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Cholesteryl n-Alkyl Carbonates

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Cholesteryl *n*-Alkyl Carbonates

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Abstract—The homologous series of cholesteryl methyl carbonate through cholesteryl eicosyl carbonate was synthesized from cholesteryl chloroformate and high-purity 1-alkanols. The mesomorphic properties were determined optically and by differential scanning calorimetry. Cholesteric mesophases and cholesteric colors of the platelet type were found throughout the series with the exception of the pentyl and hexyl carbonates, where high freezing points were encountered. The visible spectrum was exhibited by cholesteryl heptyl carbonate through cholesteryl nonadecyl carbonate. A monotropic smectic mesophase was found in cholesteryl octyl carbonate through cholesteryl octadecyl carbonate. The plots of transition temperatures and transition heats as a function of alkyl chain length reveal relationships typical of sterols with cholesteric and smectic mesophases.

In an earlier communication we reported cholesteric mesophases in several cholesteryl *n*-alkyl carbonates.(1) Some of the short chain members had been reported earlier by Vorländer's school,(2) however, the complete homologous series was never investigated. Renewed interest in connection with our studies of cholesteryl alkyl thiocarbonates,(3,4) and the advent of differential scanning calorimetry in the investigation of mesophases,(5,6) prompted us to prepare and reinvestigate the complete homologous series of cholesteryl methyl through cholesteryl eicosyl carbonate.

1. Preparation

Synthesis and purification were performed as already reported, *i.e.*, reaction of cholesteryl chloroformate and the corresponding 1-alkanol in absolute benzene in the presence of pyridine, followed by column chromatography on silica gel.(1) The 1-alkanols used were analyzed by gas liquid chromatography and found to be 99.0–99.6% pure. The

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TABLE 1 Cholesteryl Alkyl Carbonates

R (Alkyl)	Transition temperatures, °C			Transition heats, ΔH kcal/mole			Transition entropy, ΔS cal/(mole × °K)			Colors on heating, °C	Colors on cooling, °C	
	Mp	S–Ch[a]	Ch–I[b]	Mp	S–Ch[a]	Ch–I[b]	Mp	S–Ch[a]	Ch–I[b]	Platelets	Platelets	Visible spectrum
Methyl	114.0[c]	—	110.9[c]	8.02	—	0.084	20.7	—	0.21	110.8–110.9	—	—
Ethyl	83.9[d]	—	105.8[d]	5.38	—	0.089	15.1	—	0.23	105.7–105.8	—	—
Propyl	98.8[e]	—	101.0[e]	6.29	—	0.10	16.9	—	0.26	100.6–101.0	—	—
Butyl	80.2[f]	—	94.0[f]	6.08	—	0.10	17.2	—	0.27	93.7–94.0[j]	94.0–86.5	—
Pentyl	106.3	—	—[g]	7.67	—	—[g]	20.2	—	—[g]	—	—	—[l]
Hexyl	108.3	—	—[h]	7.74	—	—[h]	20.3	—	—[h]	—	—	—[l]
Heptyl	88.0	—	81.3	6.48	—	0.084	17.9	—	0.23	—	81.2–80.0	—[l]
Octyl	54.8	35.4	78.9	5.60	0.019	0.11	17.1	0.06	0.31	54.8–78.9[k]	78.0–70.0	41.0–37.3
Nonyl	79.3	45.1	77.2	7.29	—[i]	0.11	20.7	—[i]	0.31	—	77.2–66.0	50.0–45.5
Decyl	76.6	48.7	75.9	7.41	—[i]	0.14	21.2	—[i]	0.40	—	75.7–60.0	51.0–49.4
Undecyl	70.5	51.1	74.4	9.31	0.093	0.15	27.1	0.28	0.43	—	73.7–62.4	52.3–51.5
Dodecyl	61.7	51.7	72.9	10.59	0.064	0.15	31.6	0.19	0.43	—	72.9–60.0	53.0–52.1
Tridecyl	61.9	52.1	71.3	11.74	0.12	0.20	35.0	0.36	0.58	—	71.3–60.5	53.1–52.5
Tetradecyl	68.7	52.9	70.4	13.75	0.12	0.21	40.2	0.36	0.61	—	70.3–60.0	53.9–52.9
Pentadecyl	69.0	53.9	69.7	14.38	0.16	0.24	42.0	0.48	0.70	—	69.7–61.0	54.9–54.1
Hexadecyl	73.9	54.9	69.2	14.65	—[i]	0.32	42.2	—[i]	0.93	—	68.9–60.0	55.7–55.0
Heptadecyl	74.1	55.5	68.6	16.62	0.13	0.35	47.9	0.38	1.02	—	68.4–59.5	56.2–55.6
Octadecyl	78.2	55.6	67.7	16.51	—[i]	0.37	47.0	—[i]	1.08	—	67.4–62.0	56.4–55.8
Nonadecyl	78.7	—[i]	67.1	18.86	—[i]	0.38	53.6	—[i]	1.11	—	66.9–65.0	55.1–49.9
Eicosyl	80.9	—[i]	65.9	16.33	—[i]	0.44	46.1	—[i]	1.29	—	65.9–60.1	—[i]

