

Physical Properties of Two Isomers of Conjugated Linoleic Acid

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Abstract Thermal properties, powder X-ray diffraction patterns and FT-IR absorption spectra of crystals of two isomers of conjugated linoleic acid (CLA), 9-*cis*, 11-*trans*-CLA (c9t11), 10-*trans*, 12-*cis*-CLA (t10c12) were examined. To search for polymorphic modifications, we carefully performed crystallization from melt and solution phases, and isolated one type of crystalline form in c9t11 and t10c12. The melting temperature (T_m) was 14.9 °C, enthalpy of fusion (ΔH) was 38.7 kJ/mol, and entropy of fusion (ΔS) was 134 J/mol K for c9t11, and $T_m = 19.8$ °C, $\Delta H = 35.6$ kJ/mol and $\Delta S = 122$ J/mol K for t10c12. The X-ray diffraction and FT-IR measurements indicated O_{\perp} subcell packing in the crystals of c9t11 and t10c12, and long spacing values of 4.22 nm for c9t11 and 3.88 nm for t10c12. The unique molecular structures of the two isomers of CLA are discussed in comparison to the polymorphism of oleic acid, petroselinic acid, elaidic acid and linoleic acid, all of which are unsaturated fatty acids having the same carbon number of 18 as that of the two CLA isomers.

Keywords Conjugated linoleic acid · Physical property · DSC · X-ray diffraction · FT-IR absorption

Introduction

Conjugated linoleic acid (CLA) is a collective term describing a mixture of positional and geometrical isomers of linoleic acid including a conjugated double bond at various positions. It is industrially manufactured by alkali-induced conjugation of linoleic acid-rich oils such as safflower oil and sunflower oil, in the presence of propylene glycol. After conjugation, one can obtain a mixture consisting of almost equivalent amounts of the isomers, 9-*cis*, 11-*trans*-CLA (c9t11) and 10-*trans*, 12-*cis*-CLA (t10c12) [1], which have two double bonds (*cis* and *trans*) at different positions of the aliphatic chains. The two CLAs exhibit various biochemical properties, such as reduction of cancer incidence [2], beneficial effects in atherosclerosis [3], decrease in body fat content [4], and improvement of immune functions [5]. It has been reported that the biochemical properties of c9t11 and t10c12 differ such that the c9t11 isomer exhibits anti-tumor activity [6], whereas the t10c12 isomer decreases body fat [7], increases energy expenditure [8], and suppresses the development of hypertension [9].

In view of structure–function relationship, unsaturated fatty acids play important roles in functional activities of biological organisms [10], and their physicochemical properties have attracted much attention in the biophysical sciences [11]. Major factors that influence the physicochemical properties of the unsaturated fatty acids are the number, position and the configuration (*cis* or *trans*) of double bonds [12,13]. Systematic studies of polymorphic transformations of various unsaturated fatty acids in a crystalline phase have been performed. Figure 1 schematically illustrates various kinds of unsaturated fatty acids, *cis*-monounsaturated, *trans*-monounsaturated, *cis*-diunsaturated and conjugated fatty acids. In oleic acid ($C_{18:1}$,

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9-*cis*), there are four polymorphic forms (α , β_1 , β_2 and γ) [14–16]. The α and γ phases of oleic acid were also found in erucic (C_{22:1}, 13-*cis*) [17,18], gondoic (C_{20:1}, 11-*cis*) [1], asclepic (C_{18:1}, 11-*cis*) [19,20], and palmitoleic (C_{16:1}, 9-*cis*) acids [18], all of which have a *cis* double bond at odd-numbered carbon positions. Peteroselinic acid (C_{18:1}, 6-*cis*), having a *cis* double bond at even-numbered carbon positions, has two forms (LM and HM) [21–24], whose polymorphic structures are quite different from those of the other *cis*-monounsaturated fatty acids but rather similar to those of saturated fatty acids [21]. In elaidic acid (C_{18:1}, 9-*trans*), which is a *trans* isomer of oleic acid, Ueno et al. reported one crystal form [25]. However, Kaneko reported two polymorphic forms (LM and HM) [26], whose crystal structures are similar to B, C and E forms in saturated fatty acids [25]. Linoleic acid (C_{18:2}, 9,12-*cis*) has three forms (LT, MT and HT), common characteristics with the γ phase of *cis*-monounsaturated fatty acids [27]. The physical properties of conjugated unsaturated fatty acids have not been studied as much as those of mono-unsaturated and polyunsaturated fatty acids.

