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콜레스테롤 카보네이트들의 결정구조에 관한 연구

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The Crystal Structures of Cholesteryl Carbonates

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요 약

콜레스테롤 메틸카보네이트와 프로필카보네이트의 결정구조를 X-선 회절법으로 연구하였다. 이 결정들은 단사정계이고 공간군은 $P2_1$이다. 회절반점들의 세기는 흑연 단색화 장치가 있는 Enraf-Nonius CAD-4 X-선 회절계로 얻었으며, Cu-Kα X-선(λ=1.5418 Å)을 사용하였다. 콜레스테롤 메틸카보네이트의 단위세포 길이 a=17.014(1), b=7.682(1), c=10.612(1)Å,이며, β=103.05(1)°, Z=2이다. 한편 콜레스테롤 프로필카보네이트의 단위세포길이는 a=13.683(1), b=11.864(2), c=18.904(2)Å,이며, β=106.30(1)°, Z=4이다. 분자구조들은 직접법으로 풀었으며 최소자승법으로 정밀화하였다. 최종신뢰도 R값은 메틸카보네이트는 2323개의 회절반점에 대하여 0.051이고, 프로필카보네이트는 3323개의 회절반점에 대하여 0.074이다.

이들 화합물들의 콜레스테롤부분의 분자구조들은 다른 관련 화합물에서 밝혀진 구조와 잘 일치하고 있다.

위의 두 화합물을 포함하여 콜레스테롤 카보네이트들의 결정구조들은 단분자층을 이루면서 쌓여 있어서 독특한 결정구조를 보여주며 같은 계열의 알킬 카보네이트들과 일련의 유사한 결정구조의 구룹들을 보여준다. 콜레스테롤 메틸카보네이트 분자들은 monolayer를 이루면서 쌓여있으며, monolayer 중심부에서는 cholesteryl-C(17) side chain 상호작용이 강하며 layer 사이에는 카보네이트사슬들이 느슨하게 모여있다. 프로필카보네이트 결정에서는 두개의 결정학적으로 독립된 분자들(A and B)이 있다. A분자들간의 cholesterol-cholesterol상호작용과 B분자들간의 cholesteryl-C(17) side chain 상호작용들이 layer의 중심부에서 일어나며, 이들 분자들은 나사축 방향을 따라서 쌓여있다. 콜레스테롤 카보네이트의 구조들은 액체결정 상태의 특질을 가지고 있고, 이런 성질들을 결정구조와 관련하여 논의하였다.

Abstract

Cholestryl Methyl and Propyl Carbonate($CH_3OCOOC_{27}H_{45}$, $C_3H_7OCOOC_{27}H_{45}$) are monoclinic, space group $P2_1$, with a=17.014(1), b=7. 682(1), c=10.612(1)Å, β=103.05(1)°, Z=2, V=1351.16Å^3, D_c=1.09 g/cm^3, Dm=1.09 g/cm^3 for methyl carbonate, and with a=13.683(1), b=11.864(2), c=18.904(2)Å, β= 106.30(1) °, Z=4, V=2945.4Å^3, D_c=1.06 g/cm^3, Dm=1.06 g/cm^3 for propyl carbonate. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with a graphite monochromated Cu-Kα radiation. The structure was solved by direct methods and refined by full matrix least-squares methods. The final R factor was 0.051 for 2323 observed reflections for methyl carbonate and 0. 074 for 3323 observed reflections for propyl carbonate.

Compared with other cholesteryl derivatives, the cholesteryl ring and tail region of the molecules are normal. The molecules are stacked in clearly separated layers. At center of the layer, there are cholesteryl-C(17) side chain interactions. The interface region between layers is occupied by the loosely packed methyl carbonate chains.

The structures of cholesteryl propyl carbonates have two molecules(A, B) that are not related by crystal symmetry and have their tetracyclic system almost parallel to each other. Cholesteryl-cholesteryl interactions between symmetry related A-molecules, and cholesteryl-C(17) side chain interactions between symmetry related B-molecules occur at the center of the layers and these molecules stack along 2_1 screw axes. There are also C (17)chain-carbonate chain and C(17)chain-C(17)chain interactions in the interface region between layers. There is efficient packing between cholesteryl ring systems in propyl carbonates.

Temperature ranges of cholesteric mesophases of cholesteryl alkyl carbonates are narrow for methyl, pentyl and hexyl carbonates, and rather broader for ethyl and propyl carbonates. Cholesteryl-isotropic transitions change very little with chain length.

1. INTRODUCTION

X-ray crystallography is concerned with the structure of matter, in particular with how atoms and molecules are arranged in an orderly fashion in a crystalline solid[1]. X-ray diffraction studies of the individual chemical species in the crystalline state provide the most detailed knowledge concerning physical structure. Knowledgef of the structure allows one to relate structure to fuction, that is, understand physical, chemical, or biological properties and activities. It also provides the chemist with useful information for syntheses, modifications, and reaction mechanisms, and can also be used to identify very small quantities of scarce material.

Previous structural studies on cholesterol derivatives were focused on the fatty acid esters[2-7]. In this series, homologous

cholesteryl fatty acid esters with different chain lengths or different degree of unsaturation were investigated in terms of the molecular packing arrangements.

