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The Preparation of High-Purity Cholesteryl Oleyl Carbonate

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The preparation of high-purity cholesteryl oleyl carbonate for thermal radiography is described. Oleyl alcohol of 99.9% purity was obtained from olive oil *via* urea-adducts, acid soap crystallizations, fractional distillation, and subsequent reduction of methyl oleate with lithium aluminum hydride in tetrahydrofuran. The reaction of oleyl alcohol with cholesteryl chloroformate in the presence of pyridine in benzene at 0°, followed by chromatography on silica gel, results in a cholesteryl oleyl carbonate with a maximum temperature coefficient of selective reflectance of about 13,000% per °C.

Cholesteryl oleyl carbonate is a major constituent of most liquid crystal mixtures used in thermal mapping at ambient temperatures. It is a cholesteric material with a high temperature sensitivity which, unfortunately, can only be obtained with samples of high purity. The use of commercial oleyl alcohol of technical purity invariably leads to a material the properties of which change from batch to batch. Thin-layer chromatographic analysis frequently reveals the presence of eight to ten impurities. In most cases we found it almost impossible to obtain a high-purity material by recrystallization and/or chromatographic methods. We therefore started from pure natural olive oil and prepared an oleyl alcohol of greater than 99% purity. The cholesteryl oleyl carbonate synthesized from this high purity oleyl alcohol exhibited consistent optical properties and was reasonably stable for a period of several months if kept in the dark and under an inert gas. This high-purity material, used in thermal radiography,[1] exhibits a maximum temperature coefficient of 13,000% intensity change per °C (at 7000 Å).[2] In this paper we would like to report the preparation of 99+% oleyl alcohol from olive oil, the preparation of cholesteryl oleyl carbonate, and analytical investigations of its stability.

I PREPARATION OF STARTING MATERIALS

The following trivial names are used: palmitoleic acid for *(Z)-9-hexadecenoic acid*, oleic acid for *(Z)-9-octadecenoic acid*, elaidic acid for *(E)-9-octadecenoic acid*, linoleic acid for *(Z,Z)-9,12-octadecadienoic acid*, and linolenic acid for *(Z,Z,Z)-9,12,15-octadecatrienoic acid*.

a. Oleic acid California olive oil was saponified under nitrogen[3] and the isolated fatty acids were fractionated by the urea inclusion technique.[4] The resulting mixture of fatty acids was analyzed by esterifying a small sample with methanol and boron trifluoride to the corresponding methyl esters followed by gas-liquid chromatography on 10% EGSS-X.[5] Fatty acid methyl ester standards were obtained from the Hormel Institute, University of Minnesota, Austin, MN, and from Applied Science Laboratories, State College, PA. Table I shows the typical result of four urea-adduct separations (the composition of the mixtures is expressed in %). Although this method is claimed to remove all the saturated fatty acids usually found in olive oil, hexadecanoic acid was not completely removed.

TABLE I

Composition of olive oil fatty acids after urea-adduct separation

Fatty acid	Crude	Urea-adduct separations 1st	2nd	3rd	4th
Tetradecanoic	1.2	1.2	1.1	<0.1	—
Hexadecanoic	4.0	1.8	1.3	1.2	1.1
Palmitoleic	6.3	7.2	6.7	5.7	5.2
Octadecanoic	1.9	<0.1	—	—	—
Oleic	72.0	71.0	73.8	80.9	83.4
Linoleic	10.6	14.7	11.9	6.9	4.6
Linolenic	1.2	1.5	1.5	1.1	1.1
Yield (%)		73	65	63	60

Differences in the solubilities of the acid soaps of saturated, mono- and polyunsaturated fatty acids are sufficient to allow separation by recrystallization.[4] (The term "acid soap" refers to a "compound" containing one molecule of *e.g.* sodium oleate for each molecule of oleic acid). Unfortunately, this technique did not remove the hexadecanoic acid as shown in Table II. Therefore, a low-temperature crystallization[6] from acetone at $-20°$ was tried which reduced the amount of hexadecanoic acid.

The material obtained from the low-temperature crystallization from acetone had an assay of about 96% oleic acid. It was esterified with absolute methanol in the presence of hydrogen chloride[4] in a yield of 89%. B.p.

