Polymorphic Behavior of Erucic Acid[1]

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Polymorphic behavior of erucic acid was examined by differential scanning calorimetry (DSC), X-ray diffractometry (XRD) and optical microscopy. Four individual polymorphs were observed, α_1, γ_1, α and γ. The single crystals of α and α_1 were obtained from acetonitrile solutions. DSC and XRD studies exhibited reversible transformations between α and γ, and between α_1 and γ_1. The two transformations were characterized by an order (γ and γ_1)-disorder (α and α_1) transformation due to melting of the aliphatic chain between a *cis* double bond and a methyl end group, as revealed in α and γ of oleic acid. The thermodynamic stability among the four polymorphs was determined based on the transformation features and the solubility data. α_1 is most stable above 25.9 C, melting at 34.0 C. α is most stable in a range of temperature between -1.0 and 25.9 C, transforming in a crystalline state to α_1 at 31.2 C on heating. γ is most stable below -1.0 C. It can be concluded that the polymorphism of erucic acid is different from that of oleic acid with respect to the thermal and structural behaviors, although some similarities are revealed.

Unsaturated fatty acids play critical roles in biological organisms as main constituents of bio-lipids. To elucidate their physical chemical properties, the authors have recently studied the polymorphic behaviors of oleic acid, the most naturally occuring unsaturated fatty acid, using ultra-pure samples. Occurrence and phase transition (1), crystallization from solvent (2), and vibrational spectroscopic properties (3) were examined for the newly confirmed three polymorphic forms, α, β and γ. The most conspicuous property in the polymorphism of oleic acid is an order-disorder transformation of new type, which is caused by an introduction of one *cis* double bond in an aliphatic chain and, accordingly, which has not been observed in saturated fatty acids.

The present study dealt with the polymorphism of erucic acid having one *cis* double bond at the ω-9 position in 22 aliphatic carbons. In the literature, one crystal form is reported, having a melting point of 33 C (4). However, one may reasonably perceive that erucic acid may possess more polymorphs. Thorough study of erucic acid may enrich the knowledge about the polymorphism of the unsaturated fatty acids having one *cis* double bond. Conclusively, the present study identified four independent polymorphs, two of them revealing properties quite similar to those of α and γ of oleic acid.

MATERIALS AND METHODS

The erucic acid sample (>99.9%) was supplied by Nippon Oil and Fats Co. Ltd. The purity was confirmed by capillary gas liquid chromatography (GLC) (Shimadzu GC-9A, column: SP-2560, Supelco Inc., Bellefonte, Pennsylvania). Thermal behaviors of solidification, fusion and polymorphic transformation were examined by Differential Scanning Calorimeter (DSC) (Seiko-SSC 580). The X ray diffraction (XRD) patterns (Rigaku, Cu-K_α: λ = 1.542 A, Ni-filter) were taken for the samples, all of which were subjected to the same thermal treatments as DSC study.

Single crystals were grown from acetonitrile solvent in order to observe the crystal shape and to measure the solubility as well. The exact solubility values of each polymorph at different temperatures provide the most determinative data on the thermodynamic stability (2). The method of the solubility measurement was fully described in (2), e.g., the single crystal of one polymorph was put in the solution whose concentration was known, and the saturation temperature of the solution with respect to this form was searched by fluctuating the temperature of solution. In addition, solution-mediated transformation was examined to obtain complementary data for the determination of the thermodynamic stability. This transformation is caused by the growth of the more stable form at the expense of less stable ones, when all crystals were kept in a nearly saturated solution (2, 5).

Nomenclature of newly discovered polymorphs of erucic acid was given in accordance with oleic acid, taking into account the data of the polymorphic transformation, the crystal shape, the XRD pattern and the molecular structure obtained by Raman scattering spectra (unpublished).

RESULTS

DSC studies. DSC measurements were examined for the samples crystallized from melt and solution.

