Stabilizing Polymorphic Transitions of Tristearin Using Diacylglycerols and Sucrose Polyesters

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ABSTRACT: The polymorphic transitions of synthesized tristearin in the presence of selected DAG or commercial sucrose polyesters (SPE) were investigated using DSC and X-ray diffractometry. The stabilizing effects of DAG and SPE on α to β transitions of tristearin were dependent on the chemical structures of additives such as FA chain length, saturation of FA, positions and number of FA on backbones. The addition of 1,2-distearin (DS) or SPE containing 70% stearic acid with a hydrophile-lipophile balance value of 1 (S-170) to tristearin resulted in a significant stabilizing effect on the α to β transition during constant heating and storage of α forms at 53°C. The addition of 1,2-DS or S-170 also stabilized the β′ to β transitions of tristearin during constant heating and storage at 59°C. The addition of S-170 exhibited greater stabilizing effects than the addition of 1,2-DS during early stages of storage of α or β′ forms of tristearin. This study provides evidence of potential uses for SPE as additives to improve the quality and shelf life of foods containing fats by stabilizing the desirable α or β′ forms of fats.

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TAG, the major constituents of fat, exhibit characteristic polymorphic structures or forms: α, β′, and β (1,2). In commercially produced fats such as shortenings and margarines, the α and β′ forms are more desirable than β forms because the α and β′ forms result in smooth texture and good functionality (2,3). In general, the α and β′ forms of most fats are thermodynamically unstable and prone to transition to the more stable β forms, called polymorphic transition (4). Therefore, the stability of α or β′ forms is of great interest to producers of high-fat products such as butter, margarine, and chocolate.

The polymorphic transitions of natural fats and oils can be influenced by the presence of food additives such as DAG or emulsifiers (5–9). Polymorphic stability increases with the addition of DAG (5,6,8). The molecular structures of DAG, including FA chain length and the positions of FA on the glycerol backbone, are important to the stabilization of unstable polymorphic forms of fats. The addition of distearin (C18:0) exhibited the greatest stabilizing effect on β′ forms of rapeseed oil composed primarily of stearic acids with small quantities of erucic acids (LOBRA) compared with the addition of dipalmitin (C16:0) or dieicosanoin (C20:0) (5). Moreover, the addition of 1,2-DAG increased the stability of the α and β′ forms of LOBRA more than the addition of 1,3-DAG. Smith *et al.* (8) also reported that the addition of 1,2-dilaurin (C12:0) to trilaurin (C12:0) retarded the β′ to β transition more than the addition of 1,3-dilaurin. Many efforts to retard polymorphic transitions with food additives are focused on the addition of emulsifiers or surfactants such as sorbitan esters (Spans) or ethoxylated sorbitan esters (Tweens) (6,7,9–12).

Sucrose polyesters (SPE), defined as having greater than six FA esterified to the hydroxyl groups of sucrose, are lipophilic, nonabsorbable, noncaloric fat substitutes approved for use in selected foods (13). Olestra (common name for SPE) was approved by the U.S. Food and Drug Administration in 1996 to replace up to 100% of the conventional fat in savory snacks such as potato chips, cheese puffs, and crackers (14). SPE are also approved as emulsifiers in foods at less than 1% concentration (14). However, the functionality of SPE is not well studied other than as fat substitutes. Garti *et al.* (6) reported that the addition of sucrose monostearate to tristearin exhibited no effect on polymorphic transition. Elisabettini *et al.* (9) reported that the addition of 5% sucrose monostearate to tristearin retarded the α to β and β′ to β transition better than the addition of 5% sorbitan tristearate. More recently, Martini *et al.* (15) observed the retardation of the β′ to β polymorphic transition when SPE were added to hydrogenated oil at selected concentrations. The objectives of this study were to investigate and compare the effects of selected DAG and commercial SPE on the polymorphic transitions of tristearin from α to β and from β′ to β forms.