We have undertaken a series of crystal structure determinations of n-fatty acid carbonates of cholesterol. These are the structures of cholesteryl methyl carbonate, cholesteryl ethyl carbonate[8], cholesteryl propyl carbonate, cholesteryl pentyl carbonate[9] and cholesteryl hexyl carbonate[10]. From the observed crystal data [see Table 1], the modes of packing in some cholesteryl alkyl carbonates are different from those in the corresponding cholesteryl alkyl esters. Now we report the crystal structures of cholesteryl methyl carbonate and cholesteryl propyl carbonate in order to investigate the structual characteristics, packing mode and intermolecular interactions which are relevant to the liquid crystalline phases of the compound, and to make detailed comparisons with the other cholesteryl n-alkyl carbonates in the crystal line state.

The liquid crystalline behavior of cholesteryl methyl carbonate has been studied by Nuclear Magnetic Resonance Spectroscopy[11], Differential Thermal Analysis[11] and Low Angle X-ray Scattering Method[12]. The phase transformations of cholesteryl methyl carbonate are as follows:

$$\text{Solid} \xrightarrow{109^\circ C} \text{Cholesteric} \xrightarrow{112^\circ C} \text{Isotropic}$$

The phase transformations of cholesteryl propyl carbonate are in the broader range of temperature of 91 - 97°C.

2. EXPERIMENTAL

Cholesteryl methyl carbonate was obtained from Sigma Chemical Co., U. S. A. No further recrystallization was carried out. Preliminary crystal data from oscillation and the Weissenberg photographs agreed with those of Rajalakshmi, Shivaprakash and Prasad[13]. Cholesteryl propyl carbonate from Sigma Chemical Company, was recrystall-

Table 1. Crystal Data for Cholesteryl n-Alkyl Carbonates $H(CH_2)_nOCOOC_{27}H_{45}$

Compound	Space Group	Unit cell Parameter	Density (calc.)
Cholesteryl Methyl Carbonate	$P2_1$	a = 17.014(1), b = 7.682(1),	1.09g /cm^3
$CH_3OCOOC_{27}H_{45}$	Z = 2	c = 10.612(1)Å, β = 103.05(1)°	
Cholesteryl Ethyl Carbonate	$P2_1$	a = 13.552(2), b = 11.754(2),	1.06g /cm^3
2 $CH_3CH_2OCOOC_{27}H_{45}$	Z = 4	c = 18.660(1)Å, β = 105.4°	
Cholesteryl Propyl Carbonate	$P2_1$	a = 13.683(1), b = 11.864(2),	1.06g /cm^3
2 $CH_3(CH_2)_2OCOOC_{27}H_{45}$	Z = 4	c = 18.904(2)Å, β = 106.29(1)°	
Cholesteryl Pentyl Carbonate	$P2_1$	a = 12.484(3), b = 9.043(3),	1.06g /cm^3
$CH_3(CH_2)_4OCOOC_{27}H_{45}$	Z = 2	c = 14.053(3)Å, β = 94.12(2)°	
Cholesteryl Hexyl Carbonate	$P2_1$	a = 12.728(2), b = 9.184(1),	1.05g /cm^3
$CH_3(CH_2)_5OCOOC_{27}H_{45}$	Z = 2	c = 13.991(2)Å, β = 92.93(1)°	

llized from an acetone solution.

X-ray data collection was carried out using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu-Kα radiation($\lambda = 1.5418$ Å).

The structure was solved by direct method of SHELXS-86 program[14] for cholesteryl methyl carbonate. The atomic coordinates of cholesteryl propyl carbonate were taken from those of cholesteryl ethyl carbonate, because of two structures were isostructure with each other. The most of hydrogen atoms could be identified in the difference Fourier map. The remaining hydrogen atoms were geometrically fixed. In the final refinement all non-hydrogen atoms were refined anisotropically, the hydrogen atoms kept fixed with isotropic temperature factors. The refinement was carried out by the full matrix least squares method using the program SHELX-76[15] and SHELXL-93[15].

All of the crystal data, data collection and refinement procedures are listed in Table 2. All the atomic scattering factors are from the International Tables of X-Ray Crystallography[16].

The final positional coordinates for the non-hydrogen atoms are given in Table 3.

Table 2. Summary of Crystal Data, Data Collection and Refinement

Crystal Data	
$CH_3OCOOC_{27}H_{45}$	$CH_3CH_2CH_2OCOOC_{27}H_{45}$
Mw = 444.7	Mw = 472.7
Monoclinic	Monoclinic
$P2_1$	$P2_1$
α = 17.014 (1)Å	13.683(1)Å
b = 7.682 (1)Å	11.864(2)Å
c = 10.612 (1)Å	18.904(2)Å
β = 103.05 (1)°	106.30(1)°
Z = 2	4
V = 1351.2(3)Å^3	2945.4(5)Å^3
μ(Cu-Kα) = 5.34cm^{-1}	5.07cm^{-1}
Dc = 1.093 g/cm^3	1.06 g/cm^3
Dx = 1.09(floatation method in KI aq. soln.)	
Cu-Kα (graphite monochromater), λ = 1.5418Å	
Cell parameters from 25 reflections	
25° < 2θ < 74°	28° < 2θ < 70°
Parallelepiped	Parallelepiped
0.4 x 0.3 x 0.3mm	0.4 x 0.5 x 0.5mm
Colourless	Colourless
Data Collection	
$CH_3OCOOC_{27}H_{45}$	$CH_3CH_2CH_2OCOOC_{27}H_{45}$
Enraf-Nonius CAD-4 diffractometer	
$\omega/2\theta$ scans	
2θmax = 130°	
Absorption correction : none	
2458 independent measured reflections	4859
2323 observed reflections [| Fo | > 4σ | Fo |]	3323
h = -19−19	h = 0−16
k = 0−8	k = 0−13
l = 0−12	l = -22−22
3 standard reflections monitored every 3600 seconds	
Intensity decay : insignificant	
Refinement	
$CH_3OCOOC_{27}H_{45}$	$CH_3CH_2CH_2OCOOC_{27}H_{45}$
Refinement on F	
using SHELX-76	SHELXL-93
R = 0.051	R = 0.074
Rw = 0.059	Rw = 0.209
	S = 1.043
2323 reflections	3323 reflections
247 parameters	613
$\Delta\sigma_{max}$ = 0.15eÅ^{-3}	$\Delta\sigma_{max}$ = 0.31eÅ^{-3}
$\Delta\sigma_{min}$ = -0.26eÅ^{-3}	$\Delta\sigma_{min}$ = -0.26eÅ^{-3}
Extinction correction : none	

