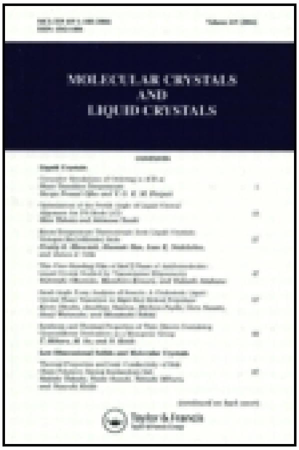

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Evaluation of Thermal Transitions in Some Cholesteryl Esters of Saturated Aliphatic Acids‡

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Abstract—The heats and temperatures of transition for fourteen cholesteryl esters of saturated aliphatic acids have been evaluated using a Perkin-Elmer Differential Scanning Calorimeter, DSC-1B. Most esters tested were first recrystallized from *n*-pentyl alcohol. Among several recrystallization solvents tested, *n*-pentyl alcohol was most effective in removing impurities and eliminating ester transitions caused by these impurities. Ester purity was determined by a recently reported technique which is based on an analysis of the complete DSC recorder scan for transitions. The transition data in this study indicate that the lowest molecular weight saturated aliphatic ester of cholesterol to show mesophase behavior is the propionate. For the formate or acetate less pure samples may be supercooled in the melt so that mesophases may be observed. New transition data for the odd esters of cholesterol from undecanoate to nonadecanoate have also been obtained. Cholesteryl eicosanoate was examined and found to have only one transition, both on heating and cooling, which may indicate that the highest members of this series do not display mesophase behavior in the pure state.

A small but definite odd-even effect in the sum of the transition entropies for each compound has been established for cholesteryl esters from nonanoate through nonadecanoate. Similarly, there is a small but definite odd-even effect for the temperatures of the crystal-mesophase transition for esters from tridecanoate through nonadecanoate.

‡ Part XXIII of the *Series on Order and Flow of Liquid Crystals.*

Experimental

Cholesteryl Esters. The ester samples come from five sources – Applied Science Laboratories, State College, Pa.; Analabs, Hampden, Connecticut; Eastman Chemicals, Kingsport, Tennessee; Aldrich, Cedar Knolls, New Jersey, and Matheson, Coleman, and Bell, E. Rutherford, New Jersey. With the exception of some esters from Applied Science Laboratories, all were recrystallized from *n*-pentyl alcohol, washed after the removal of the mother liquor in an ethanol-water solution, and vacuum dried at 50 °C. The purity that each sample attained is recorded in the table presenting the thermal transitions. The purity analysis technique applied is based on the shape of the differential scan.[1] The individual samples varied widely in mole per cent purity with all in the range of 96.0 to 99.6% pure. The best cholesterol available for esterification is obtained from animal sources and is only about 98% pure. This is thus a major limitation on the quality of available ester samples. In a previous paper by E. M. Barrall *et al.*,[2] cholesteryl esters were thought to have less than 0.1% impurity, as indicated by spectrometric analyses. Two other analytical techniques for cholesteryl ester purity applied by Arnold[3] gave values from 98.1 to 99.6% purity by one method[4] and 91.9 to 99.5% by a second method.[5] The values by Arnold are more consistent with the purities reported in this paper.

Instrumentation

The samples were analyzed on a Differential Scanning Calorimeter, Model DSC-1B, manufactured by the Perkin-Elmer Corp., Norwalk, Connecticut. The calorimeter had previously been calibrated for temperature at the applied heating rates of 1.25 and 2.50 °C/min in a temperature range of 50 to 156 °C with indium, stearic acid, and adipic acid, among other compounds. Heats of fusion were calculated by comparison with the area under the melting curve of an exceptionally pure sample of indium supplied by the Perkin-Elmer Corp. and stated as being 99.999% pure. The heat of elemental melting is well established at 6.80 cal/gm.[6] As a check on the curve area, the heat of transition of the indium was also computed from instrument parameters, as the chart ordinate represents calories/sec and the abscissa, seconds; this method gave a heat of transition of 6.89 cal/gm for indium. Two to five mg samples were weighted on a Mettler balance to 0.001 mg and enclosed in an aluminum planchet. All samples were heated to complete melting, cooled to crystallization, and reheated to isotropic liquid. Duplicate runs were made on fresh samples. All values reported are from first heating or cooling, but, except for cholesteryl tridecanoate, all samples consistently repeated the same transitions and heats on reheating.

