Nonequilibrium Transitions in Thermotropic Phases of Eicosenoic Acid Methyl Esters

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ABSTRACT: Methyl esters of *cis*-5-eicosenoic (5-EAME) and *cis*-11-eicosenoic (11-EAME) acids from the seed oil of *Limnanthes alba* (Meadowfoam) exhibit a degree of thermotropic polymorphism unobserved with shorter and longer chainlength monoenoic methyl esters. 5-EAME freezes at 264 K and melts at 266 K if cooled no lower than 215 K. 11-EAME freezes at 239 K and melts at 255 K if cooled at no lower than 240 K. Solids cooled to lower temperatures undergo phase transformation to higher-melting polymorphs (274 K, 5-EAME; 262 K, 11-EAME), and samples often exhibit double melting endotherms. Quantities of each high-melting phase vary with time at temperatures below characteristic initiation temperatures. Highly temperature-sensitive phase conversions suggest low temperature nucleation, followed by crystal growth and conversion, as reheating allows molecular motion. Once formed, both high-melting phases melt with essentially the same melting entropy. Thermodynamic and kinetic analyses imply that differences exhibited by the isomeric esters derive from aliphatic configuration distal to the double bond.
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The physical properties of aliphatic materials generally change gradually with chainlength, but relatively abrupt transitions at or near specific chainlengths are not uncommon. Unbranched alkanes thus adopt different crystal forms if their chainlengths are above or below C_{22-26} (1). With single-acid saturated triglycerides, α-phase excitation apparently occurs *via* different mechanisms if the acid chainlength is greater or less than C_{14} (2). Such polymorphic behavior, presumably due to change in stabilizing contributions from molecular conformations or intra- and intermolecular interactions, can determine form and physical properties in lipid-rich macromolecular networks as those that occur, for example, in formulated foods or in membranes of living organisms. In plants, polymorphism affects organization and differentiation processes and provides means for environmental adaptation. Often, such critical properties are associated with the presence of unsaturated or mixed lipids. Yet, knowledge of how lipid interactions regulate polymorphic behavior remains largely descriptive, even though new technology and systematic studies have begun to develop fresh insight (3–7).

Investigating the thermal properties of unusual fatty materials, we find that methyl esters of eicosenoic acids from *Limnanthes alba* (Meadowfoam), a new oilseed crop for the Pacific Northwest, exhibit a degree of thermotropic polymorphism unobserved with shorter and longer chainlength monoenoic methyl esters. The behavior of these esters emphasizes the importance of structure, double bond position, kinetic effects, and thermal conditions in achieving and maintaining selected physical properties with lipid-rich materials. Novel properties that the Meadowfoam acids can impart may prove advantageous to further investigation of factors that regulate the behavior of unsaturated lipids.

MATERIALS AND METHODS

Methyl *cis*-5-eicosenoate (5-EAME) and methyl *cis*-11-eicosenoate (11-EAME) were prepared from seed oil of *Limnanthes alba* (8) and purified by Nu-Chek-Prep (Elysian, MN). Each ester was 99+% pure. Samples, about 3 mg, were analyzed in a Perkin-Elmer (Norwalk, CT) computer-controlled DSC-2 differential scanning calorimeter in covered and crimped aluminum pans under helium with an empty covered pan as reference. Helium flow rate was 20 mL/min, and liquid nitrogen provided cooling. Cooling and heating thermograms were secured at various scan rates; e.g., 40, 10, 5, 2.5 and 0.62 K/min, but generally samples cooled at 10 K/min to selected temperatures were also reheated at 10 K/min. Heat transfers were recorded and integrated electronically.

