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Calorimetric Study of Liquid Crystalline Behavior for some 9,19–Cyclopropane Tetracyclic Triterpene Palmitates†

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A calorimetric investigation has been made of the mesomorphic behavior for the palmitate esters for four tetracyclic triterpenes-pollinastanol, 31-norcycloartanol, cycloartanol, and cycloartenol. The transition temperatures and heats were determined by differential scanning calorimetry. All the palmitates exhibit liquid-crystalline behavior. Both a smectic and a cholesteric mesophase were found with pollinastanyl, 31-norcycloartanyl and cycloartanyl esters. In addition, a second smectic mesophase was observed for 31-norcycloartanyl palmitate. Only a cholesteric mesophase was found with cycloartenyl palmitate. This suggests a disruptive effect of the C-24(25) double bond in the side chain prohibiting the formation of the more ordered smectic mesophase. The enthalpy and entropy changes at mesophase transitions are generally higher than those found heretofore for cholesteryl fatty acid esters. Values approximately twice as high as for cholesteryl palmitate were found for monotropic mesophase transitions with pollinastanyl and cycloartenyl palmitates. Substantially higher values were found with two other palmitates, where the transformation from solid to isotropic liquid involves one or two enantiotropic mesophases. The decrease of the crystal melting entropy and the formation of highly-ordered mesophases suggest an important role played by the methyl groups at C-4.

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† Part XXX of a series on Order and Flow of Liquid Crystals.
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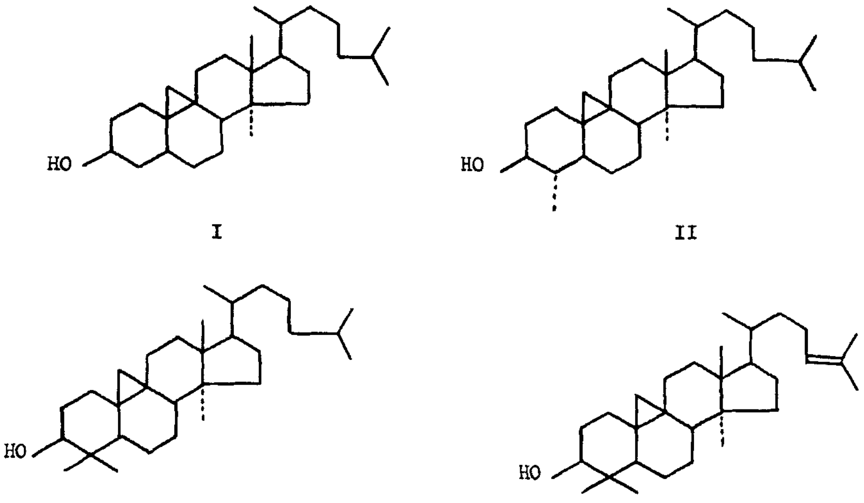
INTRODUCTION

Recent studies have established the mesomorphic properties for a number of new triterpene esters, largely even-carbon-number fatty acid esters of tetracyclic triterpenes.[1-7] These studies suggest that a critical role is played by the nucleus, fatty acyl residue and side chain in mesophase formation. Reported melting points and phase transition temperatures were determined on heating and on cooling using polarizing microscopy. No calorimetric studies on these esters have been reported heretofore.

Thermal analyses play an important role in characterization of mesomorphic substances and in the study of structure-property effects. The stepwise loss in molecular order at transition temperatures can be normally easily observed. The entropy data provide information on the magnitude of order changes associated with the transitions. The influence of various functional groups on mesomorphic properties can be revealed by comparison of data for corresponding members from selected homologous series.

Chosen for this calorimetric investigation were palmitate esters of four representative sterols possessing a 9,19-cyclopropane ring; pollinastanol, 31-norcycloaranol, cycloartanol, and cycloartenol. The structure of pollinastanol differs from that of cholesterol in containing no unsaturation, the presence of a 9,19-cyclopropane ring and a methyl group at C_{14}. Two



I

II

III

IV

FIGURE 1 Structural formulas of I, Pollinastanol; II, 31-Noncycloartanol; III, Cycloartanol; IV, Cycloartenol.

following triterpenes, 31-norcycloartanol and cycloartanol, represent mono- and di-methyl derivatives of pollinastanol with methyl groups at C_4. Cycloartenol has, in addition to two methyl groups at C_4, a double bond in the side chain at position C-24(25). The structures are shown in Figure 1.