Table 3. Fractional Atomic Coordinates($\times 10^4$) and Equivalent Isotropic Thermal Parameters for Non-hydrogen Atoms. The e. s. d.'s are in parentheses. $U_{eq.} = 1/3 \sum_i \sum_j$ Uij ai*aj*aij ($Å^2$)

Cholesteryl Methyl Carbonate.

atom	x	y	z	Ueq.
C(1)	2909(2)	7319(4)	7873(3)	.075
C(2)	3685(2)	7279(4)	8955(3)	.074
C(3)	3783(1)	5472(4)	9512(2)	.062
C(4)	3875(1)	4157(4)	8500(2)	.061
C(5)	3141(1)	4218(3)	7371(1)	.052
C(6)	2755(2)	2763(3)	6947(2)	.057
C(7)	2028(2)	2668(3)	5812(2)	.055
C(8)	1894(1)	4327(4)	5023(2)	.049
C(9)	2028(1)	5931(3)	5906(2)	.048
C(10)	2904(1)	6000	6774(2)	.053
C(11)	1778(2)	7620(4)	5155(3)	.063
C(12)	926(2)	7559(4)	4260(3)	.062
C(13)	824(1)	5994(3)	3342(2)	.049
C(14)	1024(1)	4378(3)	4195(2)	.046
C(15)	727(2)	2833(4)	3310(3)	.063
C(16)	-34(2)	3557(4)	2387(2)	.065
C(17)	-66(1)	5552(3)	2638(2)	.053
C(18)	1352(1)	6149(4)	2349(2)	.066
C(19)	3520(2)	6519(5)	5972(3)	.078
C(20)	-474(1)	6547(3)	1408(2)	.058
C(21)	-455(2)	8541(4)	1610(3)	.075
C(22)	-1351(1)	5907(4)	963(2)	.066
C(23)	-1798(1)	6517(5)	-349(2)	.073
C(24)	-2673(1)	5911(5)	-706(2)	.070
C(25)	-3156(2)	6523(5)	-2004(3)	.077
C(26)	-4056(2)	6209(7)	-2114(4)	.099
C(27)	-2896(2)	5545(9)	-3094(3)	.115
C(28)	4444(2)	5803(4)	11709(2)	.071
C(29)	5235(2)	6128(9)	13807(3)	.112
O	5171(1)	5638(4)	12503(2)	.085
O(28)	3853(1)	6268(5)	12027(2)	.099
O(3)	4523(1)	5351(3)	10545(1)	.072

Cholesteryl Propyl Carbonate(A molecule)

atom	x	y	z	Ueq
C(1A)	397(4)	-1705(5)	4048(3)	.075
C(2A)	476(4)	-1514(5)	3260(3)	.080
C(3A)	1426(4)	-844(5)	3283(3)	.082
C(4A)	1410(4)	285	3667(3)	.081
C(5A)	1280(3)	125(4)	4431(3)	.068
C(6A)	1900(4)	640(5)	5006(3)	.076
C(7A)	1827(4)	588(5)	5763(3)	.079
C(8A)	822(3)	76(4)	5829(3)	.069
C(9A)	527(3)	-932(5)	5298(3)	.067
C(10A)	393(3)	-622(4)	4496(3)	.068
C(11A)	-390(4)	-1583(5)	5426(3)	.080
C(12A)	-282(4)	-1868(5)	6240(3)	078
C(13A)	-50(4)	-833(5)	6728(3)	.074
C(14A)	899(3)	-284(5)	6610(3)	.071
C(15A)	1218(4)	588(5)	7216(3)	.086
C(16A)	938(5)	32(7)	7873(3)	.098
C(17A)	312(4)	-1037(5)	7579(3)	.079
C(18A)	-989(4)	-15(6)	6528(4)	.090
C(19A)	-606(4)	34(6)	4166(3)	.087
C(20A)	-466(5)	-1326(6)	7996(4)	.101
C(21A)	-1118(8)	-2342(9)	7685(5)	.144
C(22A)	44(8)	-1479(10)	8797(4)	.144
C(23A)	-701(9)	-1453(16)	9280(5)	.192
C(24A)	-362(8)	-1371(21)	9997(6)	.236
C(25A)	-1024(12)	-1287(20)	10476(6)	.212
C(26A)	-689(16)	-2104(19)	11111(11)	.264
C(27A)	-1079(18)	-132(20)	10735(13)	.275
O(3A)	1412(3)	-643(4)	2530(2)	.093
C(28A)	2287(6)	-380(7)	2401(4)	.102
O(28A)	3091(4)	-327(7)	2855(3)	.144
O(1A)	2102(4)	-236(6)	1677(3)	.128
C(29A)	2928(10)	16(13)	1383(6)	.190
C(30A)	2568(11)	39(17)	545(6)	.220
C(31A)	3180(16)	319(22)	172(6)	.272