EXPERIMENTAL PROCEDURES

Materials. Tristearin was synthesized from stearic acid and glycerol (16). The purity was checked by TLC. The mobile solvent of the TLC analysis was a mixture of petroleum ether/diethyl ether/acetic acid (90:10:1, by vol). The purified tristearin exhibited a single spot at a concentration of 0.001 mg/mL and an R_f value of 0.4. The melting points of α and β forms of synthesized tristearin were determined to be 56 and 73°C, respectively, using a differential scanning calorimeter (DSC-7; PerkinElmer, Norwalk, CT). Two β′ forms of tristearin were identified from a thermogram, and the melting points of β'_1 and β'_2 of tristearin were 62 and 66°C, respectively (16). The 1,3- and 1,2-isomers of dipalmitin (DP), distearin (DS), diolein

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(DO), and racemic dilinolenin (DL) were purchased from Sigma Chemical Co. (St. Louis, MO). Ryoto sugar esters (manufactured from natural sucrose and FA esters of vegetable origin) were obtained from Mitsubishi-Kasei Food Co. (Tokyo, Japan) and included sucrose laurate, sucrose myristate, sucrose palmitate, sucrose stearate, and sucrose oleate. The properties of selected commercial SPE are presented in Table 1. Five percent (w/w) of DAG and SPE were added to a tristearin melt and blended at 100°C for 10 min to destroy crystal memory and obtain a homogeneous mixture.

DSC. Thermal analyses were conducted using a differential scanning calorimeter (DSC-7; PerkinElmer). The differential scanning calorimeter was calibrated with indium, and an empty aluminum pan was used as a reference. The tristearin melt (about 5 mg) in the presence of DAG or SPE was cooled from 100 to 20°C at a rate of –20°C/min to induce α forms, held for 5 min at 20°C, and heated to 100°C at a rate of 5°C/min. To induce β′ forms, the melt was cooled to 55°C at a rate of –20°C/min, held until crystallization was complete, cooled to 20°C, and heated to 100°C at a rate of 5°C/min (9,12). The crystallization was considered to be complete when the exothermic curves of tristearin returned to the baseline.

The heats of fusion (Δ*H*) of polymorphic forms are calculated by integration of endothermic peaks from DSC curves scanned at a heating rate of 5°C/min. The Δ*H* ratios of α (α*), β′, (β′*), or β (β*) were defined as the ratio between Δ*H* values of α (β′ or β) forms of tristearin in the presence of additives and Δ*H* values of α (β′ or β) forms of pure tristearin. The α* and β′* of tristearin in the presence of additives are calculated with the following equation (11,12):

$$\alpha^*(\beta'^* \text{ or } \beta^*) = \frac{\Delta H \text{ of } \alpha\,(\beta' \text{ or } \beta) \text{ of tristearin in the presence of additives}}{\Delta H \text{ of } \alpha\,(\beta' \text{ or } \beta) \text{ of a pure tristearin}} \quad [1]$$

The α* and β* of tristearin in the presence of additives can be used as an indicator of the extent of polymorphic transition from α to β forms.

Induction and storage of polymorphic forms of tristearin. The α forms of tristearin in the presence of additives were also induced by natural cooling of the melt from 100°C to room temperature (21 ± 1°C), and the β′ forms were induced by isothermal crystallization at 55°C in a water bath (10). The induced α or β′ forms were stored at 53 and 59°C, respectively, to observe polymorphic transitions as a function of storage time.

X-ray diffractometry. The X-ray diffraction (XRD) patterns of tristearin were determined by a Philips X'Pert MPD X-ray diffractometer (Philips Analytical, Natick, MA) using a Co tube (λ = 1.7903 Å) with an Fe filter equipped with a temperature control system (T1000). The instrument settings were 35 kV with filament currents of 35 mA. The data collection for about 200 mg of tristearin was performed between 15 and 40° (2θ) with a scan speed of 0.2°/s.

RESULTS AND DISCUSSION

DAG and α to β transition of tristearin during constant heating. The addition of DAG or SPE to the tristearin melt resulted in crystallization temperatures of 47.6 ± 0.8°C and Δ*H* values of –133.4 ± 5.8 J/g, similar to the crystallization temperature and Δ*H* value of pure tristearin cooled from 100 to 20°C at a rate of –20°C/min. The fact that the Δ*H* values of tristearin in the presence of DAG or SPE were similar to the Δ*H* values of pure tristearin implies that the induction of polymorphic forms in tristearin was not changed by the addition of DAG or SPE. The XRD of tristearin cooled naturally to room temperature from a melt at 100°C in the presence of DAG or SPE exhibited short-spacing at 4.15 Å, indicating that the tristearin melt crystallized into α forms as observed in pure tristearin.

