☘The DSC Thermal Analysis of Crystallization Behavior in High Erucic Acid Rapeseed Oil

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ABSTRACT

DSC isothermal analysis is used to investigate the crystallization behavior of high erucic acid rapeseed oil (HEAR oil) in conjunction with usual cooling and heating methods. The crystallization of HEAR oil is found to be in two stages and which are accounted for by the crystallization of the α form and its transformation to the β form under isothermal cooling conditions. The α form is also transformed to the β form under constant heating rate conditions (10 K/min), but this transformation is governed by the heating rate. The crystallization behavior of HEAR oil appears to be dominated by its characteristic triglyceride structure as the transformation is completely altered by random interesterification. Further, when HEAR oil is blended with SBO, the crystallization is changed as the SBO component is increased.

INTRODUCTION

Rapeseed oil has been used as cooking oil for a long time in Japan. However, its fatty acid composition has been drastically changed since Canadian low erucic acid rapeseed oil was introduced into the edible oil market. Compared to other vegetable oils, the old type, high erucic acid rapeseed oil (HEAR) showed unique crystallization behavior. Hannewijk and Haighton (1) indicated the polymorphic behavior in HEAR oil crystals by differential thermal analysis (DTA). This uniqueness should be related to its triglyceride composition as reported by Hilditch (2) and Brockerhoff and Yurkowski (3).

The polymorphism of rapeseed oil relative to its erucic acid content had been studied by Riiner (4,5) using a differential scanning calorimeter (DSC) and a temperature programmed X-ray diffractometer (DPT camera). He suggested the following polymorphic transition in HEAR oil crystals under both constant cooling and heating conditions: (I) the sample cooled to -60 C, crystallized in the α form and transformed to the β' form upon heating at a rate of 16 C/min (4); (II) the sample rapidly cooled to -50 C, crystallized in the β_2 form and transformed to the β_1 form during heating (5). However, he described the identification of the β_2 form as tentative and mentioned that the crystals might contain the α form. Also, the sample was crystallized in the β_2 form at about -20 C with slow cooling (0.5 C/min) and remained unchanged even after further cooling.

Oil crystallization behavior appears to be greatly influenced by cooling and heating rates as was demonstrated in palm oil with a DSC (6,7). In this paper, DSC isothermal analysis is used for the first time to investigate the polymorphic behavior in HEAR oil crystals. This method is also combined with the conventional DSC cooling/heating analysis to detail the polymorphism.

EXPERIMENTAL PROCEDURE

Material

The samples used were commercial salad oils; high erucic acid rapeseed oil (HEAR), low erucic acid rapeseed oil (LEAR) and soybean oil (SBO). They were analyzed for fatty acid composition using the AOCS standard method (8). The 2-position analysis described by Luddy et al. (9) was used to determine triglyceride structure. Fatty acid composition of 1- or 3-position was calculated by the theory of 1,3 random and 2 random distribution in triglyceride. These results are shown in Table I.

The oils were interesterified to randomize fatty acid distribution in triglyceride according to Eckey's method (10,11) using 0.6% by weight of sodium methoxide at ca. 80 C under evacuated conditions. The randomized oils were refined, bleached and deodorized.

Differential Scanning Calorimetry

A Perkin Elmer Model DSC-2 was used in most cases. A piece of polyethylene terephthalate (12.0 mg) was sealed in a standard aluminum sample pan and used as a reference. A Rigaku Denki Model Low Temperature DSC was used for constant cooling investigation at lower temperatures below 233 K. Sample size was fixed at ca. 9 mg for the Perkin Elmer DSC and ca. 20 mg for the Rigaku DSC.

Before DSC analysis, the oil samples were filtered with a membrane filter (Nalgene Filter unit: 0.20μ) to eliminate dust and other foreign particles. Samples were sealed in an aluminum pan and held at 393 K for 5 min to destroy crystal nuclei before the DSC scan. The temperature of the DSC was rapidly (ca. 80 K/min) dropped and held at the desired temperature for the isothermal crystallization in the supercooled state below the melting point. The starting point was defined as the time when the indicating (green) lamp lit on the DSC front panel, which meant the system was under temperature control. The crystals generated under isothermal or constant cooling conditions were heated at a constant rate to record the DSC heating curves for the investigation of polymorphism.