Cholesteryl Propyl Carbonate(B molecule)

atom	x	y	z	Ueq
C(1B)	4950(5)	2607(10)	1408(4)	.125
C(2B)	5246(7)	2738(11)	704(4)	.137
C(3B)	6178(10)	2026(9)	749(4)	.143
C(4B)	7062(6)	2370(8)	1414(4)	.118
C(5B)	6764(5)	2306(6)	2116(4)	.094
C(6B)	7348(6)	1796(6)	2707(4)	.106
C(7B)	7134(5)	1760(6)	3434(3)	.094
C(8B)	6321(4)	2601(5)	3500(3)	.077
C(9B)	5433(4)	2595(6)	2799(3)	.086
C(10B)	5772(5)	2956(6)	2105(3)	.094
C(11B)	4511(4)	3272(8)	2887(3)	.104
C(12B)	4194(4)	3000(7)	3562(3)	.097
C(13B)	5100(4)	3141(5)	4280(3)	.079
C(14B)	5947(4)	2335(5)	4161(3)	.078

atom	x	y	z	Ueq.
C(15B)	6713(4)	2309(6)	4920(3)	.088
C(16B)	6063(4)	2375(6)	5454(3)	.088
C(17B)	4956(4)	2668(5)	4987(3)	.077
C(18B)	5468(4)	4365(5)	4378(3)	.092
C(19B)	5989(5)	4233(6)	2090(4)	.105
C(20B)	4404(4)	3377(5)	5446(3)	.082
C(21B)	3345(4)	3772(7)	5013(4)	.106
C(22B)	4335(4)	2741(6)	6133(3)	.095
C(23B)	3979(6)	3420(8)	6682(4)	.116
C(24B)	4000(6)	2707(10)	7363(4)	.133
C(25B)	3657(7)	3371(15)	7963(5)	.176
C(26B)	3905(17)	2859(33)	8609(6)	.528
C(27B)	2630(12)	3710(19)	7713(9)	.225
O(3B)	6545(6)	2204(6)	101(3)	.166
C(28B)	6453(8)	1378(11)	-350(5)	.134
O(28B)	6028(8)	531(9)	-344(5)	.196
O(1B)	6807(5)	1703(7)	-912(3)	.149
C(29B)	6733(9)	956(15)	-1474(6)	.191
C(30B)	7061(13)	1398(26)	-2199(12)	.261
C(31B)	7948(20)	1757(20)	-1892(10)	.342

3. RESULT AND DISCUSSION

The molecular conformation of cholesteryl methyl and propyl carbonate, which is drawn by the ORTEP program[17], is depicted in Figure 1. The bond distances and angles of the molecules are given in Table 4 and Table 5. Within experimental error, bond distances and angles are in agreement with those of other cholesterol compounds[19]. The estimated standard deviations in bond distances and angles are in the range 0.002 to 0.033 Å and 0.1 to 1.7°, respectively.

Selected torsion angles are given in Table 6.

Ring A and C assume chair conformation, Ring B assumes a half chair conformation and five membered ring D assumes the expected 13β, 14α-half chair conformation.

The C(17) side chains have all trans conformations. The carbonate chain has also almost fully extended conformation except B molecule of cholesteryl propyl carbonate.

Table 4. Bond Lengths(Å) for Cholesteryl Carbonates. The e.s.d.'s are in parentheses.

	Methyl Carbonate	Propyl Carbonate	
		A	B
C(1)-C(2)	1.542(5)	1.539(8)	1.504(11)
C(1)-C(10)	1.544(3)	1.540(8)	1.529(10)
C(2)-C(3)	1.504(4)	1.514(8)	1.512(16)
C(3)-C(4)	1.508(4)	1.528(6)	1.536(13)
C(3)-O(3)	1.473(2)	1.438(7)	1.463(11)
C(4)-C(5)	1.524(2)	1.515(8)	1.496(10)
C(5)=C(6)	1.322(3)	1.326(7)	1.323(10)
C(5)-C(10)	1.524(2)	1.537(6)	1.556(9)
C(6)-C(7)	1.521(4)	1.464(8)	1.484(9)
C(7)-C(8)	1.513(4)	1.540(7)	1.525(9)
C(8)-C(9)	1.533(4)	1.540(8)	1.527(8)
C(8)-C(14)	1.541(2)	1.511(8)	1.511(8)
C(9)-C(10)	1.566(2)	1.520(8)	1.568(8)
C(9)-C(11)	1.532(4)	1.549(7)	1.543(9)
C(10)-C(19)	1.545(4)	1.544(7)	1.546(10)
C(11)-C(12)	1.544(5)	1.543(8)	1.494(8)
C(12)-C(13)	1.532(4)	1.515(8)	1.570(8)
C(13)-C(14)	1.528(3)	1.523(7)	1.567(8)
C(13)-C(17)	1.567(2)	1.564(8)	1.512(8)
C(13)-C(18)	1.537(3)	1.570(8)	1.531(8)
C(14)-C(15)	1.527(4)	1.515(8)	1.522(8)
C(15)-C(16)	1.540(4)	1.546(8)	1.523(8)
C(16)-C(17)	1.559(4)	1.544(10)	1.564(8)
C(17)-C(20)	1.536(3)	1.530(9)	1.547(8)
C(20)-C(21)	1.545(4)	1.516(13)	1.525(8)
C(20)-C(22)	1.540(3)	1.491(10)	1.529(8)
C(22)-C(23)	1.503(3)	1.548(14)	1.498(10)
C(23)-C(24)	1.524(3)	1.307(14)	1.534(12)
C(24)-C(25)	1.511(4)	1.452(18)	1.557(15)
C(25)-C(26)	1.529(5)	1.512(27)	1.321(23)
C(25)-C(27)	1.526(5)	1.464(33)	1.410(19)
C(28)-O	1.337(4)	1.324(9)	1.282(13)
C(28)=O(28)	1.185(4)	1.192(9)	1.162(16)
C(28)-O(3)	1.319(3)	1.332(9)	1.343(11)
C(29)-O	1.414(4)	1.425(14)	1.364(16)
C(29)-C(30)	1.522(15)	1.644(25)	
C(30)-C(31)	1.280(23)	1.263(32)	