The accuracy of transition heats presented can be estimated from multiple runs on Fisher triple point benzoic acid that ranged from 35.0 to 35.6 cal/gm. A previous investigation by adiabatic calorimetry gave a value for benzoic acid of 35.2 cal/gm.[7] Accepting this figure for the mean permitted, a standard deviation of 0.23 cal/gm was calculated. A 95% reliability requires two standard deviations or ± 0.46 cal/gm. Conversion of this figure to per cent of sample heat gives an expected accuracy of ± 1.3%. This estimate is satisfactory for the sizable calorie change on heating the crystalline material through its initial transition because the ordinate scale can always be adjusted to give a large full curve on the chart. However, all mesophase-isotropic transitions had to be run on a scale of maximum sensitivity smaller than in normal melting. (Attenuation at different sensitivities was checked for error.) In addition, the specific heat before and after each mesophase transition is abnormally high which alters the baseline slope. From a comparison of the mesophase data reported here for cholesteryl myristate with that of other investigations, such as Barrall *et al.*[8] and M. Leclerq *et al.*,[9] a good accuracy of ± 0.02 cal/gm can be anticipated. Conversion of this value to per cent would suggest accuracy ranging anywhere from ± 3.3% for nonadecanoate to 11.8% for the smallest heat reported which is for the cholesteric-isotropic liquid transition of cholesteryl propionate.

The precision of transition temperatures presented here can be estimated from multiple tests made over a period of weeks on the three cholesteryl transitions of a 98.1% purity myristate. The transition ranges for each were from 70.0 to 71.0 °C, 77.3 to 78.2° C, and 82.8 to 83.7 °C. The expected precision then is approximately ± 0.5 °C. These transition temperatures on cholesteryl myristate are compared with those of Martire,[10] Friedel,[11] Gray,[12] Arnold[13] and Barrall[2] in Table 1. The cholesteryl myristate sample of

TABLE 1 Transition temperatures for cholesteryl myristate

Transition	Transition temperature, °C Martire[(1)]	Friedel[(2)]	Gray[(2)]	Arnold[(3)]	Barrall[(1)]	This work[(1)]
Crystal-smectic	69.8	72	71	71.0	73.6	70.5
Smectic-cholesteric	79.0	78	81	79.1	79.7	77.8
Cholesteric-isotropic liquid	84.2	83	86.5	84.6	85.5	83.2

(1) Transition determined by DSC.
(2) Transition determined by optical technique.
(3) Transition determined by equilibrium calorimetry.

Martire *et al.*[10] had a 98.8% purity, as determined by the Perkin-Elmer Corp. method of analyzing the shape of the differential scan.[13,14] This sample and that of these investigations are likely comparable in purity, since the purity analysis technique developed for this work generally gives somewhat lower purity values on the same sample than the Perkin-Elmer method.[1] The transition temperatures reported by Barrall *et al.* are higher than those reported here, as are all other cholesteryl ester melting temperatures reported in this same study.[2] The methods of calibration and operation of the DSC are likely the determining factors, rather than purity, for the higher transition temperatures reported previously by Barrall *et al.*[2]

Results

The temperatures and heats of transition of fourteen cholesteryl esters derived from saturated aliphatic acids of varying chain length are presented in Table 2, columns one and two. Values for unesterified cholesterol are listed first, followed by the esters from the shortest, formate, of carbon tail length one, to eicosanoate, of carbon tail length twenty. Eight of these esters have been measured previously by E. M. Barrall *et al.*[2,15] Their results are shown for comparison in columns three and four. The per cent difference in ΔH between these new and the published values is presented in column five. The purity as estimated by the analysis of the DSC curve shape is presented in column six. The final two columns show the calculated entropies of transition and the sum of all transition entropies for each compound. The thermodynamics of each compound studied will be discussed separately.

Cholesterol. The series, in theory, can be considered to begin with an ester having a carbon tail length of zero, or the parent compound, an alcohol. However, the transition temperature column in Table 2 clearly shows the significant difference of cholesterol from the remainder of the true ester series. That is, there is a melting temperature decline of 50 °C between cholesterol and the first ester, the formate. The high melt temperature of cholesterol demonstrates a structural stability to thermal energy that is lost on esterification. The cholesterol, received from Analabs, has one transition and exhibited no mesophases on either heating or cooling which is consistent with the literature.[16]

Cholesteryl Formate. This ester exhibited only simple melting and melt recrystallization. It did not appear to form mesophases. Neither the original compound from Aldrich nor a sample recrystallized from *n*-pentyl alcohol showed an additional transition as suggested by E. M. Barrall *et al.*[2] One of these authors (EMB) has recently found that the formate ester can be supercooled sufficiently to give a mesophase transition of 0.08 cal/gm at 57.1 °C.