Figure 1 shows DSC data of melt-cooling and successive heating between 50 and -50 C at a rate of 2 C/min. Sharp peaks at 32.0 C (cooling) and 34.0 C

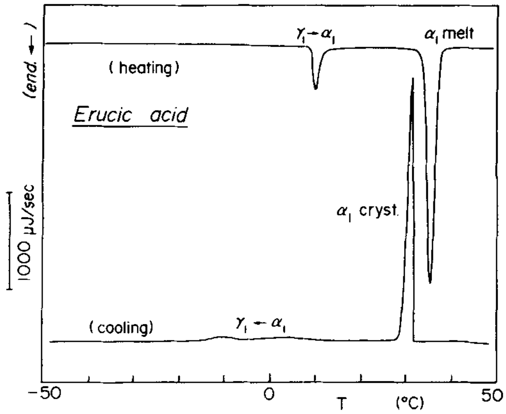

FIG. 1. DSC thermograms of α_1 and γ_1 of erucic acid with a cooling/heating rate of 2 C/min.

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(heating) correspond to the solidification and the fusion of a high-temperature polymorph, respectively. Far below these two peaks, a broad peak appeared in a wide range of temperature (20 ∼ -30 C) on cooling at 10 C/min, whereas on reheating, a sharp endothermic peak appeared at 9.0 C by 2 C/min. These two peaks were found to correspond to a polymorphic transformation between low-temperature and high-temperature polymorphs named γ_1 (low-temperature) and α_1 (high-temperature). The peak of the $\alpha_1 \rightarrow \gamma_1$ transformation on cooling was always broader than the sharp peak of $\gamma_1 \rightarrow \alpha_1$ at 9.0 C on heating, indicating peculiar property of the solid-state transformation. Therefore, more detailed DSC analyses were carried out on these two forms.

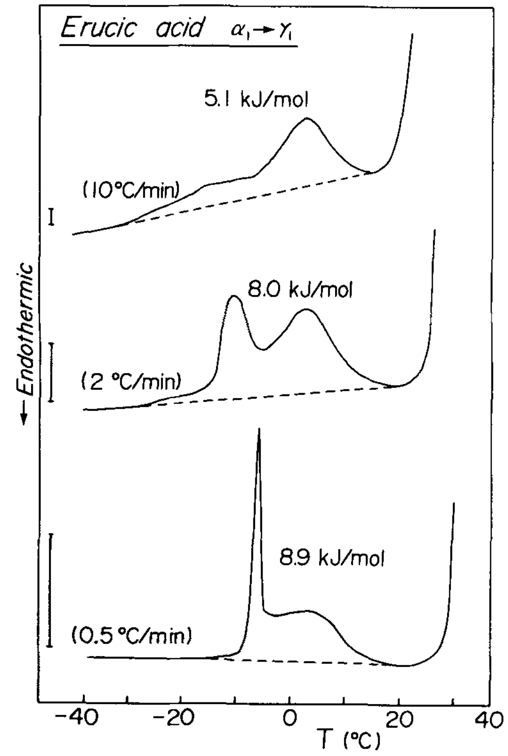

FIG. 2. DSC thermograms and ΔH_t values of the $\alpha_1 \rightarrow \gamma_1$ transformation of erucic acid with three cooling rates, 10 C/min, 2 C/min and 0.5 C/min.

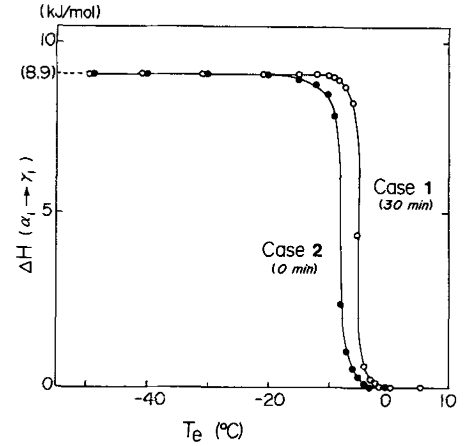

FIG. 3. ΔH_t values of the $\gamma_1 \rightarrow \alpha_1$ transformation as a function of T_e (see text).