TABLE II

Composition of olive oil fatty acids after additional acid soap crystallization and low-temperature crystallization from acetone

Fatty acid	4th Urea adduct	Acid soap cryst. 1st	2nd	3rd	Acetone
Hexadecanoic	3.1	3.8	4.0	4.1	2.2
Palmitoleic	3.9	1.1	0.5	0.2	0.2
Oleic	85.0	92.2	93.0	93.8	96.0
Linoleic	4.8	1.5	1.2	0.9	0.8
Linolenic	0.6	0.4	0.2	0.1	<0.1
Yield (%)		70	91	94	81

148–150° (0.1 Torr); $[n]_D^{25}$ 1.4512 (lit.[4] 1.4510). To remove the last impurities it was distilled *in vacuo* with a reflux ratio of about 10:1 in a vacuum-jacketed 50-cm distillation column filled with stainless steel helices. After several distillations gas chromatographic analysis indicated a purity of 99.9+ %. Figure 1 shows traces of the gas chromatographic analyses of the final product and the crude mixture.

Thin-Layer Chromatography (TLC)—*Cis-trans* isomers of higher fatty acids cannot be completely resolved by gas-liquid chromatography.† Therefore, we used thin-layer chromatographic methods as additional purity checks for methyl oleate.

In partition chromatography of fatty acids or their methyl esters, both direct and reversed phase, "critical pairs" occur because the presence of a double bond gives a change in partition coefficient about equivalent to that produced by a reduction in chain length by two methylene groups.[7,8] Thus, methyl hexadecanoate and methyl oleate cannot be resolved. On silver nitrate-impregnated silica gel the resolution is based on the degree of unsaturation.[9] However, a two-dimensional method has been reported[10,11] using a reversed-phase separation in the first dimension, followed by impregnation with silver nitrate before the second development in the second dimension, which separates methyl esters of fatty acids according to chain length, structure, and configuration. This method allows the complete analysis of fatty acids differing not only in chain length and in the degree of unsaturation, but also in the position and configuration of the double bonds.

The application of this method indicates that oleic acid prepared as outlined above does not contain detectable amounts of the *trans*-isomer, elaidic acid, nor any other saturated or unsaturated fatty acid as depicted in Figure 2.

† See "Note added in proof" after References!

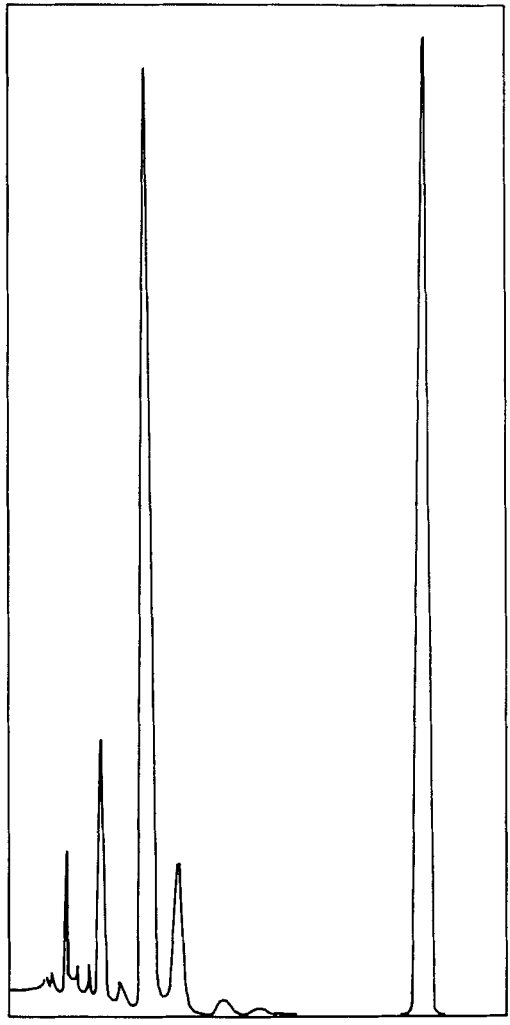


FIGURE 1 Gas-chromatographic analyses of fatty acid methyl esters on 10% EGSS-X. Left: fatty acids from olive oil; right: pure methyl oleate.