The choice of palmitate esters represents a convenient way of studying the mesomorphic behavior at fixed fatty acid ester chain composition and by alternating the structure of the nucleus and side chain. Palmitic acid esters were chosen also due to the fact that they exhibit a well-defined cholesteric mesophase in other steroid esters.

The calorimetric investigations were conducted at the University of Massachusetts, Amherst. The esters were prepared and characterized by optical means at the St. Louis University School of Medicine.

MATERIALS AND METHODS

Pollinastanol and 31-norcycloartanol were isolated from the pollen of *taraxacum dens leonis* and purified and characterized as described elsewhere.[2,7] Cycloartenol and cycloartanol were also isolated from the same source. They were separated from 31-norcycloartanol and pollinastanol by thin layer and column chromatography as described previously.[2,7] Cycloartenol and cycloartanol cochromatographed. Due to the presence in cycloartenol of a double bond in the side chain at position 24, separation of cycloartenol from cycloartanol was affected by argentation chromatography of their acetates. The acetate of the mixture was prepared and chromatographed on a neutral alumina column impregnated with 12% $AgNO_3$. Elution was carried out using petroleum ether-benzene mixtures. Cycloartanyl acetate was first eluted with the ratio 7:3 of the solvent mixture and when no more residue was eluted the ratio was changed to 3:7. Cycloartenyl acetate was eluted with the latter mixture.

Pure cycloartanyl acetate

Cycloartanyl acetate obtained from the column still contained traces of cycloartenyl acetate. Hydrogenation using platinum oxide was performed to reduce any cycloartenyl acetate to cycloartanyl acetate. The compound thus obtained had a purity of over 99.5% and was characterized by GLC-MS and by direct comparison with a hydrogenated sample of cycloartenol obtained from a previous experiment from the seeds *strychnos nux-vomica.*[1] Free cycloartanol was obtained by saponification of its acetate.

Pure cycloartenyl acetate

The crude cycloartenyl acetate obtained from a $AgNO_3$ chromatographic column was crystallized several times from methanol until the purity rose to approximately 98%. Free cycloartenol was prepared by saponification of the acetate and subsequently purified by crystallization from ethyl acetate. The purified cycloartenol was identical with an authentic sample of cycloartenol previously obtained from the seeds of *strychnos nux-vomica.*[1]

The palmitate of each of the triterpenes was prepared according to the method previously adopted.[2,7]

EXPERIMENTAL

The first experiments were carried out on a DSC-1B; the final results were obtained using a DSC-2, both instruments manufactured by Perkin-Elmer, Norwalk, Connecticut. Recorder Model 56 was used for thermogram registration.

The DSC-1B was calibrated using the known transition temperatures and heats for high-purity indium, benzoic acid, naphthalene, and p-nitrotoluene. Transition heats were determined by measuring the areas under transition peaks with a planimeter (Gellman Instruments, Germany). The chart area was calibrated in calories per unit using the standard samples.

The DSC-2 was similarly calibrated with lead, tin, indium, naphthalene and p-nitrotoluene. It has a highly-improved linearity in temperature programming. The average calibrated correction from 0-150° C is only 0.1-0.2° C. The lower noise level, improved base line linearity and reproducibility of the DSC-2 allows the use of higher sensitivities. The quantity available for some of the esters was only 2-4 mgs requiring the higher sensitivities.

The transition temperatures and heats represent an average of at least three determinations. The mesophase transitions were determined both on cooling from the isotropic liquid and on reheating from a mesophase.

The melting points were obtained by correcting the peak maxima temperatures for thermal lag using the slope of the leading edge for an indium sample heated at the same rate and sensitivity. Temperatures are uncorrected peak temperatures obtained at high sensitivity and at slow scanning rate. The correction is negligible and within the precision of determination.