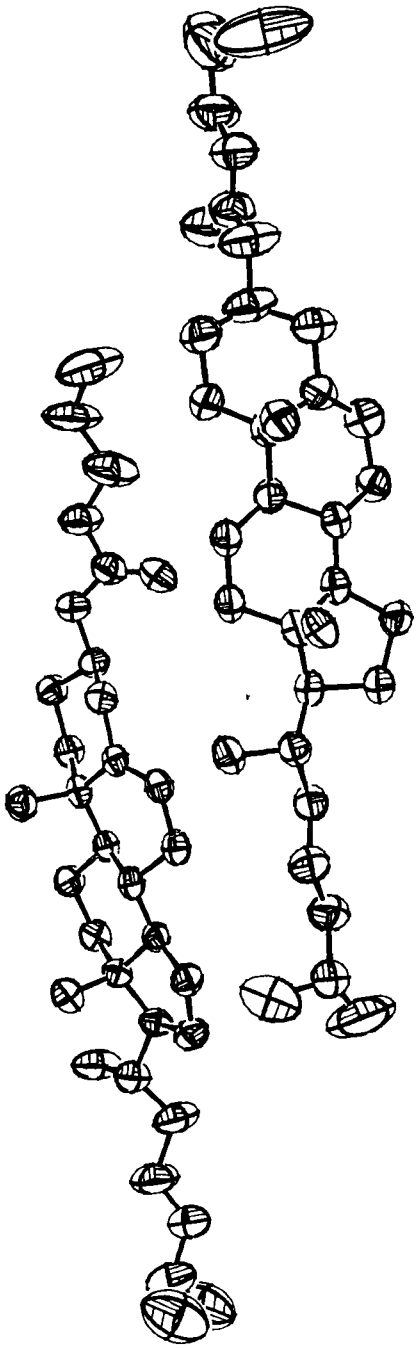

Fig. 1 Molecular Conformation with Atomic Numbering in Cholesteryl Methyl Carbonate

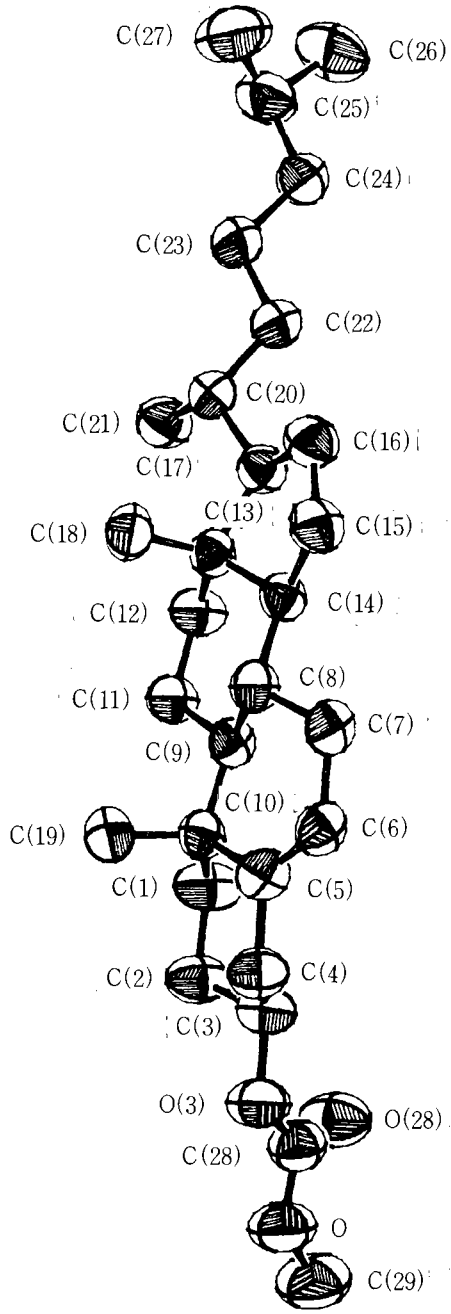

Fig. 1 Molecular Conformation in Cholesteryl Propyl Carbonate left : A molecule, right : B molecule

Table 5. Bond Angles(°) for Cholesteryl Carbonate. The e. s. d.'s are in parentheses.