b. Oleyl alcohol The methyl oleate was reduced to oleyl alcohol in nearly quantitative yield with lithium aluminum hydride.[4] Because stirring became difficult on the reduction of 200-g batches of methyl oleate, diethyl ether was replaced by tetrahydrofuran. The complex was decomposed with aqueous sodium hydroxide,[12] and all operations carried out in a nitrogen atmosphere. Yield: 96%; bp 148–150° (0.1 Torr): $[n]_D^{20}$ 1.4607. Gas chromatographic analysis (as the acetate) on 10% EGSS-X confirmed a purity of 99.9%.

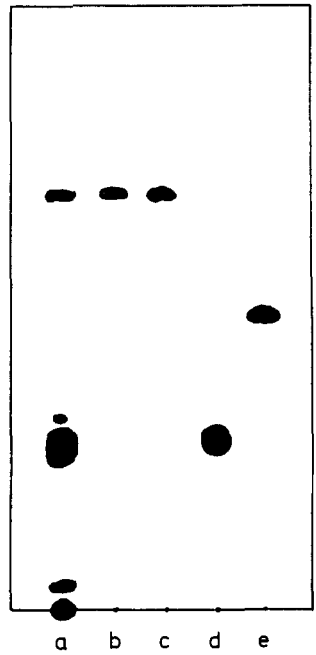


FIGURE 2 TLC on silica gel HR with 25% $AgNO_3$, developed with benzene/hexane 1:1. a) technical methyl oleate; b) methyl hexadecanoate; c) methyl octadecanoate; d) pure methyl oleate; e) methyl elaidate.

c. Cholesterol It is known that cholesterol, in the presence of air, deteriorates under the influence of heat and light. The complexity of cholesterol autoxidation was not recognized until the advent of TLC and progress is still being made in the identification of the oxidation products.[13,14] Commercial cholesterol reveals several autoxidation products on two-dimensional TLC on silica gel[13] which cannot be removed by recrystallization (Figure 3). Similarly, cholesterol originally purified by the bromination-debromination method of Fieser[15] and then kept at room temperature and in the dark for a period of several years, also reveals autoxidation products. However, the freshly prepared sample is chromatographically homogeneous after recrystallization from ethanol.

d. Cholesteryl chloroformate was obtained from purified cholesterol and phosgene according to a published procedure.[16] It was recrystallized twice from ethyl acetate, avoiding prolonged boiling since it decomposes into 3β-chlorocholest-5-ene.[17] Since cholesteryl chloroformate hydrolyzes on both alumina and silica gel,[18] a thin-layer chromatographic analysis was