The DSC heating curves of tristearin after cooling from 100 to 20°C in the presence of selected DAG are presented in Figure 1. In the DSC heating curve of pure tristearin, the first endothermic peak at 56°C represents the melting of α forms induced by cooling a melt, and the second peak at 73°C represents the melting of β forms crystallized after melting of α forms during constant heating. The exothermic peak between the two endothermic peaks reflects a series of crystallization, melting, and polymorphic transitions: α to β′ transition, crystallization into β′ forms, melting of β′ forms, β′ to β transition, and crystallization into β forms during constant heating (7).

Tristearin in the presence of solid DP or DS at room temperature exhibited α form peak areas equivalent to the peak areas of α forms in pure tristearin, and β form peak areas smaller than the peak areas for β forms in pure tristearin. Tristearin in the presence of 1,3-DS exhibited DSC profiles similar to pure tristearin; however, tristearin in the presence of 1,2-DS exhibited altered

TABLE 1
Properties of Selected Commercial Sucrose Polyesters[a]

Sucrose polyester	Ryoto name	Approximate HLB[b]	Approximate % FA	Approximate % polyester
Sucrose laurate	L-595	5	95	70
	L-1695	16	95	20
Sucrose myristate	M-1695	16	95	20
Sucrose palmitate	P-1670	16	70	20
Sucrose stearate	S-170	1	70	100
	S-570	5	70	70
	S-1670	16	70	25
Sucrose oleate	O-1570	15	70	30

[a]From Ryoto (Mitsubishi-Kasei Food Co., Tokyo, Japan) sugar ester technical information (2000).
[b]Hydrophile-lipophile balance values.

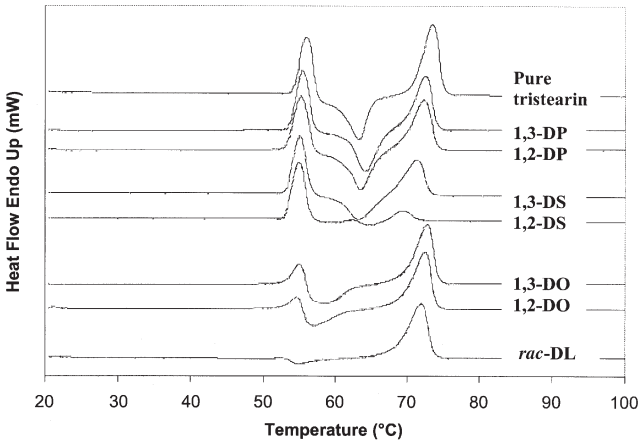

FIG. 1. DSC heating curves of tristearin in the presence of 5% 1,3- or 1,2-dipalmitin (DP), distearin (DS), diolein (DO), and racemic dilinolenin (*rac*-DL).

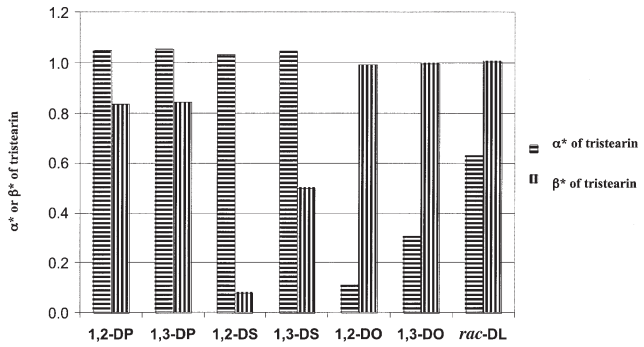

FIG. 2. The α* and β* of tristearin in the presence of 5% 1,3- or 1,2-DP, DS, DO, and *rac*-DL. The α* (or β*) = Δ*H* of α (or β) in the presence of DAG/Δ*H* of α (or β) of pure tristearin. For abbreviations see Figure 1.