Cholesteryl Acetate. The original compound from Matheson,

TABLE 2 Cholesteryl ester transition values

Sample	Measured ΔH Temp (°C)	Cal/gm	Reference ΔH[1] Temp (°C)[2]	Cal/gm	% Diff. ΔH	% Purity Estimate[3]	ΔS Cal/mol/°K	ΔS total Cal/mole/°K
Cholesterol	147.0	16.0	148.5[14]			98.0	14.7	14.7
Cholesteryl Formate	96.6	12.6	97.3	12.8[4]	-1.6	99.1	14.5	14.5
Cholesteryl Acetate	114.6	11.4	118.2	11.2[5]	1.8	99.4	12.6	12.6
Cholesteryl Propionate								
Cry-Chol Trans	97.2	13.3	99	12.5[6]	2.9[6]	99.6	15.9	
Chol-Iso Trans	113.0	0.17	115.3	0.23	-26		0.20	16.1
Cholesteryl Nonanoate								
Cry-Chol Trans	77.8	11.4	80.8	10.2[7]	12	98.5	17.1	
Chol-Iso Trans	91.7	0.25	93.0	0.22	14		0.36	17.5
Cholesteryl Undecanoate[8]								
Cry-Iso Trans	91.5	16.0				99.6	24.3	
Chol-Sm Trans[9]	78.9	0.37					0.58	
Iso-Chol Trans[9]	87.9	0.32					0.50	24.3
Cholesteryl Laurate								
Cry-Iso Trans	91.3	13.4	99.0	17.7	-24	98.7	20.9	
Chol-Sm Trans[9]	80.2	0.40	80.7	0.86	-54		0.64	
Iso-Chol Trans[9]	87.2	0.31	87.4	0.70	-56		0.49	20.9
Cholesteryl Tridecanoate								
Cry-Sm Trans	63.4	16.4				96.4	28.4	
Sm-Chol Trans	77.5	0.54					0.90	
Chol-Iso Trans	83.5	0.32					0.52	29.8
Cholesteryl Myristate								
Cry-Sm Trans	70.5	18.6	73.6	18.7	-0.5	98.1	32.6	
Sm-Chol Trans	77.8	0.56	79.7	0.52	7.0		0.95	
Chol-Iso Trans	83.2	0.41	85.5	0.41	0.0		0.69	34.2
Cholesteryl Pentadecanoate[8]								
Cry-Sm Trans	70.3	19.4				96.0	34.5	
Sm-Chol Trans	77.1	0.63					1.10	
Chol-Iso Trans	81.8	0.38					0.65	36.0
Cholesteryl Palmitate								
Cry-Chol Trans[10]	77.3	22.4	79.7[13]	23.2[13]	-1.6[12]	97.1	40.0	
Chol-Iso Trans	81.6	0.45					0.80	40.8

Cholesteryl Heptadecanoate(8)								
Cry-Chol Trans(11)	76.3	22.8				98.4	41.6	
Chol-Iso Trans	79.7	0.49					0.89	42.5
Cholesteryl Stearate								
Cry-Iso Trans	81.8	25.8	85.1(12)	25.5(12)	1.2	98.2	47.4	
Chol-Sm Trans(9)	69.6	0.60					1.14	
Iso-Chol Trans(9)	74.4	0.60	71	0.54	11		1.13	47.4
Cholesteryl Nonadecanoate(8)								
Cry-Iso Trans	80.4	26.3				98.6	49.6	
Chol-Sm Trans(9)	71.8	0.68					1.28	
Iso-Chol Trans(9)	75.6	0.60					1.15	49.6
Cholesteryl Eicosanoate	83.0	26.2				97.7	50.1	50.1

(1) E. M. Barrall *et al.*,[2,8,15] are the source of these values.

(2) All values reported in the above Table are from DSC curves except the reference temperatures, which are from DTA curves.[2]

(3) Purity estimates are derived from the shape of the DSC curves.[1]

(4) Barrall *et al.* reported a second transition on cooling of 0.08 cal/gm at 57.1 °C.

(5) Barrall *et al.* detected another transition at 81–87 °C of 4.89 cal/gm.

(6) Barrall *et al.* reported another transition at 110 °C of 0.43 cal/gm on first heating. The % ΔH difference is based on the sum of 12.5 cal/gm and this value of 0.43 cal/gm.

(7) Barrall *et al.*,[2] M. Leclerq *et al.*,[9] and these investigators report an additional transition on cooling of 0.11 cal/gm at 66 °C, 0.16 cal/gm at 76.5 °C, or 0.14 cal/gm at 74.6 °C respectively.

(8) The values reported for the C^{11}, C^{13}, C^{15}, C^{17}, and C^{19} saturated aliphatic acid have no known reference for comparison.

(9) These values can only be obtained from the cooling curves.

(10) Cry-Sm and Sm-Chol transition separable only from cooling curves. Chol-Sm transition equals 0.58 cal/gm at 75.6 °C on cooling; ΔS equals 1.04 cal/mole/°K.

(11) Cry-Sm and Sm-Chol transitions separable only from cooling curves. Chol-Sm transition equals 0.69 cal/gm at 74.8 °C on cooling; ΔS equals 1.26 cal/mole/°K.

(12) For comparison purposes, the measured ΔH for the cry-chol and chol-iso transitions are added together.

(13) Barrall *et al.* originally did not resolve this transition into two components as achieved here, although a recent result by one of the authors achieved this separation.

(14) *Handbook of Chemistry and Physics*, 47th Edition, Chemical Rubber Publishing Co. (1966–67).

Coleman, and Bell exhibited the multiple transition behavior suggested by Barrall *et al.*[2] However, after *n*-pentyl alcohol recrystallization, only one transition appeared on melting, on melt recrystallization, and on remelting.