	Methyl Carbonate	Propyl Carbonate	
		A	B
C(3)-C(2)-C(1)	108.2(2)	110.1(4)	109.0(8)
C(4)-C(3)-C(2)	111.0(2)	110.2(4)	110.8(8)
C(5)-C(4)-C(3)	109.9(2)	111.4(3)	111.4(7)
C(5)-C(10)-C(1)	108.6(2)	108.1(4)	107.8(6)
C(6)=C(5)-C(4)	119.9(2)	120.4(4)	121.4(7)
C(7)-C(6)=C(5)	124.2(2)	125.4(5)	124.4(7)
C(8)-C(7)-C(6)	113.1(2)	113.8(5)	113.3(5)
C(9)-C(8)-C(7)	110.9(2)	109.3(4)	110.3(5)
C(9)-C(10)-C(1)	108.0(2)	109.3(4)	109.1(5)
C(9)-C(10)-C(5)	110.0(1)	110.0(4)	108.4(5)
C(10)-C(1)-C(2)	114.1(2)	115.0(5)	114.8(6)
C(10)-C(5)-C(4)	116.6(2)	117.1(4)	114.6(6)
C(10)-C(5)-C(6)	123.6(2)	122.5(5)	123.8(6)
C(10)-C(9)-C(8)	112.2(1)	113.5(4)	112.0(4)
C(11)-C(9)-C(8)	112.2(2)	111.2(4)	112.3(5)
C(11)-C(9)-C(10)	113.1(2)	113.5(4)	113.0(5)
C(12)-C(11)-C(9)	114.0(2)	114.2(4)	115.0(6)
C(13)-C(12)-C(11)	111.8(2)	112.0(5)	111.6(4)
C(13)-C(14)-C(8)	114.6(2)	115.8(4)	115.3(5)
C(14)-C(8)-C(7)	110.0(2)	111.8(4)	110.8(5)
C(14)-C(8)-C(9)	108.6(2)	110.5(4)	110.2(4)
C(14)-C(13)-C(12)	106.4(2)	107.4(4)	104.3(5)
C(15)-C(14)-C(8)	118.2(2)	118.2(5)	118.7(4)
C(15)-C(14)-C(13)	105.6(2)	104.9(4)	102.6(4)
C(16)-C(15)-C(14)	103.0(2)	103.4(5)	104.3(4)
C(16)-C(17)-C(13)	103.1(2)	103.0(4)	103.6(4)
C(17)-C(13)-C(12)	115.6(2)	116.8(5)	117.2(5)
C(17)-C(13)-C(14)	99.8(2)	100.4(4)	100.7(4)
C(17)-C(16)-C(15)	107.7(2)	107.4(5)	106.9(4)
C(18)-C(13)-C(12)	112.0(2)	109.7(5)	111.1(5)
C(18)-C(13)-C(14)	112.4(2)	112.0(5)	111.4(4)
C(18)-C(13)-C(17)	110.0(2)	110.2(5)	111.4(5)
C(19)-C(10)-C(1)	111.0(2)	109.8(4)	110.4(6)
C(19)-C(10)-C(5)	108.2(2)	107.8(4)	108.3(5)
C(19)-C(10)-C(9)	111.0(2)	111.8(4)	112.7(5)
C(20)-C(17)-C(13)	120.0(2)	120.0(5)	119.9(5)
C(20)-C(17)-C(16)	111.8(2)	113.3(5)	110.6(4)
C(21)-C(20)-C(17)	112.6(2)	113.4(6)	114.0(5)
C(22)-C(20)-C(17)	108.8(2)	110.8(6)	111.4(5)
C(22)-C(20)-C(21)	110.3(2)	110.7(7)	109.4(5)
C(23)-C(22)-C(20)	115.9(2)	113.5(8)	115.7(6)
C(24)-C(23)-C(22)	113.3(2)	120.8(10)	110.6(7)
C(25)-C(24)-C(23)	115.5(2)	123.3(11)	113.3(10)
C(26)-C(25)-C(24)	110.4(3)	110.3(16)	113.0(18)
C(27)-C(25)-C(24)	110.3(3)	111.9(19)	112.0(10)
C(27)-C(25)-C(26)	108.8(3)	111.5(15)	114.5(14)
C(28)-O(3)-C(3)	115.5(2)	117.3(5)	117.0(8)
O(28)=C(28)-O	124.9(2)	127.1(7)	127.6(10)
O(3)-C(3)-C(2)	110.6(2)	106.6(4)	110.8(7)
O(3)-C(3)-C(4)	106.2(2)	109.1(5)	105.7(9)
O(3)-C(28)-O	106.9(3)	107.4(6)	108.5(10)
O(3)-C(28)=O(28)	128.2(3)	125.4(7)	123.3(10)
C(29)-O-C(28)		119.0(7)	117.7(10)
C(30)-C(29)-O		110.4(10)	117.6(15)
C(31)-C(30)-C(29)		120.5(13)	100.2(17)

Table 6. Selected Torsion Angles(°) in Cholesteryl Carbonate. The e. s. d.'s are in parentheses.