It is quite interesting to study the physical properties of CLA isomers in comparison to those of the above mono-unsaturated fatty acids. In the present paper, we report the

results of experiments on physical properties of CLA isomers, t10c12 and c9t11, using pure samples.

Experimental Procedures

Materials

Samples of c9t11 (>98% purity) and t10c12 (>98% purity) were purchased from Matreya, LLC (PA, USA). Acetonitrile (>99.5 % purity) and *n*-decane (>97% purity) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Four types of crystallization were carried out. The sample was melted and held for 10 min at 40 °C and then cooled rapidly and stored at –20 °C (rapid-melt crystallization). The melted sample was cooled at 1 °C/min and stored at –20 °C (slow-melt crystallization). The sample was dissolved in *n*-decane or acetonitrile at 50 °C and stored at –20 °C (*n*-decane solution) or –5 °C (acetonitrile solution) without stirring. The crystallized sample was filtered at the stored temperature under reduced pressure in a low-temperature thermostatic chamber (PG-2KP: Espec Corp., Osaka, Japan).

Differential Scanning Calorimetry (DSC)

Thermal analyses were performed using a DSC6220 (Seiko Instruments Inc., Chiba, Japan). The crystallized sample (about 3 mg) was weighed in an aluminum pan. The heating scan was recorded from –30 °C to 60 °C at a rate of 2 °C/min.

X-Ray Diffraction (XRD)

A powder XRD study was performed using a RINT-TTR (Rigaku Co., Tokyo, Japan) equipped with a vertical goniometer and rotator anode, and measured by Cu-K α (0.154 nm) radiation with an Ni-filter, 6.0 kW (30 kV, 200 mA). The melted sample was first mounted on an XRD plate at 40 °C, and then placed in a temperature-controlled vacuum sample holder and cooled to –20 °C. Finally, the sample was subjected to XRD every 5 °C during heating from –20 °C to 20 °C. The solvent-crystallized sample was measured by XRD at 5 °C.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR measurement was performed using a μ -IR 8000 (Shimadzu Co., Kyoto, Japan). The CLA samples were sandwiched between two KBr plates and placed in a