TABLE I

Fatty Acid Composition of High Erucic Rapeseed Oil, Low Erucic Rapeseed Oil and Soybean Oil

Sample	Triglyceride position	Fatty acid composition (weight %)											
		16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	20:2	22:0	22:1	22:2
High erucic rapeseed oil	total	3.5	0.3	1.0	14.8	13.7	8.0	0.8	8.5	0.6	0.6	46.2	1.1
	2	0.6	0.4	–	36.1	38.3	20.3	–	2.0	–	–	2.3	–
	1 or 3[a]	5.0	0.3	1.5	4.2	1.4	1.9	1.2	11.8	0.9	0.9	68.2	1.7
Low erucic rapeseed oil	total	3.4	0.3	1.5	54.1	21.9	13.6	0.5	–	–	0.4	4.3	–
Soybean oil	total	10.3	–	4.0	21.2	56.3	7.7	0.2	–	–	–	–	–

[a]Calculated by the theory of 1,3 random and 2 random distribution in triglyceride.

RESULTS AND DISCUSSION

Polymorphism under Constant Cooling Mode

Oil crystallization is greatly influenced by the cooling mode. HEAR oil crystallization also seems to be influenced by the cooling rate. The crystallization behavior was investigated at cooling rates of ca. 80, 10 and 0.31 K/min. The crystals generated at the different rates were melted at a heating rate of 10 K/min to reveal their crystal forms. These cooling and heating curves are shown in Figure 1.

All three cooling curves in Figure 1 show a sharp exothermal peak at 210, 238 and 252 K. These may be caused by the α form crystallization. The difference in temperature is due to the temperature lag of the instrument at different cooling rates. Riiner indicated that HEAR oil crystallized to α form or, in some cases, to β_2 form (5). The α form converted to β_2 form which converted to β_1 form as the temperature was increased (5). This also is supported by a small endothermal peak at 252 K in the DSC heating curve of Figure 1-1. This peak seems to be the melting of the α crystals because of the lowest temperature peak. The crystallization by such a rapid cooling as ca. 80 K/min is solidified in α form, but it may partially remain in a glassy state. Thus, the endothermal peak is very small.

At the slow cooling rate (10 K/min), a more complete conversion from liquid to β_2 form is able to take place before the sample is cooled below temperatures at which crystallization takes place easily. In the heating curve of Figure 1-2 the endothermal peak appears at 265 K, but start of melting is found to be at 239 K. This broad peak may consist of fusion of the α and β_2 crystals. Most of the α form rapidly converts to the β_2 form melting at 265 K. It is probably the same polymorphism as in the rapid cooling mode (ca. 80 K/min) but just a different amount. The β_2 form crystals are transformed to the β_1 form by recrystallization (the exothermal peak at 270 K) under the heating mode of 10 K/min.

Due to the slower cooling rate, Figure 1-3 at point (B) this conversion ($\alpha \rightarrow \beta_2 \rightarrow \beta_1$) is nearly completed. The heating curve from 240 K (point B) after the second exothermal peak shows that the α crystals have had time to convert to the higher melting form and finally to the β_1 form. However, the very slow cooling condition may tend to promote separation of higher and lower melting components. In the heating curve of Figure 1-3, the endothermal peak at 278 K is probably the fusion of the β_1 form of the
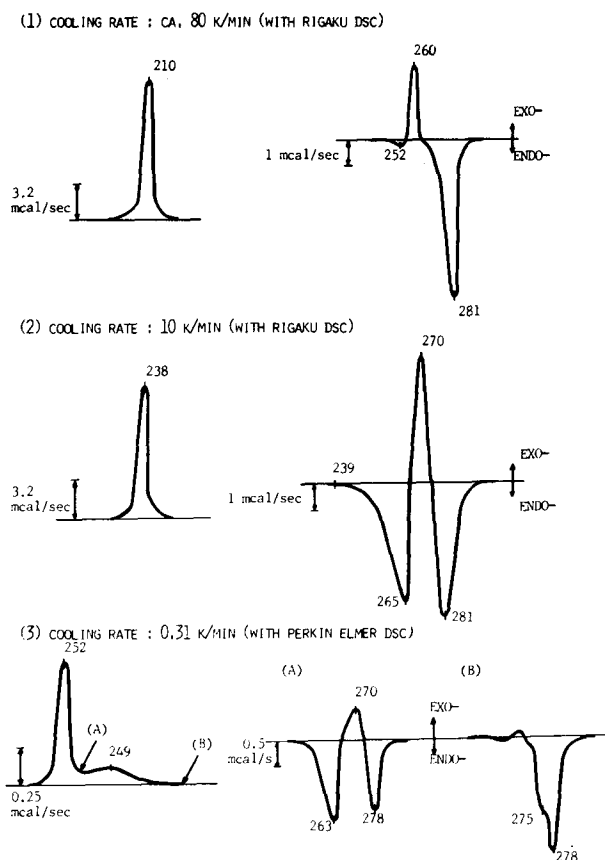
FIG. 1. DSC cooling curves (left side) and heating curves (right side) of high erucic rapeseed oil. Heating rate: 10 K/min.