(a) Smectic–cholesteric transition. (b) Cholesteric–isotropic transition. (c) Reported:⁽²⁾ 114°; 104.5°. (d) Reported:⁽²⁾ 83.2°; 103.8°. (e) Reported:⁽²⁾ 99.0°; 101.4°. (f) Reported:⁽²⁾ 77.8°; 89–90°. (g) Freezes at 103°. (h) Freezes at 95°. (i) Not observable due to crystallization of sample. (j) Regular cholesteric colors (blue): 80.2–93.7°. (k) Regular cholesteric colors (blue). (l) Quenching the sample in ice water produces the visible spectrum.

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physical properties of compounds not previously reported are listed in the Experimental Section. The calorimetric data and optical observations are tabulated in Table 1.

2. Mesomorphic Behavior

As previously discussed,(6) we identified mesophases by optical means and determined temperatures of phase transitions by both optical and thermal methods. The transition temperatures and the transition heats were measured to determine their dependence on chain length.

IDENTIFICATION OF MESOPHASES

Using the combination of a polarizing microscope under conoscopic and orthoscopic operating conditions and a Mettler FP-2 hot stage, the samples were studied in transmitted and reflected light. We observed monotropic and enantiotropic cholesteric–isotropic phase transitions in all members with the exception of cholesteryl pentyl and hexyl carbonates, where crystallization interfered. We also observed a " platelet " texture exhibiting mostly green and blue colors. In the lower members of the series these platelets generally formed on heating, in the higher members on cooling. This phenomenon will be discussed later in more detail. On further cooling the intensely colored platelets disappeared and were followed by a monotropic cholesteric color band exhibiting the complete visible spectrum for cholesteryl octyl through nonadecyl carbonates. Cholesteryl pentyl, hexyl and heptyl carbonates showed cholesteric colors only when the samples were undercooled by quenching in ice water. A monotropic smectic–cholesteric transition was observed with cholesteryl octyl through octadecyl carbonates. This transition could not be observed in the last two members of this homologous series, because the freezing points were higher than their extrapolated smectic–cholesteric transition temperatures.

In summary, the optical investigation established the existence of a cholesteric mesophase for all members, and a monotropic smectic mesophase for cholesteryl octyl carbonate and higher members of this series, with the noted exceptions where crystallization interfered.

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Determination of Transition Temperatures

The transition temperatures were measured with a modified differential scanning calorimeter(6) (DSC-1, Perkin-Elmer Corp.). A detailed discussion about measurement uncertainties in determining transition temperatures and transition heats has been reported by this laboratory.(4) A comparison of data obtained by optical observation and differential scanning calorimetry showed a close agreement (± 1°) between the values obtained by either method.

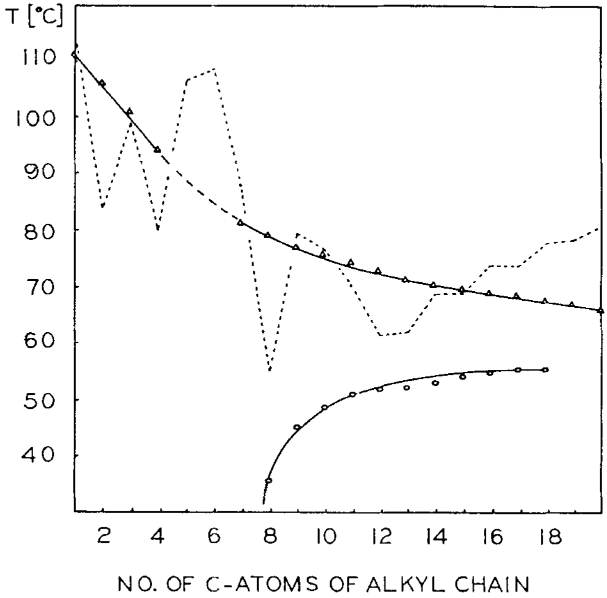

Figure 1. Transition temperatures of cholesteryl alkyl carbonates: – – –, melting points; —△—, cholesteric–isotropic transitions; —○—, smectic–cholesteric transitions.

