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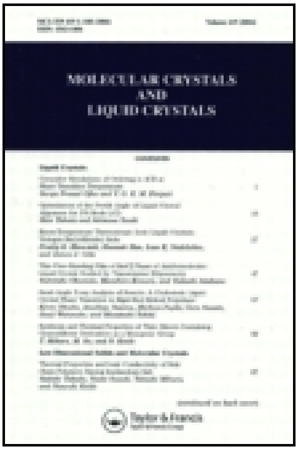

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Study of Phase Transitions Involving the Mesophases of Cholesteryl Linoleate

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Study of Phase Transitions Involving the Mesophases of Cholesteryl Linoleate

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An investigation of the structural properties of cholesteryl linoleate was performed by using several techniques. In particular, the following phase transitions occurring in the cholesteryl linoleate were investigated by X-ray diffraction, DSC and polarizing microscopy: solid-isotropic liquid, isotropic liquid-cholesteric, cholesteric-smectic. This study follows a previous similar one on the cholesteryl oleate. Both these substances are interesting for their peculiar physical properties and biological implications. As in the case of cholesteryl oleate the smectic phase appears to be S_A. The structural properties of cholesteryl linoleate appear to be similar to those of cholesteryl oleate as expected; in spite of some observed differences which should be attributed to the presence of two double bonds in the cholesteryl linoleate instead of a single one in the cholesteryl oleate. A phase coexistence was observed during the solid-isotropic liquid phase transition. Strong pretransitional effects were observed at the cholesteric-smectic phase transition. In particular, the longitudinal coherence length $\xi_\parallel$ appears to diverge as the critical temperature is approached in the cholesteric phase by cooling the sample.

INTRODUCTION

The cholesteryl esters are interesting because in addition to their peculiar physical properties, such as their mesomorphism, including the "blue phase", they show important biological properties. In fact, they are contained in appreciable proportion in the serum lipoproteins and in the lipids of the atherosclerotic lesions, as discussed in detail in Ref. 2.

The structural properties and the phase transitions involving the mesophases of the cholesteryl oleate were recently investigated mainly by X-ray diffraction.[1] In particular, the solid-isotropic liquid, the isotropic liquid-cholesteric, and the cholesteric-smectic phase transitions were investigated.

Strong pretransitional effects were observed at the solid-isotropic liquid phase transition and at the cholesteric-smectic phase transition. Both the longitudinal coherence length $\xi_\parallel$ and the transversal coherence length $\xi_\perp$ were determined as a function of temperature. The longitudinal coherence length $\xi_\parallel$ diverges at the cholesteric-smectic phase transition as the critical temperature is approached in the cholesteric phase, whereas the transversal coherence length $\xi_\perp$ increases abruptly at the same transition. Furthermore, it seems that the smectic phase should be a smectic A, on the basis of the temperature dependence of angular position of the low angle diffraction peak.

The present paper reports the results of a similar investigation on cholesteryl linoleate. This substance was chosen because it constitutes, together with cholesteryl oleate, 60%–80% of the cholesteryl esters contained in the above mentioned biological substances.[2] Moreover, the cholesteryl linoleate is particularly interesting because it could exist in a liquid crystalline state at body temperature, and therefore, could present the function of storage lipid as discussed by Small.[2]

After a preliminary thermodynamic analysis, X-ray diffraction analysis was used to investigate the solid-isotropic liquid, the isotropic liquid-cholesteric, and the cholesteric-smectic phase transitions.

2. THERMODYNAMIC ANALYSIS AND OPTICAL MICROSCOPY OBSERVATIONS

The cholesteryl linoleate was already investigated by differential scanning calorimetry (DSC) by Small[2] and by Armitage[3] using 99% pure samples. Nevertheless, we thought it suitable to carry out again a DSC preliminary analysis on our 99% pure samples before performing the X-ray diffraction study, as it was the case for the cholesteryl oleate.