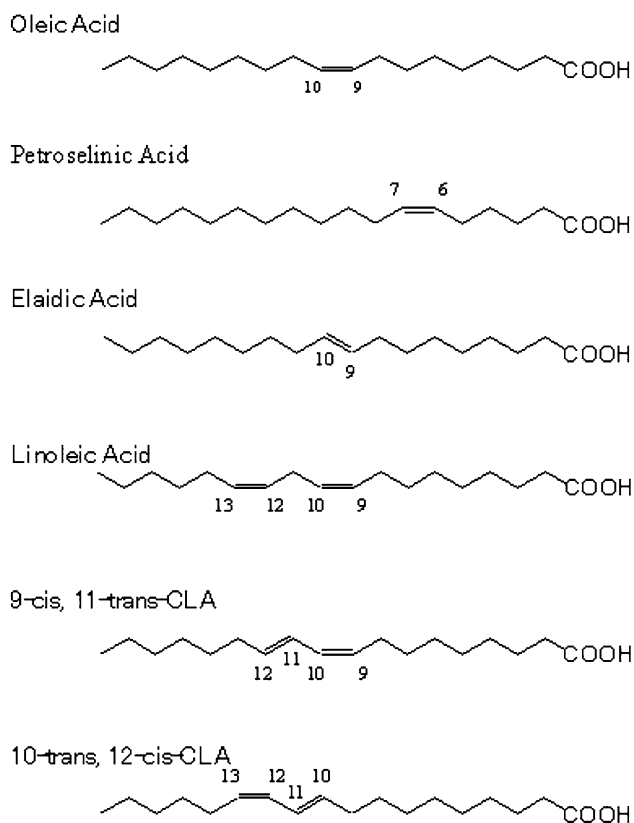


Fig. 1 A schematic illustration of six unsaturated fatty acids

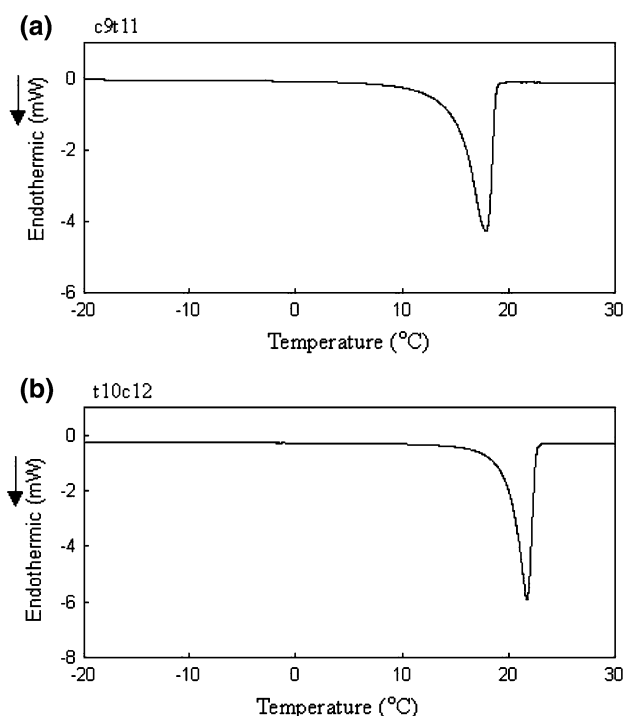


Fig. 2 DSC heating thermograms of **a** c9t11 crystals and **b** t10c12 crystals, both obtained by rapid-melt crystallization

handmade cell holder. The FT-IR spectra were recorded with 128 scans at 4 cm^{-1} resolution after the following temperature variation. First, the sample was cooled from $45\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C}/\text{min}$, and FT-IR measurement was performed every $5\text{ }^{\circ}\text{C}$ during heating from $-15\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$ while holding the temperature for more than 5 min at every measured point. The heating rate was $2\text{ }^{\circ}\text{C}/\text{min}$ between every measuring temperature.

Results and Discussion

Figure 2 plots the DSC heating thermo-peaks of c9t11 and t10c12, which were crystallized by rapid-melt crystallization. A large endothermic peak corresponding to the melting of the crystallized samples with T_m (melting temperature) at $14.9\text{ }^{\circ}\text{C}$ (onset temperature) for c9t11, and $19.8\text{ }^{\circ}\text{C}$ (onset temperature) for t10c12 was observed for each CLA isomer. The enthalpy (ΔH) and entropy (ΔS) of

fusion of two CLA isomers were calculated from Fig. 1, as summarized in Table 1. ΔH was obtained from the area of the endothermic peak and ΔS was calculated by the calculation type ($\Delta S = \Delta H/T_m$). The values of T_m , ΔH and ΔS obtained using the crystals formed by slow-melt crystallization and crystallization from acetonitrile and *n*-decane solutions were the same as those using the crystals formed by rapid-melt crystallization, both for c9t11 and t10c12.

Figure 3a,b present the XRD short- and long-spacing patterns of c9t11 and t10c12, which were crystallized by rapid-melt crystallization. Long-spacing values were calculated as 4.22 nm for c9t11 (Fig. 3a) and 3.88 nm for t10c12 (Fig. 3b) taken at $5\text{ }^{\circ}\text{C}$. The strong peaks of (001), (003) and (005) reflections of the two CLA crystals suggest that the two crystals are stacked in a double-chain-length structure. A strong peak (0.398 nm) and six medium peaks (0.377 , 0.413 , 0.424 , 0.435 , 0.455 and 0.469 nm) were obtained for the short-spacing pattern of c9t11. In t10c12, a strong peak (0.421 nm) and three medium peaks (0.375 , 0.400 and 0.404 nm) were obtained in the short-spacing spectra. The exact values and intensity ratios of the short-spacing peaks are summarized in Table 1. Based on the long- and short-spacing patterns of the two CLA crystals, we concluded that the crystal structures of the two CLAs are significantly different. In particular, the long-chain axis of t10c12 is more inclined than that of c9t11 with respect to the lamellar plane because the long spacing of t10c12 was 0.3 nm shorter than that of c9t11, which may approximately correspond to an inclination angle of the long-chain CLA molecules about 7° .