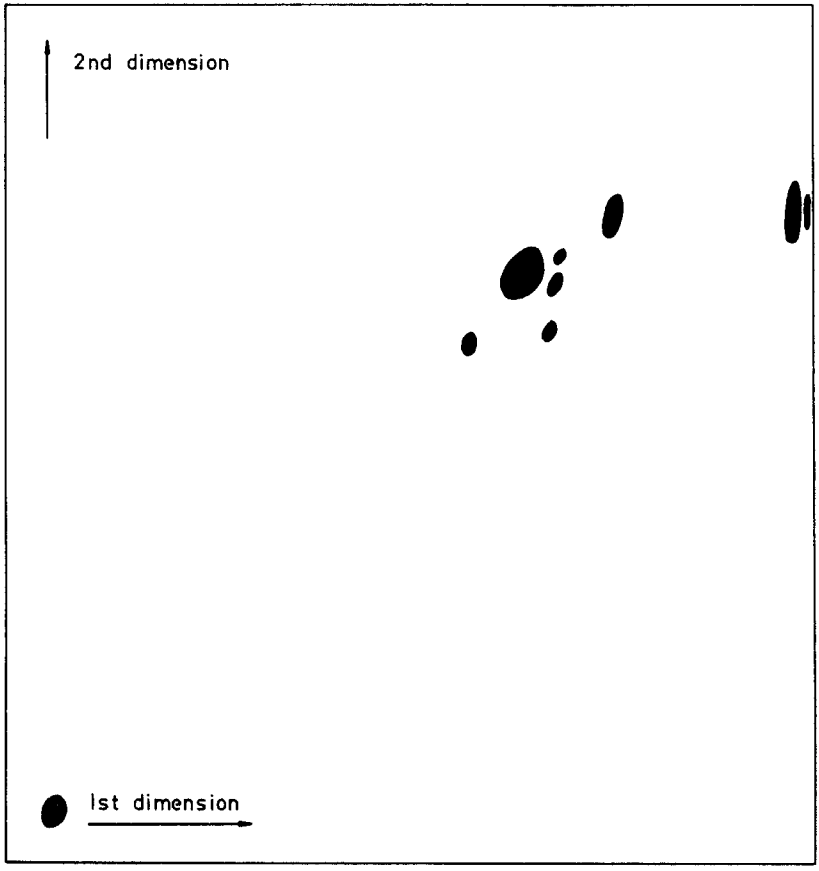


FIGURE 3 TLC of autoxidation products of 4 year-old cholesterol on silica gel HR. First dimension ethyl acetate/heptane 1:1; second dimension acetone/heptane 1:1. Four irrigations each in each dimension.

precluded. A small sample was therefore saponified under nitrogen. The isolated cholesterol was uniform on two dimensional TLC.

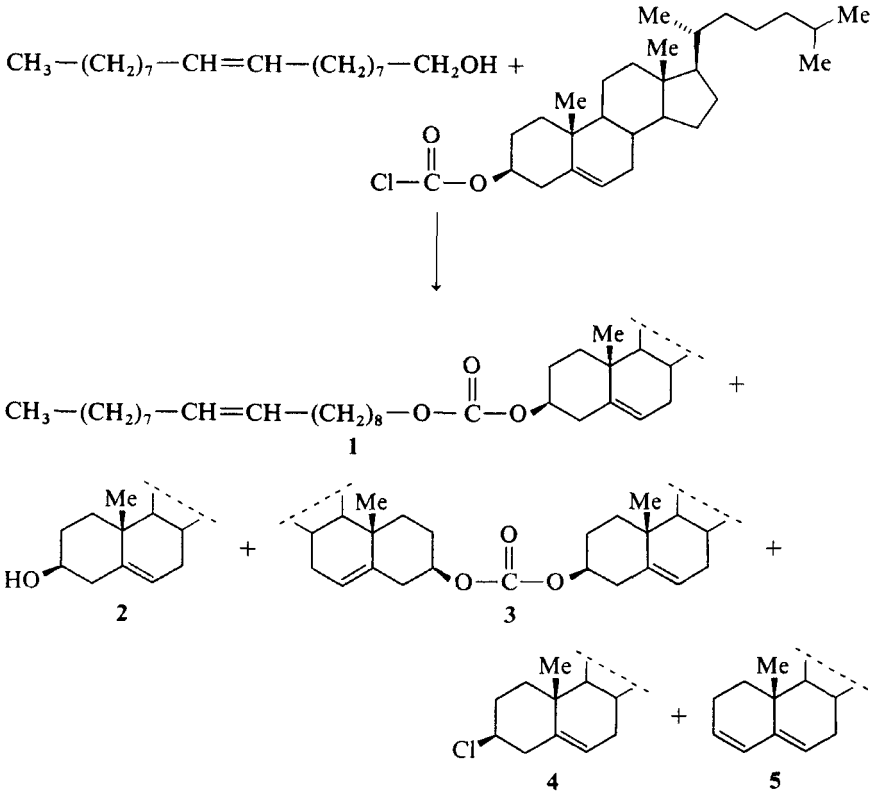
Commercially available cholesteryl chloroformate (Aldrich, Eastman) was analyzed in the same manner and found to contain minute amounts of impurities which could be removed by about two recrystallizations from ethyl acetate (slow rate of cooling to room temperature).

In order to further confirm the equal purity of these two samples of cholesteryl chloroformate, we prepared the respective cholesteryl octyl carbonates.[19] Since we did not observe any differences in their mesomorphic and optical properties, we used commercial cholesteryl chloroformate

which we recrystallized twice from ethyl acetate prior to the preparation of cholesteryl oleyl carbonate.