RESULTS

Polymorphism. The distinct thermal behavior of the methyl esters from Meadowfoam acids was first noted when 5-EAME and other monoenoic acid esters, including methyl *cis*-9-octadecenoate (9-EAME) and methyl *cis*-13-docosenoate (13-EAME), were frozen and melted at different rates. Freezing thermograms for the monoenoic acid esters (Table 1) exhibited some drift of freezing point and ΔH with scan rate, but were highly consistent in terms of the number and shape of transitions regardless of cooling rate. Similarly, 9-EAME and 13-EAME showed little or no variation in their melting endotherms when reheated from 100 K over a range of scan rates from 0.62 to 40 degree/min even though both underwent minor solid-phase transitions before melting sharply. In marked contrast, remelting 5-EAME from 100 K produced thermograms in

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TABLE 1
Freezing Transitions of Monoenoic Acid Methyl Esters[a]

	Liquid → Solid			Solid → Solid		
Cooling rate (degree/min)	$-T_f$ K	ΔH_f kJ/mol; kcal/mol	ΔS_f J/mol K (cal/mol K)	T_t K	ΔH_t kJ/mol; kcal/mol	ΔS_t J/mol K (cal/mol K)
Methyl *cis*-9-Octadecenoate						
0.62	229	−40.7 (−9.7)	−177.8 (−42.5)			
2.5	227	−39.4 (−9.4)	−173.8 (−41.5)			
10	224	−36.7 (−8.8)	−163.8 (−39.1)			
Methyl *cis*-5-Eicosenoate						
2.5	265	−29.2 (−7.0)	−110.1 (−26.3)	253	−1.3 (−0.3)	−5.0 (−1.2)
				222	−2.1 (−0.5)	−9.2 (−2.2)
10	264	−30.6 (−7.3)	−116.1 (−27.7)	252	−0.6 (−0.2)	−2.6 (−0.6)
				222	−1.3 (−0.3)	−5.9 (−1.4)
				161	tr	
Methyl *cis*-11-Eicosenoate						
10	239	−48.9 (−11.7)	−204.6 (−48.9)			
Methyl *cis*-13-Docosenoate						
10	259	−54.8 (−13.1)	−211.5 (−50.5)	249	−1.9 (−0.4)	−7.4 (−1.8)
				240	−1.2 (−0.3)	−5.0 (−1.2)

[a] Cooled to 100 K; T_f, freezing temperature; T_t, transition temperature; ΔH_f, transition enthalpy; ΔS_t, transition entropy.

which the presence of a high-melting endotherm and a change in melting enthalpy both depended on cooling or heating rate. When heated rapidly (40 degree/min), the sample melted entirely at a lower temperature than when heated slowly (*ca.* 1 degree/min). Intermediate rates produced scans with two endotherms. 11-EAME behaved similarly. Table 2 gives data on samples reheated at 10 degree/min.

The novel quality of 5-EAME and 11-EAME polymorphism was more obvious when samples were reheated from progressively lower temperatures. Figure 1 records results obtained with 5-EAME; Figure 2, those with 11-EAME. Briefly, 5-EAME cooled to 215 K or above and 11-EAME cooled to 240 K or above exhibited single principal melting endotherms. Samples cooled to lower temperatures, however, exhibited additional principal endotherms and penultimate exotherms that changed with the appearance and increased presence of higher-melting forms. Scans from 185 and 205 K, especially, exemplify exothermic shifts that accompanied the changes in final endotherms (Fig. 1). These changes in samples that had experienced lower temperatures presumably result from delayed crystallization of 5-EAME and 11-EAME into their respective most stable forms. Comparison of heats of fusion and kinetic analyses (discussed later) are not inconsistent with this presumption.

Thermodynamics. As with the unusual thermograms exhibited by 5-EAME (Fig. 1) and 11-EAME (Fig. 2), comparisons of freezing and melting enthalpies for 5-EAME (Tables 1 and 3) and 11-EAME (Tables 1 and 4) also revealed the different thermotropisms in samples of 5-EAME frozen at 220 K and above or in 11-EAME frozen at 240 K and above. These materials melted with enthalpies that duplicated their corresponding principal freezing enthalpies—for 5-EAME, 30 kJ/mol (7 kcal/mol) melting vs. 30 kJ/mol (7 kcal/mol) freezing, for 11-EAME, 50 kJ/mol (12 kcal/mol) melting vs. 49 kJ/mol (12 kcal/mol) freezing.