Cholesteryl Propionate. In this work, this ester had the minimum carbon length for the observation of the cholesteric mesophase. The heat absorbed at the cholesteric-isotropic liquid transition is small but reproducible both on heating, cooling, and on reheating. The high purity of this sample originally obtained from Eastman Chemical was achieved by two recrystallizations from *n*-pentyl alcohol. Despite its 99.6% purity, the transition temperature remains below that stated by E. M. Barrall *et al.*[2] All data in the table are from melting curves of original crystals unless otherwise stated. Barrall *et al.*[2] detected an additional transition on first heating the crystalline material, i.e. two mesophases, one of which was a solid-solid transition, but this transition did not appear upon reheating. H. Arnold[3] reports only two transitions at 99.6 and 114 °C of 11.8 and 0.43 cal/gm respectively (one mesophase). This compound appears to form only a single mesophase which can be formed reversibly on either heating or cooling.

Cholesteryl Nonanoate. In this investigation, three transitions were observed. As with other experimenters, viz. M. Leclerq *et al.*[9] and E. M. Barrall,[2] a small third transition on cooling from the melt, in this case of 0.14 cal/gm at 74.6 °C, occurred. The sample studied here was obtained from Eastman Chemicals. It was recrystallized twice from *n*-pentyl alcohol.

Cholesteryl Undecanoate. This ester exhibits three transitions on heating, cooling, and reheating. This means the reversible formation of two mesophases likely to be identified as smectic and cholesteric. A quite pure sample of 99.6 mole % was received from Applied Science Laboratories. The DSC traces were unusually clear and sharp on the sample as received.

There are no known previous studies of either the heats or transition temperatures for this compound. This is the case for all the higher odd carbon length esterified acids.*

Cholesteryl Laurate. This ester and the next in the series, the tridecanoate, demonstrate a similar form of instability, that is the impure material exhibits on heating a reproducible exothermic recrystallization between two other endothermic crystallization processes. The laurate exhibits this behavior both on heating and on reheating. This unusual behavior has been described in detail by E. M. Barrall *et al.*[15] Importantly, after recrystallization of the Eastman cholesteryl laurate from *n*-pentyl alcohol, only one endothermic transition on heating occurs, but three exothermic transitions (smectic and cholesteric mesophases) form on cooling. The heat absorbed on melting is substantially smaller than what would have been estimated from a knowledge of the heats of transition of the nearest two even carbon esters, the decanoate and the myristate. H. Arnold[3] reports a similarly small heat of 13.9 cal/gm. Transition temperatures by Barrall *et al.*,[15] Arnold,[3] Gray,[12] and these investigators are compared in Table 3.

TABLE 3 Transition temperatures for cholesteryl laurate

Transition	Transition temperature, °C			This
	Gray[(1)]	Arnold[(2)]	Barrall[(3)]	work[(3)]
Crystal-isotropic liquid	93	91.3	98.9	91.3
Isotropic liquid-cholesteric	90	88.6	87.4	87.2
Cholesteric-smectic	83.5	81.4	80.6	80.2

(1) Transitions determined by optical techniques.
(2) Transitions determined by equilibrium calorimetry.
(3) Transitions determined by DSC.

Cholesteryl Tridecanoate. This is the only ester for which endothermic transitions obtained on heating the recrystallized material could not be repeated on reheating the same melt recrystallized sample. Instead the tridecanoate displays on second heating two sizable endothermic transitions between an exothermic transition, similar to the laurate, as well as a final mesophase-isotropic transition. An initial attempt to purify the ester from *n*-pentyl alcohol failed when an unexpected ester degradation occurred at the standard drying temperature of 50 °C as detected by its DSC trace. None of the other esters dried in the presence of minute quantities of water at this temperature under vacuum displayed this instability. The three transitions from the original crystalline material, including two mesophases, are listed in Table 2.

Cholesteryl Myristate. This ester is highly regular and exhibits three distinct and reversible transitions on heating, cooling, and reheating. The compound analyzed was a relatively high purity sample from Applied Science Laboratories. The compound is difficult to purify further by recrystallization with common alcohols. Cholesteryl myristate has been studied extensively by DSC and can be considered a reference compound. It has now become the most widely studied of all esters of cholesterol.

Cholesteryl Pentadecanoate. Almost a twin of cholesteryl myristate, this ester has three distinct transitions in heating, cooling, and reheating and at almost the same temperatures as the myristate. Note in Table 2 that with the next four higher members of the series, the odd carbon ester takes on the same characteristics of its even number predecessor in the molecular weight series. These characteristics are in the number, reversibility of formation, and the monotropic nature of the mesophases formed.

Cholesteryl Palmitate. On first heating and reheating this ester, only two distinct transitions were observed. These were the crystal-cholesteric and cholesteric-isotropic liquid transitions. Barrall *et al.* did not resolve these transitions into two separate maxima in the heating curves. One of these authors (EMB) has performed experiments which indicate that this ester has three optically different crystalline forms.