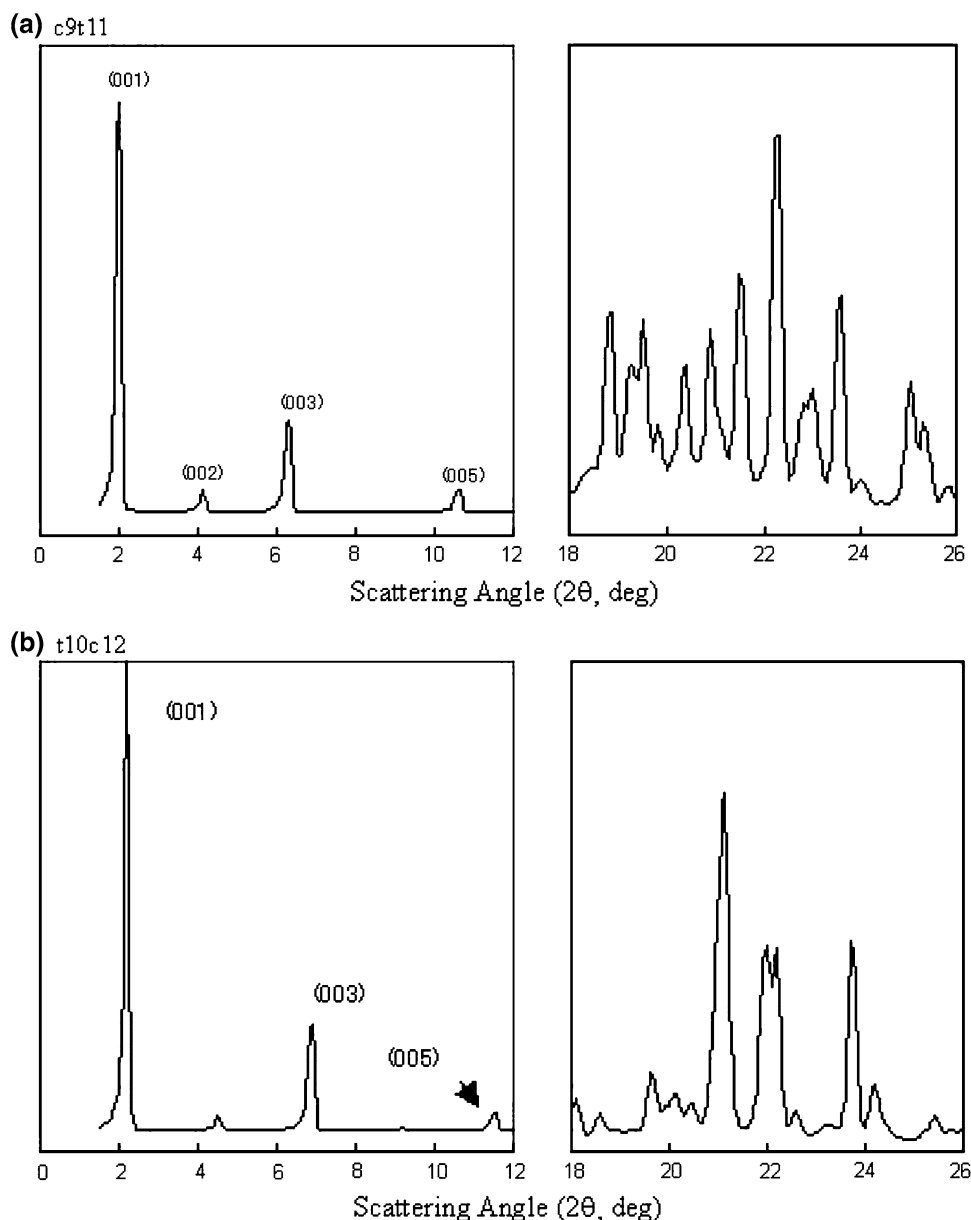
Figure 4 plots the FT-IR spectra of c9t11 and t10c12 taken at $5\text{ }^{\circ}\text{C}$. In Fig. 4a for c9t11, the split spectra at 737 and 727 cm^{-1} of the CH_2 rocking mode and the split spectra at $1,468$ and $1,456\text{ cm}^{-1}$ of the CH_2 scissoring mode indicate the presence of an O_{\perp} -type subcell structure. However, the wave numbers of the split peaks differed from those of the typical O_{\perp} subcell structures of fatty acids. For example, in petroselinic acid and elaidic acid, wave numbers of 731 and 721 cm^{-1} were obtained for the CH_2 rocking mode, and $1,473$ and $1,463\text{ cm}^{-1}$, for the CH_2 scissoring mode [21,25]. Despite this small discrepancy, we may conclude that the subcell packing of the two CLA crystals is O_{\perp} .