Figure 2 shows enlarged thermograms of the exothermic peaks of the $\alpha_1 \rightarrow \gamma_1$ transformation examined by three cooling rates, 10, 2 and 0.5 C/min. The enthalpy values of transformation (ΔH_t) are also shown. Three marks are noted: (a) each thermogram involves two sub-peaks, the higher between 20 and -4 C and the lower between -4 and -30 C; (b) relative size of the lower sub-peak increased at the expense of the higher peak with decreasing cooling rate, and (c) a total exothermic latent heat covering the two subpeaks increased with decreasing cooling rate, 5.1 kJ/mol at 10 C/min and 8.9 kJ/mol at 0.5 C/min). The latter value equals the heat of $\gamma_1 \rightarrow \alpha_1$ transformation obtained by the heating (Fig. 1).

Figure 3 shows ΔH_t ($\gamma_1 \rightarrow \alpha_1$) values for the samples which underwent different computer-programmed thermal treatments. The melt (50 C) was cooled to various temperatures (T_e) at 2 C/min, then the crystal was heated to induce the $\gamma_1 \rightarrow \alpha_1$ transformation by 2 C/min, either after keeping the sample at T_e for 30 min (case 1), or soon after T_e was reached (case 2). It is clear that ΔH_t is highly dependent on T_e. No transformation was detectable at T_e > -2.0 C. ΔH_t rapidly increased when the sample was cooled below -4 C, and reached the largest value of 8.9 kJ/mol at T_e < -20 C, regardless of two thermal treatments. At -2 C < T_e < -20 C, the values of ΔH_t in case 1 were higher than those of the samples in case 2. Specifically, the sample which was kept at T_e = -10 C for 30 min gave rise to ΔH_t = 8.9 kJ/mol, which is the largest value. The thermal hysterisis phenomena shown in Figure 1, and the dependence on the cooling rate shown in Figure 2, indicate certain relaxation processes involved in the $\alpha_1 \rightarrow \gamma_1$ transformation.

The crystals grown from acetonitrile solutions revealed two kinds of DSC data, depending on the temperature and the rate of crystallization. DSC data of the crystal grown above 26 C were the same as those of the melt-grown crystal. This was true regardless of solute concentration and the crystallization rate. Hence, it can be concluded that the α_1 form was produced exclusively in this range of temperature. On the contrary, two crystalline forms exhibiting different DSC data were crystallized below 26 C, indicating the occurrence of two polymorphs. The crystals, which were grown rapidly from highly concentrated solution, exhibited DSC data identical to the α_1 form. However, another crystal appeared and increased in number of precipitates at the expense of α_1 by decreasing the rate of crystallization. Figure 4 shows the cooling and heating DSC data (2 c/min) of the single crystal which was obtained from acetonitrile solution by very slow cooling from 20 to 18 C (see below). A sharp exothermic peak appeared at -2.3 C on cooling, Δ H value being 8.6 kJ/mol. On heating, two endothermic peaks were revealed, the smaller with ΔH_t = 8.8 kJ/mol at -1.0 C, and the larger with ca. 53 kJ/mol at 34 C. The peak at -1.0 C indicates a solid-state transformation between another couple of polymorphs. Hence, α (high-temperature) and γ (low-temperature) were nomenclated to these two forms, according to the reasons given below.

The peak at 34 C first seems to mean the fusion of α.

TABLE 1

Enthalpy (ΔH) and Entropy (ΔS) of Fusion (f), Dissolution (d) in Acetonitrile, and Solid-state Transformation of α, γ, α_1 and γ_1 Polymorphs of Erucic Acid[a]

Erucic acid				Oleic acid			
	T (°C)	ΔH (kJ/mol)	ΔS (j/mol•K)		T (°C)	ΔH (kJ/mol)	ΔS (J/mol•K)
α_1 (f)	34.0	51.0	166.2	α (f)	13.3	39.6	138.4
α_1 (d)	-	94.5	264.9	β (f)	16.2	51.9	179.3
α (d)	-	106.5	305.1	α (d)	-	59.4	222.9
				β (d)	-	76.0	279.7
Solid state transformation							
$\alpha \rightarrow \alpha_1$	31.2	5.4	17.6				
$\gamma_1 \rightleftharpoons \alpha_1$	9.0	8.9	31.6				
$\gamma \rightleftharpoons \alpha$	-1.0	8.8	32.3	$\gamma \rightleftharpoons \alpha$	-2.2	8.8	32.3

[a] Oleic acid polymorphs data are also shown (1,2).