Cholesteryl Heptadecanoate. This ester exhibits phase behavior in common with its even predecessor, cholesteryl palmitate, and has similar transition temperatures. The cholesteric-smetic transition occurs only on cooling. The sample received from Applied Science Laboratories was only about 93.8 mole per cent pure but one recrystallization from *n*-pentyl alcohol markedly increased the purity to 98.4%

Cholesteryl Stearate. Only one transition appears on first heating and on reheating this ester. However two mesophases, a smectic and a cholesteric, are obtained on cooling at a rate of 2.5 °C/min. However, if the cooling rate is slowed to 1.25 °C/min, the cholesteric-smectic transition is lost in the transition to the crystalline form. The slower heating rate permits crystal formation at a higher temperature. Barrall *et al.* did not resolve the cholesteric-smectic transition. The Analabs sample improved somewhat with recrystallization.

Cholesteryl Nonadecanoate. Again, this ester is a close replicate of the even carbon predecessor in the series. The common features include the loss of the cholesteric-smectic transition on cooling by changing the cooling rate from 2.5 to 1.25 °C/min; transition temperatures are also very similar. The sample came from Applied Science Laboratories in good quality and was tested as received.

Cholesteryl Eicosanoate. This ester exhibited only one transition on heating, cooling, and reheating. These features thus may likely mark the termination of the series where mesophases are formed by cholesterol esters of saturated aliphatic acids. The sample was tested as received from Analabs. The purity of the sample, as calculated from shape of the DSC trace, was estimated to be 97.7%.

Discussion of Results. The sum of transition entropies for each compound, (see Table 2, column eight), is plotted against number of carbons in esterified acid in Fig. 1. An inspection of data shows that from the nine carbon acid through the nineteenth, there appears to be a minor but real odd-even effect. The odd-carbon acid esters differs from the next in the series by 6.3 ± 0.8 cal/mole/°K in this range. The even carbon esterified acids from fourteen to eighteen are separated from each other by about 6.6 cal/mole/°K. Using the data for the ten carbon esterified acid from Barrall *et al.*[15] of 20.8 cal/mole/°K, a difference is found from the fourteen carbon esterified acid of 13.4 cal/mole/°K. This is about the value that would be expected for regularity, i.e., twice 6.6 cal/mole/°K. Bondi[17] has indicated that there can be a linear relationship between total entropy of fusion and the number of carbons atoms in a chain for a homologous series, and that for *n*-paraffins, there is an odd-even effect. This part of the series can

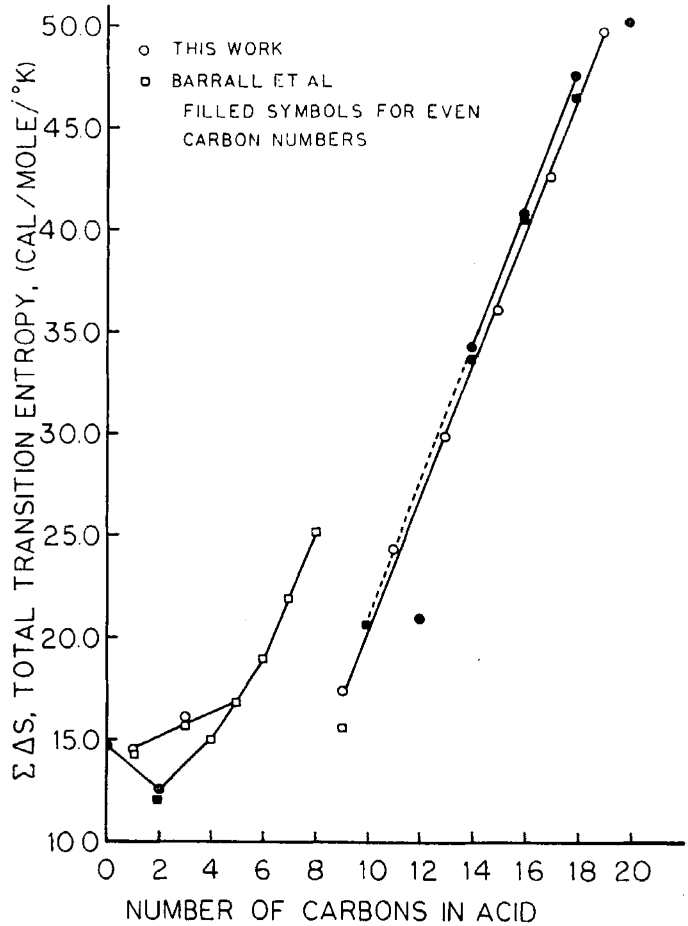

Figure 1. Aliphatic esters of cholesterol; total transition entropies.

be correlated in a similar manner. The resulting equations are, given that N_c is the chain length, $\sum \Delta S_T$, the total entropy, and R, the gas constant:

$$(N_c = 10, 14, 16, 18) \qquad \sum \Delta S_{T/R} = -6.04 + 1.66 N_c$$
$$(N_c = 9, 11, 13, 15, 17, 19) \qquad \sum \Delta S_{T/R} = -5.54 + 1.58 N_c$$

The equation form is the same as for the n-paraffin series but the large negative constant is characteristic of the n-alkyl benzene series and indicates that initial members of the series will deviate from this regular behavior. The twelve carbon esterified acid, the cholesteryl laurate, is over 6 cal/mole/°K too low. This large deviation is not too well understood at present. The value given by Arnold[3] for cholesteryl laurate is only 0.8 cal/mole/°K higher than that of these investigations. Arnold has indicated, by the second of his purity determinations,[5] that his cholesteryl laurate contained 8.1% impurity. Should the level of impurity be this high, such a sample could be dramatically lower in entropy than that of a high purity sample. Barrall *et al.* indicate in their data[15] that the total entropy increases from the third to the eighth carbon esterified acid reaching a value of 25.7 cal/mole/°K.

