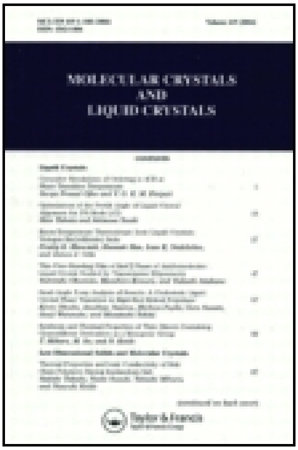

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Mesomorphism of Homologous Series

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Mesomorphism of Homologous Series

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Abstract—Problems associated with the molecular interpretation of mesomorphic behavior within a given or between different homologous series and possible effects of impurities on mesomorphic properties are considered. The temperatures and enthalpies of phase transitions were determined for the first twenty cholesteryl esters and compared with the results of corresponding thiocholesteryl esters. The investigated compounds had a purity of 99 mole percent or better. With two exceptions, the thiocholesterols exhibited higher clearing temperatures, but generally lower heats of clearing. Smectic phases were observed for cholesteryl octanoate and higher members, while for thiocholesterol these phases started with the heptanoate. The study of ω-phenyl cholesteryl esters (first 8 members) showed that all members exhibit cholesteric mesophases except the acetate. The values of heats of clearing lie on two well separated curves, one for odd and the other one for even values of chain length. The corresponding ω-phenyl thiocholesteryl esters exhibit higher clearing points for odd values of acid chain length. For even chain length only the octanoate exhibited a mesomorphic phase. Because of the lack of knowledge about molecular arrangement and interactions in cholesteric mesophases, the effects of the sulfur substitutions on mesomorphic behavior cannot be explained.

Homologous series are usually studied to obtain empirical rules relating molecular features with properties of the mesomorphic state. Within a given homologous series, systematic variations of transition temperatures in the melt indicate changes in molecular polarizability and molecular dimensions; while differences of such temperatures for corresponding members of different homologous series suggest in addition the influence of certain functional groups. To interpret such effects information is needed about molecular arrangements and molecular interactions in mesomorphic states.

For nematic and smectic homologous series Gray[1] succeeded by using customary concepts of molecular arrangement and by approximating complex molecular interactions with lateral and terminal attractions between neighboring molecules. These ordering forces, which are strongly dependent on molecular separation, have to compete with disordering thermal fluctuations. The molecular layer structure of smectic phases occurs in temperature regions where lateral attraction dominates, while the parallel molecular arrangement in nematic phases exists in a temperature interval with predominant terminal interactions. By chemical substitution the ordering interactions between molecules can be changed directly by altering molecular forces or indirectly by varying the distance between neighbouring molecules. In this way Gray used substituents as probes to determine molecular features responsible for the mesomorphic behavior. However, this deductive approach did not succeed for homologous series exhibiting cholesteric mesophases, because the molecular interactions are more complex—as indicated by the unusual optical properties of plane textures—and because no useful concept of molecular arrangement common to all cholesteric textures is known. These problems could be circumvented by studying a large number of homologous series and by deriving from the results not only critical molecular features but also—with an inductive approach—molecular arrangements and interactions. But this is not possible, since relatively few cholesteric homologous series were investigated and since some of these contained intolerable amounts of impurities. The effect of the latter is demonstrated in Fig. 1, which shows scanning calorimetry recordings of heating power versus temperature for commercial and chromatographic standard cholesteryl palmitate. The less pure commercial compound exhibits sluggish smectic-cholesteric and cholesteric-liquid transitions, resulting in the lowering of transition temperatures by about 5 °C. Obviously, only compounds of high purity permit a meaningful comparison of mesomorphic properties and thus allow an appraisal of the effects caused by molecular alterations.

