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Thermal Transitions of Cholesteryl Esters of C_{18} Aliphatic Acids

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Thermal Transitions of Cholesteryl Esters of C_{18} Aliphatic Acids†

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The studying of physical properties for cholesteryl esters of C_{18} aliphatic acids is of both fundamental and practical interest. The physical chemistry is of interest because of the mesophase or liquid crystal behavior that can be potentially exhibited, by analogy with other esters of cholesterol. Moreover, systematic studies on these esters are rare.(1,2) From a practical view, the cholesteryl ester content of human β-lipoprotein blood serum is ~24.1% cholesteryl oleate (18:1) and ~46.8% cholesteryl linoleate (18:2).(3) Recent studies at the Massachusetts Institute of Technology have indicated that measuring the amounts of cholesterol-bearing β-lipoprotein may be more important than measuring the amount of blood cholesterol itself in characterizing coronary heart disease.(4) β-Lipoprotein contains cholesterol predominantly in the esterified state, containing only about 11.5% free cholesterol compared with 58.2% esterified cholesterol.(3)

This study reports two independent calorimetric investigations on the C_{18} aliphatic esters of cholesterol. The two approaches have been conducted in separate laboratories with different instrumentation being employed. In addition the sample esters were obtained

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† These results were presented in part by D. M. Small at the 158th American Chemical Society Meeting, New York, Sept. 1969.

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from different sources. Purification and purity analyses also varied. The following paragraphs describe separately the methods developed in the two laboratories. The comparative results of transition temperatures and heats are given in Table 1.

The cholesteryl stearate (18 : 0), oleate, and linoleate esters tested at the University of Massachusetts were obtained from Applied Science Laboratories, State College, Pennsylvania. The linolenate (18 : 3) ester came from Mann Research Laboratories, 136 Liberty Street, New York. The cholesteryl stearate and linoleate were recrystallized from an efficient recrystallization solvent, *n*-pentyl alcohol, washed after removal of the mother liquor in an ethanol-water solution and vacuum dried at 25 °C. The recrystallization solvent was selected after a careful screening of different solvent efficiencies for purification of cholesteryl esters.(5) The samples were analyzed for heats and temperatures of transition on a Differential Scanning Calorimeter, Model DSC-1B, manufactured by the Perkin–Elmer Corporation, Norwalk, Connecticut. The DSC calibration procedure has been previously described.(1) The heats and temperatures of transition can be markedly dependent on level of purity. An estimate of sample purity has been made for each ester by a technique based on the shape of the DSC curves.(6) The differences in purity reported for these samples from those studied at the Boston University Medical Center are expected to be due more to differences in analytical procedure than to real differences between samples.

Each of the cholesteryl esters studied at the Boston University Medical Center were obtained from the Fatty Acid Project, The Hormel Institute, Austin, Minnesota, and tested upon receipt without further purification. An assay for all the esters indicates 99% + purity. Each sample was tested by thin layer chromatography in a system which separates cholesteryl esters by their degree of unsaturation. Each ester was found to give a single spot which corresponded to the proper degree of unsaturation. 2.5–7 mg samples were analyzed at 10 °C per minute in a DSC cell on a Model 900 Differential Thermal Analyzer manufactured by E. I. DuPont de Nemours, Wilmington, Delaware. These cholesteryl esters were also subjected to polarized microscopic examination to identify the mesophases. The transitions of the mesophases were exhibited both upon cooling

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TABLE 1 Cholesteryl Esters of C_{18} Aliphatic Acids, Temperatures and Heats of Transition†