higher melting major component and the shoulder at 275 K is the fusion of the β_1 form of the lower melting component. The separation probably results from the unique fatty acid composition of HEAR oil, as shown in Table I.

Polymorphism under Isothermal Crystallization

DSC isothermal crystallization curves of HEAR oil are shown in Figure 2. There are two exothermal peaks which can be easily distinguished at crystallization temperatures of 249-255 K. They are respectively termed peak-A and
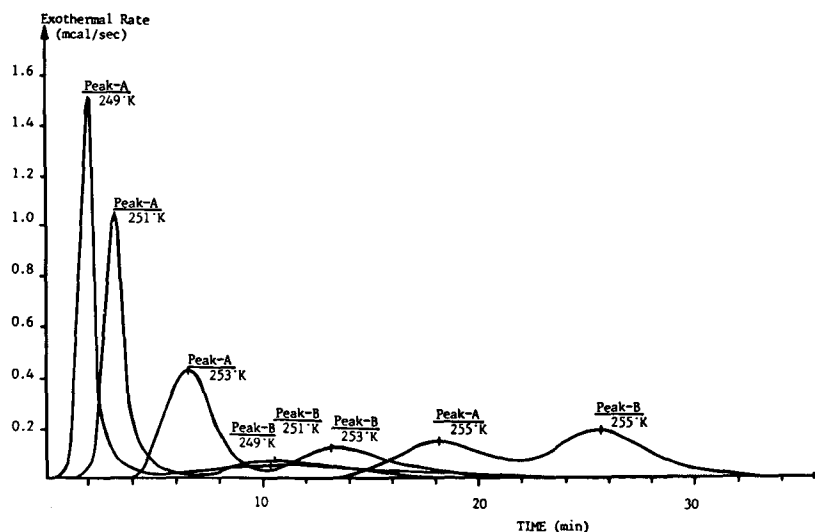
FIG. 2. DSC isothermal crystallization curves of high erucic rapeseed oil.

peak-B in order of generation in Figure 2. The heating curves at rates of 2.5, 10 and 40 K/min obtained after each exothermal peak are used to investigate the crystal forms corresponding to peak-A and peak-B as shown in Figure 3. The heating curve at a rate of 10 K/min after peak-A shows the same pattern as the heating curve shown in Figure 1-2 or 1-3 (A). The heating curve after peak-B shows only the endothermal peak at 278 K with a shoulder at 274 K. This pattern appears to be coincident with the heating curve of Figure 1-3 (B).

It would appear in the previous section that the poly-morphism of HEAR oil consists of the α form which melts around 252 K, the β_2 form which melts around 265 K, and the β_1 form which melts around 278 K. The α form seems to convert rather quickly at or below its melting point to the β_2 form as long as solid α form is present. The β_2 to β_1 conversion seems to be slower at the α melting point but increase in rate as the temperature is increased. At or near the β_2 melting point, it is very fast. In Figure 2, the very rapid solidification at both crystallization temperatures of 249 and 251 K is probably the α form crystallization. At a crystallization temperature of 253 K, most of the solidification seems to be from the liquid directly to the β_2 form while at 255 K or higher temperature.

In Figure 3, after peak-A heating at 40 K/min, the major melting peak appears at 267 K which corresponds to the β_2 form shown by Riiner from X-ray data (5). Accordingly, the small melting peak at 279 K corresponds to the β_1 form of Riiner (5). At the slow heating rate of 2.5 K/min, HEAR oil is eventually converted to the highest melting form β_1. This crystal form contains the major component melting at 277 K and the minor component melting at 271 K, which is essentially what has happened after peak-B. Thus, the isothermal crystallization exhibits the same behavior as the slow cooling crystallization.