The enthalpy and entropy changes for individual transitions are listed in Table I. All indications are that the samples were stable during the tests. Insufficient material was available, however, for analysis after testing.

TABLE I

Transition temperatures and calorimetry

Palmitate ester transition	Temp. °C	ΔH cal/g	ΔH kcal/mol	ΔS cal/mol/°K	ΔH Total kcal/mol	ΔS Total cal/mol/°K
Pollinastanyl					13.80	41.59
Solid-Isotropic	58.7	21.6	13.80	41.59		
Smectic-Cholesteric	44.4	0.89	0.57	1.79		
Cholesteric-Isotropic	50.3	0.75	0.48	1.48		
31-Norcycloartanyl					14.69	43.02
Solid-Cholesteric	67.7	16.05	10.48	30.75		
Cholesteric-Isotropic	70.2	6.45	4.21	12.27		
Smectic-Cholesteric	62.2	3.25	2.12	6.33		
Smectic-Smectic	55.5	1.65	1.08	3.28		
Cycloartanyl					13.85	41.85
Solid-Smectic	53.2	12.5	8.33	25.55		
Smectic-Cholesteric	61.5	3.42	2.28	6.82		
Cholesteric-Isotropic	68.9	4.86	3.24	9.48		
Cycloartenyl					14.32	43.66
Solid-Isotropic	54.8	21.53	14.32	43.66		
Cholesteric-Isotropic	44.6	0.72	0.48	1.51		

The temperatures and heats of the solid-isotropic liquid or of the solid-mesophase transition are given for the highest melting polymorph. All listed transition temperatures are those determined on heating the solid or on reheating from a mesophase in the case of monotropic behavior. ΔH(Total)[ΔS(Total)] represents the enthalpy (entropy) change for the total solid-isotropic liquid transformation.

INDIVIDUAL ESTERS

Pollinastanyl palmitate

Only a single transition, a solid-isotropic conversion at 58.7° C, was found on heating a sample prepared by crystallization from acetone (see Figure 2a). On cooling the isotropic liquid, two mesophase transitions were observed before massive crystallization took place at 23° C (Figure 2b). Figures 2c and 2d illustrate cooling of the isotropic liquid until mesophases were observed and subsequent reheating from mesophases to isotropic liquid on the DSC-2 at 5°/min cooling and heating rate and high sensitivity. Supercooling of mesophase transitions decreased at lower cooling rates and only approximately 1.5° C for both transitions was found at a cooling rate of 0.6°/min.