However, a shoulder peak at the low-temperature side is detectable. To separate the shoulder peak from the main peak, DSC heating thermogram by 0.2 C/min was measured as shown separately in Figure 4. The smaller peak appeared at 31.2 C with $\Delta H_t = 5.4$ kJ/mol and the larger one at 34.0 C with the enthalpy of fusion (ΔH_f) of 51.0 kJ/mol. Because the latter peak is equivalent to the melting of α_1, the endothermic peak at 31.2 C means the transformation from α to α_1.

Consequently the four polymorphs, α, γ, α_1 and γ_1, of erucic acid were identified by the DSC study. The thermal data are summarized in Table 1.

X ray Diffraction. The XRD patterns of the four polymorphs and their relative intensities are shown in Figure 5 and Table 2, respectively.

In case of the $\alpha \rightleftharpoons \gamma$ transformation, the short spacing spectra changed drastically by cooling α below -3 C (Fig. 5a), and the long spacing value was decreasd by 0.7 Å. In contrast, subtle changes were detectable between α_1 (22 C) and γ_1, which was kept at -20 C for one hr (Fig. 5b). On cooling two major peaks (denoted by *) looked unchanged, although their lattice parameters were decreased. The long spacing was largely changed from 46.5 Å (α_1, 22 C) to 44.0 Å (γ_1, -20 C).

Single crystal growth. The single crystals of α_1 and α of erucic acid were grown from acetonitrile solutions around 18 C (Fig. 6). α_1 revealed a rhombohedral shape, whereas α had an elongated hexagonal shape. The crystal shapes of γ and γ_1 were not available in the present study, because the crystallization of these two forms below -3 C was so difficult.

Solubility. The solubilities of α_1 and α in acetonitrile increased with increasing temperature, the differences being rather small (Table 3 and Fig. 7). To accurately determine the crossing point of the two solubilities, the solution-mediated transformation between α_1 and α was examined. At 25.9 C, (an arrow in Fig. 7), no transformation occurred, meaning that the solubilities of α and α_1 have the same value at this temperature.

The molar fraction (X) of the solubility and 1/T (1/K) was plotted on straight lines for the two polymorphs. Then, the enthalpy (ΔH_d) and entropy (ΔS_d) of dissolution were obtained (Table 1).

TABLE 2

X-ray Long and Short Spacing Spectra of α, γ, α_1 and γ_1 of Erucic Acid[a]

	Long spacing	Short spacing
α	50.3(vs)	3.74(s), 3.92(vs), 4.11(s) 4.30(s), 4.37(m), 4.46(w)
γ	49.6(vs)	3.68(w), 3.91(vs), 4.04(s) 3.73(s), 4.26(m), 4.71(s)
α_1	46.5(vs)	3.40(w), 3.56(s), 3.73(vs) 3.93(w), 4.04(w), 4.21(m) 4.40(m), 4.60(m)
γ_1	44.0(vs)	3.30(w), 3.48(vs), 3.66(vs) 3.77(m), 3.98(w), 4.18(m) 4.32(m), 4.55(m)

[a] Unit, Angstrom.

vs, very strong; s, strong; m, medium, w, weak.

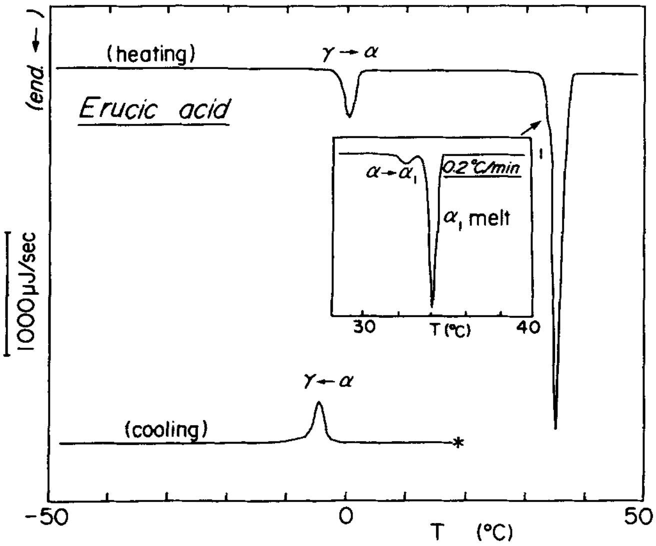

FIG. 4. DSC thermograms of α, γ and α_1 of erucic acid for the crystal grown from acetonitrile at 18 C.