Polymorphism Influenced by Triglyceride Composition

The unique polymorphic behavior of HEAR oil crystals probably results from the triglyceride structure: erucic acid in 1- or 3-position as shown in Table I. HEAR oil
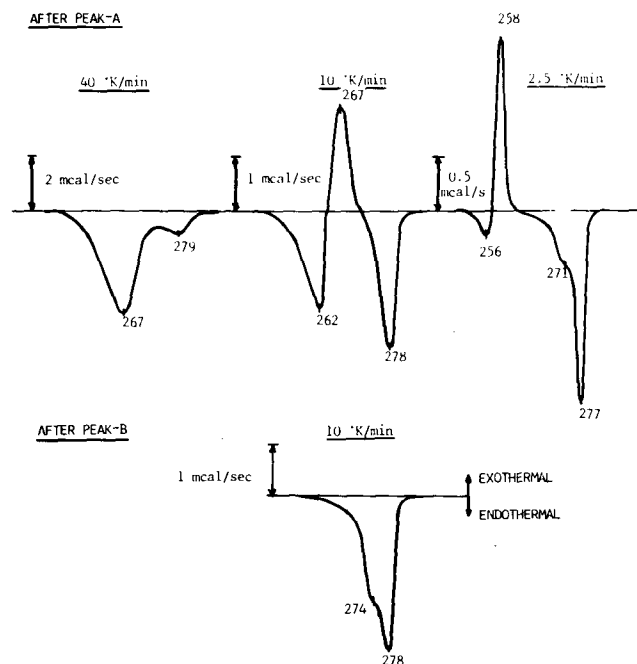

FIG. 3. DSC heating curves, initiated after peak-A and peak-B of isothermal crystallization at 249 K (Ref. Fig. 2).
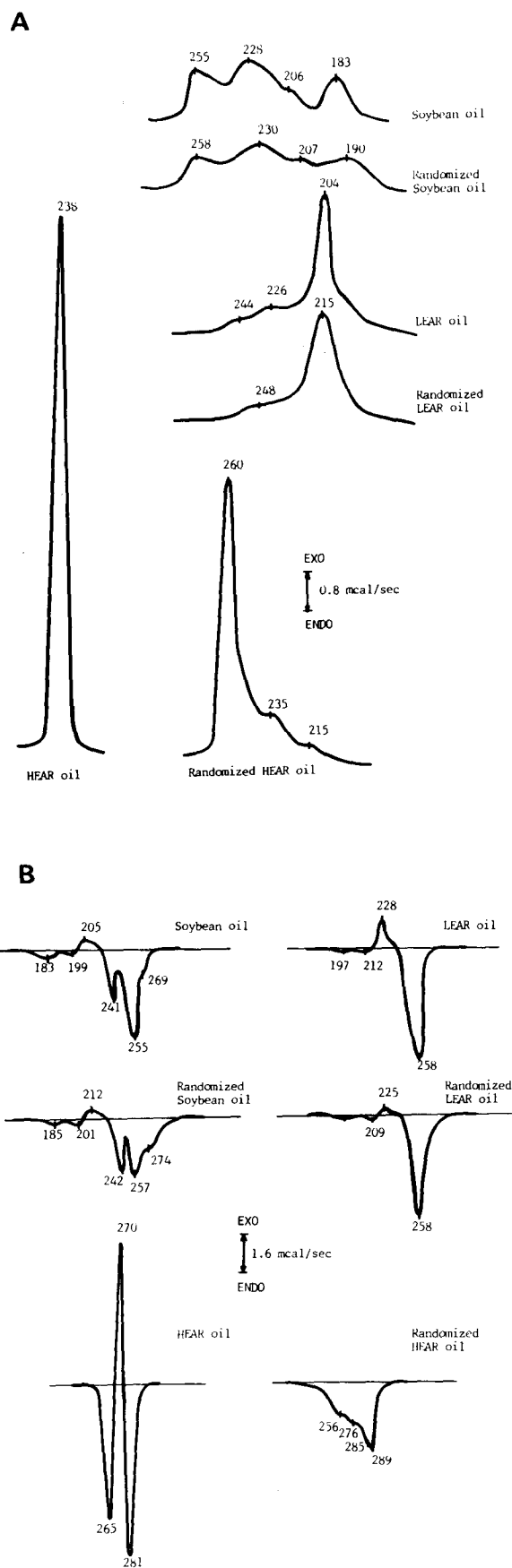