Esters that experienced lower temperatures, however, melted with higher enthalpies that increased along with the appearance of higher-melting forms and additional energy absorption or loss during solid–solid transformations and further crystal organization. The highest values were obtained with esters that had converted entirely to their higher-melting forms: 5-EAME melted (274 K) with ΔH_m = 61.2 kJ/mol (14.6 kcal/mol); 11-EAME (262 K), 59.7 kJ/mol (14.3 kcal/mol). Complete melting of both compounds involved essentially the same entropic change; i.e., *ca.* 225 J/mol K (54 cal/mol K), which implies that both esters undergo the same type of intramolecular disruption upon melting in spite of the entropic differences that they exhibit upon freezing.

TABLE 2
Melting Transitions of Methyl *cis*-9-Octadecenoate (9-EAME) and Methyl *cis*-13-Docosenoate (13-EAME)[a]

Initial Temperature K	Solid → Solid $-T_t$ K	Solid → Solid ΔH_t kJ/mol; kcal/mol	Solid → Solid ΔS_t J/mol K (cal/mol K)	Solid → Liquid T_m K	Solid → Liquid ΔH_m kJ/mol; kcal/mol	Solid → Liquid ΔS_m J/mol K (cal/mol K)
9-EAME						
100	227	1.3 (0.3)	6.3 (1.5)			
	232	–5.0 (–1.2)	–22.2 (–5.3)	249	51.1 (12.2)	204.7 (48.9)
100[b]				249	49.7 (11.9)	199.7 (47.7)
13-EAME						
100	246	3.3 (0.8)	13.6 (3.2)			
	260	0.2 (0.1)	0.8 (0.2)	270	55.9 (13.4)	207.2 (49.5)
100[c]	260	trace	trace	21	54.7 (13.1)	201.3 (48.1)

[a] Cooled and heated at 10 K/min; T_t, transition temperature; T_m, melting temperature; H_m, melting enthalpy; S_m, melting entropy. See Table 1 for other abbreviations.
[b] Tempered at 240 K for 20 min during heating.
[c] Tempered at 255 K for 30 min during heating.

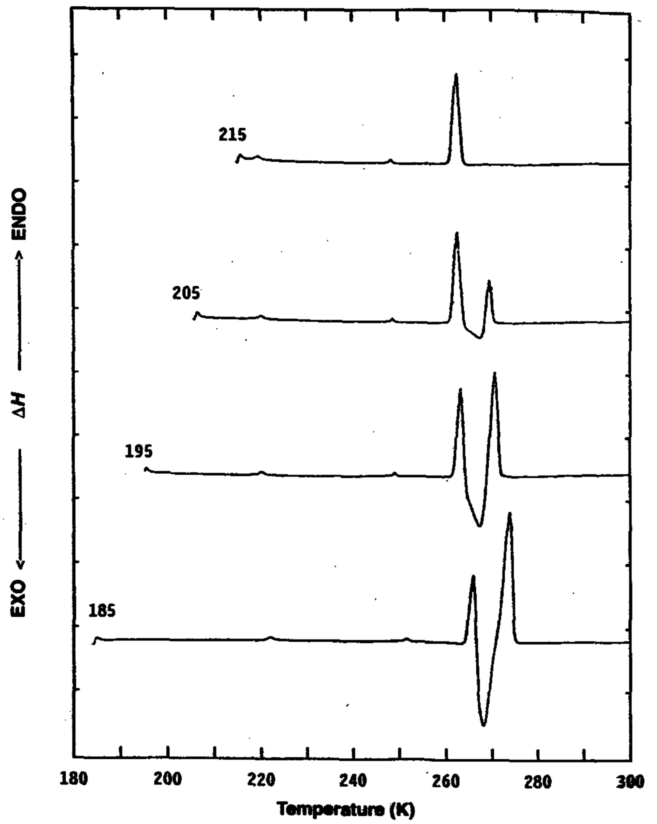

FIG. 1. Effect of cooling on thermal behavior of methyl *cis*-5-eicosenoate. Sample reheated at 10 K/min after cooling at 10 K/min to indicated temperature.