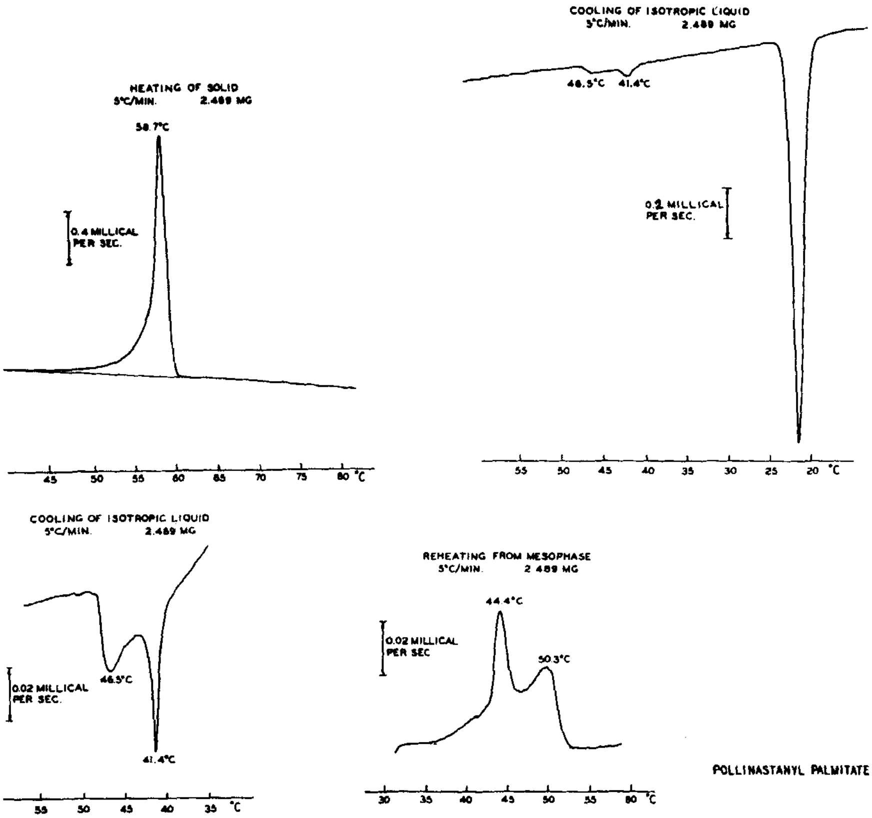


FIGURE 2 Transitions for pollinastanyl palmitate.

31-Norcycloartanyl palmitate

Two crystal modifications have been observed as well as liquid crystalline behavior. Results on heating depended on thermal history. The stable modification melted at 67.7° C to the cholesteric mesophase which immediately converted to the isotropic liquid. The cholesteric-isotropic transition was noted as only a shoulder on the tail of the melting endotherm (see Figure 3a).

Complicated behavior was found on cooling the isotropic liquid and on subsequent reheating from the mesophase. On cooling from 80° C, one large exotherm was observed followed by an overlapping, very small one, before the massive crystallization took place at approximately 30° C. The first change on cooling, indicated by a deflection of the DSC trace at 68° C, gives a peak at 62.2° C and a small exotherm at 55.5° C. When cooling was termin-

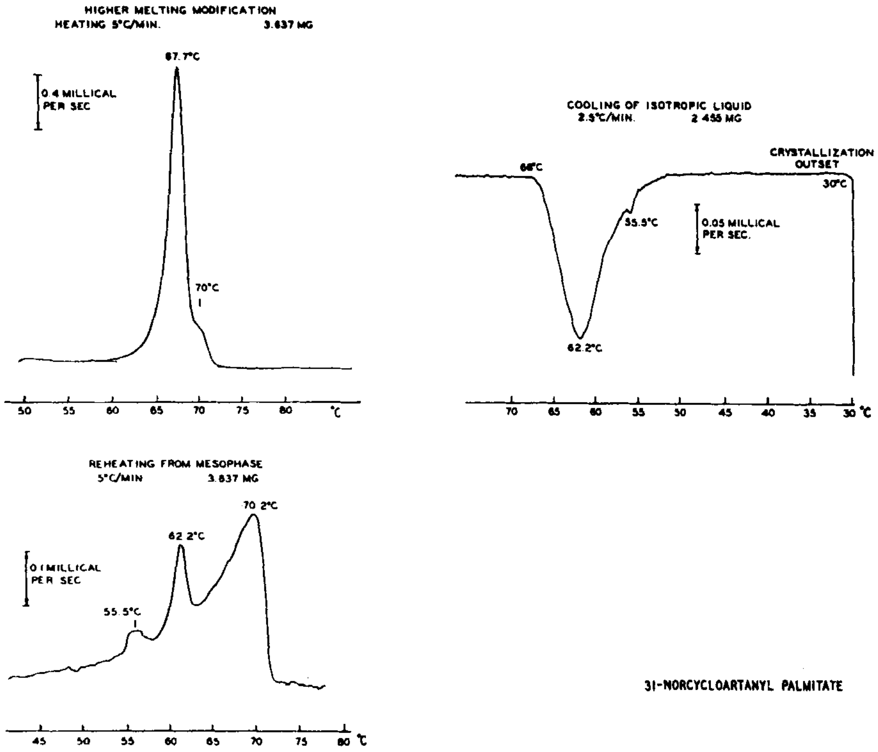


FIGURE 3 Transitions for 31-norcycloartanyl palmitate.

ated before crystallization, for example at 40° C, the sample reheated from mesophase, three peak maxima appeared at 55.5, 62.2 and 70.2° C.