FIG. 4. (A) DSC cooling curves of high erucic rapeseed oil, low erucic rapeseed oil, soybean oil and their random interesterified oils. Cooling rate: 10 K/min. (B) DSC heating curves of samples crystal-lized at 10 K/min as shown in A. Heating rate: 10 K/min.
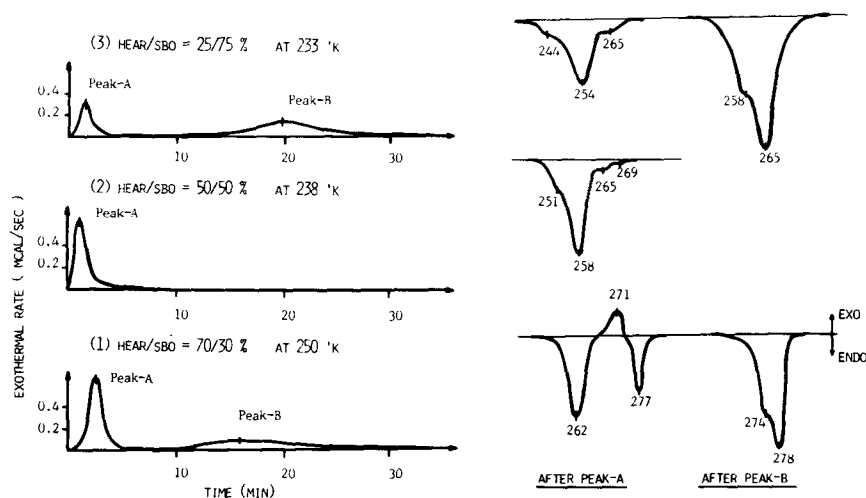
FIG. 5. DSC isothermal crystallization curves and heating curves (right side) of HEAR/SBO blend oils.

crystallization can be changed by a random interesterification. The randomized HEAR oil shows a higher freezing point (260 K) than HEAR oil (238 K) as shown in Figure 4A. Also, the randomized oil does not show a recrystallization peak upon heating at 10 K/min in Figure 4B. This peak is very characteristic of HEAR oil in the heating curve. However, the polymorphic behavior of SBO and LEAR oil is not much changed by a random interesterification as shown in Figures 4A and 4B. Therefore, it can be deduced that the unique polymorphic behavior of HEAR oil crystals is due to the location of erucic acid in the triglyceride.

The crystallization behavior is also influenced by the blend of SBO as well as by interesterification. The polymorphic behavior in the crystals of HEAR and SBO blends were investigated by the DSC isothermal method. The results are shown in Figure 5. The HEAR/SBO = 70/30% blend shows two exothermal peaks and its polymorphic behavior is the same as HEAR oil. When the ratio of HEAR oil is reduced to 50%, the HEAR/SBO = 50/50% blend shows only one exothermal peak under the isothermal condition at 238-248 K for 2 hr.

When the ratio of HEAR oil is reduced to less than 25%, two exothermal peaks are again observed in the blend oils. However, pure SBO shows only one peak. There is a turning point in the property of crystallization of HEAR/SBO blends, which occurs around HEAR/SBO = 50/50%.

The DSC heating curves (10 K/min) initiated at a stage after peak-A or B are shown in Figure 5 (right side). The HEAR/SBO = 70/30% blend shows the same heating curves as HEAR oil does. When the ratio of HEAR oil is reduced to 50 or 25%, the heating curve of peak-A crystals shows only an endothermal peak and no recrystallization peak.

The crystal form of this peak-A appears to be different from that of the HEAR/SBO = 70/30% blend or HEAR oil. For the HEAR/SBO = 25/75% blend, the heating curve of peak-B crystals shows a large endothermal peak, in which peak-A crystals may participate as the melting peak. This peak-B seems to be due to the crystal formation, but not to the transformation.

It can be concluded that the DSC isothermal method is appropriate not only for HEAR oil but also for other fats and oils to investigate their polymorphic behavior.

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