Table 1 Thermodynamic data and X-ray diffraction patterns of two CLA isomers

	T_m ($^{\circ}\text{C}$)	ΔH (kJ/mol)	ΔS (J/mol K)	Long spacing (nm)	Short spacing (nm)
c9t11	14.9	38.7	134	4.22	0.469(m), 0.455(m), 0.435(m), 0.425(m), 0.413(m), 0.398(s), 0.390(w), 0.386(w), 0.377(m), 0.356(w), 0.352(w)
t10c12	19.8	35.6	122	3.88	0.453(vw), 0.441(vw), 0.433(vw), 0.421(s), 0.404(m), 0.400(m), 0.375(m), 0.367(vw)

T_m melting point, ΔH enthalpy of fusion and ΔS entropy of fusion. *s* strong; *m* medium; *w* weak; *vw* very weak

Fig. 3 X-ray diffraction short and long spacing patterns of **a** c9t11 and **b** t10c12



It is worth discussing the physical properties of the crystals of the two CLA isomers in comparison with the other unsaturated fatty acids having 18 carbon atoms. Table 2 summarizes the subcell structures, melting points (T_m), enthalpy (ΔH) and entropy (ΔS) of fusion of the polymorphic forms of four unsaturated fatty acids and the two CLA isomers, and long-spacing values of the crystals of major unsaturated fatty acids having 18 carbon atoms are shown in Table 3.

Our first concern is the subcell structure, since it reflects the lateral packing of the long-chain molecules of the fatty acids [13]. Saturated fatty acids usually possess the O_{\perp} subcell (although not shown here). The subcell structures, however, of mono-unsaturated fatty acid revealed remarkable diversity and their occurrence was influenced

by many factors such as polymorphism, conformation (*cis* or *trans*) of double bond, parity (odd or even) of the position of the bond in the total fatty acid chain, etc. [13]. In the *trans*-fatty acid, (elaidic acid), the O_{\perp} subcell was also observed, and this can easily be understood by taking into account of similar all-*trans* conformation of the aliphatic chains of the saturated and *trans*-unsaturated fatty acids. The *cis*-monounsaturated fatty acids revealed parallel-type subcells such as $T_{//}$, $O'_{//}$ and $M_{//}$, and $O'_{//}$ was most frequently observed in such as oleic acid and linoleic acid (Table 2), and also in gondoic acid and asclepic acid [13]. However, an exception revealing the O_{\perp} subcell was observed in the LM form of petroselinic acid, which has the *cis*-double bond at the 6th carbon atoms from $-\text{COOH}$ group. The *cis*-monounsaturated fatty acids revealing the