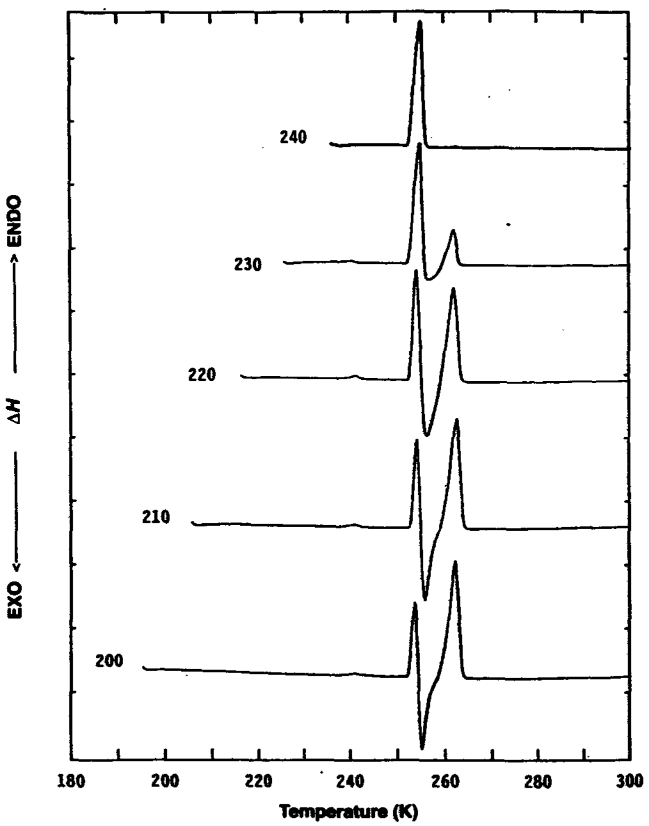

FIG. 2. Effect of cooling on thermal behavior of methyl *cis*-11-eicosenoate. Conditions as in Figure 1.

TABLE 3
Effect of Cooling on Methyl *cis*-5-Eicosenoate (5-EAME) Transitions[a]

	Sold → Solid[b]			Solid → Liquid		
Lowest Temperature K	$-T_t$ K	ΔH_t kJ/mol; kcal/mol	ΔS_t J/mol K (cal/mol K)	T_m K	ΔH_m kJ/mol; kcal/mol	ΔS_m J/mol K (cal/mol K)
220				266	29.7	111.8
					(7.1)	(26.7)
210	262	29.7	113.4			
		(7.1	(27.1)			
	267	–1.7	–6.3	269	1.3	4.6
		(–0.4)	(–1.5)		(0.3)	(1.1)
200	264	27.2	103.0			
		(6.5)	(24.6)			
	269	–17.2	–63.6	273	19.3	70.3
		(–4.1)	(-15.2)			
					(4.6)	(16.8)
190	266	20.1	75.8			
		(4.8)	(18.1)			
	268	–41.0	–152.8	274	53.6	195.5
		(–9.8)	(–36.5)			
					(12.8)	(46.7)
180	266	18.0	67.8			
		(4.3)	(16.2)			
	268	–41.4	–154.4	274	55.7	203.4
		(–9.9)	(–36.9)			
					(13.3)	(48.6)
100	267	17.2	64.0			
		(4.1)	(15.3)			
	268	–23.9	–89.6	275	59.9	218.1
		(–5.7)	(–21.4)		(14.3)	(52.1)

[a] Cooled and heated at 10 K/min. See Tables 1 and 2 for other abbreviations.
[b] Samples also exhibited minor endotherms (*ca.* 0.4 kJ/mol) near 220 and 250 K.