Figures 3b and 3c are DSC traces obtained on cooling and reheating. They suggest that this ester forms two smectic and one cholesteric mesophase. The changes occur over broad temperature ranges. The total enthalpy change for all three transitions on heating, 11.35 cal/g, equals the two peaks on cooling. Thus the isotropic-cholesteric transition supercools and the transition with peak at 62.2° C represents the combined isotropic-cholesteric and cholesteric-smectic transition. No separation was achieved at a lower cooling rate of 0.6°/min.

The transition characteristics are given in Table I. They are higher for the smectic-cholesteric and cholesteric-isotropic transitions than for the corresponding cholesteryl fatty acid ester[8–12] or for pollinastanyl and cycloartenyl palmitates from this series. Such transition heats are comparable to fusion heats and yield questionable phase identification. Additional studies by polarizing microscopy are necessary.

Crystallization from acetone produced only a lower melting modification which was stable at ambient. No transformation to the higher melting form was observed. A sharp melting was found at 61° C followed by a broad one with a peak at 71° C (Figure 4a). The shape is typical for melting of two component systems.[13–17] This suggests the presence of a higher melting substance and continuous melting up to near 75° C.

This ester was found to be of high purity (99%). However, some decomposition or other changes might take place prior to study. Melting of both solid polymorphs was, therefore, also examined with a polarizing microscope with a Mettler hot stage. No evidence was found for melting of a second compound and no solid was observed on reheating from the mesophase. Above 76° C, only the isotropic liquid is observed. No supercooling of mesophase transitions was found on cooling. The cholesteric mesophase appeared at 76-75° C and the smectic at 66-65° C. The smectic-smectic transition was not confirmed by polarizing microscopy. The transition

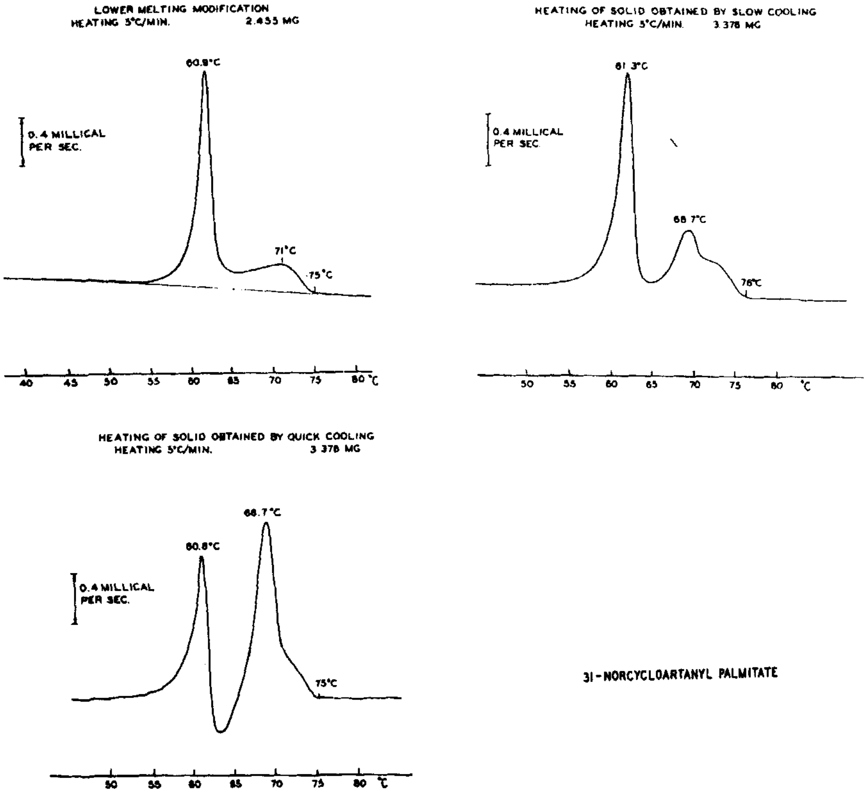


FIGURE 4 Transitions for 31-norcycloartanyl palmitate.

temperatures on heating and the appearance of both mesophases on cooling agrees with previous results by optical means, see Table II. Liquid crystals can nucleate and orient at glass surfaces and therefore between glass plates could perform differently than in a DSC cell. The difference might also be due to the slow rate of phase conversion. The DSC peak maxima represent temperatures for higher transformation rates, whereas temperatures found by optical methods correspond to the disappearance of the last traces. In this respect indications of the beginning and the end of transformations in the DSC traces are in good agreement with temperatures established by microscopic observations.