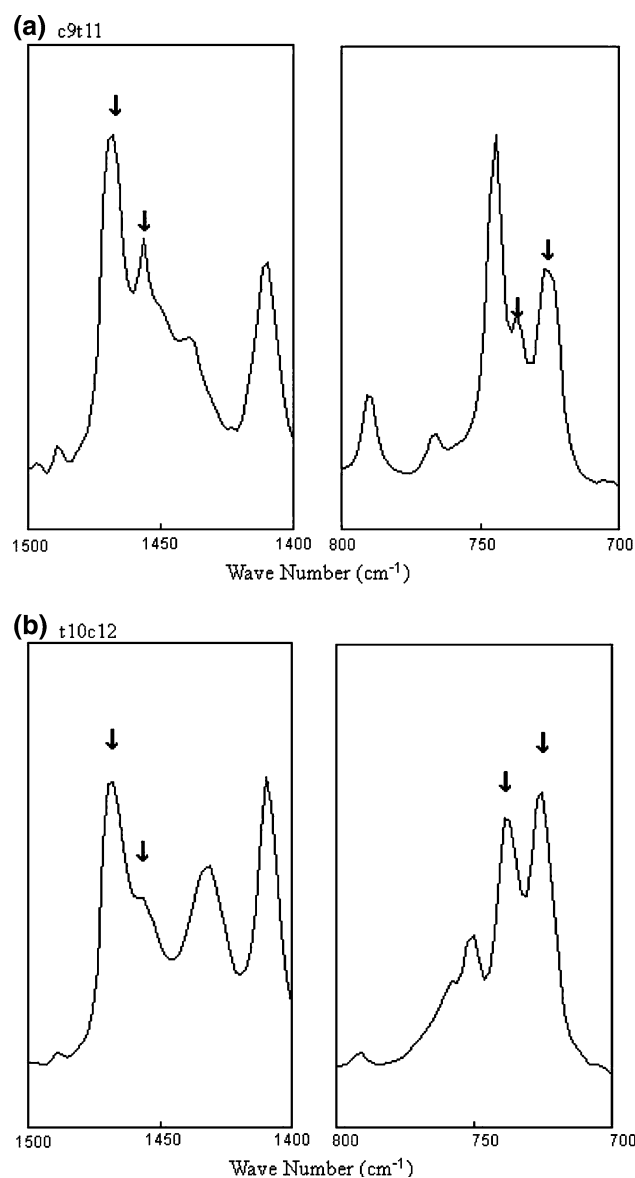


Fig. 4 FT-IR absorption spectra of **a** c9t11 and **b** t10c12

parallel-type subcells have the *cis*-double bond at the odd-numbered carbon positions, but petroselinic acid has the double bond at the even-numbered carbon position. Furthermore, olefinic configuration of petroselinic acid LM form, expressed by internal angles of (157° , *cis*, -160°) was largely different from those of the other *cis*-unsaturated fatty acids which are of the type of skew-*cis*-skew' [13]. In the present study, the subcell structures of t10c12 and c9t11 were assumed to be O_\perp because of the split peaks of CH_2 rocking and the CH_2 scissoring modes in the FT-IR spectra. As for t10c12, the XRD short-spacing pattern was quite similar to those of the LM form of petroselinic acid [21] and the I form of elaidic acid [25]. These results indicate that molecular interactions of the two CLA isomers revealed in the subcell structure are closer to those of the

Table 2 Molecular properties of six C_{18} unsaturated fatty acids [23–25]

Fatty acid	Form	Subcell	T_m ($^\circ\text{C}$)	ΔH (kJ/mol)	ΔS (J/mol K)
Oleic acid	γ	$O'_{//}$	– ^a	–	–
	α	$O'_{//} + \perp$ -like	13.3	39.6	138
	β_2	// type	16.0	48.9	169
	β_1	$T_{//}$	16.3	57.9	200
Petroselinic acid	LM	O_\perp	–	–	–
	HM	O_\perp -like + $M_{//}$	30.5	47.5	156
Elaidic acid	I	O_\perp	44.5	53.6	169
Linoleic acid	LT	$O'_{//}$	–	–	–
	MT	$O'_{//}$	–	–	–
	HT	$O'_{//}$	–7.2	33.6	121
CLA (c9t11)		O_\perp	14.9	38.7	134
CLA (t10c12)		O_\perp	19.8	35.6	122

^a Transformation into other polymorphs

Table 3 Long-spacing values of major unsaturated fatty acids having 18 carbon atoms [20,23,25]

Fatty acid (polymorph)	Long spacing (nm)
Oleic acid (β_1 form)	4.12
Petroselinic acid (LM form)	4.40
Linoleic acid (HT form)	4.20
α -linolenic acid (HT form)	4.11
Elaidic acid (I form)	4.91