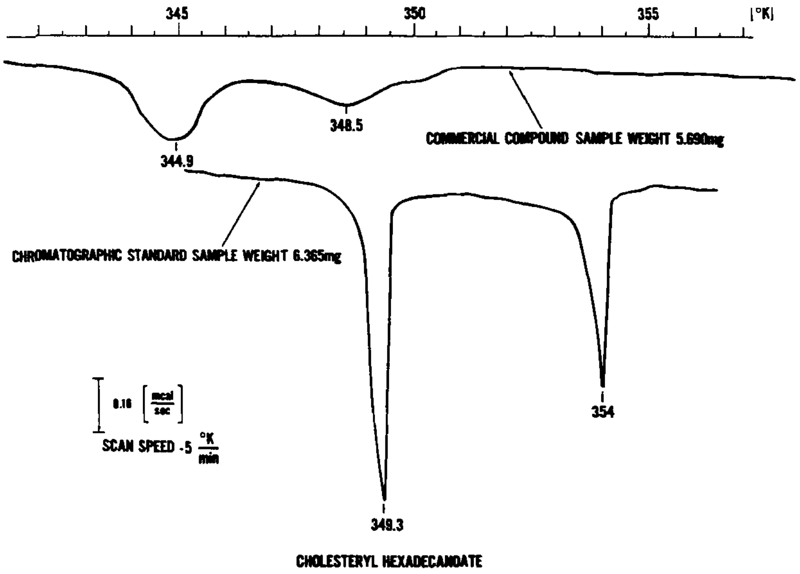

Figure 1. Influence of purification on transitions in the melt

The purity of cholesteryl derivatives and thus of the compounds exhibiting most of the known cholesteric mesophases was significantly improved in 1952 by Fieser's purification method[2] and around 1966 by gas chromatographed alcohols and mercaptans of 99% purity and better. Therefore, the known series of esters and ω-phenyl esters of cholesterol were investigated again on compounds of higher purity in addition to the corresponding thiocholesterols. To determine transition temperatures and identify mesophases, differential thermal calorimetry[3] and polarizing microscopy were used, as described elsewhere[4].

Esters of Cholesterol and Thiocholesterol

Elser and Pohlmann[5] synthesized the thiocholesteryl esters from acids of at least 99% purity. They also prepared cholesteryl formate, butyrate, and eicosanoate and purified by column chromatography commercial cholesteryl hexanoate, heptanoate, octanoate, and eicosanoate. All the other cholesteryl esters were chromatographic standard compounds, obtained from Applied Science Laboratories. The results of many spot checks performed with a special gas-chromatographic method[6] support the purity estimate of 99% or better for all investigated compounds.

Transition Temperatures

Figure 2 shows the transition temperatures of the two homologous series.‡ The relation between lower temperature limit of the melted state and chain length is indicated for heating by the " melting point curve " and for cooling by the " freezing curve ". The latter refers to the beginning of freezing obtained for a cooling rate of 10 °C per minute. In spite of the high purity the compounds exhibit melting points dependent on thermal history and unusually low freezing points. However, the same thermal history such as freezing rate and storage time yields reproducible melting points even for solid phases, which apparently are not in thermal equilibrium. Figure 2 shows only the high melting

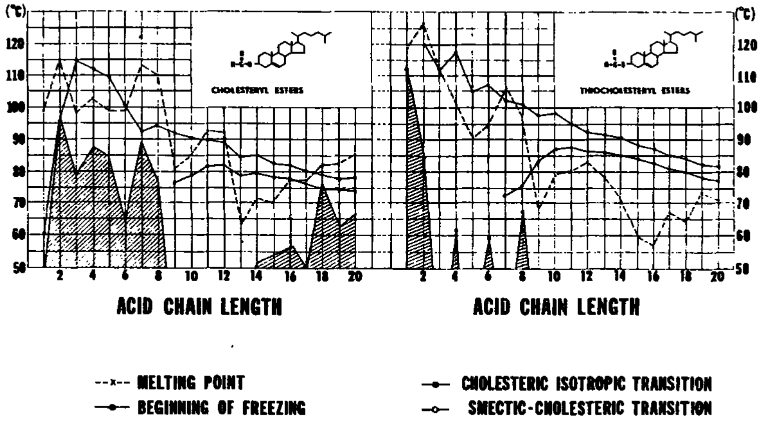

Figure 2. Transition temperatures of the esters of cholesterol and thiocholesterol

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‡ The results of the measurements conducted on thiocholesteryl esters were reported in another context.[3]

temperatures associated with the presumably more stable phases. The large under-cooling effect indicates that the molecular order of monotropic mesophases may delay if not prevent nucleation. Since molecular interactions are much stronger in the solid than in the melt, more accurate melting and freezing points are not required for the study of mesophases.

The clearing point curve of the cholesteryl esters exhibits a maximum for propionate and thereafter a steady decrease with chain length. Contrary to Gray's findings[7] these data do not fit well two separate clearing curves, i.e. one for odd and one for even chain length. However, this is the case for at least the first half of the thiocholesteryl ester series. It may be possible that thiocholesteryl formate is not mesomorphic because the low branch of this clearing point curve (not shown in Fig. 2), associated with odd acid chain lengths, lies below the freezing line.

Furthermore, this odd-even effect may also be the reason why thiocholesteryl propionate and pentanoate are the only thiocholesteryl esters with clearing temperatures that are lower than the values of corresponding cholesteryl esters. Such considerations will be of more than descriptive value once odd-even effects can be explained for homologous series with cholesteric mesophases. The substitution of the σ-bonded oxygen in cholesteryl esters by sulfur results in an increase of smectic-cholesteric transition temperatures, and causes the existence of smectic phases in heptanoate and octanoate. This transformation from cholesteryl to thiocholesteryl esters only slightly affects the shape of the curve representing the dependence between smectic-cholesteric transition temperature and chain length. In addition, the transition temperatures are raised so that cholesteric mesophases, existing above smectic phases, occur within about the same temperature intervals. Figure 3 shows for both series that these intervals approach a constant value with increasing chain length. The curve for S-alkyl thiocholesteryl carbonates and other results[8] indicates that this behavior may be typical for homologous sterol series and that smectic phases may generally occur above heptanoate.