Crystallization from melt results in a mixture of both modifications. Their relative amounts varies with cooling rate and thermal history. Figure 4b illustrates immediate reheating after cooling at 0.6°/min to 0° C. Both endotherms are distinct and followed by a shoulder for the cholesteric-isotropic transition. The lower melting form converts to the cholesteric mesophase which is unstable in the presence of the higher melting form.

TABLE II

Transition temperatures transition temperatures (°C)

	University of Massachusetts			St. Louis University	
	DSC-2	Microscopy		Microscopy	
Palmitate ester transition	Heating	Heating	Cooling	Heating	Cooling
Pollinastanyl				(7)	
Solid-Isotropic	58.7	—	—	59–60	—
Smectic-Cholesteric	44.4	—	—	—	48
Cholesteric-Isotropic	50.3	—	—	—	49
31-Norcycloartanyl				(2)	
Solid-Cholesteric[a]	60.9	61	—	62	—
Solid-Cholesteric[b]	67.7	68	—	—	—
Cholesteric-Isotropic	70.2	76	76–75	75	78
Smectic-Cholesteric	62.2	64–65	66–65	65	68
Smectic-Smectic	55.5	—	—	—	—
Smectic-Solid	—	—	—	—	27
Cycloartanyl				(5)	
Solid-Cholesteric	—	—	—	52	—
Solid-Smectic	53.2	53.5	—	—	—
Smectic-Cholesteric	61.5	63–64	63	—	—
Cholesteric-Isotropic	68.9	71–72	71	—	72
Cycloartenyl				(1,5)	
Solid-Isotropic	54.8	—	—	54–55	—
Cholesteric-Isotropic	44.6	—	—	52.5	53

[a] Lower melting crystal modification.

[b] Higher melting crystal modification.

Accordingly, spontaneous crystallization ensues accompanied by an exothermic evolution of heat. The extent of this transformation depends on the amount of the higher form present. This was evident on heating the solid after quick cooling or prolonged standing at ambient temperature resulting in a larger amount of the higher form (Figure 4c). The solid produced by a quick cooling and a few days standing at ambient temperature melted only as the higher modification.

The higher melting form would be expected to appear on slow cooling. It is not clear how far this effect is due to impurities or only due to different nucleation rates for the polymorphs. When solid is formed from the melt, some amount of higher modification is always present.

Cycloartanyl palmitate

Three transitions occur on heating (see Figure 5a). They are the solid-smectic and two smaller endotherms, a smectic-cholesteric and a cholesteric-