Freezing (Table 1) leaves 5-EAME more disordered than 11-EAME by *ca.* 90 J/mol K (22 cal/mol K). If freezing involved only quenching of intramolecular rotation, the entropic difference between 5-EAME and 11-EAME would amount to 10 rotational centers, i.e., 11 carbons (2). Accordingly, it is tempting to conjecture that freezing at 264 K leaves much of the 14-carbon chain distal to the double bond in 5-EAME trapped in configurations that are energetically disfavored below 220 K. Alternatively, of course, the same behavior would be realized if about 40% of the molecules remained completely disordered among a population ordered like 11-EAME.

Once initiated by exposure to lower temperatures, and with adequate subsequent excitation, the disordered crystal structure of 5-EAME apparently converts to essentially the same kind of structure that 11-EAME adopts more readily. In samples cooled to 100 K, conversion of 11-EAME to the highest-melting form requires less endergonic and exergonic change than does the conversion of 5-EAME (Tables 3 and 4). This conversion also occurs at a lower temperature with 11-EAME (256 K) than with 5-EAME (268 K). In each case, the solid–solid transformation to a higher-melting form is predetermined by events at much lower temperatures, and once the conversion is initiated, transformation of essentially the entire molecular population follows.

The 10 K difference between melting points for the isomeric esters can likely be attributed to variation in intermolecular order allowed by differences in double bond location. It is analogous to the melting point difference that Hagemann *et al.* (9) observed with single-acid triglycerides of the Δ5 and Δ11 isomers of octadecenoic acid.

Phase initiation and development. The appearance and growth of higher-temperature melting endotherms as samples are cooled to lower temperatures (Figs. 1 and 2) suggests initiation of high-melting phases at critical temperatures during cooling. Tempering experiments (Table 5) reinforce this conviction, and indicate that the initiation temperatures for 5-EAME and 11-EAME lie well below their principal freezing exotherms at 264 and 239 K, respectively. As ΔH_m data in Table 5 show, a 10-degree decrease in temperature produces a 20- to 30-fold increase in formation of the higher-melting forms in samples tempered for 30 min. For 5-EAME, this increase occurred between 220 and 210 K, for 11-EAME, between 240 and 230 K. These temperatures help define the composition of freshly formed solids.

Even more useful is knowledge of rates at which such solids transform with further cooling. Accordingly, optimum melting enthalpies for 5-EAME and 11-EAME were used to calculate for each ester and each temperature a rate constant-time product, $k_t t$, from $k_t t = \ln[a/(a - x)]$, where $a = 1$ and $x =$

TABLE 4
Effect of Cooling on Methyl *cis*-11-Eicosenoate (11-EAME) Transitions[a]

Lowest Temperature K	Sold → Solid[b] $-T_t$ $-T_t$ K	ΔH_t kJ/mol; kcal/mol	ΔS_t J/mol K (cal/mol K)	Solid → Liquid T_m K	ΔH_m kJ/mol; kcal/mol	ΔS_m J/mol K (cal/mol K)
240				255	49.8 (11.9)	195.5 (46.7)
230	255	43.9 (10.5)	172.4 (41.2)			
	257	-7.1 (-1.7)	-27.6 (-6.6)	262	13.4 (3.2)	51.1 (12.2)
220	254	32.2 (7.7)	126.8 (30.3)			
	256	-25.5 (-6.1)	-100.0 (-23.9)	262	42.7 (10.2)	163.2 (39.0)
210	254	23.0 (5.5)	90.4 (21.6)			
	256	-26.0 (-6.2)	-101.7 (-24.3)	262	54.4 (13.0)	207.2 (49.5)
200	254	18.8 (4.5)	74.1 (17.7)			
	255	-22.6 (-5.4)	-88.7 (-21.2)	262	56.5	215.1
100	255	3.3 (0.8)	12.8 (3.1)			
	256	-11.4 (-2.7)	-44.5 (-10.6)	264	57.8 (13.8)	218.4 (52.2)