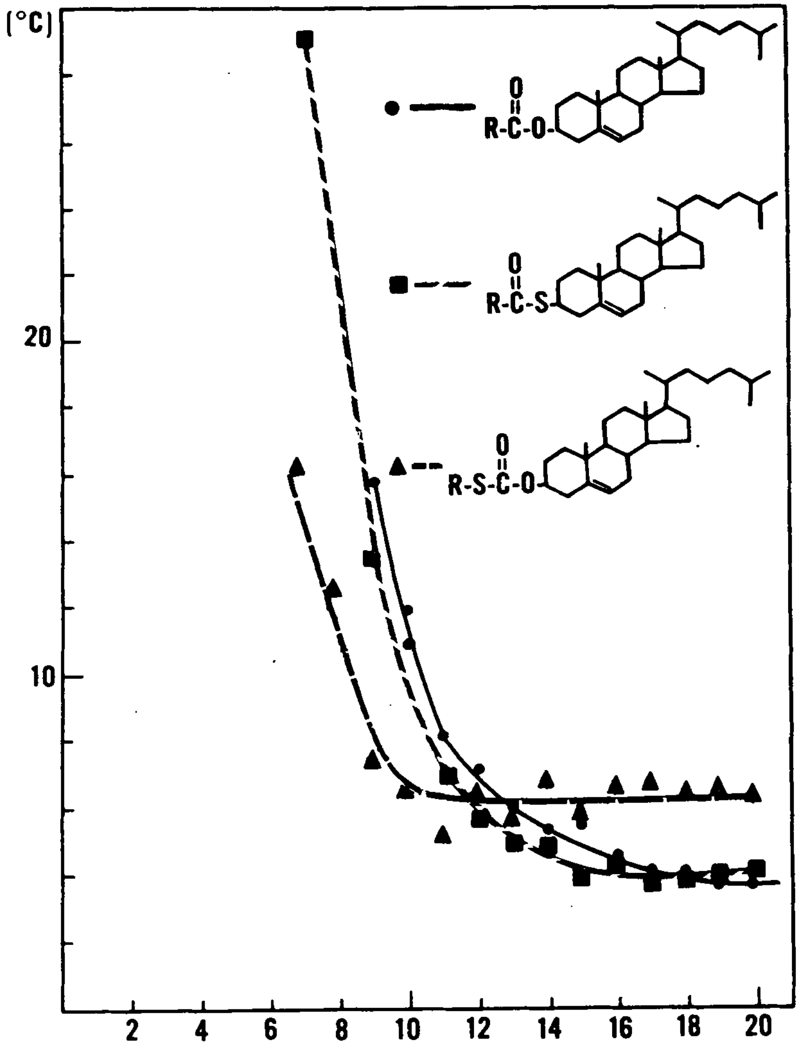

Figure 3. Temperature range of cholesteric mesophases

All transition temperatures in the melt were determined with a modified differential scanning calorimeter (DSC I, Perkin Elmer Corp.) at a scan rate of 10 °C per minute for heating and for cooling. Since the temperature calibration of the calorimeter holds only for heating, the transition temperatures obtained for cooling must be corrected for the thermal lag of the instrument, i.e., 2.8 ± 0.2 °C have to be added. Depending on the compound this results in a temperature reversibility of transitions in the melt ranging from 0.2 °C to 1.2 °C. The discrepancy between these data and the optically determined reversibility of a few tenths of a degree reported in the literature[7] or obtained in optical tests on the investigated materials, may be caused by variations in the instruments, by lack of thermal equilibrium of the sample, and by impurity effects. The latter possibility is most unlikely in this case.

In Table 1 the transition temperatures of cholesteryl esters are compared with Gray's results[7] obtained by purely optical means. Except for the discrepancy of 7.8 °C for pentanoate, most of the values agree within less than 3 °C. All discrepancies may be caused by impurity differences of the acids used for the preparation of the compounds.

Other investigators[9] also studied cholesteryl esters with the differential scanning calorimeter DSC I. Part of their results is presented in Table 2, where the last two columns were added to show the differences of the respective transition temperatures in the melt, obtained for heating and cooling. Because of the satisfactory purity of the compounds, these temperature differences are primarily due to the thermal lag of the instrument.‡

Since the calibration of the DSC I pertains only to heating runs, the transition temperatures taken on cooling have to be corrected for the thermal lag. For materials of high purity the latter is approximately equal to the difference of the transition temperatures obtained for a temperature reversible phase on heating and cooling (for example see last column of Table 2). If the temperature of another reversible transition is known only for cooling at

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‡ The amount of thermal lag cannot be related to published data[8] because the latter were obtained from a modified DSC I.