II CHOLESTERYL OLEYL CARBONATE (1)

This was prepared from cholesteryl chloroformate, oleyl alcohol, and pyridine in absolute benzene under nitrogen and in the dark. By-products of this reaction are cholesterol (**2**), dicholesteryl carbonate (**3**), 3β-chloro-cholest-5-ene (**4**), and cholesta-3,5-diene (**5**):



The reaction products and their identification by TLC is shown in Figure 4. Column chromatography allows an easy separation of cholesteryl oleyl carbonate (**1**) from the much faster migrating **4** and **5**, while cholesterol (**2**) is retained on the column. But dicholesteryl carbonate (**3**) tails into the cholesteryl oleyl carbonate fractions. Chromatography on silver nitrate-impregnated silica gel finally results in a clear separation (see Figure 5) of

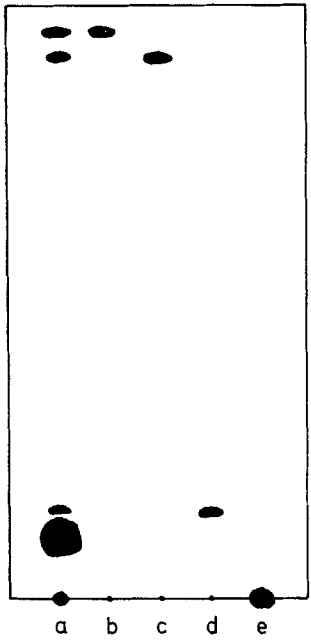


FIGURE 4 TLC of crude reaction product of preparation of cholesteryl oleyl carbonate on silica gel HR with benzene/hexane 15:85. a) reaction product; b) cholesta-3,5-diene; c) 3β-chlorocholest-5-ene; d) dicholesteryl carbonate; e) cholesterol.

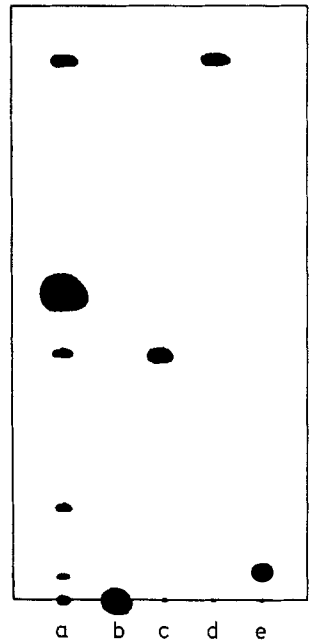


FIGURE 5 TLC of crude reaction product of preparation of cholesteryl oleyl carbonate on silica gel HR with 25% $AgNO_3$ with benzene/hexane 1:1. a) reaction product; b) cholesta-3,5-diene; c) 3β-chlorocholest-5-ene; d) dicholesteryl carbonate; e) cholesterol.

1 and **3**. (Some of the R_F-values observed, especially that of cholesta-3,5-diene, vary with the age of the silver nitrate-impregnated silica gel layer).

To avoid two successive column chromatographic separations we loaded the column (10 cm × 120 cm) with 1 Kg of 25% silver nitrate-impregnated silica gel followed by 3.5 Kg of regular silica gel for the chromatography of a 250 g-batch of crude reaction product and eluted using a gradient program. Starting with 100% hexane and gradually changing to a mixture containing 30% benzene, we obtained a reasonable yield of pure cholesteryl oleyl carbonate. The fractions were monitored by TLC. The head fractions containing some dicholesteryl carbonate were rechromatographed or combined with another batch.

On searching for optimum reaction conditions, we found that considerably less dicholesteryl carbonate was produced if the reaction was carried out at 0° for a period of 12 hr in the dark and if the solvent of the filtered solution was removed below 35° *in vacuo*. The chromatography could then be carried out on regular silica gel.