	Methyl Carbonate	Propyl Carbonate	
		A	B
(1) Steroid Skeleton			
Ring A			
C(1)-C(2)	-58.3(2)	57.2(5)	59.4(8)
C(2)-C(3)	61.7(2)	-58.2(5)	-58.1(9)
C(3)-C(4)	-58.5(2)	55.5(4)	55.9(8)
C(4)-C(5)	52.0(2)	-51.5(4)	-52.5(7)
C(5)-C(10)	-46.8(2)	46.5(4)	49.7(7)
C(10)-C(1)	49.7(2)	-48.9(5)	-53.4(7)
Ring B			
C(5)=C(6)	0.1(2)	-0.9(5)	0.8(6)
C(6)-C(7)	12.6(2)	-12.1(5)	-14.1(7)
C(7)-C(8)	-41.5(2)	40.2(5)	43.5(6)
C(8)-C(9)	59.8(2)	-59.0(5)	-61.6(5)
C(9)-C(10)	-45.7(2)	45.9(4)	46.4(5)
C(5)-C(10)	16.4(2)	-15.9(5)	-16.8(7)
Ring C			
C(8)-C(9)	-50.6(2)	48.3(4)	47.3(5)
C(9)-C(11)	50.1(2)	-48.7(5)	-49.1(6)

	Methyl Carbonate	Propyl Carbonate	
		A	B
C(11)-C(12)	-53.4(2)	53.5(5)	55.5(5)
C(12)-C(13)	56.1(2)	-55.2(5)	-57.4(5)
C(13)-C(14)	-61.5(2)	59.2(5)	60.6(5)
C(8)-C(14)	59.2(2)	-56.4(5)	-57.1(5)
Ring D			
C(13)-C(14)	46.2(2)	-46.1(4)	-46.9(5)
C(14)-C(15)	-34.5(2)	34.7(5)	35.1(5)
C(15)-C(16)	8.7(2)	-9.3(5)	-10.7(4)
C(16)-C(17)	19.1(2)	-18.4(5)	-18.8(5)
C(13)-C(17)	-38.9(2)	38.6(5)	39.5(4)
(2) Chain			
C(1)-C(2)-C(3)-O(3)	179.4(3)	-176.6(6)	-175.1(11)
C(2)-C(3)-O(3)-C(28)	86.4(3)	-160.2(7)	-111.5(11)
O(28)=C(28)-O(3)-C(3)	1.2(3)	2.3(7)	7.5(12)
O-C(28)-O(3)-C(3)	-179.0(3)	179.7(8)	178.7(12)
C(4)-C(3)-O(3)-C(28)	-153.0(3)	80.7(6)	128.5(11)
O(3)-C(28)-O-C(29)	177.5(4)	-177.8(10)	177.0(13)
O(28)=C(28)-O-C(29)	-2.6(3)	-0.4(9)	-5.4(12)
O(3)-C(3)-C(4)-C(5)	-178.8(2)	172.3(6)	176.0(10)
C(28)-O-C(29)-C(30)		174.8(14)	171.1(17)
O-C(29)-C(30)-C(31)		175.7(20)	54.2(18)
(3) Tail			
C(13)-C(17)-C(20)-C(21)	-54.8(2)	55.1(7)	55.3(6)
C(13)-C(17)-C(20)-C(22)	-177.5(2)	-179.7(8)	179.7(7)
C(16)-C(17)-C(20)-C(21)	-175.6(3)	177.2(8)	175.8(7)
C(16)-C(17)-C(20)-C(22)	61.7(2)	-57.6(7)	-59.9(5)
C(17)-C(20)-C(22)-C(23)	-170.0(3)	164.5(11)	169.9(7)
C(21)-C(20)-C(22)-C(23)	66.1(2)	-68.8(10)	-63.2(6)
C(20)-C(22)-C(23)-C(24)	-177.3(3)	-167.6(17)	-176.8(9)
C(22)-C(23)-C(24)-C(25)	178.6(3)	176.8(24)	178.9(10)
C(23)-C(24)-C(25)-C(26)	-166.6(4)	132.1(23)	-164.6(18)
C(23)-C(24)-C(25)-C(27)	73.2(3)	-103.1(22)	64.3(12)

The crystal structures of cholesteryl alkyl carbonates with chain length C_1-C_6 except for C_4 are compared in Figure 2. The crystal structures of cholesteryl ethyl and propyl carbonate are isostructural with each other, as well as those of pentyl and hexyl carbonates.

As shown in Figure 2, the molecules of the cholesteryl methyl carbonate are stacked in clearly separated layers. The adjacent molecules in a layer are related by the 2_1 screw axis and are therefore oriented antiparallel to each other. At center of the layers there are cholesteryl-C(17)side chain interactions. The interface region between layers is occupied by the loosely packed methyl carbonate chains. Each layer is made up of rows of molecules with all molecular long axes parallel to the [1 0 1] direction. This packing type is similar to those of cholesteryl bromide[20], chloride[20] and methyl ether[18].