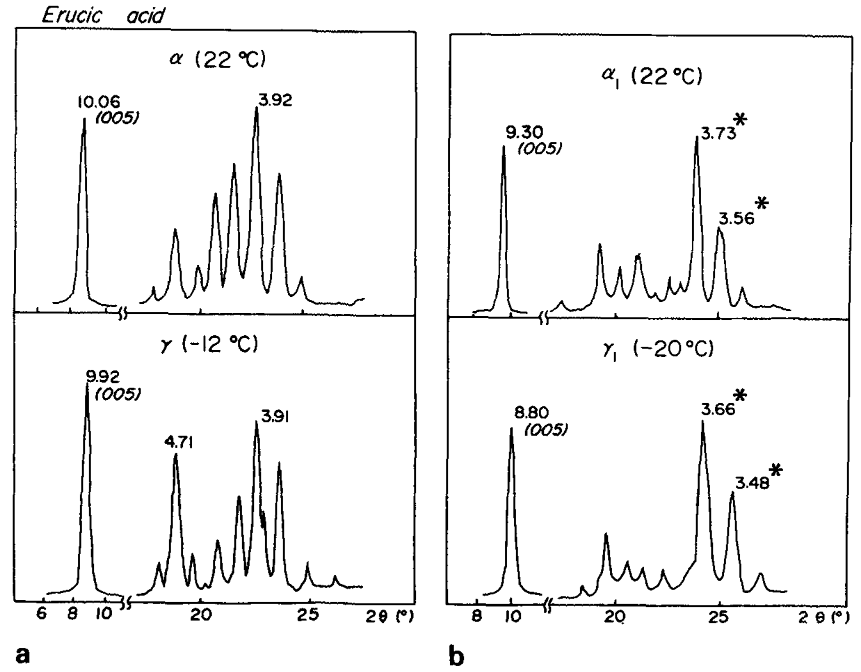

FIG. 5. X-ray diffraction patterns of (a), α and γ, and (b), α_1 and γ_1 of erucic acid. (unit, Angstrom).

DISCUSSION

Nomenclature of polymorphs. The nomenclature of the new polymorphs of erucic acid was given primarily in accordance with the polymorphism of oleic acid (1-3). In doing so, we paid most attention to the nature of molecular disordering in the aliphatic chain between the *cis* double bond and the methyl end group (ω chain). This is because the molecular disordering of this type is one of the most significant characteristics commonly observed in oleic, erucic and palmitoleic acids (3). The subcell structure may also be utilized for the nomenclature. However, the authors did not use this principle. The lateral packing of the molecularly disordered hydrocarbon chain may be rather nonspecific as revealed in a rotator phase of n-paraffin crystals (6). Therefore, the subcell structure of the polymorph whose ω-chain is disordered cannot be defined as a whole, e.g., in the case of α of oleic acid.

First, α and γ of erucic acid were named in the same manner as oleic acid, because their physical properties are quite similar to α and γ of oleic acid as fully discussed below: the XRD patterns, the crystal habits and the thermal behavior. The Raman spectra also were taken into account (3).

Second, the name of α_1 was chosen so that the conformational disordering in the ω-chain identical to α of oleic acid was meant in the nomenclature. Namely, the detailed analyses of the Raman data of α_1 showed the disordered conformation in the ω-chain which is a most typical characteristic of α of oleic acid. Therefore, a suffixed name of α_1 was given, because it is more stable than α above 25.9 C. The interplanar angle of α_1 is the same as those of β of oleic acid which approximately assumes the triclinic structure (3). However, there is no conformational disordering in β of oleic acid, hence the nomenclature using β was not used. As for γ_1, no similarity to γ was detectable. However, γ_1 and α_1 undergo the reversible solid-state transformation, having the same nature of order-disorder transition as $\gamma \rightleftharpoons \alpha$ of oleic and erucic acids. Thus, a suffixed name of γ_1 was selected.