Table 1 Transition Temperatures [°C]

	Cholesterol				Thiocholesterol	
	S—Ch		Ch—I		S—Ch	Ch—I
Alkanoates	Gray[7]		Gray[7]			
Formate	—	—	60.5	60.4	—	—
Acetate	—	—	94.5	95.4	—	119.5
Propionate	—	—	116	114.1	—	111.1
Butyrate	—	—	113	111.8	—	117.6
Pentanoate	—	—	101.5	109.3	—	104.7
Hexanoate	—	—	101.5	100.4	—	107.7
Heptanoate	< 92.5	—	95.5	92.7	73.1	102.1
Octanoate	69.5	—	96.5	94.7	76.6	100.8
Nonanoate	77.5	76.3	92	92.1	84.0	97.5
Decanoate	81.5	79.0	92.5	90.9	87.4	98.3
Undecanoate	...	81.9	...	90.0	88.1	95.0
Dodecanoate	83.5	82.1	90	89.2	86.7	92.3
Tridecanoate	...	78.8	...	84.8	86.5	91.4
Tetradecanoate	81	79.9	86.5	85.2	85.5	90.4
Pentadecanoate	...	78.3	...	82.9	84.3	88.3
Hexadecanoate	78.5	78.1	83	82.6	83.0	87.3
Heptadecanoate	...	76.5	...	80.6	81.2	85.0
Octadecanoate	75.5	75.1	79.5	79.2	80.2	84.2
Nonadecanoate	...	74.2	...	77.8	78.3	82.4
Eicosanoate	...	74.3	...	78.1	77.1	81.3

— mesophase not observed ... not measured

S—Ch smectic-cholesteric Ch—I cholesteric-isotropic liquid

TABLE 2 Transition Temperatures and Heats of Transition

Cholesteryl Ester	Second Heating						Cooling						Thermal Lag	
	T_1	H_1	T_2	H_2	T_3	H_3	T_1'	H_1'	T_2'	H_2'	T_3'	H_3'	T_2-T_2'	T_3-T_3'
Formate	...	...	...	...	97.0	12.7	50.0	8.6	...	...	97.1	0.2	...	NA
Acetate	...	...	...	...	110.9	10.7	92–98	10.7	...	...	...	...	...	...
n-Propionate	101.6	13.0	...	...	115.2	0.23	66.3	11.1	...	...	108.7	0.43	...	6.5
n-Heptanoate	...	...	...	...	116.0	17.0	87	16.8	95	a	...	...	...	...
n-Nonanoate	74	a	80.7	10.1	93.0	0.23	b	...	66	0.11	86	0.23	NA	7
n-Decanoate	87.2	13.3	...	...	91.4	0.28	b	...	68.5	0.18	81.9	0.30	...	10.5
Myristate	73.6	18.7	80.0	0.52	85.6	0.41	36.7	16.8	70.0	0.56	76.4	0.44	10	9.2
Palmitate	...	...	...	...	79.6	22.7	47	17.5	64	0.57	70.0	0.46	...	NA
Stearate	...	...	...	...	85.0	25.2	67	25.8	a	...	71	0.54	...	NA

T— temperatures in °C.

H— transition heats in cal/g.

Subscript 1, 2 and 3 correspond to solid-smectic, smectic-cholesteric and cholesteric-isotropic transitions. In cases of a single transition, the solid-isotropic liquid is listed as transition 3.

a— Not resolved.

b— Not measured owing to supercooling

NA—Not applicable, because heating and cooling temperatures cannot refer to the same phase transition. (Notice difference of transition heats.)

Note: Data taken from (9).

the same scan speed, adding this thermal lag results in an approximately corrected transition temperature. This procedure yields a smectic-cholesteric transition temperature of 73 °C for nonanoate and of 79 °C for decanoate. These results and the transition temperatures obtained for heating agree within a few degrees centigrade with the values in Table 1. However, the investigators mistook the melting process of nonanoate, occurring at 80.7 °C with a latent heat of 10.1 cal/g, for the smectic-cholesteric transition and claim for the formate a clearing point of 97.1 °C, i.e., a temperature 36.6 °C higher than reported in Table 1. Since they do not present evidence for the latter other than the respective endotherm, this high temperature endotherm may not indicate a clearing point but only a trivial effect such as a high freezing impurity. To avoid such errors and ambiguities, the temperature reversibility of transitions in the melt has to be determined whether a calorimetric or an optical method is applied. Furthermore, unusual findings such as transitions in the melt, with transition heats comparable to the heat of fusion, and significant deviations from literature results should always be carefully studied by polarizing microscopy.

Transition Heats

The dependence of enthalpy of fusion on thermal history indicates the lack of thermal equilibrium in the solid state. Figure 4 shows only the high enthalpy values because they correspond to the highest thermal stability obtained in the solid state during these experiments. Disregarding minor variations, the latent heat and the corresponding entropy of fusion, presented in Fig. 5, increase with chain length for both homologous series, but increase much less for thiocholesteryl esters, above dodecanoate. Figure 6 shows the enthalpies and Fig. 7 the entropies of transitions in the melt. Because of small signals and because of difficulties in defining a proper base line, these small enthalpy values have an estimated accuracy of only ± 20%. The curves associated with the cholesteric-isotropic liquid transition increase