The heating rate of a typical thermogram was 2.5°K/min. The volume of the containers was 20 μl. The linoleate samples were supplied, enveloped by dry ice, by Serva. The claimed purity was better then 99%. Moreover, the same precautions of the sample handling were taken as in the case of cholesteryl oleate.[1]

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The following phase diagram was obtained

$$\begin{tikzcd}
{} & S_A \arrow[l, dashed] \arrow[r, leftarrow, shift left, "30.5^\circ \pm 0.5^\circ C"] \arrow[r, shift right] & Ch \arrow[dr, leftarrow, shift left, "32.5^\circ C \pm 0.5^\circ C"] \arrow[dr, shift right] & \\
Cr \arrow[rrr, "41^\circ \pm 0.5^\circ C"'] & & & I
\end{tikzcd}$$

The transition temperature is defined as the temperature at which the peak maximum occurs. The obtained crystal isotropic liquid transition temperature of 41°C ±0.5°C, is slightly smaller than the value 42°C ±0.5°C found by Small,[2] and the value 41.5°C found by Armitage.[3] A similar behavior was already found for cholesteryl oleate.[1] However, the discrepancy in the present case is of the order of magnitude of the experimental uncertainties. Moreover, the full width at half maximum of the DSC peak associated to the crystal-isotropic liquid phase transition is $\Delta T_{1/2} \cong 1.3$°C. Previous measurements on two different series of samples supplied, enveloped by dry ice, by Serva and by Sigma gave $\Delta T_{1/2} \cong 2.5$°C, in spite of the claimed purity, better than 99%. It is possible that a loss of purity occurred during the transportation of these samples. The experimental data obtained for these two series of samples showed the same qualitative behavior, but some slight quantitative discrepancy as compared to the data reported below, concerning the more recent and more pure series of samples.

Table I reports the average DSC data; the transition temperatures were corrected for heating rate. The transition temperatures, isotropic liquid-cholesteric, and cholesteric-smectic are slightly lower as compared to those reported in Refs. 2 and 3, as it was the case for cholesteryl oleate. A satisfactory agreement exists concerning the transition enthalpies with the data reported in Ref. 3. DSC data are not reported for the transition S_A-solid phase, as this transition does not occur immediately by cooling the sample to room temperature, but only after an annealing of several days (several minutes in the case of cholesteryl oleate), as already reported by Small.[2]

TABLE I

Phase transition	T(°C)	ΔH (cal/g)	 (Kcal/mole)	ΔS cal/mole T°(K)
Crystal-Isotropic Liquid	41°	10.23 ± 0.4	6.64 ± 0.3	21.14 ± 1.5
Isotropic Liquid-Cholesteric	32.5°	0.23 ± 0.03	0.15 ± 0.02	0.48 ± 0.05
Cholesteric-Smectic	30.5°	0.64 ± 0.08	0.41 ± 0.04	1.38 ± 0.13

Measured enthalpies and entropies for the different phase transitions of Cholesteryl linoleate.

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Some optical observations, with crossed polarizers, were performed by using a polarizing microscope (Leitz Ortolux 2 Pol), before carrying out X-ray diffraction experiments. By heating the crystalline sample, with a heating rate 1°K/min, small isotropic regions begin to appear at 37°C and slightly grow as a function of temperature until a rapid enlargement is observed at 40°C. Some birefringent crystallites remain visible till 41.5°C.

On cooling the sample from the isotropic liquid, some droplets having a negative sign of birefringence appear at ~32.8°C on a dark background, whereas "bâtonnets" appear at ~31.5°C and transform into a fine birefringent texture which covers the whole field and corresponds to the cholesteric phase. A fan-shaped texture with positive sign of birefringence appears at 30.5°C indicating the formation of the smectic phase. On further heating of the sample a good reversibility of the same liquid crystalline transitions and textures are observed, with a satisfactory reproducibility of both these physical characteristics. Moreover, the smectic phase which is obtained by cooling the cholesteryl linoleate is quite stable at room temperature, while the smectic phase of cholesteryl oleate is unstable[1] under the same conditions. If the sample is held for two or more days at −2°C, recrystallization occurs.

3. X-RAY DIFFRACTION RESULTS

The X-ray diffraction measurements were performed with the same apparatus and the same procedure as reported in Ref. 1.

The heating or cooling rates were ~1°C/min. The equilibration time at each temperature was 10 min, and for some temperatures it was checked that no change in the diffraction pattern occurred when the measurement was repeated after 30 min.

3.1. The solid-isotropic liquid transition

The crystal structure of cholesteryl linoleate ($C_{45}H_{76}O_2$) is presently unknown due to difficulty in producing single crystals.[4] The molecule of cholesteryl linoleate differs from the one of the cholesteryl oleate for the presence of a second double bond at the C_{12} atom of the chain.

Figure 1 reports the typical diffraction patterns obtained in the solid, isotropic liquid, cholesteric, and smectic phases.* Figure 2a reports the normalized intensities associated to the Bragg peaks corresponding to $Q = 0.37$ Å^{-1}, $Q = 1.28$ Å^{-1}, and $Q = 1.37$ Å^{-1}, respectively. The quantity Q is defined as $Q = (4\pi/\lambda) \sin\theta$ where λ is the X-ray wavelength

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*From the analysis of the powder diffraction pattern in solid phase it appears that the crystallographic organization of the cholesterol linoleate is not inostructural with cholesterol oleate.