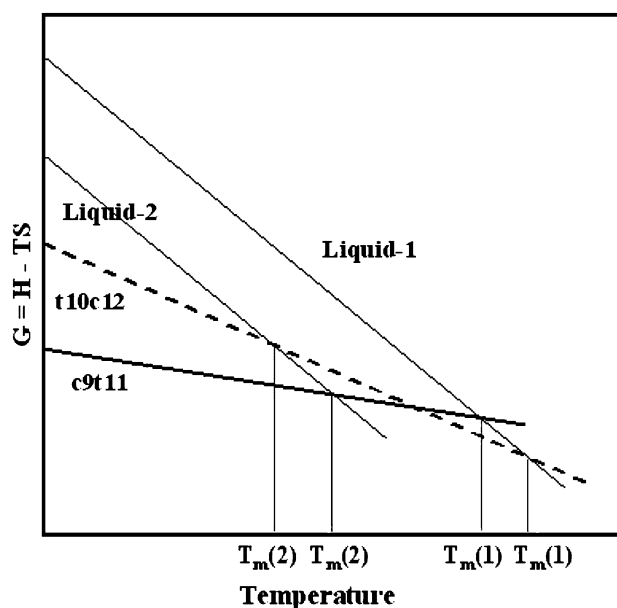


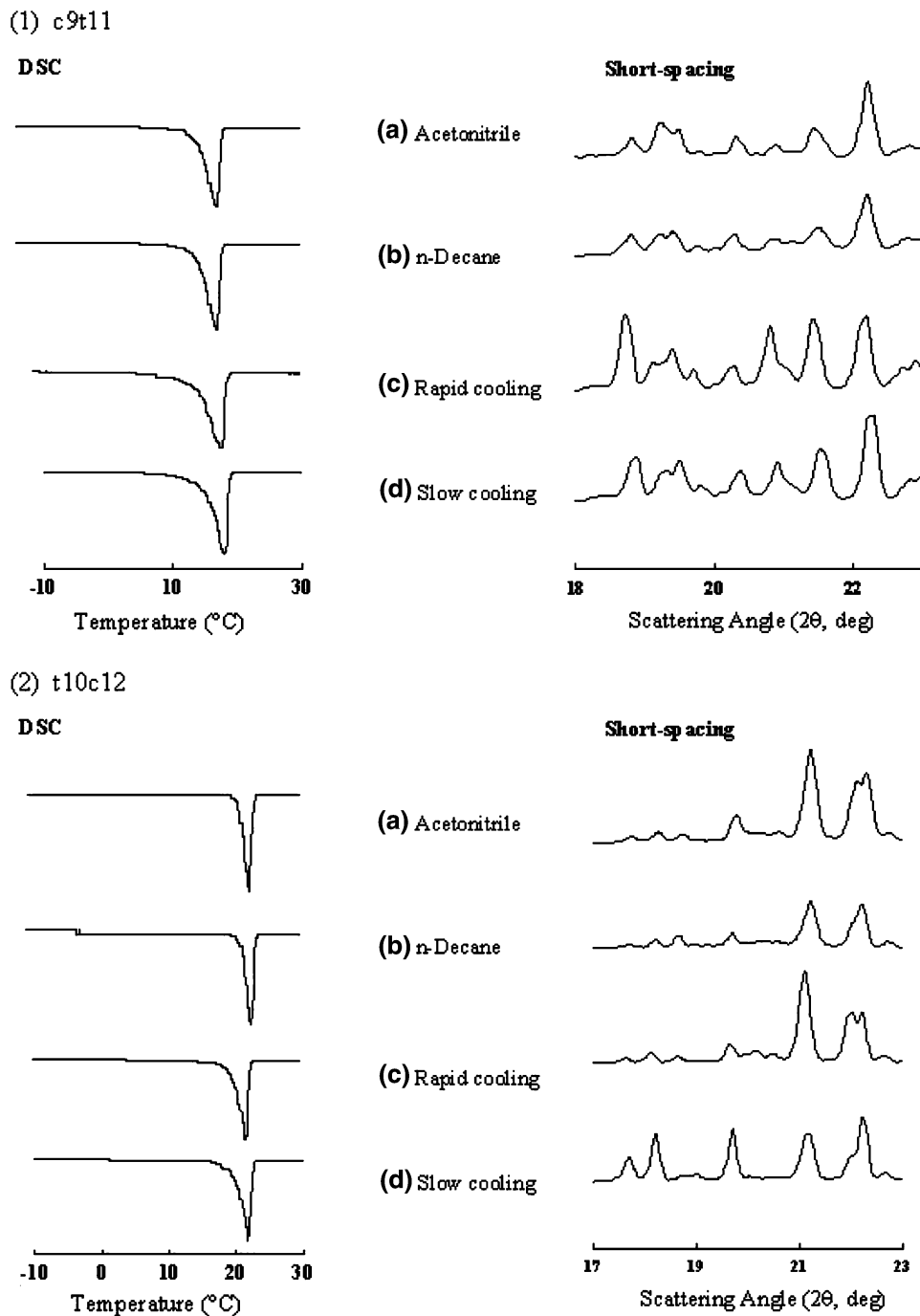
Fig. 5 Relationship among Gibbs free energy values (G) of crystal phases of two CLA isomers and liquid phase as a function of temperature

saturated and *trans*-unsaturated fatty acids than those of the *cis*-unsaturated fatty acids with an exception of the LM form of petroselinic acid. We expect that the presence of *trans*-double bonds combined with the *cis*-double bond in a conjugated manner may cause such interactions, although further consideration is necessary to fully clarify this.