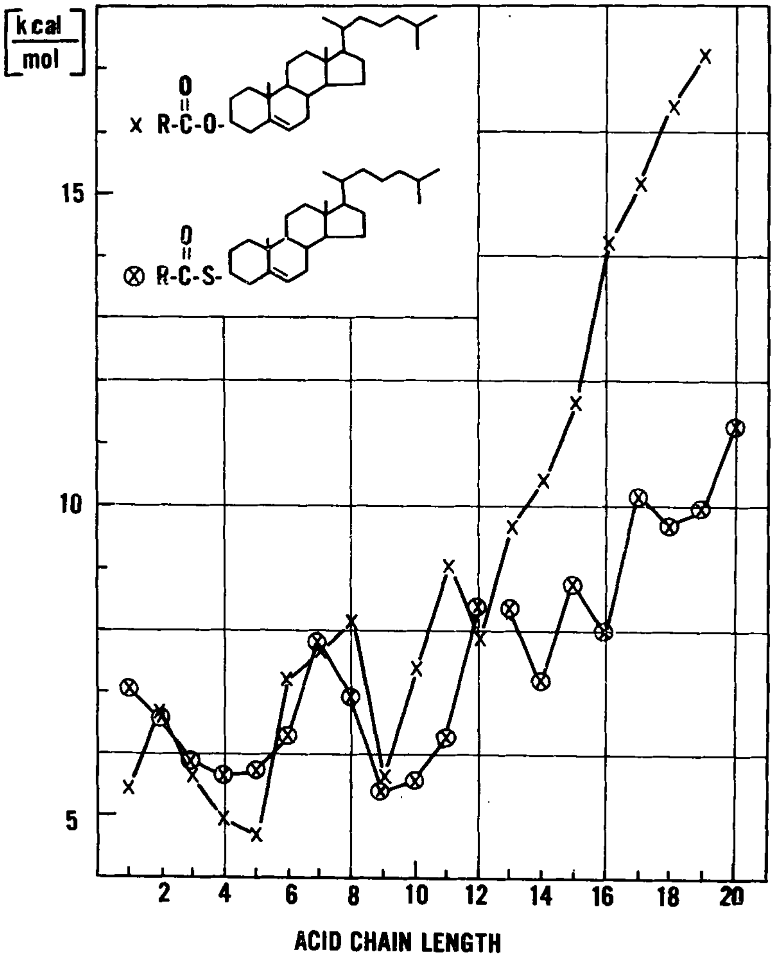

Figure 4. Enthalpy of fusion of the esters of cholesterol and thiocholesterol

with chain length in a bumpy form for cholesteryl esters and in the shape of an ascending zig-zag line for thiocholesteryl esters. The latter supports the existence of the odd-even effect already inferred from the curve of clearing temperatures (see Fig. 2). Furthermore, the thiocholesteryl esters exhibit lower enthalpy and entropy values than the corresponding cholesteryl esters, a result akin to observations at the melting points.