[a]Cooled and heated at 10 K/min. See Tables 1 and 2 for other abbreviations.
[b]Samples also exhibited minor endotherm near 240 K.

mole fraction in the highest-melting form. Plots of the calculated products (given in Fig. 3) identified initiation temperatures consistent with the predictions from tempering experiments. The sigmoid shape of these plots further indicates substantial temperature sensitivity, as would be typical of new phase nucleation (10) and rate control by different component processes at different temperatures. Because the two transformations exhibited nearly the same temperature sensitivity, division of each $k_r t$ by the time (seconds) spent below an ester's initiation temperature and its corresponding melting point allowed comparison of approximate rate constants and identified temperatures for optimum conversion—namely, 0.0034 s^{-1} at 186 K for 5-EAME and 0.0052 s^{-1} at 207 K for 11-EAME. Obviously, these values are useful only for comparison purposes. It remains for other methodology to establish how accurately they represent true phase conversion rates.

DISCUSSION

That relatively slow transformation processes initiated in solids at specific temperatures can determine the recrystallization behavior of phases melting at much higher temperatures is an interesting and exploitable premise that offers insight into how thermal history determines lipid properties. It implies that routes taken from the molten state through solid phases and back to the melt may not be reversible and that critical responses to conditions along the way determine the course of such a hysteretic cycle. This concept and that of crucial phase sequences from triglyceride polymorphism (11) or similar concepts from solid-state physics and metallurgy (12–14) are especially pertinent to food processing and storage, where texture and quality can depend on thermal history. They also offer plausible molecular explanation for responses of nonhomeothermic organisms to short-term environmental variation as, for example, in frost resistance, heat tolerance, and vernalization of crop plants, where substantial physiological change results from brief exposure to extreme conditions. In the case of 5-EAME and 11-EAME, low-temperature initiation establishes conditions that later, upon reheating, produce solid-phase structure different from that obtained in solids cooled only slightly below the freezing point. It remains to be seen if the transformations that these esters undergo involve major changes in unit cell dimensions of the type that accompany fat bloom in processed foods or that would be sufficient to perturb bioprocesses in live tissue.

Obviously, lipid polymorphic transformations are kinetic events that derive character from contexts in which they are observed. While our cooling and reheating experiments correlate the appearance of high-melting phases with cooling below specific temperatures, tempering experiments (Table 5) suggest that these phases will also form at other temperatures below the freezing point if given enough time. Perhaps,

TABLE 5
Effect of Tempering on Methyl *cis*-5-Eicosenoate (5-EAME) and Methyl *cis*-11-Eicosenoate (11-EAME) Transitions[a]