The structures of cholesteryl ethyl and propyl carbonates have two molecules(A, B) that are not related by crystal symmetry and have their tetracyclic system almost parallel to each other. Cholesteryl-cholesteryl interactions between symmetry related A- molecules, and cholesteryl-C(17)side chain interactions between symmetry related B-molecules occur at the center of the layers and these molecules stack along 2_1 screw axes. There are also C(17)chain-carbonate chain and C(17)chain-C(17)chain interactions in the interface region between layers. In the structures of cholesteryl pentyl and hexyl carbonates, there is efficient packing between the cholesteryl ring systems within stacks of molecules at the center of the monolayers. This type of packing has been designated as monolayers type II by B. M. Craven.[21]

Crystal structures of cholesteryl n-alkyl carbonates with chain lengthC_1-C_6 except for C_4, which has not been determined yet,

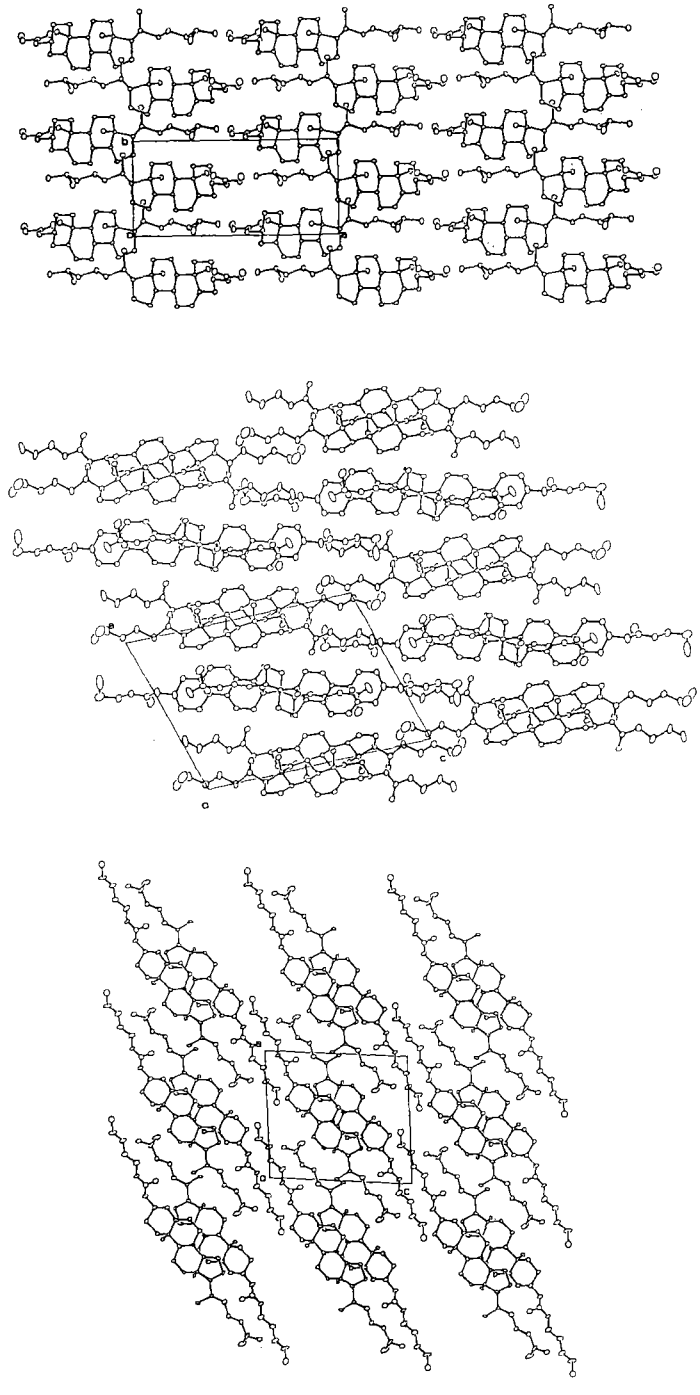

Fig. 2 Molecular Packing of n-Alkyl Carbonate
top : Cholesteryl Methyl Carbonate
middle : Cholesteryl Propyl Carbonate
bottom : Cholesteryl Pentyl Carbonate

can be classified as three types of monolayer. At the center of monolayer three kinds of molecular interactions occur; cholesteryl-chain interactions in the methyl carbonate, cholesteryl-cholesteryl and cholesteryl-chain interactions in the ethyl and propyl carbonates, and cholesteryl cholesteryl interactions in pentyl and hexyl carbonates. As the carbonate chain length increases, cholesteryl-cholesteryl interaction becomes predominant.

Temperature ranges of cholesteric mesophases of cholesteryl n-alkyl carbonates are listed in Table 7. The temperatures were measured by differential scanning calorimeter, DSC 700 of the STANTON REDCROFT. The cholesteric-isotropic transition temperature is relatively constant. The temperature ranges are narrow for methyl, pentyl and hexyl carbonates, and are rather broader for ethyl and propyl carbonates. Cholesteryl -isotropic transitions change very little with chain length.

In the crystal, the cholesteryl methyl and propyl carbonates are stabilized by nonbonded van der Waal's forces.

ACKNOWLEDGEMENT

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Table 7. Temperature Ranges of Cholesteric Mesophases of Cholesteryl n-Alkyl Carbonates. $H(CH_2)_nOCOOC_{27}H_{45}$

	Cholesteric Range(℃)	
	from reference	measured
Cholesteryl Methyl Carbonate	109 – 112[12]	109 – 114
Cholesteryl Ethyl Carbonate	83 – 105[12]	78 – 107
Cholesteryl Propyl Carbonate		91 – 97
Cholesteryl Pentyl Carbonate	98 – 102[23]	100 – 106
Cholesteryl Hexyl Carbonate	106 – 108[23]	101 – 107

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