In Fig. 1 the transition temperatures of the cholesteryl alkyl carbonates are plotted as a function of alkyl chain length. Since the melting points are usually affected by the thermal history,(4) only the high melting points of the presumably more stable crystal modification are reported. They show the expected erratic behavior, while the curves of the cholesteric–isotropic and smectic-cholesteric transition temperatures indicate a definite relationship between transition temperatures and the length of the 3β-side chain. As a

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matter of fact, the deviations from an idealized curve by the lower members of the homologous series of cholesteryl alkanoates,(7) S-cholesteryl alkanethioates,(8) and cholesteryl S-alkyl thiocarbonates(4) do not occur in this series.

TRANSITION HEATS

Figure 2 shows the relationship between the heats of fusion and the alkyl chain length. As in other homologous series of this type, a general increase of the heats of fusion with increasing chain length is observed.

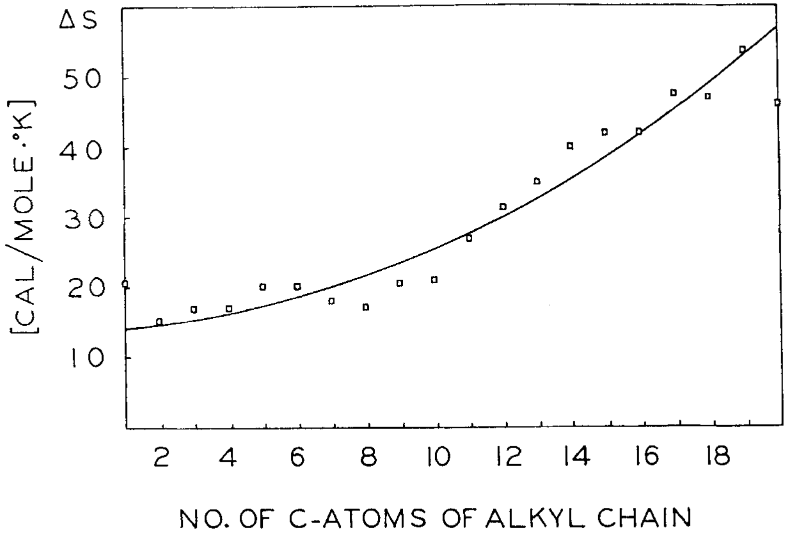

Figure 2. Entropy of fusion.

The transition entropies in the melt, depicted in Fig. 3, also show a general upward trend with increasing chain length. The heats of the smectic–cholesteric phase transitions are lower than those of the cholesteric–isotropic phase transitions, and the two curves do not overlap as found in the series of cholesteryl S-alkyl thiocarbonates.(4)

OPTICAL OBSERVATIONS

In order to illustrate the optical properties of the cholesteric members of this series, we selected cholesteryl butyl carbonate—mp 80.2°, cp 94.05°—which has an enantiotropic cholesteric mesophase.

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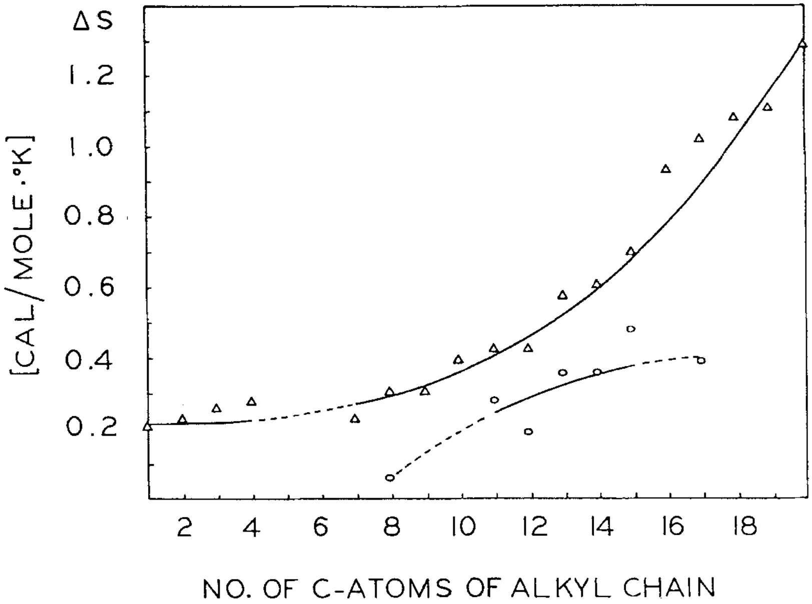