	Sold → Solid			Solid → Liquid		
K/min	$-T_t$ K	ΔH_t kJ/mol; kcal/mol	ΔS_t J/mol K (cal/mol K)	T_m K	ΔH_m kJ/mol; kcal/mol	ΔS_m J/mol K (cal/mol K)
5-EAME						
220/30	266	28.9 (6.9)	108.4 (25.9)			
	270	−2.5 (−0.6)	−9.2 (−2.2)	273	2.5 (0.6)	9.2 (2.2)
220/60	266	26.4 (6.3)	99.2 (23.7)			
	271	−22.2 (−5.3)	−82.0 (−19.6)	274	25.1 (6.0)	91.7 (21.9)
210/30	265	10.5 (2.5)	39.3 (9.4)			
	267	−34.7 (−8.3)	−130.2 (−31.1)	273	58.6 (14.0)	214.3 (51.2)
210/60	265	1.3 (0.3)	4.6 (1.1)			
	266	−20.1 (−4.8)	−75.8 (−18.1)	274	60.3 (14.4)	220.2 (52.6)
11-EAME						
240/30	255	49.8 (11.9)	195.5 (46.7)			
	257	−0.8 (−0.2)	−3.3 (−0.8)	262	0.8 (0.2)	3.3 (0.8)
240/60	255	41.9 (10.0)	164.5 (39.3)			
	257	−1.3 (−0.3)	−5.0 (−1.2)	262	9.6 (2.3)	36.8 (8.8)
230/30	255	38.1 (9.1)	149.8 (35.8)			
	257	−14.6 (−3.5)	−56.9 (−13.6)	262	25.5 (6.1)	97.5 (23.3)
230/60	255	38.1 (9.1)	149.8 (35.8)			
	257	−13.8 (−3.3)	−54.0 (-12.9)	262	25.1 (6.0)	95.8 (22.9)

[a]Cooled and heated at 10 K/min. See Tables 1 and 2 for other abbreviations.

under proper time-temperature conditions, other monoenoic fatty acid esters are capable of similar behavior, even though the 9-EAME and 13-EAME that we examined were not unusual.

Certainly, the marked temperature sensitivity of phase transformation rates exhibited by 5-EAME and 11-EAME imparts unusual character to these isomeric eicosenoates. This temperature sensitivity makes us suspect that the observed low temperature initiation of higher-melting phases is equivalent to nucleation (10), but the molecular nature of the change is not known. Results with 11-EAME suggest that some definite temperature-related event (or more than one) is involved. When cooled to 230 K and tempered for 30 or 60 min (Table 5), 11-EAME behaved quite differently than when cooled to slightly lower temperatures for much shorter times. Tempering 11-EAME at 230 K produced less than half the expected quantity of high-melting phase. Under analogous conditions, 5-EAME transformed completely to the high-melting form.

Given this difference in tempering behavior between 5-EAME and 11-EAME, it is interesting to compare exotherms exhibited by the two compounds as they were reheated from lower and lower temperatures (Figs. 1 and 2). The exotherm in the scan of 5-EAME from 195 K, for example, is shaped essentially opposite that in the scan of 11-EAME from 200 K. Even though both esters eventually assume configurations that cause them to melt with the same melting entropy, they appear to do so through different, as yet unresolved, intermediates or conversion paths that become kinetically significant at characteristic temperatures. Double bond location differences and different pseudo-linear chain orientations (15) might allow such behavior.

5-EAME and 11-EAME exhibit another curious difference pertinent to the impact of unsaturation on physical properties and the sequence of molecular events through which these esters form high-melting phases. First-order rate constants from data on samples tempered at 220 and 240 K for 30 and 50 min

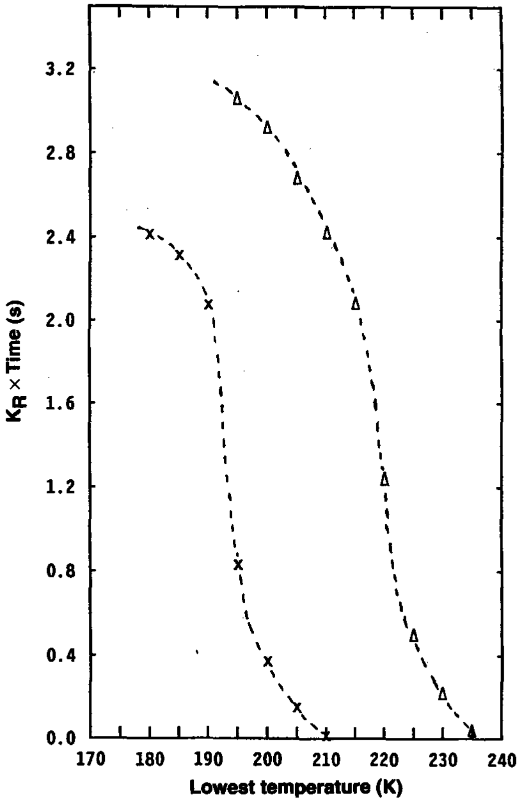

FIG. 3. Temperature effect on first-order rate constant-time product for high-melting phase formation in methyl *cis*-5-eicosenoate (-X- - -X-) and methyl *cis*-11-eicosenoate (-Δ- - -Δ-). Conditions as in Figure.1.