III STABILITY

Cholesteryl oleyl carbonate, prepared in the above manner, is reasonably stable for a period of a few months, if it is kept in the dark and under an inert gas. But it is quite sensitive to autoxidation, as was found by other investigators also.[20,21] This is vividly demonstrated in Figure 6. TLC reveals two impurities, only one of which could be identified as dicholesteryl

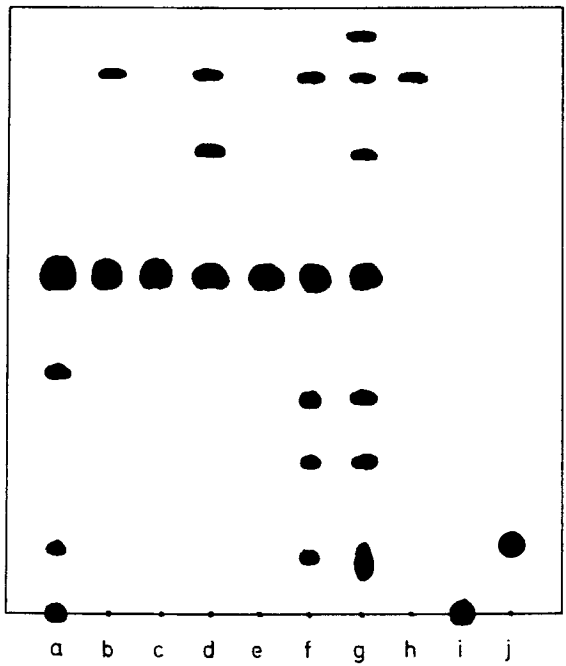


FIGURE 6 TLC of cholesteryl oleyl carbonate on silica gel HR with 25% $AgNO_3$ with benzene/hexane 1:1. a) reaction mixture of synthesis; b) after chromatography on silica gel; c) after rechromatography on silica gel impregnated with 25% $AgNO_3$; d) stored for 2 months at −35° in the dark; e) rechromatographed on silica gel with 25% $AgNO_3$; f) 10% chloroform solution, kept at 0° for 3 months and frequently exposed to air; g) same solution, after 5 months; h) dicholesteryl carbonate; i) cholesta-3,5-diene; j) cholesterol.

carbonate. If the sample has not been exposed to air for too long a period of time, rechromatography will result in a material with the same optical properties as a freshly prepared sample. However, further exposure to air and light eventually results in a material which can no longer be repurified by chromatographic methods in a reasonable yield.

IV EXPERIMENTAL PART

The following combination of instruments was used in the column chromatographic purification of cholesteryl oleyl carbonate: a 10 cm I.D. × 120 cm long chromatographic column with Teflon end plates,[22] a programmed gradient pump,[23] and a preparative fraction collector[24] which was modified to hold twelve 1,000-ml Erlenmeyer flasks. All connections were made with Teflon tubing. Silica gel[25] was used without pretreatment. About 4.5 Kg of silica gel were needed for one filling. The solvents used for elution were benzene and technical (95%) *n*-hexane[26] which were dried over molecular sieve prior to elution. The chromatographic column was wrapped with aluminum foil to exclude light and the fraction collector was purged with nitrogen. The fractions eluted were monitored by TLC.

Our original procedure to process a batch of about 320 g of crude cholesteryl oleyl carbonate was the following: The gradient pump was programmed to start with hexane and to deliver 800 ml/hr. The pump was then adjusted continuously over 10 steps (one step/hour) with a setting of 70% hexane and 30% benzene at the 11th step, and elution was continued at this ratio. While cholesta-3,5-diene and 3β-chlorocholest-5-ene were separated completely, dicholesteryl carbonate tailed appreciably into the cholesteryl oleyl carbonate. After many experiments we achieved the best separation with the following setting: the gradient pump is programmed to deliver hexane in the first five steps, and then 70% hexane and 30% benzene from step six on continuously. This setting resulted in considerably less tailing of the dicholesteryl carbonate into the main fractions of cholesteryl oleyl carbonate.