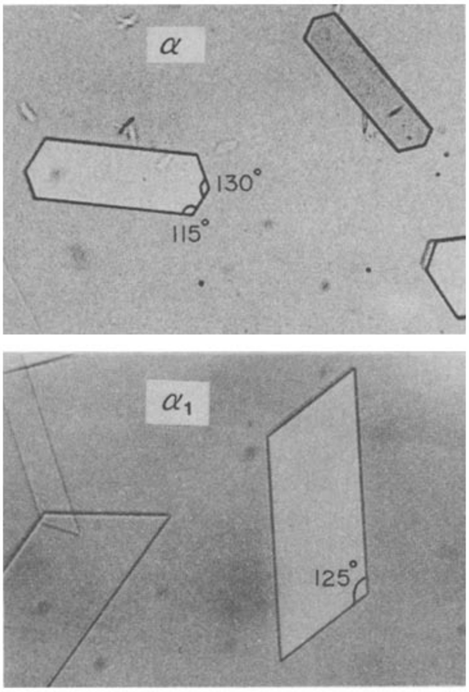

FIG. 6. Single crystals of α and α_1 of erucic acid grown from acetonitrile.

Thermodynamic stability and polymorphic transformation. The stability relationship was determined by the solubility data and the solid-state transformation. As for α and α_1, the solubilities (Fig. 7) clearly show that α_1 is more stable above 25.9 C, and vice versa below that temperature. The solid-state transformations are somewhat complicated. The reversible transformations of $\gamma \rightleftharpoons \alpha$ and $\gamma_1 \rightleftharpoons \alpha_1$ mean that α_1 is more stable than γ_1 above 9.0 C, and that α is more stable than γ above -1.0 C.

Then a problem arises on the stability among γ_1, α and γ below 9.0 C. To examine the stability between γ_1 and γ, the XRD study was carried out using γ_1 as a starting form at -20 C. After keeping the sample for several hours, the XRD pattern characteristic of γ appeared and increased in size at the expense of those of γ_1 due to the solid-state transformation which occurs very slowly. When the sample exhibiting the XRD peaks of both γ_1 and γ was heated in DSC at 2 C/min, two endothermic peaks appeared at -1.0 C and 9.0 C, corresponding to the transformations of $\gamma \rightarrow \alpha$ and $\gamma_1 \rightarrow \alpha_1$, respectively. This means that γ is more stable than γ_1 at -20 C. As for the stability between α and γ_1, the solution-mediated transformation (2) at 2.0 C, which is located between the transformation temperatures of $\gamma \rightarrow \alpha$ and $\gamma_1 \rightarrow \alpha_1$, provided that the solubility of α is lower than that of γ_1, as the transformation underwent from γ_1 to α.

Consequently, crystal Gibbs energies (G) of the four polymorphs against temperature (T) may be drawn in a range of temperature from -20 to 34 C (Fig. 8) in a qualitative manner. According to this G-T relationship, one may argue the following transformation pathways: $\gamma_1 \rightleftharpoons \alpha_1$, $\gamma \rightleftharpoons \alpha$, $\alpha \rightarrow \alpha_1$ and $\gamma_1 \rightarrow \alpha$ occurred in the solid state, among which only $\gamma_1 \rightarrow \alpha$ is irreversible because $\alpha_1 \rightarrow \alpha$ actually occurred according to the solubility relationship (Fig. 7). Hence, the G values may cross at temperatures of the reversible transformation and at the crossing point of the solubilities. Irreversible also was $\gamma_1 \rightarrow \alpha$ as examined in the acetonitrile solution at 2 C. The two irreversible conversions proved that both γ_1 and α_1 are less stable than γ and α below 25.9 C, as illustrated in the larger G values.