Compound transition	Boston University		University of Massachusetts		
	Temp. (°C)	Cal/gm.	Temp. (°C)	Cal/gm.	% Purity estimate‡
Cholesteryl stearate (18:0)					
Crystal-isotropic	82.0	21.4	81.8	25.8	98.2
Isotropic-cholesteric	75.5	0.66	74.4	0.60	
Cholesteric-smectic	71.2	0.57	69.6	0.60	
Cholesteryl-oleate (18:1)					
Crystal-isotropic	50.5	8.6	50.0	11.2	98.8
Isotropic-cholesteric	47.5	0.25	46.4	0.18	
Cholesteric-smectic	42.0	0.56	41.8	0.37	
Cholesteryl linoleate (18:2)					
Crystal-isotropic	42.0	8.0	42.6	11.0	97.4
Isotropic-cholesteric	36.5	0.27	35.1	0.20	
Cholesteric-smectic	34.0	0.78	34.0	0.54	
Cholesteryl linolenate (18:3)					
Crystal-isotropic	35.5	6.2	34.8	‖	>95
Isotropic-cholesteric	29.0	1.1§	34.8	0.16	
Cholesteric-smectic	27.5	0.76	33.0	0.68	

† All mesophase transitions occurred only on cooling the sample from the melt or on reheating from the mesophase.

‡ Purity estimates are derived from the shape of the DSC curves.(6)

§ Estimated because of poor separation of the mesophase transitions.

‖ An endothermic followed by an exothermic change occurred prior to the transition which interfered with the calculation of transition heat.

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of the isotropic liquid and on reheating from the smectic mesophase (with the exception of cholesteryl stearate which recrystallized immediately below the cholesteric-smectic transition). Some of these data have been published elsewhere.(7) The results given here are an average value of several determinations. The reported crystal-isotropic liquid transitions are the values obtained on heating after premelting and cooling the sample to −40 °C. The mesophase transitions are the averages of the heating and cooling transitions.

The temperatures and heats of transition of the four cholesteryl esters of C_{18} aliphatic acids are presented in Table 1. Columns 1 and 2 are the results from the Boston University Medical Center. Columns 3 and 4 of Table 1 report the independent results from the University of Massachusetts for which an estimate of ester purity by the method given in Ref. (6) is also listed in Table 1, column 5. The esters are tabulated according to acid unsaturation starting with the totally saturated stearate and ending with the triply unsaturated linolenate. The trend of temperatures of transition for the cholesteryl esters of C_{18} aliphatic acids are plotted against the number of unsaturated bonds in Fig. 1. All of the esters exhibited three transitions: the crystal-isotropic liquid on heating, the isotropic liquid-cholesteric, and the cholesteric-smectic on cooling. The mesophases were thus monotropic. The specific mesophase types, identified optically, are analogous to mesophases observed for the saturated esters of cholesterol. Each transition type is connected by a dotted line in Fig. 1.

The general trend for each type of transition shows the temperature of transition decreasing with increasing unsaturation. This decline in temperature of transition is particularly sharp in going from zero to one unsaturation, amounting to about a 30 °C drop for the major and the two mesophase transitions. Comparison of the results from the two laboratories shows substantial agreement with the University of Massachusetts temperatures averaging 0.5 °C lower. Exceptions are the mesophase transitions of cholesteryl linolenate. The results from Boston University Medical Center indicate that the mesophase transitions of this ester are lower, 5.2 and 5.5 °C, and continue the downward trend of the transition temperature versus the degree of unsaturation plot (Fig. 1) in an almost linear manner. This may indicate the presence of some trans double bonds in the University