These investigators feel that the above odd-even effect is real, particularly since the total entropy data for the even carbon esters is comparable to that of Barrall *et al.*,[2] Arnold,[3] and M. Leclerq *et al.*[9] The purity of the samples and crystal morphology of the solid phase remains, however, the major problem in cholesteryl ester transition evaluations. The cholesteryl pentadecanoate, of 96.0% purity, is judged to have the largest error in the crystalline-smectic transition, probably low by 4 to 5%.

The smectic-cholesteric transition entropies from Table 2, for both the measured and the reference data, are plotted against number of carbons in esterified acid in Fig. 2. An estimated curve has been drawn through the data so that its general trend can be followed. Odd-even effects cannot be established, possibly because there is a $\pm$ 0.03 cal/mole/°K deviation in each value, that could be larger than the effect itself. The smectic-cholesteric entropy of transition becomes small at an esterified carbon length of 9. The sharp downward slope of the curve at length 9 may indicate that the smectic transition begins here rather than at length 7 as reported by Gray.[16]

The cholesteric-isotropic liquid transition entropies from Table 2, for both the measured and the reference data are presented *vs.* number of carbons in esterified acid in Fig. 3. As in Fig. 1, two distinct upward sloping curves are formed with a break between cholesteryl octanoate and nonanoate. For reasons similar to that

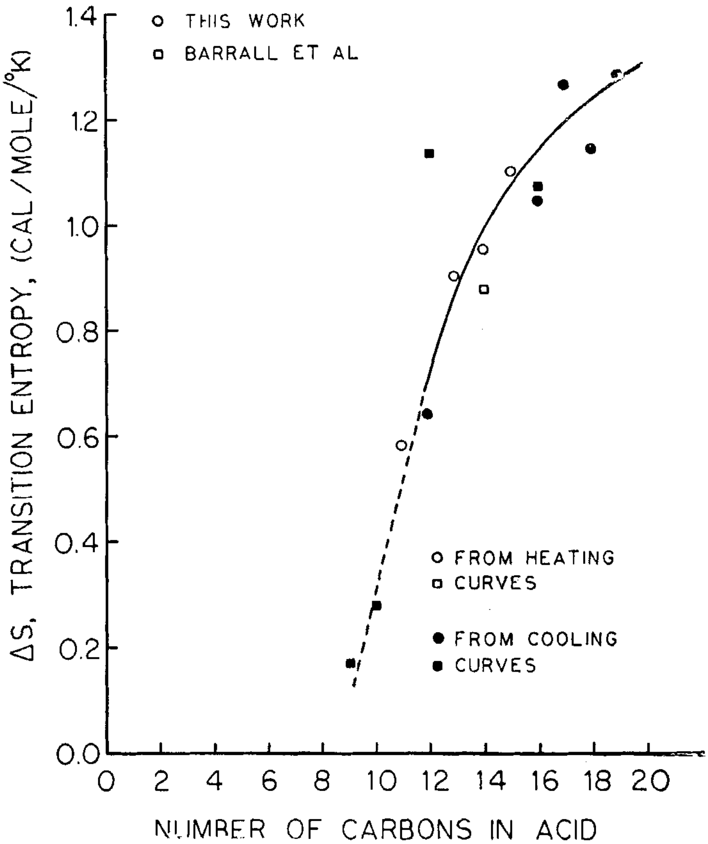

Figure 2. Aliphatic esters of cholesterol; smectic-cholesteric transition entropies.

for the smectic-cholesteric transitions, odd-even effects are not discernible. While Barrall *et al.*[2] and Gray[16] have indicated that cholesteryl formate and acetate have a mesophase transition, this investigation determined that the first cholesteryl ester exhibiting a mesophase is the propionate. Gray[16] reports that cholesteryl acetate has a cholesteric-isotropic liquid transition on cooling at 94.5 °C, but a 99.4% pure cholesteryl acetate became crystalline at 102.5 °C, 8 °C above the mesophase transition reported by Gray.