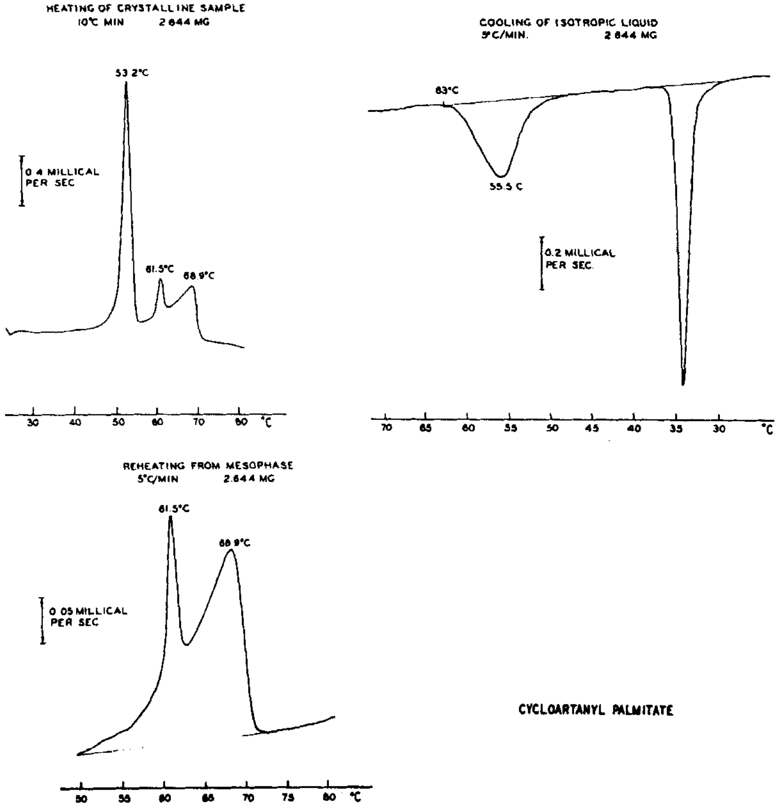


FIGURE 5 Transitions for cycloartanyl palmitate.

isotropic transition. On cooling the isotropic liquid from 90° C, only one exotherm was observed before solidification took place at 34° C (Figure 5b). From the transition heat, this exotherm corresponds to the combined isotropic-cholesteric and cholesteric-smectic transition. This is similar to results on 31-norcycloartanyl palmitate. If the first change on cooling, at 63° C, in Figure 5b is taken as the beginning of the isotropic-cholesteric transition and the peak maximum temperature for the cholesteric-smectic transition temperature, the supercooling is 6° C for each transition for cooling at 5°/min. This is 4.4-5° C for 31-norcycloartanyl palmitate for the same conditions. On cooling at 0.6° C/min, no supercooling was noticed for the cholesteric-smectic transition. The beginning of the combined transition, however, remained unchanged at 63° C.

Microscopy was consistent with high sample purity. Transition temperatures are given in Table II. The optical observations showed a difference on cooling between slide-and-cover and in the DSC. Each mesophase was seen at about 2° higher than temperatures for the maxima in thermograms. A smectic mesophase was found by both optical and calorimetric methods. The same solid is formed from melt or solution.

Cycloartenyl palmitate

This ester exhibits polymorphism in the solid state as well as liquid crystalline behavior. It can be crystallized in two or three different crystal modifications with melting points 39, 51-52, and 54.8° C.

Samples crystallized from acetone or methanol-ether provided the highest melting form.

Only the cholesteric mesophase was observed on cooling the isotropic liquid (Figure 6). Supercooling of the transition is 0.5° C for cooling at a rate of 5°/min. The cholesteric mesophase is stable upon further cooling to near 36-37° C where sharp crystallization occurs.

Changes dependent on thermal history are observed upon reheating. The lower melting forms can be obtained by quick cooling. They are unstable and transform spontaneously into the stable modification. After three weeks at ambient temperature, only the highest melting form was observed.

Only a cholesteric mesophase was found in our separate study at St. Louis University (Table II). The isotropic-cholesteric transition temperature, 51° C, is substantially higher. This suggests, in accordance with results for 31-norcycloartanyl and cycloartanyl palmitates, that the cholesteric mesophase forms again on cooling between slide and cover at higher temperatures than that found with DSC.

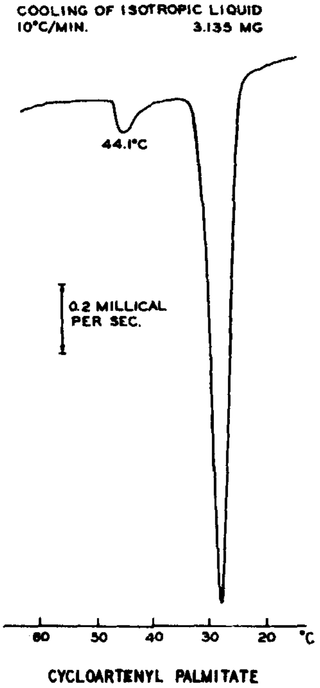


FIGURE 6 Transitions for cycloartenyl palmitate.