DSC profiles in that a small endothermic peak appeared near 62°C and the endothermic peak for β forms at 73°C decreased. The endothermic peak at 62°C can be interpreted as the endothermic peak for β′ forms. Therefore, the addition of 1,2-DS may retard the polymorphic transition sufficiently to form substantial intermediate β′ forms during polymorphic transition.

On the other hand, tristearin in the presence of liquid DO or DL at room temperature exhibited smaller peak areas for α forms than the peak areas for α forms of pure tristearin, and equivalent peak areas for β forms. Since quantities of crystallized tristearin were not altered by the addition of DO or DL during cooling of the melt from 100 to 20°C, the small endothermic peaks for α forms of tristearin in the presence of DO or DL imply that the α to β transitions of tristearin were promoted by the addition of DO or DL during constant heating. Garti *et al.* (6) reported that emulsifiers containing unsaturated FA promoted polymorphic transitions probably because tilted unsaturated FA resulted in greater tristearin mobility, decreasing the interactions between emulsifier and tristearin.

The α* and β* of tristearin in the presence of DAG are presented in Figure 2. The α* of tristearin in the presence of DP or DS are greater than 1, and the β* are less than 1. Interpretation of the results indicates that DP or DS co-crystallizes with tristearin and stabilizes α forms of tristearin and, as a result, retards the transition to more stable β forms. The addition of DS to tristearin melts resulted in a greater reduction in the β* than the addition of DP. The addition of 1,2-DS produced a greater reduction in β* than the addition of 1,3-DS. On the other hand, the addition of DO or DL to tristearin melts produced α* less than 1, and produced β* of 1, representative of promoting an α to β transition during constant heating of tristearin.

These results confirm that the effects of DAG on the α to β′ transition of tristearin are dependent on the chemical structure of DAG, such as saturation of FA, FA chain length, and the position of FA on the glycerol backbone. The solid DAG containing the saturated FA, DP or DS, retarded the α to β transition of tristearin, whereas the liquid DAG containing the unsaturated FA, DO or DL, promoted the α to β transition of tristearin. Liquid emulsifiers and surfactants promote or produce only small effects on polymorphic transitions of tristearin (11,12). DS isomers containing a FA chain length equivalent to tristearin retarded the α to β transition to the greatest extent compared with the tested solid DAG. Moreover, 1,2-DS exhibited a more effective retardation of the α to β transition of tristearin than 1,3-DS as reported by Hernqvist *et al.* (5) and Smith *et al.* (8). The greater stabilizing effect of 1,2-DAG when compared with 1,3-DAG may be attributed to the fact that 1,2-DAG crystallize into the β′ form with orthorhombic chain packing, whereas 1,3-DAG crystallize into β forms with triclinic packing (5). Moreover, the molecular structure of 1,2-DAG is better fitted to the tristearin crystal structure than 1,3-DAG, producing retardation of the polymorphic transitions.

SPE and the α to β transition of tristearin during constant heating. The effects of SPE containing selected FA chain lengths and with hydrophile-lipophile balance (HLB) values on α to β transitions of tristearin are presented in Figure 3. Among the tested SPE, S-170 and S-570, containing stearic acid with HLB values of 1 and 5, respectively, retarded the α

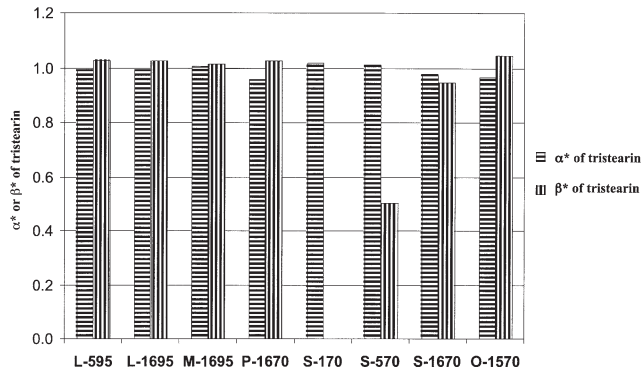

FIG. 3. The α* and β* of tristearin in the presence of sucrose polyesters. The α* (or β*) = Δ*H* of α (or β) in the presence of sucrose polyesters/Δ*H* of α (or β) of pure tristearin. For properties of the commercial sucrose polyesters used in these experiments, see Table 1.