As for $\alpha \rightarrow \alpha_1$, the solid state transformation occurred at 31.2 C, which is far above the crossing point of their Gibbs energies (25.9 C). This discrepancy may be ascribed to certain steric hindrance involved in the solid-state transformation. This steric hindrance needs a certain amount of thermal excitation energy for the conversion, causing the actual transformation far above the turning point of the Gibbs energy. It in turn prevents the conversion from α_1 to α below 25.9 C. The similar feature was seen between B and C polymorphs of stearic acid; G(C) is higher than G(B) above 32 C (7), yet the irreversible B→C transformation occurred at 54 C (8). Recent study clarified (9) that the change in the molecular conformation and the rotation of the unit cell and subcell axes are involved in the B→C transition of stearic acid. It can be inferred that appreciable structural rearrangements may be needed during the $\alpha \rightarrow \alpha_1$ transformation of erucic acid.

The thermal data of erucic acid can be discussed in comparison to those of oleic acid and other typical long-chain compounds, together with the physical properties whose details will be presented below.

TABLE 3

Solubilities of α and α_1 Polymorphs of Erucic Acid in Acetonitrile: C_0 (g solute/100 g solvent) and X (molar fraction)

α			α_1		
T (°C)	C_0	X	T (°C)	C_0	X
17.2	0.545	0.660	15.1	0.500	0.606
18.8	0.675	0.818	18.2	0.700	0.845
20.0	0.774	0.937	22.3	1.200	1.045
21.2	0.940	1.138	23.7	1.400	1.694
22.1	1.069	1.294	26.0	1.870	2.262
23.2	1.259	1.524	26.6	1.952	2.361
24.1	1.398	1.692	26.9	2.059	2.490
24.7	1.590	1.924	27.4	2.199	2.659
24.8	1.615	1.954	28.0	2.390	2.889
25.3	1.710	2.069	28.6	2.600	3.142
			29.0	2.700	3.275

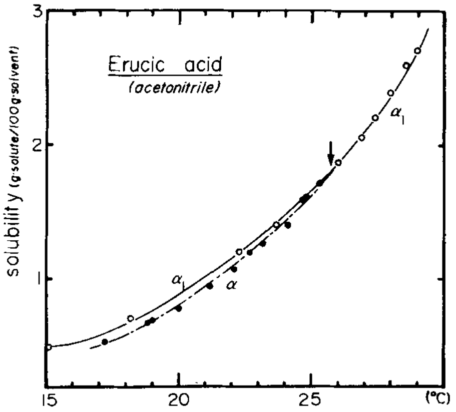

FIG. 7. Solubilities of α and α_1 of erucic acid in acetonitrile.

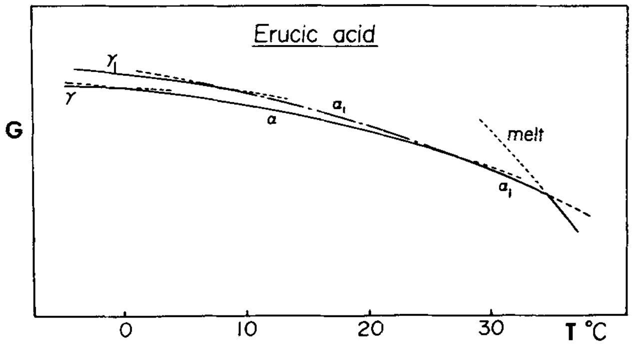

FIG. 8. A relationship between Gibbs energy (G) and temperature (T) of γ_1, α_1, γ and α of erucic acid.

As for the fusion, α_1 cannot be compared simply with α of oleic acid, because of a remarkable dissimilarity in the polymorphic structures; instead, the α forms of the two acids may be compared with each other because their physical properties are quite similar. Although $\Delta H_f(\alpha)$ of erucic acid is not available, it was reasonably estimated by adding $\Delta H_t(\alpha\text{-}\alpha_1)$ = 5.4 kJ/mol to $\Delta H_f(\alpha_1)$ = 51.0 kJ/mol, as 56.4 kJ/mol. This value is larger than $\Delta H_f(\alpha)$ of oleic acid by 16.8 kJ/mol. However, this difference can be explained by an increase in the chain length by 4 in the carboxyl-sided aliphatic chain which may be conformationally ordered. ΔH_f per one

CH_2 of the *trans* aliphatic chains is approximately 4 kJ/mol (6), which accounts for the difference in ΔH_f between the α forms of oleic and erucic acids.