The temperatures at which the major or largest transition

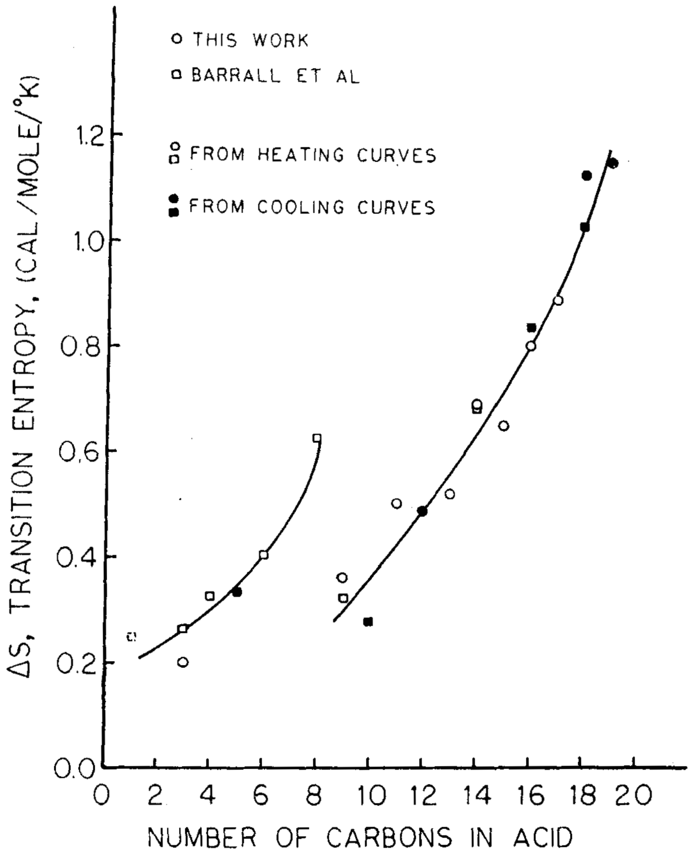

Figure 3. Aliphatic esters of cholesterol; cholesteric-isotropic liquid transition entropies.

entropy occurs is plotted against the number of carbons in esterified acid for lengths from 9 to 20 in Fig. 4. The minor odd-even effect is apparent in acid carbon lengths 13 to 19. The relatively high transition temperatures of the decanoate, undecanoate, and laurate may be related to the fact that all three exhibit mesophase behavior only on cooling from the melt. In Figs. 5 and 6, the data for the temperature at which the smectic-cholesteric and cholesteric-isotropic liquid transitions appeared *vs.* number of carbons in esterified acid for lengths 9 through 20 is presented. The smectic-cholesteric transition temperatures form the general shape

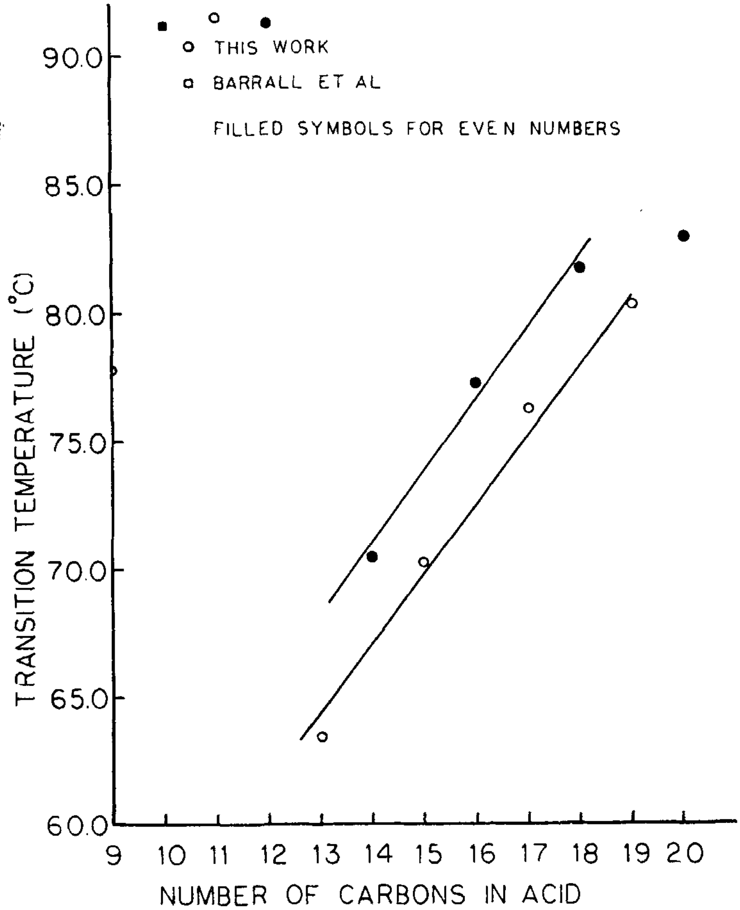

Figure 4. Aliphatic esters of cholesterol; temperature for major transition.

of a horseshoe with a maximum at cholesteryl laurate, and agrees with the graphical presentation of Gray.[16] In the case of the cholesteric-isotropic liquid transition, the suggested trend of the data is a downward sloping line from nonanoate to nonadecanoate.