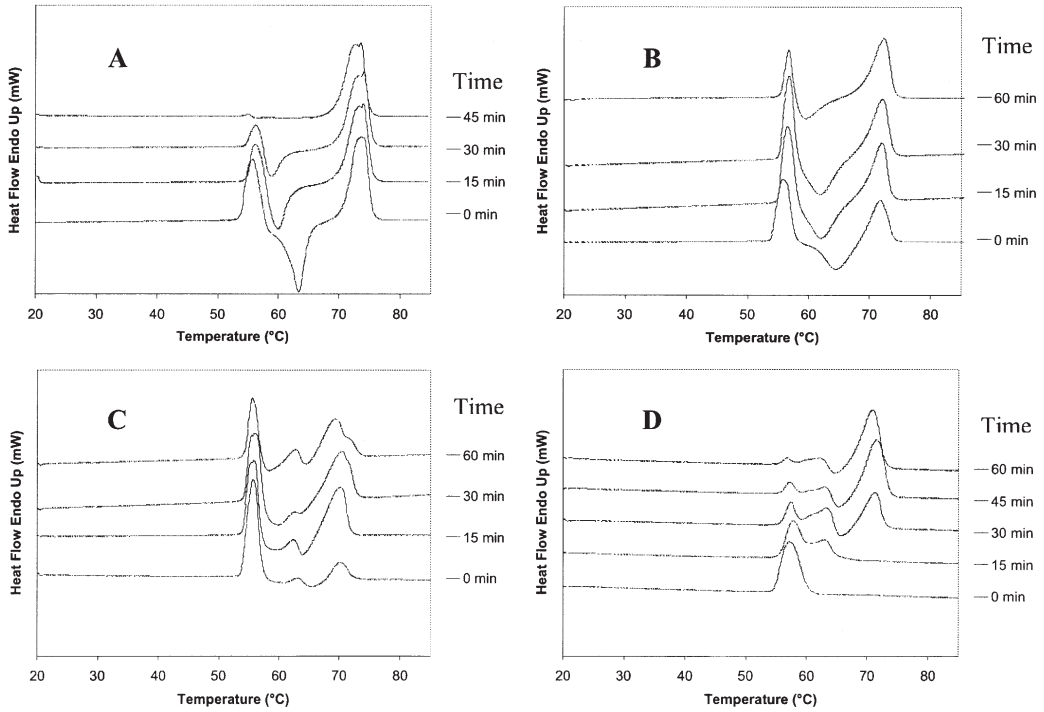

FIG. 4. DSC curves of α forms of pure tristearin (A), in the presence of 1,3-DS (B), 1,2-DS (C), and S-170 (D) stored at 53°C. For abbreviations see Figure 1.

to β transition of tristearin, reducing the β′*. SPE other than S-170 and S-570 exhibited little effect on the α to β transition of tristearin. The retardation effects of SPE containing stearic acids on α to β transitions of tristearin increased as the HLB values decreased. The addition of S-170 with an HLB value of 1 to tristearin exhibited the maximal stabilizing effects on the α to β′ transition of tristearin. The DSC heating curves of tristearin in the presence of S-170 exhibited a single endothermic peak for α forms with no endothermic peak for β forms, as presented in Figure 4D, implying that polymorphic transition to the more stable β forms was inhibited during a constant heating rate of 5°C/min.