The ΔH_t and ΔS_t values for $\gamma_1 \rightarrow \alpha_1$ and $\gamma \rightarrow \alpha$ of erucic acid are almost the same as those of $\gamma \rightarrow \alpha$ of oleic acid. This is quite consistent with the mutual nature of the order-disorder transformation in the ω-chain involving nine carbons. Highly-resolved Raman data indicate that α of the two acids has the same pattern, while the disordering in α_1 of erucic acid is less enhanced (unpublished). This is reflected in smaller values of ΔS_t for $\gamma_1 \rightarrow \alpha_1$.

Polymorphic structures. The structures of the four polymorphs of erucic acid are discussed mainly based on the XRD data and the crystal habits, in comparison to the oleic acid polymorphs.

The XRD patterns of γ and α are almost identical to γ and α of oleic acid (1): three strong peaks of α; 4.30 Å, 3.92 Å and 3.74 Å, and three strong peaks of γ; 4.71 Å, 3.91 Å and 3.73 Å. No superposition of the long spacing spectra with higher indices gave rise to a confusion in the short spacing spectra. Therefore, the subcell structures of γ and α or erucic and oleic acids must be the same. The crystal habit of α, which is the same between the two acids, also supports this. As for the long spacing, α is longer than γ by 0.7 Å. This difference is a bit smaller than those of oleic acid; 43.3 Å (α) and 41.9 Å (γ). It is inferred that the increase in the long spacing of α of oleic acid may be due primarily to the disordering in the ω-chain. This assumption can also be applied to two couples of polymorphs of γ/α, and γ_1/α_1 of erucic acid; in each couple, the interlamellar distance of the disordered form is longer than that of the ordered form.

The DSC melting peak of α_1 (34.0 C) is close to the crystal which was determined as a triclinic structure by Craven (4). The lattice parameters are a = 9.88 Å, b = 5.17 Å, c = 47.8 Å, α = 102°, β = 91° and γ = 87°, which yield the interlamellar distance (long spacing) very close to the observed value of 46.4 A of α_1. Hence, it is concluded that α_1 is equivalent to the crystal examined by Craven. As for γ_1, its XRD short spacing pattern does not differ from α_1, being singly decreased by $0.04 \sim 0.06$ Å. This reduction must be a simple lattice constriction due to different temperatures examined. However, the long spacing of γ_1 is shorter than α_1 by 2.5 Å, which is appreciably large compared to the difference between γ and α. Hence, one may assume that the transformation from α_1 to γ_1 is accompanied with the decrease in the chain inclination with respect to the basal surface, the change in the subcell structure being rather small. In addition, the disordering in the methyl-sided alkyl chain is introduced, as the detailed Raman bands indicate. The peculiar thermal hysterisis exhibited in $\alpha_1 \rightarrow \gamma_1$ transition (Figs. 2 and 3) may be related to the lattice displacements and the molecular re-ordering discussed here.

Finally, the interplanar angles of the lateral faces of α_1 of erucic acid are 55° and 125° which are the same values of β of oleic acid (2). This means a similarity in the subcell structure, yet dissimilarity was seen in some points: (a) growth forms of crystal are rhombohedral in α_1, but needle-like in β; (b) the XRD short spacing spectra are largely different, and (c) there is no conformation disordering in oleic acid β. Hence, one may conceive that the detailed molecular structures of α_1 and β would be very different.

To conclude, four polymorphs of erucic acid were identified in the present study. Two of them, γ and α, revealed the same features as γ and α of oleic acid, undergoing the transformation characterized by the conformational disordering in the ω-chain. The other two forms, γ_1 and α_1, also revealed the order-disorder transformation like $\gamma \rightleftharpoons \alpha$, but neither form revealed the complete similarity in the crystal structures to γ and α, and to the third form γ of oleic acid as well. The successive solid-state transformations resulted in the single melting of the high-temperature form of α_1. In the case of oleic acid, double melting of α and β was observed. From the similarity or dissimilarity between oleic and erucic acids presented here, one may predict that the polymorphism of one *cis*-double bonded unsaturated acid may differ from one acid to others, depending on the position of the double bond in the aliphatic chain.

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