DISCUSSION

All palmitates investigated exhibit liquid-crystalline behavior. Both smectic and cholesteric mesophases were found with the pollinastanyl ester and with its mono- and di-methyl derivatives (on carbon 4 in ring A) of 31-nor-cycloartanyl and cycloartanyl palmitates. In addition, a smectic-smectic transition was observed with 31-norcycloartanyl palmitate. Only a cholesteric mesophase was found with cycloartenyl palmitate. This suggests a disruptive effect of the C-24(25) double bond in the side chain prohibiting the formation of the more ordered smectic mesophase but still permitting the organization of molecules in the cholesteric mesophase.

It is known that mesophase formation is dependent upon critical structural requirements and that small structural changes can cause major differences in mesomorphic behavior. In this respect the alteration of the configuration of the side chain can destroy the ability of a given ester to form mesophases. The importance of a double bond in different positions has been shown in several studies.[1–7,18]

The entropy changes for the total solid-isotropic transitions are similar and ie in the range 41.6–43.8 cal/mol/°K. The corresponding value for cholesteryl palmitate is 40.0–42.9 cal/mol/°K.[10,11,19–22] It shows that the presence or absence of the nuclear double bond at C-5, 9,19-cyclopropane ring, or methyl substituents at C-4 or C-14, as well as the double bond in position C-24(25) does not have a larger effect on the total order. The way in which the total order change is realized, however, is strongly dependent on structure.

Both mesophases for the pollinastanyl ester are monotropic. The entropy changes for the smectic-cholesteric and cholesteric-isotropic transitions, 1.79 and 1.48 cal/mol/°K, are almost twice as high as 1.04–1.32 and 0.78–0.89 cal/mol/°K for cholesteryl palmitate.[10,11,19–21]

Substantially higher enthalpy and entropy changes for mesophase transitions were found for mono- and di-substituted pollinastanyl palmitate where the transformation from solid to isotropic liquid involves one or two enantiotropic mesophases. For the former, the entropy change for the cholesteric-isotropic liquid transition is 28.5% of the solid-isotropic liquid transition entropy. When both monotropic transitions are considered, this value reaches 51%. For the latter ester, this represents 22.8% for the cholesteric-isotropic transition and 38.9% for both mesophase transitions. In both esters the entropy for the cholesteric-isotropic transition is larger than for the smectic-cholesteric transformation.

This suggests the important role of the methyl groups at C-4. The decrease of the crystal melting entropy and the formation of highly-ordered mesophases indicate a marked change in the geometrical arrangement and density packing in the solid state. When both methyl groups at C-4 double bond C-24(25) are present, the solid melts directly to isotropic liquid and only a cholesteric mesophase is formed on cooling.

The entropy changes connected with mesophase transitions are unusually high as compared with cholesteryl fatty acid esters. Some general conclusions concerning the magnitudes of the transition enthalpies and entropies for phase changes have been drawn in recent reviews of liquid crystal thermodynamics.[23–25] The solid-mesophase transition enthalpy is usually an order of magnitude larger than the enthalpy changes connected with loss of order at all mesophase transitions. The smallest enthalpy changes are usually for the transformation of the nematic or the cholesteric mesophase to the isotropic liquid.

However, exceptions have been observed. The entropy changes for the smectic-isotropic transition for 4-methyloxy,4′-dodecyloxy-trans-stilbene accounts for 38% of the total entropy change.[26] The sum of mesophase transition entropies represents 31.6% of the total change for n-amyl dodecyloxybenzylidenaminocinnamate. The smectic-isotropic transition entropy in 4,4′-di-n-dodecyloxyazoxybenzene accounts for 20% of the solid-isotropic liquid transition entropy.[27,28] With bis(4′-n-octyloxybenzal)-1,4-phenylenediamine the entropy change for five smectic and a nematic mesophase was found to represent 48% of the total transformation entropy.[29]

There has not been previously reported, however, such a high percentage for the nematic or exclusively the cholesteric mesophase. In addition, for 31-norcycloartanyl and cycloartanyl palmitates the transition entropies are higher for the cholesteric-isotropic transition than for the smectic cholesteric. In this case, the cholesteric mesophase more resembles a smectic mesophase[20] than a nematic.[24]

From Figures 2-5, and in accordance with microscopy, prominent pre- and post-transitional effects are evident in specific heats. The mesophase transitions are broader than melting transitions.

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