The polymorphic transitions of tristearin in the presence of SPE were also dependent on the molecular structure of the SPE, especially the FA chain length and the number of FA esterified on the sucrose molecules. The HLB values of SPE are related to the number of FA esterified to sucrose molecules in that the SPE with low HLB values have a greater hydrophobicity and number of FA esterified to sucrose, whereas the SPE with high HLB values are largely composed of monoesters (Table 1). SPE containing FA with chain lengths equivalent to tristearin and containing large numbers of FA esterified to sucrose exhibited the most effective retardation effects on the α to β transition. S-170, containing approximately 100% polyesters, may maximize the interaction of FA among SPE and tristearin in the solid state. Also, with an HLB value of 1, S-170 may incorporate into the tristearin melt more easily owing to hydrophobicity and the small HLB value, and co-crystallize with tristearin. The interaction of S-170 sucrose FA polyesters with tristearin in the solid state may contribute to stabilization of α forms, resulting in retardation of the α to β transition of tristearin. Elisabettini *et al*. (9) reported that sucrose monostearate exhibited more retardation on the polymorphic transition of tristearin than emulsifiers such as 1-monostearin or sorbitan tristearate. However, we observed that sucrose monostearate (S-1670), containing 75% monoesters, exhibited little effect on the polymorphic transition previously reported by Garti *et al*. (6).

The fact that DAG or SPE containing saturated FA with chain lengths equivalent to tristearin exhibited stabilizing effects on polymorphic transitions implies that the FA chain length of additives may be the most important factor contributing to the stability of polymorphic transitions. DAG or SPE co-crystallize with tristearin and penetrate into the crystal lattice, resulting in maximum interactions of C18 resulting in FA chains between DAG or SPE and tristearin. The steric hindrance between C18 FA chains may hold and stabilize the hexagonal subcell packing structure of α forms, resulting in retardation of the polymorphic transition to β forms. The positions of the FA on DAG and the number of FA esterified to SPE are also important. However, the position and number of FA play a role in affecting polymorphic transitions only when the additives contain a FA chain length equivalent to that of tristearin. The addition of 1,2-DP to tristearin exhibited a stabilizing effect equivalent to the addition of 1,3-DP. Likewise, little difference in the stability of transition was observed with the addition of L-595 and L-1695 to tristearin (refer to Table 1).

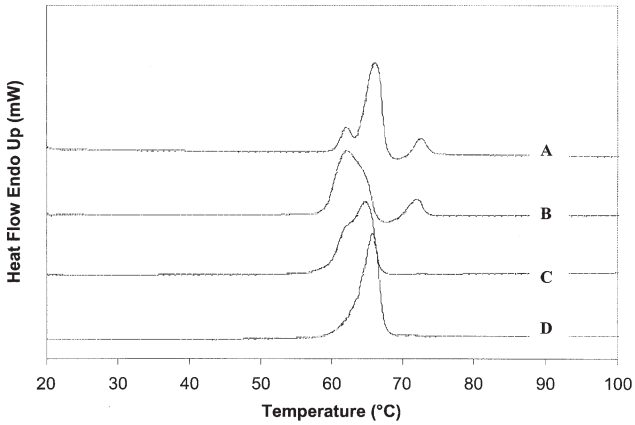

FIG. 5. DSC curves of β′ forms of pure tristearin (A) and of tristearin in the presence of 1,3-DS (B), 1,2-DS (C), and S-170 (D) after isothermal crystallization at 55°C. For abbreviations see Figure 1.

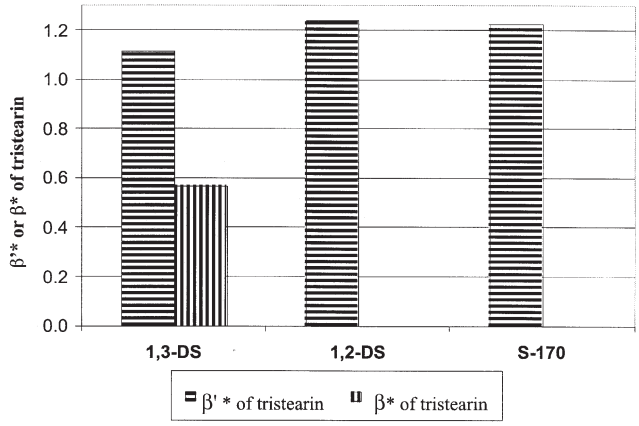

FIG. 6. The β′* and β* of tristearin in the presence of 1,3-DS, 1,2-DS, and S-170. The β′* (or β*) = Δ*H* of β′ (or β) in the presence of additives/Δ*H* of β′ (or β) of pure tristearin.