Cholesteryl oleyl carbonate

A solution of 39.6 g (0.5 mole) of dry pyridine in 250 ml of absolute benzene was added over a period of 3 hr to a stirred solution of 224.5 g (0.5 mole) of cholesteryl chloroformate and 134.3 g (0.5 mole) of oleyl alcohol in 1,000 ml of absolute benzene under nitrogen. The reaction flask was protected from light and was cooled with ice water. After the addition was complete, stirring was continued overnight. The reaction mixture was then filtered and the solvent stripped from the filtrate in a rotary evaporator at a temperature of 30°.

Yield: 340 g (100%).

The crude material was dissolved in about 750 ml of hexane and the solution put onto the chromatographic column. The chromatographic procedure used is discussed in the preceding general part. The fractions with pure cholesteryl oleyl carbonate were combined, filtered, and the pure material isolated.

Yield: 265 g (78%). By re-chromatography of the fractions contaminated with dicholesteryl carbonate on a smaller column the yield could be increased to about 85%. The analytical sample was obtained by recrystallization from acetone at $-35°$, where small flakes were obtained.

Anal.: Calcd for $C_{46}H_{80}O_3$ (681.1) C, 81.11; 11.84; O, 7.04.

Found: C, 80.97; H, 11.75; O, 7.12.

V PHASE TRANSITIONS IN THE MELT

Figure 7 depicts the thermograms of the transitions in the melt of high-purity cholesteryl oleyl carbonate obtained with a scan rate of 10°K/min. On heating, a mesophase–mesophase transition occurs at 16.3° and the cholesteric–isotropic phase transition at 28.8°, while on cooling the corresponding exotherms are observed at 24.3° and 10.8°, respectively (see Table III).

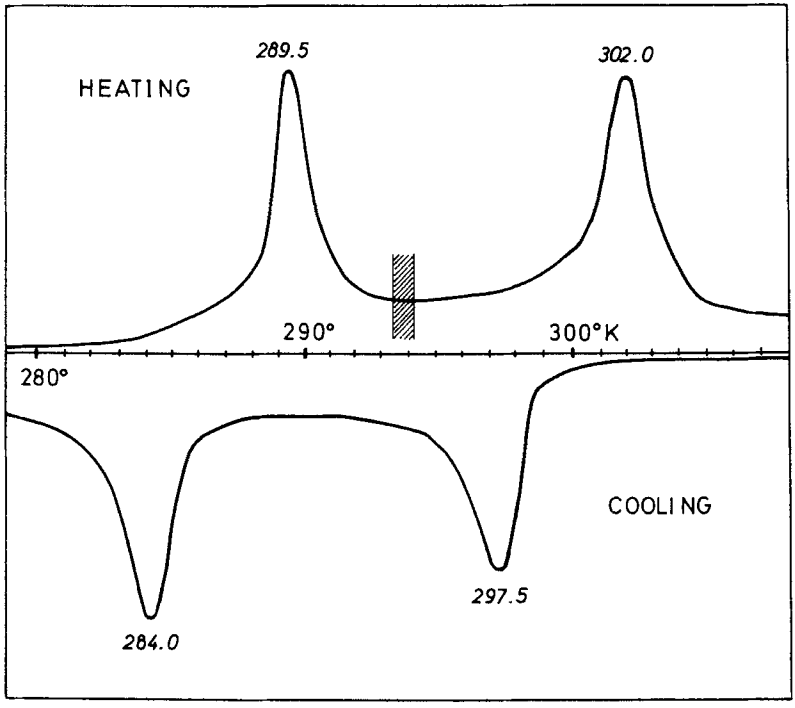


FIGURE 7 Transitions in the melt on heating and cooling; sample weight 15.03 mg. Shaded area: visible spectrum of selectively reflected light.

TABLE III

Phase transitions in the melt and corresponding changes of entropy (ΔH) and enthalpy (ΔS) of high-purity cholesteryl oleyl carbonate

Transition	T (°K)	T (°C)	ΔH (kcal · mole^{-1})	ΔS (cal · mole^{-1} · °K^{-1})
a) *Heating*				
S–Ch	289.5	16.3	0.18	0.65
Ch–I	302.0	28.8	0.20	0.74
b) *Cooling*				
I–Ch	297.5	24.3	0.16	0.58
Ch–S	284.0	10.8	0.16	0.58