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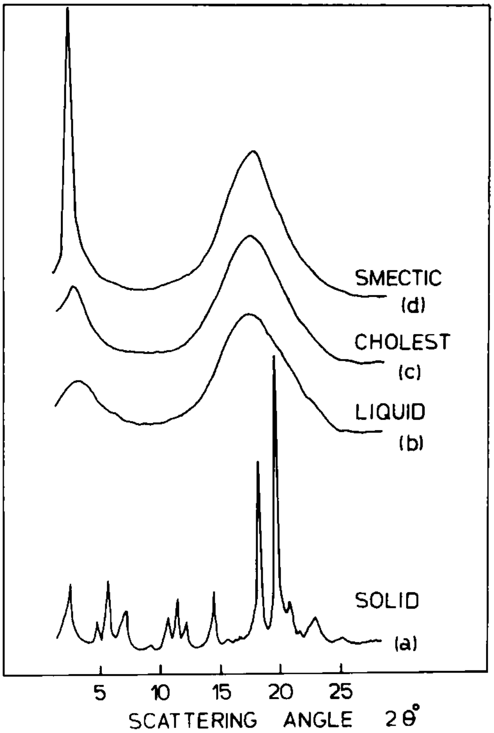

FIGURE 1 X-ray diffraction patterns obtained by cholesteryl linoleate in the solid phase (a), in the liquid phase (b), in the cholesteric phase (c), and in the smectic phase (d).

and 2θ is the take-off angle. A temperature dependence is observed similar to the case of cholesteryl oleate. Figure 2b reports the observed full width at half maximum for the three reflections as a function of temperature. No dramatic change is observed, as in the case of the cholesteryl oleate. Figure 2c reports the scattered intensities at $Q = 1.23$ Å^{-1} corresponding to the large Q diffuse peak of the isotropic liquid phase. A continuous increase of the diffuse radiation intensity is observed, as it was the case for the cholesteryl oleate, in the temperature interval 37°C–41°C. The optical microscopy data reported in Section 2 suggest that this temperature interval corresponds to a phase coexistence. This interpretation presumably applies to the cholesteryl oleate as well.

3.2. The isotropic liquid-cholesteric and cholesteric-smectic phase transitions

By cooling the sample from the isotropic liquid phase, the transitions to the cholesteric and to the smectic phase were investigated in the same way as

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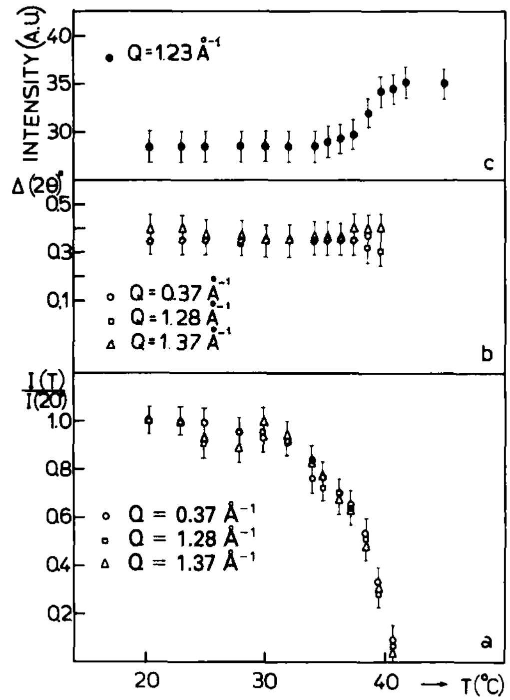

FIGURE 2 Solid-isotropic liquid transition. (a) Intensities of peaks at $Q = 0.37$ Å^{-1}, $Q = 1.28$ Å^{-1} and $Q = 1.37$ Å^{-1}, normalized to the intensities at 20°C, as a function of temperature. (b) Full width at half maximum at $Q = 0.37$ Å^{-1}, $Q = 1.28$ Å^{-1} and $Q = 1.37$ Å^{-1}. (c) Intensities of diffuse peak at $Q = 1.23$ Å^{-1} *vs* temperature.

with cholesteryl oleate. Similar results were obtained so that the interpretation of the data is largely based on the considerations and definitions reported in Ref. 1, to which the reader should refer.