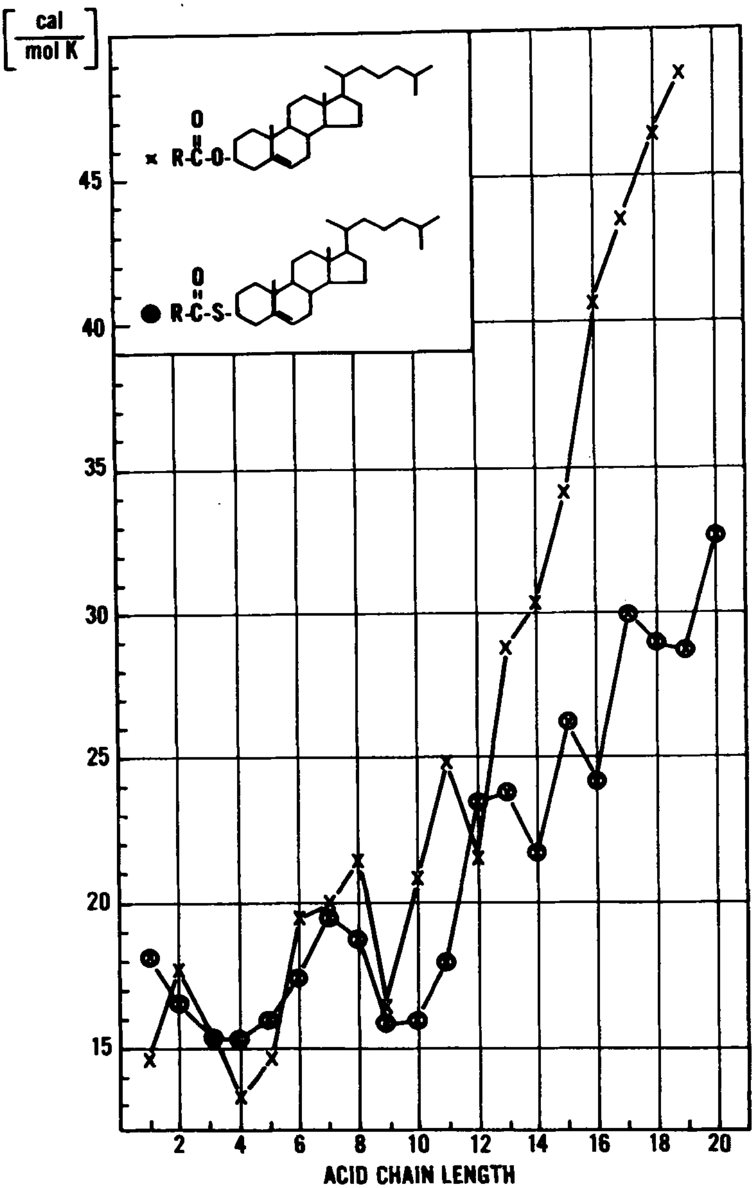

Figure 5. Entropy of fusion of the esters of cholesterol and thiocholesterol

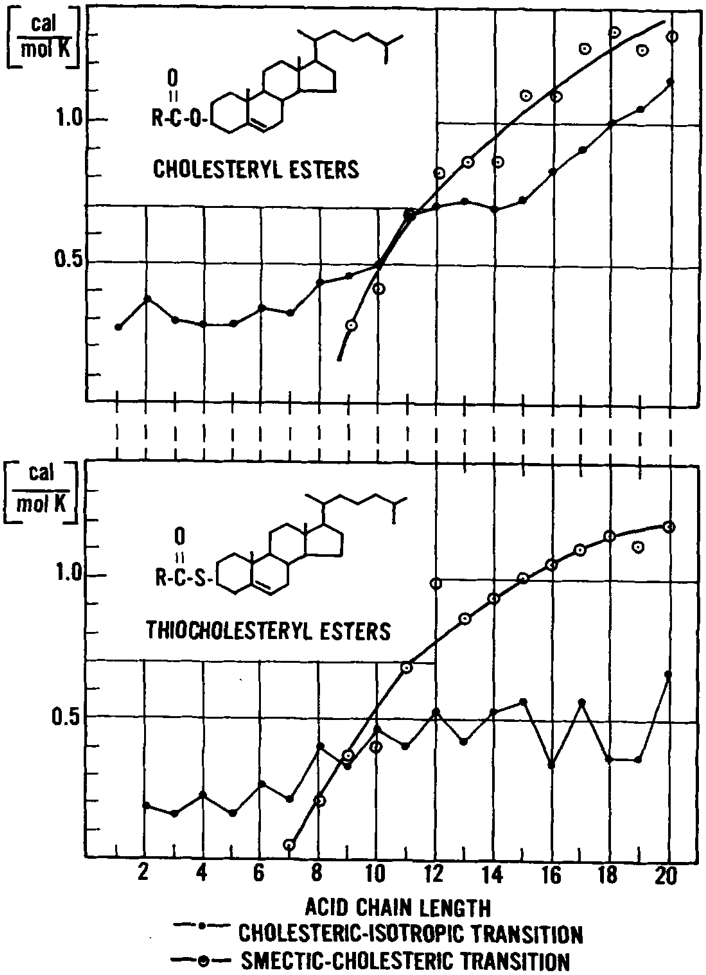

Figure 6. Enthalpy changes at transitions in the melt of the esters of cholesterol and thiocholesterol

However, the two homologous series show comparatively small differences of these quantities at smectic-cholesteric transitions except for low chain length, where the curves for cholesteryl esters have a greater slope. If these curves are extrapolated towards shorter chain length, the occurrence of a smectic mesophase may