The unusually high temperature difference of the transition temperatures obtained on heating and cooling is partially caused by the thermal lag of the instrument of about 2.6°K associated with a scan rate of 10°K/min.[27] The remaining difference of about 2°K for both phase transitions may represent undercooling caused by the high viscosity of the material. This conclusion is supported by the broad shape of the transition peaks indicating a sluggish phase transition and by microscopic observations of thin films (sandwiched between glass slides) exhibiting poor alignment in response to mechanical disturbance and the freezing-in of cholesteric colors upon fast cooling. Under the microscope the cholesteric-isotropic phase transition appeared at 29.3°. The difference of 0.5° between this result and the calorimetric measurement lies within the uncertainty with which the end point of the phase transition can be determined from the shape of the peak of the thermogram. The smectic mesophase could not be verified optically. Apparently, the high viscosity of the sample prevented the appearance of characteristic textures needed for the identification of the smectic mesophase. But previous experience with numerous cholesteric steryl derivatives implies that the mesophase–mesophase transition at 16.3° should be a cholesteric–smectic phase transition. Furthermore, Maidachenko[28] identified a smectic mesophase and reports the following transition temperatures for a cholesteryl oleyl carbonate prepared from oleyl chloroformate and cholesterol: S–Ch 17°; Ch–I 34°.

The visible spectrum of selectively reflected light occurs in the temperature interval of 20.3–21.1°, *i.e.*, about 4° above the cholesteric–smectic phase transition. The latter differs from observations that the visible spectrum of other temperature-sensitive cholesteric materials occurs in the pretransitional region of the cholesteric–smectic phase transition. But considering the sluggishness of the phase transition, we believe that the calorimetric data were obtained under non-equilibrium conditions and that therefore the color band may still be in the pretransitional region.

VI OPTICAL PROPERTIES

We will briefly discuss only some aspects of the unusual optical properties because a detailed discussion of the temperature sensitivity of the selective reflection has already appeared.[2] The high-purity cholesteryl oleyl carbonate exhibits the visible spectrum of selectively reflected light at 20.3–21.1°. With its temperature coefficient of about 13,000%/°C at 7000 Å it permits the visible detection of temperature differences of a millidegree Celsius.

High-purity cholesteryl oleyl carbonate does not align very well on a glass surface and, therefore, does not display the vivid colors usually observed with commercial samples. However, better alignment and brighter colors can be obtained on calendered Mylar® films (calendering of Mylar apparently results in an aligned polar surface as indicated by large regions of uniform birefringence. Cast Mylar films do not align at all). Improved alignment and increased selective reflectance are also obtained by adding small amounts of other cholesteric compounds. The addition of 0.5–1.0% of either 3β-chlorocholest-5-ene or cholesteryl nonanoate results in brilliant colors and does not affect the temperature interval and the region of the color band.

On exposure of high-purity cholesteryl oleyl carbonate to air and light, the color band shifts gradually toward lower temperatures and eventually the selective reflectance disappears. This deterioration can be significantly reduced by sandwiching and sealing the cholesteric film between Mylar sheets. We observed that such thin films retained their selective reflectance within approximately the same temperature region after over five years of storage in the dark.

The major drawback of cholesteryl oleyl carbonate, either obtained commercially or prepared from the many grades of commercial oleyl alcohol, is the fact that both the width of the color band and its temperature range are strongly dependent upon the impurities in the oleyl alcohol. We have observed temperature intervals of the visible spectrum of selectively reflected light of 2° to 4° in the temperature range of 5° to 20°. In contrast, the high-purity cholesteryl oleyl carbonate has a reproducible well-defined temperature region of the selective reflectance close to ambient. Although the alignment is poorer and the selective reflectance lower, both can easily be increased by the addition of small amounts of other cholesteric materials without altering width or range of the color band. The exhaustive process required to prepare oleyl alcohol of high purity is more than adequately compensated with the advantage of obtaining a reproducible material necessary for critical temperature measurements.

Acknowledgments

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Note added in proof: A baseline separation of methyl oleate and methyl elaidate has been achieved on the cyanosilicone stationary phase OV-275 (Supelco, Inc., Bellefonte, PA, Bulletin 721 C).