Conclusions

1. In this work, cholesteryl propionate appears to be the first member of the series to exhibit mesophase behavior in the pure

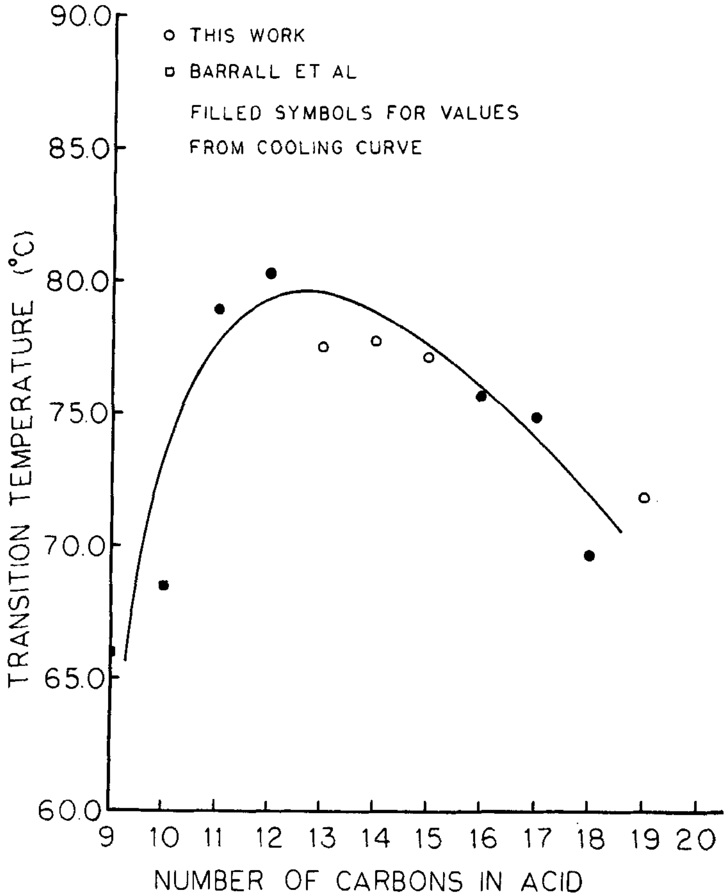

Figure 5. Aliphatic esters of cholesterol; temperature for smectic-cholesteric transition.

state. The first two pure esters, the formate and acetate, exhibited only one transition on both heating and cooling, except for less pure and supercooled samples.

2. From the undecanoate to the nonadecanoate ester, all members have two distinguishable mesophases obtained both from heating and cooling. In optical studies on the even esters,[16] these mesophases have been identified as smectic-cholesteric and cholesteric-isotropic liquid transitions. By analogy, it may be

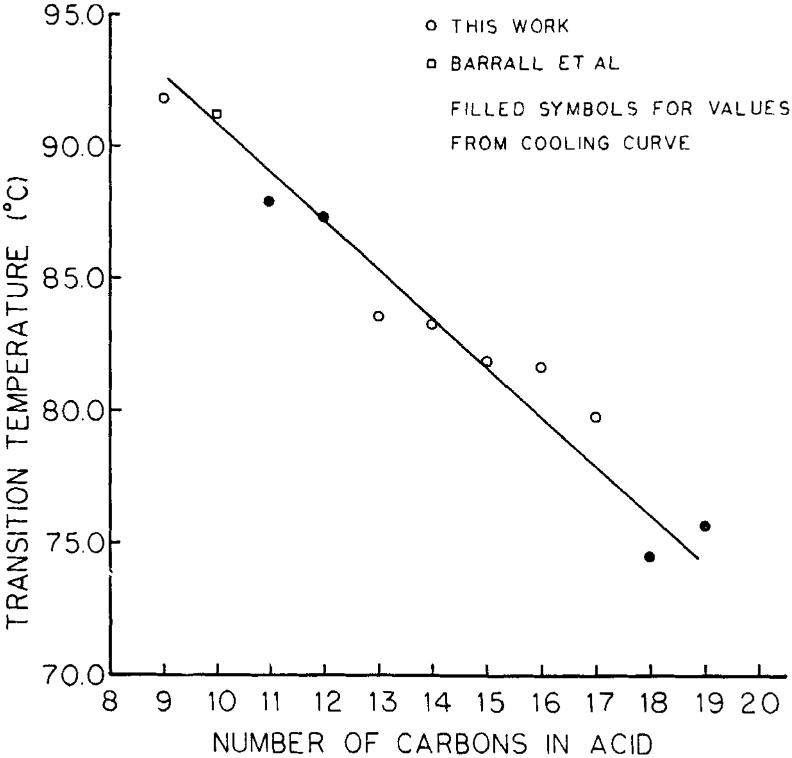

Figure 6. Aliphatic esters of cholesterol; temperature for cholesteric-isotropic liquid transition.

suggested that the mesophases of the odd esters may also be smectic-cholesteric and cholesteric-isotropic liquid transitions.

3. Cholesteryl eicosanoate has only one transition under all conditions. This may indicate that higher members of this series do not display mesophase behavior in the pure state.

4. There is a small but definite odd-even effect in the sum of transition entropies for each compound. This behavior is established for cholesteryl nonanoate up through cholesteryl nonadecanoate. Cholesteryl laurate exhibits deviating behavior in all tests run and in previous reports on this compound.[3,15]

5. Similarly, there is a small but definite odd-even effect in the temperatures of the major calorimetric transition (crystal-mesophase) for compounds from tridecanoate through nonadecanoate.

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* After this paper was accepted, a valuable study on many of these compounds has appeared:
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