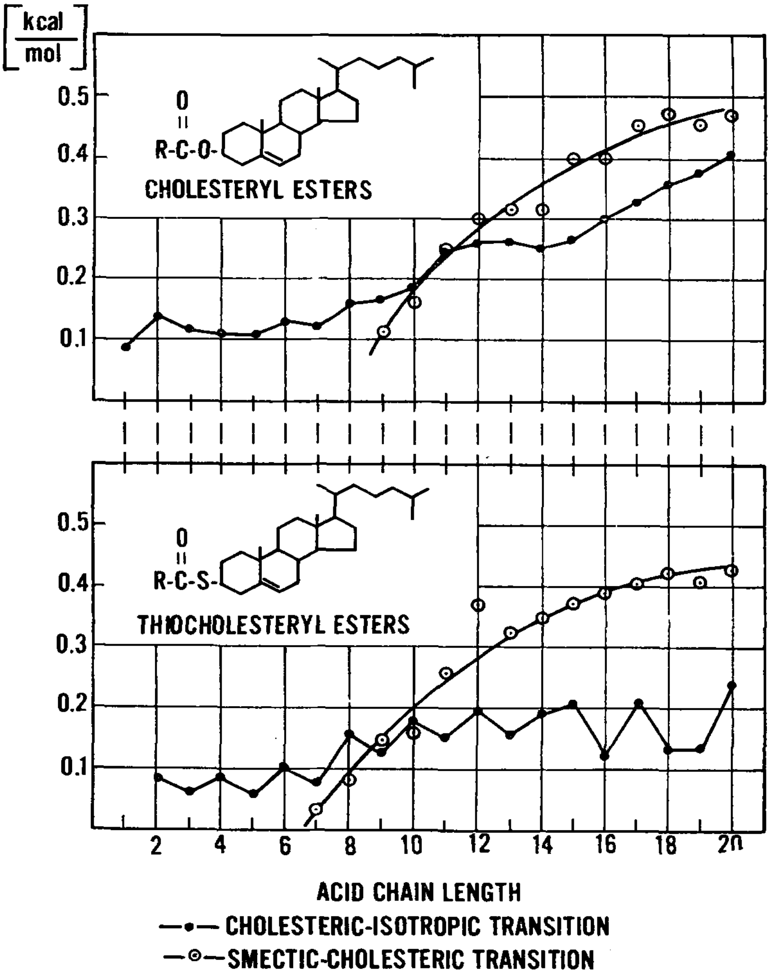

Figure 7. Entropy changes at transitions in the melt of the esters of cholesterol and thiocholesterol

be indicated for octanoate, but not for lower members. A similar extrapolation based on data in Fig. 2 yields a smectic-cholesteric transition temperature of 70 °C for octanoate, a temperature only 0.5 °C higher than reported by Gray. However, this phase was not observed in spite of undercooling to 50 °C. Since rapid cooling was required for this test, non-equilibrium phenomena could have prevented the occurrence of the smectic mesophase. The presence of different impurities may be responsible for the discrepancies of these data and Gray's results. Inspection of Figs. 6 and 7 shows that no smectic mesophases should be anticipated for members lower than thiocholesteryl heptanoate. This is also supported by the latent heat of 25 cal/mol obtained for the smectic-cholesteric transition of thiocholesteryl heptanoate, because this value is smaller than the lowest one reported for transitions in the melt.[10]

The ω-Phenyl Esters of Cholesterol and Thiocholesterol

Elser and Pohlmann[11] modified Staab's esterification method[12] to synthesize the ω-phenyl esters under conditions not conducive to the formation of impurities. They estimate a purity of 99% or better for the investigated materials.

Transition Temperatures

Figure 8 shows the transition temperatures of the investigated ω-phenyl esters. The " melting curve " and the " freezing curve ", both describing the lower temperature limit of the melted state, were determined under the same conditions as discussed for Fig. 2. All high temperature mesophases of both series are cholesteric.

The clearing point curve of the cholesterol series consists of two branches: the upper one apparently related to odd and the lower one associated with even values of the acid chain length. The branches tend to approach each other with increasing chain length. The ω-phenyl cholesteryl acetate may not be mesomorphic because the extrapolation of the lower branch yields a clearing point lying about 50 °C below the freezing point. Only the octanoate (the highest member of the series) exhibits a smectic mesophase. This conforms with our experience that all homologous sterol series with cholesteric mesophases show smectic behavior above octanoate.

The clearing points of the upper branch agree within a few

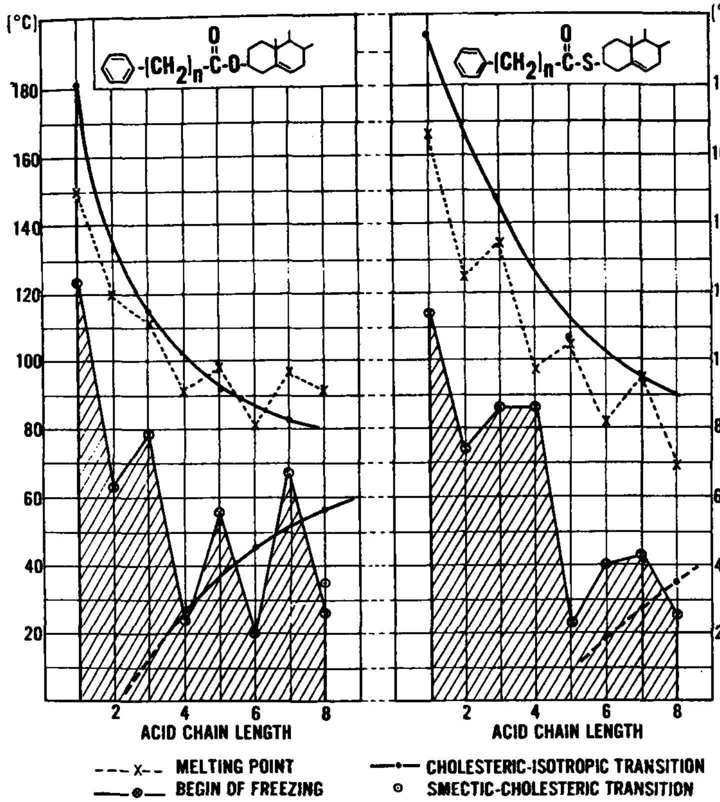

Figure 8. Transition temperatures of the ω-phenyl esters of cholesterol and thiocholesterol

degrees with the values obtained by Fergason,[13] who studied the first 5 members of the ω-phenyl cholesteryl esters. Since he did not observe a mesophase for the propionate, he concluded that these ω-phenyl esters are only mesomorphic for odd values of the acid chain length. The difference of the results can be explained by the large number and the higher purity of the materials discussed in this paper.