Figure 3. Entropies of transitions in the melt: —△—, cholesteric–isotropic transitions; —○—, smectic–isotropic transitions.

All observations were made with a Leitz Ortholux Polarizing Microscope utilizing polarized reflected light. A programmed Mettler FP-2 hot stage was used for temperature control. The photographs were obtained with high-speed Ektachrome color film (ASA 125) and an optical magnification of 70 × .

On heating, the crystals melt at 80.2° and the cholesteric focal-conic texture appears. On disturbing the sample, the focal-conic texture changes to the typical plane texture which exhibits a strong blue color. This color disappears at 93.7° and a green, grainy texture forms (Fig. 4) which changes rapidly to the larger aggregates depicted in Fig. 5, which we would like to call " platelets ". They have the angular appearance of crystals and do not increase in size with rising temperature. This change from the plane texture to the green platelets is very distinct and as reversible with temperature as a phase transition. However, differential scanning calorimetry does not indicate a change in specific heat or enthalpy, even when operated close to the limit of sensitivity (0.2×10^{-3} cal/°C × sec at a scan rate of 10 °C/min). On application of light pressure, the platelets dis-

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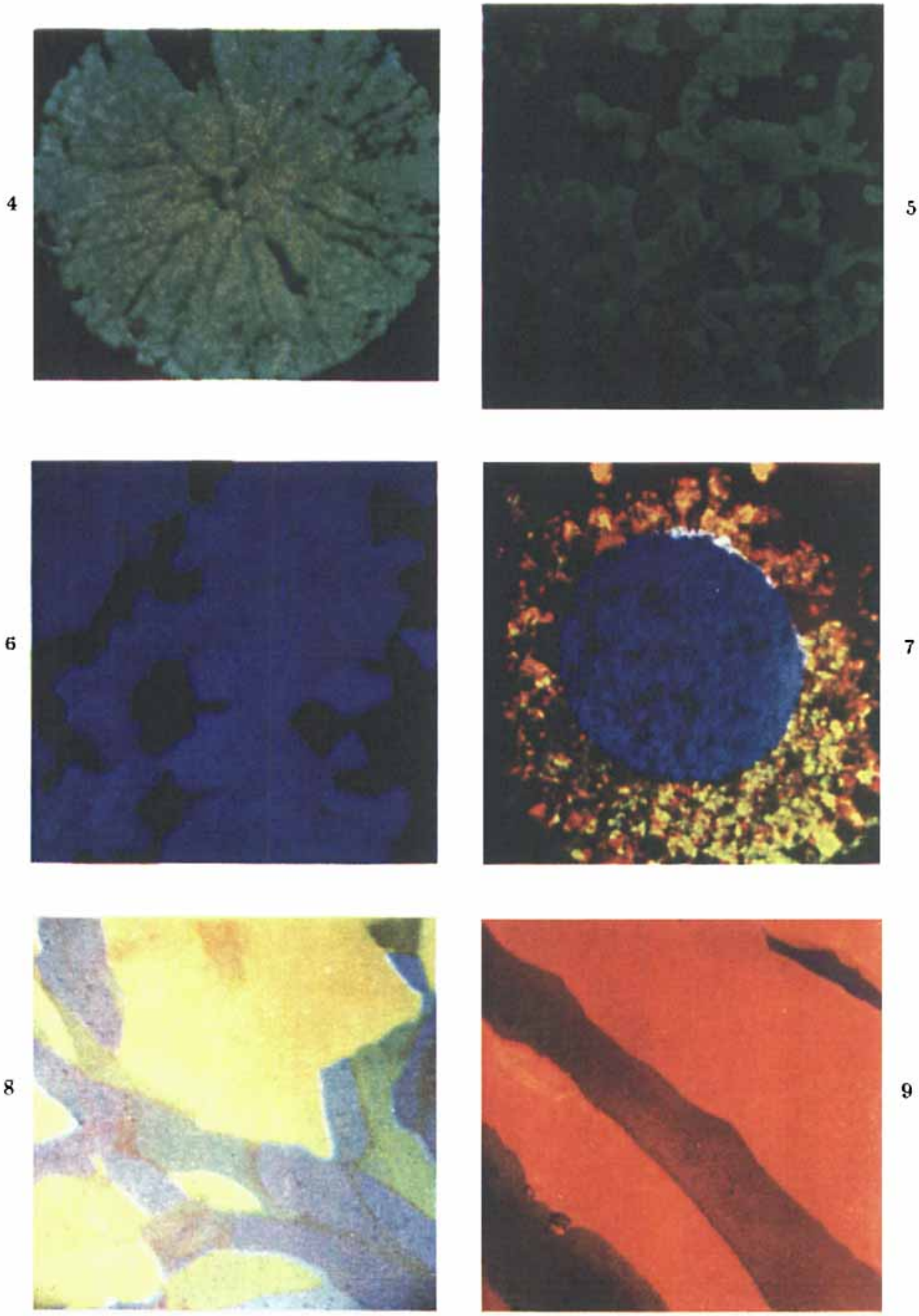