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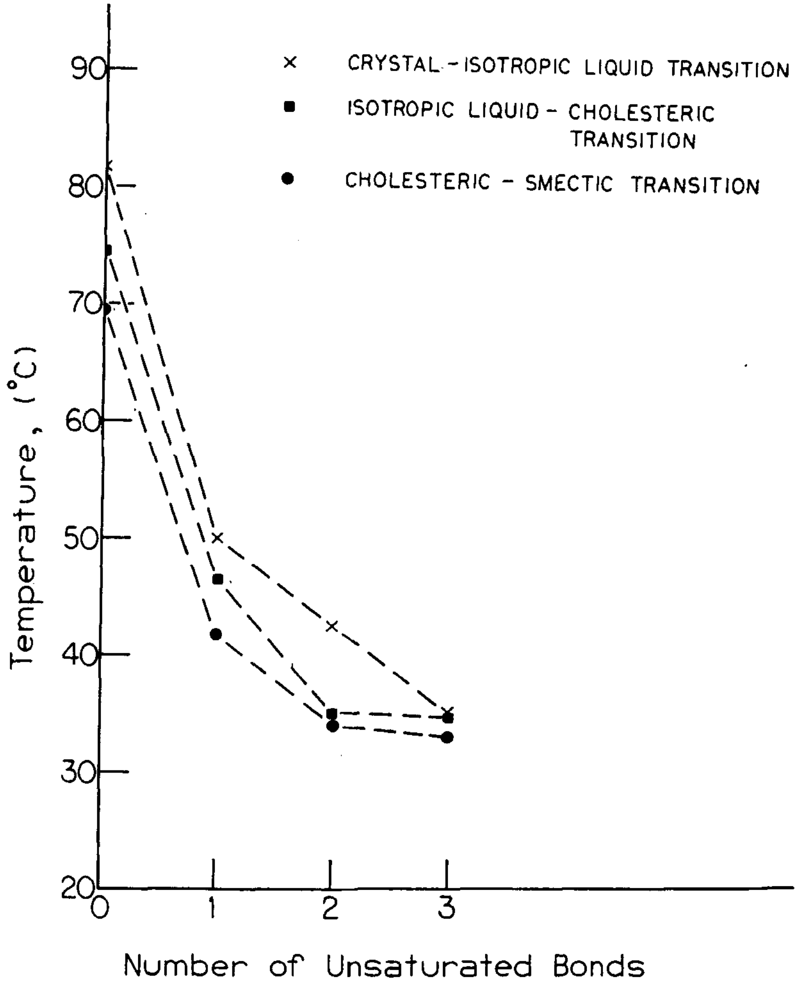

Figure 1. Temperature of transition vs unsaturation.

of Massachusetts sample, whereas the Boston University Medical Center sample may have contained only *cis* double bonds.

The heats of transition for these esters exhibit less regular behavior, see Table 1. The data may be subject to revision due to hypersensitivity of transition behavior to ester purity. The mesophase transition heats obtained in the two laboratories are in good accord, generally agreeing to 0.1 cal/gm. There is, however, a distinct difference between sets of values for the crystal-isotropic

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transition with the Boston University Medical Center results being generally about 20% lower. The three unsaturated esters studied at the University of Massachusetts all exhibit the same, within measurement precision, 0.18 ± 0.02 cal/gm heat for the isotropic liquid-cholesteric mesophase transition. Additional sets of transition temperatures and heats have been reported on only one of these compounds, the stearate ester.(1,2,8–10) A comparison among these four recent sets of transition temperatures indicates that the values reported here are all within the range of previous results. The average value found here, 82 °C, for the crystal-isotropic transition is in particularly good agreement with four previously reported values of 82–83 °C.(1,2,8–10) The transition entropies previously reported for the stearate are also in good accord with the data given here. Heretofore entropies in Kcal/mole have been given in the range of 46.5–47.5 for the crystal-isotropic transition, 1.19–1.26 for the smectic-cholesteric and 1.00–1.13 for the cholesteric-isotropic transition.(1,2,8–10)

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REFERENCES

1. Davis, G. J. and Porter, R. S., *Mol. Cryst. and Liq. Cryst.*, to be published.
2. Ennulat, R. D., *Mol. Cryst. and Liq. Cryst.* **8**, 247 (1969).
3. Smith, E. B., Evans, P. H. and Downham, M. D., *J. Atheroscler. Res.* **7**, 171 (1967).
4. *Chemical and Engineering News*, November 17, 1969, p. 39.
5. Davis, G. J. and Porter, R. S., *Mol. Cryst. and Liq. Cryst.*, **6** 377 (1970).
6. Davis, G. J. and Porter, R. S., *J. Thermal Analysis*, to be published.
7. Small, D. M., in *Surface Chemistry of Biological Systems*, Ed. Blank, M., Plenum Publishing Co., New York 1970, pp. 55–84.
8. Barrall, E. M., II, Porter, R. S., and Johnson, J. F., *J. Phys. Chem.* **71**, 224 and 895 (1967).
9. Sell, P. J. and Newmann, A. W., *Z. physik. Chem. Neue Folge* **65**, 13 (1969).
10. Gray, G. W., *J. Chem. Soc.* 3733 (1956).