermolecular C–C distances less than 4.0 Å of which the shortest is C(18)–C(23) of 3.803 Å (*Table* 5). Interactions between adjacent stacks within a monolayer involve atoms C(11), C(12), C(18), C(19) and C(20) from one stack and the cholesteryl chain atoms C(20) through C(27) in another. The projecting methyl groups C(19), C(21) and particularly C(18) appear to have an important interlocking function for the cholesteryl packing arrangement.

The efficiency of cholesteryl packing arrangements is in contrast to the packing of the hexanoate chains. The hexanoate chains are loosely packed to form the monolayer interface region. The chains from adjacent monolayers are deeply interdigitated. In traversing the interface, there are hexanoate chains side by side.

Table 5. Intermolecular distances less than 4.0 Å.

C(2)···C(26)	1 /	1	0	−1	3.841
C(6)···C(18)	2*/	1	0	1	3.842
C(7)···C(18)	2 /	1	0	1	3.945
C(11)···C(27)	2 /	0	0	1	3.892
C(12)···C(27)	2 /	0	0	1	3.874
C(16)···C(33)	1 /	−1	0	1	3.967
C(18)···C(23)	2 /	0	−1	1	3.803
C(18)···C(24)	2 /	0	−1	1	3.993
C(19)···C(26)	2 /	0	−1	1	3.870

* Distance is between C(6) at symmetry position 1 (x, y, z) and C(18) at symmetry position 2$(-x, 1/2+y, -z)$ and translated 1 unit cell along *a*, 0 unit cell along *b*, 1 unit cell along *c*.

Three general types of packing arrangements have been observed for cholesteryl esters. The three arrangements are chain–chain packing, the preferred stacking of cholesterol moieties,

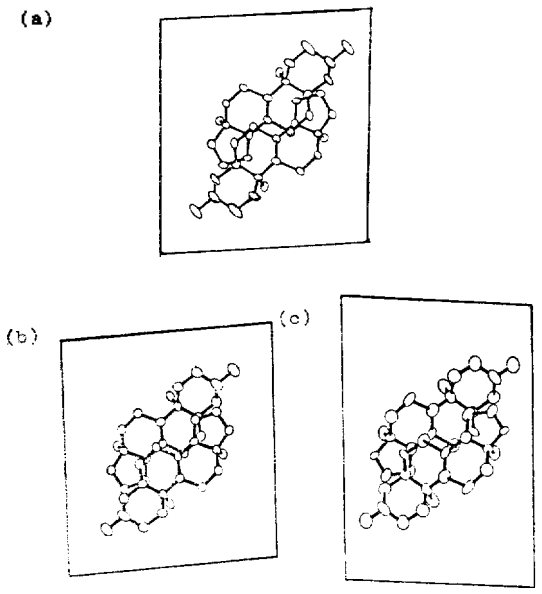

Fig. 4. The crystallographic [010] projections of the cholesterol tetracyclic ring systems of cholesteryl hexanoate (a), cholesteryl octanoate (b), and cholesteryl-oleate (c).

and chain-cholesterol packing.

The crystal structure discussed here belongs to monolayers Type II in which a close packing of antiparallel cholesteryl groups is predominant. Esters with this structure are the *n*-alkanoates with six, seven and eight carbon atoms, the chloroformate[12] and oleate[3] as well as cholesteryl iodide[13].

For medium chain-length *n*-alkanoate esters with nine through twelve carbon atoms and cholesteryl palmitoleate, a different monolayer structure is found (Type I). In monolayers of Type I there are two molecules A and B which are not related by crystal symmetry and have their tetracyclic systems almost perpendicular to each other. Compared with monolayers of Type II, cholesteryl-cholesteryl interactions are reduced to the stacking of tetracyclic systems of B molecules. However, there are important cholesteryl-alkyl chain interactions which do not occur in the other two crystal structure types.

For longer chain *n*-alkanoate esters with thirteen to eighteen carbon atoms and cholesteryl 17-bromoheptadecanoate[14], the preferred structure is the bilayer arrangements. In cholesteryl myristate, the bilayers contain two molecules not related by crystal symmetry. At the center of the bilayers, there is a regular packing of alkanoate chains with a recognizable orthorhombic subcell structure. An important feature of the bilayer structure which is lacking in the two monolayer structure types, is the efficient packing of the ester chains.

Cystals with Type II monolayers melt to give an isotropic liquid with an intermediate cholesteric phase. Cholesteryl-cholesteryl interactions may be the principle crystal packing forces since these forces may be greater than any other interactions involving the small ester chains.

REFERENCES

1. B. M. Craven and G. T. DeTitta, *J. Chem. Soc. Perkin Trans.* II, 817 (1976).
2. B. M. Craven and N. G. Guerina, *Chemistry and Physics of Lipids*, **24**, 157 (1979).
3. B. M. Craven and N. G. Guerina, *Chemistry and Physics of Lipids*, **24**, 91 (1979).
4. V. Pattabhi and B. M. Craven, *J. Lipid Research*, **20**, 753 (1979).
5. N. G. Guerina and B. M. Craven, *J. Chem. Soc. Perkin Trans*, II, 1414 (1979).
6. P. Sawzik and B. M. Craven, *Acta Cryst.*, B35, 895 (1979).
7. P. Sawzik and B. M. Craven, *Acta Cryst.*, B35, 789 (1979).
8. J. A. W. Barnard and J. E. Lydon, *Mol. Cryst. Liq. Cryst.*, **26**, 285 (1974).
9. G. W. Gray, *J. Chem. Soc.*, 3733 (1956).
10. D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).
11. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

12. R. J. Chandross and J. Bordner, *Acta Cryst.*, B **34**, 2872 (1978).
13. C. H. Carlisle and D. Crowfoot, *Proc. Roy. Soc.*, **184**A, 64 (1945).
14. S. Abrahamsson and B. Dahlen, *Chemistry and Physics of Lipids*, **20**, 43 (1977).