Figure 3 reports the maximum intensity of the diffuse peak, which in the smectic phase becomes a Bragg peak centered at $Q = 0.177$ Å^{-1}, as a function of temperature. A divergence of this intensity appears, which should be attributed to increasing order parameter fluctuations (increase of the cybotactic cluster dimensions). Figure 4 reports the longitudinal coherence length $\xi_\parallel$ as a function of temperature; also, in this case, a divergence is observed as in Ref. 1.

Figure 5 reports the position in Q units of the low angle Bragg peak in the smectic phase and of the corresponding diffuse peak in the cholesteric

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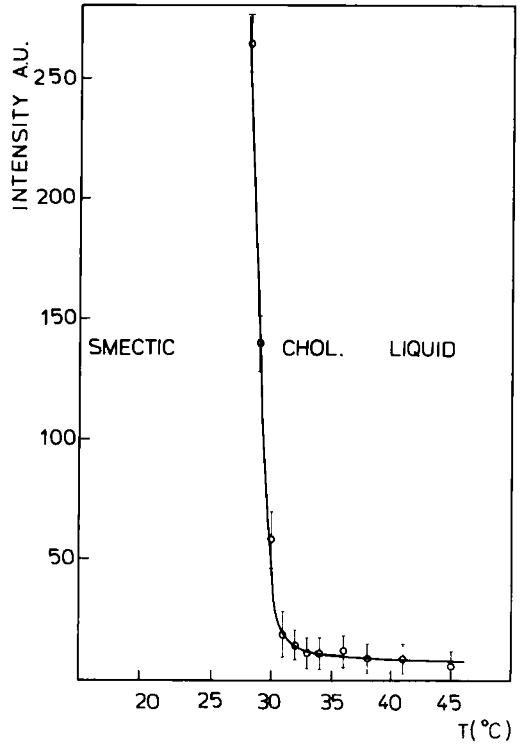

FIGURE 3 Maximum intensity of the small angle peak *vs* temperature.

and isotropic liquid phases. In the smectic phase it is possible to apply the Bragg law and an interplanar distance $d = 35.5$ Å is obtained, i.e. slightly smaller than that of the cholesteryl oleate. This fact can be explained by the existence of the double kink (instead of a single one) which should reduce the molecular length. The temperature dependence of Q_p in the cholesteric and isotropic liquid phases is similar in this case to the one observed in Ref. 1 so that similar conclusions can be derived. In particular, the smectic phase is likely to be of type A. The Q_p value observed in the isotropic liquid phase is much larger in the present experiment as compared to cholesteryl oleate. The variation cannot be explained taking into account the small change in the interplanar distance, i.e., in the molecular length. Therefore, it is necessary to assume that the center of mass of two adjacent molecules in the direction of the molecular length are located at a smaller distance in

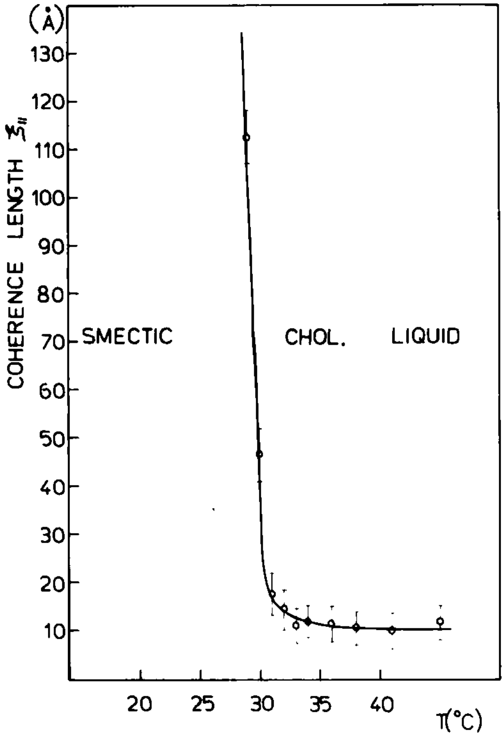

FIGURE 4 Longitudinal coherence length $\xi_{\parallel}$ *vs* temperature.