Figures 4–9. Platelet texture, as observed with cholesteryl butyl carbonate.

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appear briefly and come back immediately whether the pressure is released or not. The platelets are very bright when observed with reflected light. In transmission, however, the color is extremely faint and the shape of the platelets becomes barely visible.

Figure 6: On heating, the green platelets which are separated by black areas, change to violet platelets just below the clearing point.

Within a narrow temperature range ($<0.1°$) there seems to be a gradation of colors from violet to indigo and blue. The platelets disappear at 94.05°, the cholesteric–isotropic transition point.

On slow cooling from the isotropic state, violet platelets appear at 94.05°. They do not pass through a grainy structure as the green platelets do when they form out of the plane texture. With slowly decreasing temperature green platelets form at 93.8°, which change to a yellowish green at 93.7°, to yellow at 93.6°, to orange at 93.5°, to gold at 93.4°, and to red at 93.4°. The focal-conic texture grows into the platelets at 92.5° and the last platelets disappear at 86.5°.

Figure 7: This photograph was obtained on cooling the sample slowly from the isotropic state and shows platelets of various colors. Originally, green platelets formed leaving a black circle in the center. A slight decrease in temperature changed the color of some of the green platelets to yellow and gold, while violet platelets formed in the center. This phenomenon was reversible on very careful manipulation of heating and cooling.

Figures 8, 9: We observed another unusual platelet-like texture, depicted in the last two photographs. If the temperature is kept constant after both green and violet platelets are obtained on heating, regions of blue, green, and yellow start to grow into the black areas. On careful heating, the green areas change to blue, then violet, and then black; the already blue areas change to violet and then black. A surface effect can be ruled out, because it is reversible with temperature and does not show a storage effect. The texture appears with the same features on cooling, but the arrangement of the yellow, green and blue areas is different. We also observed that large colored areas and platelets appeared together. On further cooling, the focal-conic texture grows into this pattern and eventually replaces the platelet texture.

Since these textures are sensitive to thermal and mechanical history, and since some of the texture changes are slow, it is difficult

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to determine the degree of thermal equilibrium of the textures during the experiments. But some of the major features are reproducible, reversible and quite distinct.

3. Discussion

The shape of the transition curves is typical for homologous series of sterol derivatives exhibiting cholesteric and smectic mesophases and showing no odd–even effect(9,10) in their chain length dependence. The exceptionally smooth relationship between mesomorphic transition temperatures and the chain length of our cholesteryl alkyl carbonates supports Gray's arguments about purity in homologous series.(11) We therefore can conclude that the impurity content of these compounds is negligible. The cholesteric–isotropic transition temperatures decrease with chain length, while the smectic–cholesteric transition temperatures first increase steeply and then level off. This behavior of the smectic–cholesteric transition curve has not been observed in our other series investigated. There we found an increase and then a decrease of about the same rate as the decrease of the cholesteric–isotropic transition temperatures, resulting in an almost constant temperature interval of the cholesteric mesophase for higher members. But since our investigation ended with the eicosyl carbonate, no definite conclusion can be drawn because the trend of the smectic–cholesteric transition curve might reverse itself with higher members.