Stability of α forms of tristearin in the presence of DS or S-170 at 53°C. The α forms of tristearin were induced by natural cooling of tristearin melts to room temperature in the presence of DS isomers or S-170 SPE and stored at 53°C to study the stability of α forms in the presence of DS isomers and S-170. The storage of α forms at 53°C allows transformation to the β forms through solid–solid transition because the temperature is below the α form melting point of 56°C (7). The DSC curves of α forms of tristearin stored at 53°C as a function of storage time are presented in Figure 4. The lifetime of α forms of pure tristearin at 53°C was 45 min (Fig. 4A). The addition of 1,3-DS to tristearin resulted in a slower decrease in the areas under α peaks than the area under the peak of pure tristearin, and about 40% of the peak area for α forms remained after 60 min (Fig. 4B). The intermediate β′ peak was not detected during storage of tristearin in the presence of 1,3-DS, indicating that the α forms transformed rapidly to the β forms, as observed with pure tristearin. The addition of 1,2-DS to tristearin resulted in about 67% of the peak area for α forms remaining after 60 min, indicating a greater stabilizing effect of 1,2-DS on the α forms of tristearin than of 1,3-DS (Fig. 4C). The appearance of the endothermic peak at 62°C in tristearin in the presence of 1,2-DS during storage at 53°C can be interpreted as stabilization of β′ forms as well as α forms of tristearin. The addition of S-170 to tristearin produced stabilization of the α forms of tristearin similar to the addition of 1,2-DS to tristearin; the peaks for β′ forms were observed for 60 min of storage at 53°C (Fig. 4D). Greater stability of α forms was observed on the addition of S-170 to tristearin than on the addition of 1,2-DS to tristearin during 15 min of storage at 53°C. However, after 30 min of storage of tristearin in the presence of S-170, the α forms of tristearin started transforming to the β forms, and about 9% of the α forms of tristearin remained after storage at 53°C for 60 min. The addition of S-170 to tristearin stabilizes the relatively unstable α and β′ forms of tristearin more than does the addition of 1,2-DS to tristearin during early stages of storage at 53°C.

Induction of β′ forms of tristearin in the presence of DS or S-170. The β′ forms of tristearin crystallized in the presence of DS isomers or S-170 were induced by isothermal crystallization at 55°C. The isothermal crystallization of pure tristearin at 55°C was completed in about 25 min, whereas the addition of DS isomers and S-170 to tristearin increased the crystallization time for β′ forms to about 90 min and 24 h, respectively. Unlike crystallization of tristearin into α forms, crystallization into β′ forms of tristearin in the presence of DS or S-170 increased crystallization time tremendously. The increased crystallization time may be due to the crystallization into a more stable subcell structure of β′ forms. DS or S-170 may co-crystallize into stabilized orthorhombic subcell packing with long crystallization time. The identification of co-crystallized β′ forms of tristearin with DS or S-170 is presented in Figure 5. The DSC curves of the β′ forms of pure tristearin crystallized at 55°C for 25 min exhibited two peaks: one for β'_1 forms at 66°C and the other for β'_2 forms at 62°C, as observed by Elisabettini *et al.* (9). Although the crystalline structures between the two β'_1 and β'_2 forms of TAG are not resolved (17), β'_1 forms are more stable than β'_2 forms (4). The addition of DS isomers also produced peaks for β'_1 and β'_2 forms. The addition of 1,3-DS resulted in larger quantities of β'_2 forms than β'_1 forms, and the addition of 1,2-DS resulted in larger quantities of β'_1 forms than β'_2 forms. No peak for β'_2 forms was detected in the DSC curves of tristearin in the presence of S-170, indicating that the addition of S-170 induced primarily β'_1 forms rather than β'_2 forms. However, no differences in the XRD patterns of the induced β'_1 and β'_2 forms in the presence of DS isomers or S-170 were observed, producing the short-spacing at 4.2 and 3.8 Å equivalent to the short-spacing patterns of pure β′ forms of tristearin.