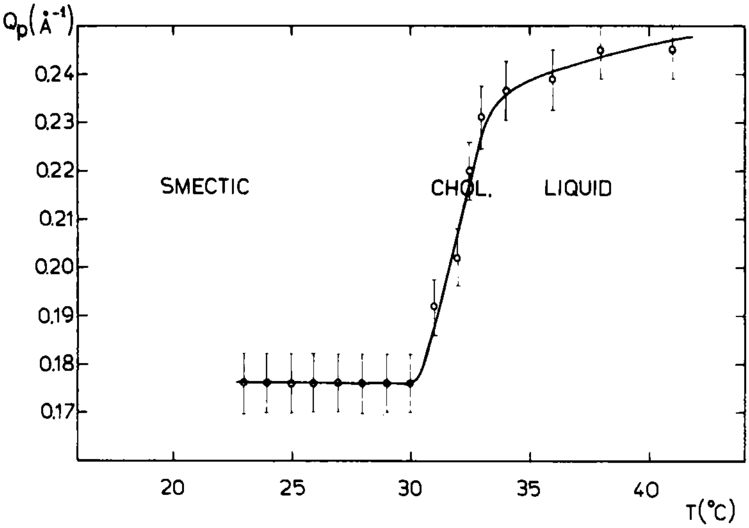

FIGURE 5 Position Q_p of the low angle Bragg peak in the smectic phase and of the corresponding diffuse peak in the cholesteric and isotropic liquid phases as a function of temperature.

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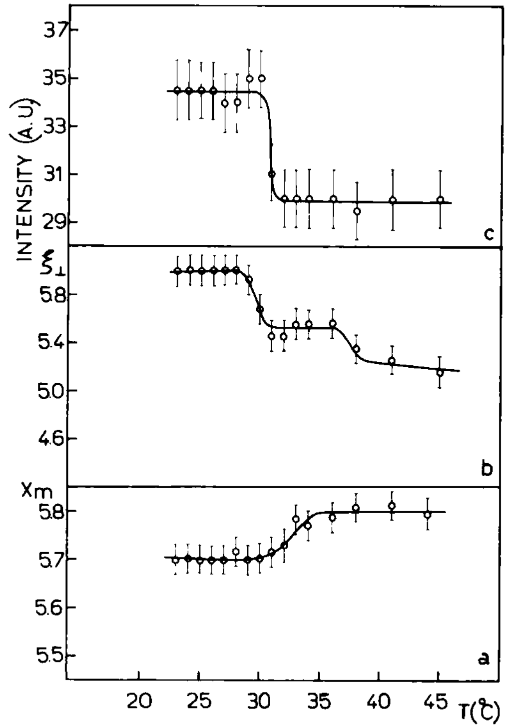

FIGURE 6 Isotropic liquid-cholesteric and cholesteric-smectic transitions: (a) Intermolecular lateral distance as a function of temperature. (b) Transversal coherence length $\xi_\perp$ vs temperature. (c) Maximum intensity of the large angle diffuse peak vs temperature.

the cholesteryl linoleate as compared to the cholesteryl oleate. This fact and the strong temperature dependence of the Q_p value inside the cholesteric phase will be investigated in more detail in the future.

Figure 6 reports the transversal coherence length $\xi_\perp$, the intensity of the large Q diffuse peak, and the intermolecular lateral distance x_m, as a function of temperature. Some differences are observed as compared to the cholesteryl oleate. In particular, the x_m values appear in this case larger than in the previous experiment. This can be explained by the presence of a double kink which implies a larger lateral surface for each molecule. Moreover, an appreciable decrease of x_m appears during the cooling inside the cholesteric phase, whereas no appreciable change is observed in the isotropic liquid and in the smectic A phase. A slight difference appears in the absolute values and temperature dependence of $\xi_\perp$, which is lower in the case of cholesteryl linoleate. This fact suggests that the presence of a double kink makes the short range lateral organization of molecules more difficult.

Finally a continuous change in $\xi_\perp$ is observed at the cholesteric-S_A phase transition, whereas an abrupt change was observed in cholesteryl oleate.

CONCLUSIONS

The different phase transitions of cholesteryl linoleate were investigated by X-ray diffraction after a preliminary analysis by DSC and polarizing microscopy. This last technique showed a phase coexistence in a temperature interval of few degrees at the solid-isotropic liquid phase transition. This fact is to be correlated with the progressive decrease of X-ray Bragg peak intensity occurring in the same temperature interval. The smectic phase seems to be a smectic A as it was the case for the cholesteryl oleate.[1] The longitudinal coherence length $\xi_\parallel$ and the low angle peak maximum intensity appear to diverge at the cholesteric-smectic A phase transition in a similar way to the cholesteryl oleate. In general, as expected, the observed structural properties are similar to those of the cholesteryl oleate. However, some differences exist, concerning the absolute values of the different physical quantities and some specific structural aspects. These differences should be attributed to the presence of a double kink (two double bonds) in the cholesteryl linoleate as compared to a single one in the cholesteryl oleate molecule.

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