(Table 5) show that 5-EAME converts to the high-melting form some three times faster than does 11-EAME when both are above their initiation temperatures. This comparison contrasts sharply with the comparison of rates for samples cooled to lower temperatures. In initiated samples, 11-EAME converts some 1.5 times faster than 5-EAME. This reversal of rates raises the question whether the double bonds in these two esters are located such that different portions of the molecules participate in crystallization under different conditions.

If the rate comparisons of 5-EAME and 11-EAME are carried further, i.e., by preparing Arrhenius plots of ln k_r vs. $1/T$, determining frequency factors from high-temperature portions of the plots (Y-intercepts), and calculating activation entropies (16) at temperatures that correspond to low-melting endotherms of 5-EAME (265 K) and 11-EAME (254 K), the $\Delta S^{\ddagger}$ for formation of high-melting 5-EAME is some 50–60 J/mol K (12–14 cal/mol K) greater than that for 11-EAME. This entropic difference, which could account in part for the slower conversion of 5-EAME, would be equivalent to 5–6 rotational centers (6–7 carbons) if such activation involves only rotations within aliphatic chains (2). Again, it is tempting to conjecture that the differences observed with 5-EAME vs. 11-EAME arise for configurational differences in portions of the aliphatic chains distal to the double bonds in these compounds.

Our experience with isomeric eicosenoic acid esters is in some ways analogous to experience of Sato and colleagues (17–19) with ultra-pure monoenoic acids. These workers observed a diversity of polymorphic behavior depending both on chainlength and double bond position. With palmitoleic (*cis*-9-hexadecenoic) acid, oleic (*cis*-9-octadecenoic) acid, asclepic (*cis*-11-octadecenoic) acid, and erucic (*cis*-13-docosenoic) acid, they found from two to four polymorphs that differed due to "interfacial melting," i.e., order–disorder transformations in aliphatic chain segments distal to the double bond and including the methyl group. Curiously, petroselinic (*cis*-6-octadecenoic) acid and methyl oleate each exhibited two forms but showed no evidence of "interfacial melting." The polymorphs of these latter compounds seemed instead to represent different subcell packings. Accordingly, Sato and colleagues (17–19) inferred that double bond location closer to the methyl group is a prerequisite for "interfacial melting." Their results, which differentiate between methyl-side and carboxyl-side aliphatic structure in monoenoic acids, provide additional evidence of the importance of methylene interactions in determining crystal structure (20), and they point out the inherently greater stability of carboxyl-side aliphatic structure when chainlengths are equal on either side of the *cis* double bond. Our data are consistent.

In general, our data also agree with conclusions of Cevc (21) from theoretical considerations of double bond effects on the phase-transition temperatures of unsaturated phosphatidylcholines. The 262 K phase of 11-EAME, which has a longer carboxyl-side chain, forms quicker with slightly less entropic change than the 274 K phase of 5-EAME, which has a longer methyl-side chain. The 274 K phase of 5-EAME, however, melts at a higher temperature with a larger melting enthalpy even though melting apparently involves the same type of intramolecular disruption.

Just as we observed critical initiation temperatures, Hiramatso *et al.* (19) observed that with asclepic acid, specific pressure conditions can give rise to additional polymorphs. This experience, plus their results with petroselinic acid and methyl oleate, affirm our conviction that the polymorphism we observe represents different crystal forms with distinct nucleation and growth properties.

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