The ω-phenyl esters of thiocholesterol show a similar behavior. The substitution of sulfur for the σ-bonded oxygen moves the two branches apart. The clearing temperatures for odd chain length are increased, while the clearing temperatures of the lower branch are decreased. The latter apparently is shifted so far into the freezing region that only the octanoate exhibits an observable mesophase. Of course, higher members have to be studied to prove the existence of the lower branch.

Transition Heats

The heats of fusion of the ω-phenyl esters depend on thermal history, a behavior observed not only for ordinary esters but also for most mesomorphic sterols investigated in our laboratory. For reasons described previously, Fig. 9 shows only the high enthalpy and entropy values. These results are generally higher and less varying with chain length than those obtained for the corresponding esters of cholesterol and thiocholesterol. Like the transition temperatures the heats of clearing of ω-phenyl esters of cholesterol form a curve of high values for odd and a curve of low values for

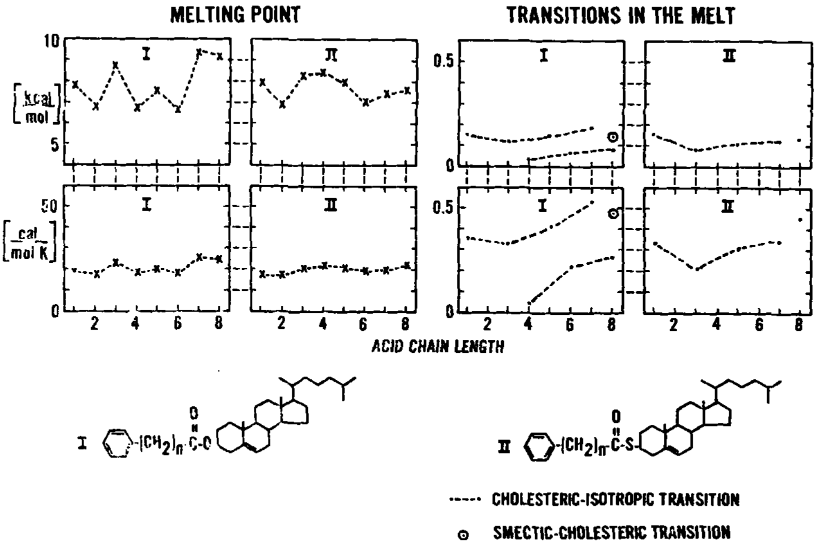

Figure 9. Transition enthalpies and entropies of the ω-phenyl esters of cholesterol and thiocholesterol

even chain length. The associated entropy curves are even more separated. The entropy data of ω-phenyl esters of thio-cholesterol indicate that two such curves may exist for higher members.

Summary and Discussion

The substitution of the σ-bonded oxygen by sulfur in cholesteryl esters increases most transition temperatures in the melt, decreases heats of clearing, introduces an odd-even effect for temperatures and heats of clearing, and causes the existence of a smectic mesophase for heptanoate and octanoate. Such a substitution for ω-phenyl esters of cholesterol raises the clearing points for odd, but lowers them for even acid chain length. Phenyl-substitution on the acid chain, i.e., the transformation from alkanoates to ω-phenyl alkanoates of cholesterol, results in the largest known odd-even effect in temperatures and heats of clearing. The substitution of oxygen for sulfur in cholesteryl esters and in carbonates of stigmasterol, cholestanol, and cholesterol[8] increases the thermal stability of the smectic mesophases. These results suggest that the lateral interactions between the molecules are increased relatively to their terminal attractions. However, as Elser pointed out, other data indicate a reduction of the force constant of the carbonyl groups, thus implying a weakening of lateral attractions.[8] More experimental evidence may be required to explain this contradiction.

The effect of molecular alterations on the properties of cholesteric mesophases cannot be explained, since neither the arrangement of nor the interaction between molecules is known. The molecular features, responsible for the occurrence of cholesteric mesophases, may be obtained from empirical studies of homologous series, if the data are independent of impurities. In spite of 99% purity of the investigated compounds the plots of temperatures and transitions in the melt versus chain length show a few large deviations from a best fit. Impurity checks with gas chromatography[6] indicate only the presence of close homologues. The effects of homologues were studied on a sample of cholesteryl nonanoate containing 0.1 mol of cholesteryl decanoate. This added impurity increased the smectic-cholesteric transition temperature by 0.4 °C but did not affect the clearing temperature. Because of this result and because of an homologue content of 0.01 mol or less in the investigated materials, large deviations from the best fit of the data may be caused by other impurities. Since acids of 99% purity or better were mostly used in the preparation of the compounds, some of these discrepancies may be only explainable by the presence of unknown impurities of the cholesterol. Progress in gas chromatography is imminent to detect this source of error.

Acknowledgments

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