Effect of addition of DS or S-170 on β′ to β transition of tristearin. The β′* and β* of tristearin in the presence of DS isomers and S-170 are presented in Figure 6. The addition of DS isomers or S-170 to tristearin increased the β′* and decreased the β*, indicating the β′ to β transitions of tristearin were retarded by the addition of DS or S-170. The addition of 1,2-DS

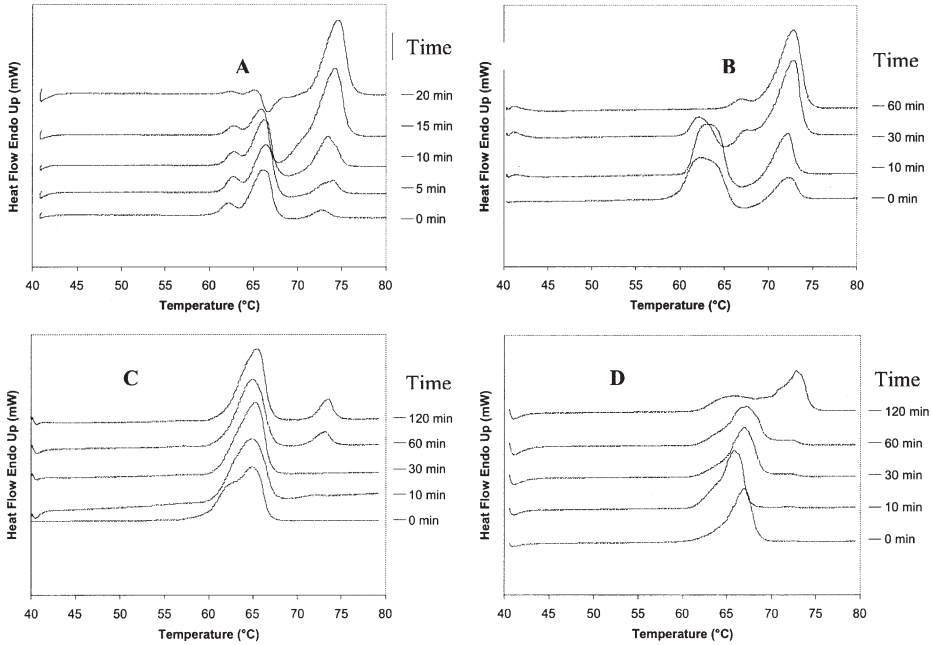

FIG. 7. DSC curves of β′ forms of pure tristearin (A) and of tristearin in the presence of 1,3-DS (B), 1,2-DS (C), and S-170 (D) stored at 59°C. For abbreviations see Figure 1.

exhibited a greater stabilizing effect on the β′ to β transition of tristearin than the addition of 1,3-DS. The addition of 1,2-DS or S-170 completely inhibited the β′ to β transition, observed as zero Δ*H* values of β form during constant heating of tristearin in the presence of 1,2-DS or S-170.

The induced β′ forms of tristearin in the presence of DS or S-170 were stored at 59°C to accelerate polymorphic transition to the β forms (Fig. 7). As storage time at 59°C increased, the area under the endothermic peaks for β′ forms decreased and the area under the endothermic peaks for β forms increased, indicating the β′ to β transition of tristearin occurred during storage. The β′ forms of pure tristearin transformed to β forms in 20 min at 59°C. The addition of DS isomers to tristearin stabilized the β′ forms. The addition of 1,2-DS produced a greater stabilizing effect than the addition of 1,3-DS. The β′ forms of tristearin in the presence of 1,3-DS transformed to β forms after 60 min, whereas about 96% of the β′ forms of tristearin in the presence of 1,2-DS were preserved after 120 min. The addition of S-170 to tristearin produced a greater stabilizing effect than the addition of 1,2-DS after 60 min, exhibiting smaller peak areas for β forms than the peak areas of β forms after addition of 1,2-DS. However, the β′ forms of tristearin in the presence of S-170 rapidly transformed to β forms after 60 min, resulting in preservation of about 32% of the β′ forms after 120 min. The addition of S-170 to the tristearin melt exhibited greater stabilizing effects than the addition of 1,2-DS during initial storage of α or β′ forms of tristearin, implying that SPE may be used to improve the shelf life of fats or foods containing fats by stabilizing the desirable α or β′ forms of the fats.

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