The two textures, platelet and platelet-like, have not been reported in any other series of sterol derivatives investigated. The platelets, extensively investigated with cholesteryl butyl carbonate, have the appearance of a texture. We notice a distinct transition from either the plane cholesteric texture or the cholesteric focal-conic texture on heating, and a transition from the isotropic state of the platelets on cooling, followed by the apperance of the focal-conic texture and the visible spectrum in other members of this series. The relationship between these two textures could not be established, but it might be possible to clarify this question whenever other members of this series form uniform areas large enough for further optical measurements.

None of the observed textures described here in detail can yet be explained on the basis of structural arrangements in the cholesteric mesophase. However, we hope that this information will stimulate

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other researchers to investigate the unique optical properties of cholesteryl alkyl carbonates.

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4. Experimental Section

(A) Purity of Starting Materials

Commercial cholesteryl chloroformate(12) was recrystallized twice from ethyl acetate. A small sample was saponified under nitrogen and the isolated cholesterol analyzed by two-dimensional thin-layer chromatography(13) where only one spot and no impurities were detected.

The 1-alkanols used were purchased: methanol, propanol, 1-pentanol, 1-hexanol, 1-heptadecanol, and 1-nonadecanol from Columbia Organic Chem. Co., Inc., Columbia, S.C. (Fluka A.G., Switzerland), the remainder from Chemical Samples Co., Columbus, Ohio. Gas chromatographic analyses were performed using the following phases: 3% OV-17, 1% OV-1, and 3% XE-61 on silanized support (6-ft glass columns). All the alkanols had a purity of 99.4–99.7% with the exception of 1-tridecanol, 1-pentadecanol, 1-heptadecanol, and 1-nonadecanol, which were only 99.0–99.2% pure.

(B) Purity of Cholesteryl Alkyl Carbonates

Thin-layer chromatographic analyses were used throughout the experiments to monitor the purity of the compounds, and a detailed discussion about various aspects of the analysis of homologous series has appeared elsewhere.(4) Considering these facts, we can safely assume a minimum purity of 99% for all the members investigated.

(C) Preparation of Compounds

Although a general procedure was previously published,(1) a short outline will be given in the following since some members of this series have not been reported.

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Cholesteryl tridecyl carbonate: To a stirred solution of 2.00 g (0.01 mol) of 1-tridecanol and 4.49 g (0.01 mol) of cholesteryl chloroformate in 50 ml of absolute benzene a solution of 0.8 g (0.01 mol) of pyridine was added within 30 min at room temperature. Stirring was continued for 2 hr at room temperature and for an additional 2 hr under reflux. Then the cooled reaction mixture was filtered, the solvent distilled off, and the residue chromatographed on silica gel (45 × 350 mm; Merck, 0.05–0.2 mm). Elution with benzene/hexane (30/70), combination of the fractions containing the tridecyl carbonate, evaporation of the solvent, and recrystallization of the residue from ethanol/2-butanone yielded 4.4 g (72%) of colorless needles, mp 61.9°, cp 71.35°.

Calc'd for $C_{41}H_{72}O_3$ (613.1): C, 80.31; H, 11.86; O, 7.82.
Found:(14) C, 80.21; H, 11.73; O, 7.79.

Cholesteryl pentadecyl carbonate: Yield 74%; mp 69.05°; cp 69.7°.
Calc'd for $C_{43}H_{76}O_3$ (641.2): C, 80.54; H, 11.97; O, 7.48.
Found: C, 80.42; H, 12.11; O, 7.45.

Cholesteryl heptadecyl carbonate: Yield 72%; mp 74.1°; cp 68.65°.
Calc'd for $C_{45}H_{80}O_3$ (669.2): C, 80.75; H, 12.07; O, 7.16.
Found: C, 80.70; H, 11.93; O, 7.31.

Cholesteryl nonadecyl carbonate: Yield 71%; mp 78.75°; cp 67.15°.
Calc'd for $C_{47}H_{84}O_3$ (697.3): C, 80.95; H, 12.16; O, 6.87.
Found: C, 80.88; H, 12.11; O, 6.79.

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