As to the thermal properties, we first compare T_m of *c9t11* and *t10c12*. The T_m of *c9t11* was 4.9 °C lower than that of *t10c12*. Gunstone and Ismail clarified that the melting point of the mono-unsaturated fatty acid is

decreased using *cis*- and *trans*-monounsaturated fatty acid isomers due to the conversion of the double-bond conformation from *trans* to *cis*, the double-bond position shifting from even-numbered carbon positions to odd-numbered positions, and the double-bond position shifting from end positions of the fatty acid chain to central positions [12,13,26]. The fact that T_m of *t10c12* was higher than that of *c9t11* is consistent with this interpretation. In more detail, shifting the *cis*-double bond from the 9th position to the 12th position increases T_m by 14 °C, whereas shifting

Fig. 6 Comparison of DSC heating thermograms and X-ray diffraction short-spacing patterns of CLA isomers crystals obtained by four different crystallization conditions: **a** acetonitrile solution, **b** *n*-decane solution, **c** rapid cooling from melt, **d** slow cooling from melt



the *trans*-double bond from the 11th position to the 10th position decreases T_m by 9 °C. Simple summation of the above increase and decrease of T_m equals 5 °C, which is almost the same as the difference in T_m between c9t11 and t10c12 obtained in the present study.

As indicated in Table 2, the values of T_m , ΔH and ΔS for c9t11 and t10c12 fall between those of oleic acid and linoleic acid (HT form), yet the values of ΔH and ΔS of t10c12 were smaller than those of c9t11, even though T_m of t10c12 was higher than that of c9t11. c9t11's *cis* double bond position is identical to that of oleic acid, and it has the same number of double bonds as linoleic acid, except for the presence of a *trans*-double bond in c9t11. ΔH of t10c12 was larger than that of linoleic acid (HT form). However, its ΔS was almost the same as that of linoleic acid.

Thus, we may note that ΔH and ΔS of t10c12 were smaller than ΔH and ΔS of c9t11 by 3.1 kJ/mol and 12 J/mol K, even though T_m of t10c12 was 4.9 °C higher than the T_m of c9t11. This is explained by taking into account the Gibbs free energy ($G = H - TS$, H ; enthalpy and S ; entropy) and temperature (T) relationship. Basically, ΔH and ΔS are the differences in G at $T = 0$ and $S = -(\partial G/\partial T)_P$ between the crystal and liquid phases. If we reasonably assume that there is no appreciable difference in the G values of the liquid phases of c9t11 and t10c12, we may schematically draw two possible G - T relationships of c9t11, t10c12 and liquid as shown in Fig. 5. Figure 5 does not represent the phase diagram of two polymorphic forms of one substance. However, the following results obtained by the present study, that the H and S values of t10c12 are larger than those of c9t11, and thereby the values of ΔH and ΔS of t10c12 are smaller than those of c9t11, may be argued in the G - T relationships illustrated in Fig. 5. When the G - T line of liquid is placed at the line of liquid-1, T_m of c9t11 lies below that of t10c12, but the opposite occurs with the liquid-2 line. The present result would suggest that the G - T line follows that of liquid-1. These phenomenological understandings should be fully investigated by more microscopic structural analysis of the crystalline phases of the two CLA isomers.

With regard to polymorphism, we performed careful crystallization of the two CLA isomers under four conditions: two melt-crystallization conditions (rapid and slow cooling) and two solvent crystallization conditions (in acetonitrile solution and in *n*-decane solution). As mentioned before, two or more multiple polymorphic forms have been found in almost all fatty acids, both in saturated or unsaturated acids. In the CLA isomers of c9t11 and t10c12, however, only one crystalline form was observed in the DSC and XRD experiments using the crystals obtained under different crystallization conditions. Figure 6 compares the XRD short-spacing patterns and DSC heating thermopeaks of CLA isomer crystals formed by four

different crystallization conditions. Based on previous work on polymorphism of the *cis*-monounsaturated fatty acids having multiple polymorphic modifications, we first assumed that rapid-melt crystallization might cause the crystallization of metastable forms, whereas solvent crystallization might cause the more stable forms, if the CLA isomers exhibit polymorphism. However, four different types of crystallization (rapid-melt crystallization, slow-melt crystallization, solution crystallization with acetonitrile and *n*-decane) produced just one form for each CLA isomer, since no detectable differences in the XRD and DSC patterns were observed between the crystals obtained by four different conditions. Therefore, we concluded that the two CLA isomers do not exhibit polymorphism. It seems that the presence of conjugated double bonds may not allow the CLA molecule packing to be sufficiently diversified to reveal polymorphic modifications.

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