

# Synthesis and Physicochemical Characterization of Mixed Diacid Triglycerides That Contain Elaidic Acid

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**ABSTRACT:** The synthesis of symmetrical and asymmetrical palmito- and stearo-elaidic triglycerides (PEP, SES, EPP, PEE, ESS, and SEE, in which P = palmitic, S = stearic, and E = elaidic acid) was undertaken to investigate their polymorphism. The chemical pathways and the purification steps, including crystallization and adsorption chromatography, are described. The different chromatographic analyses (gas-liquid chromatography: carbon number profile and fatty acid methyl ester profile, and high-performance liquid chromatography) revealed that the purity of the synthesized products was superior to 99% except for SES (>96%). The thermal behavior, as well as the polymorphism of these triglycerides, has been investigated by means of differential scanning calorimetry and powder X-ray diffraction spectroscopy at variable temperatures. The six compounds crystallize according to a double chainlength packing. The most stable polymorphic form of palmito-elaidic triglycerides belongs to the  $\beta'$  variety, whereas the stearo-elaidic triglycerides are  $\beta$  stable.

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**KEY WORDS:** Elaidic acid, mixed diacid triglycerides, polymorphism, synthesis.

Natural fats are known for their complex thermal and structural behavior, which is closely related to their major components: triglycerides. Triglycerides are characterized by multiple melting due to polymorphism. Basically, they exhibit three different polymorphic forms:  $\alpha$ ,  $\beta'$  and  $\beta$ , which are easily pointed out by X-ray measurements. In crude oils and fats, triglycerides are almost exclusively derived from saturated and *cis* unsaturated fatty acids. Their polymorphism has been widely investigated (1).

To diversify their use, natural fats and oils are industrially transformed according to different techniques, such as hydrogenation, fractionation, and interesterification (2). Hydrogenation aims at reducing the degree of unsaturation of the

oil. Because this process raises the melting point, consistency as well as stability against oxidation of the final product is improved. However, positional isomerization of the *cis* double bond takes place and leads to the occurrence of *trans* isomers as by-products (3). Such isomers drastically change the physicochemical characteristics of refined fats.

Because hydrogenated fats are largely used in the food industry (margarine, shortenings, etc.) and because little is known about the physicochemical behavior of triglycerides that contain *trans* fatty acids, we investigated the polymorphism of such triglycerides. We focused on triglycerides that contain palmitic and stearic acids—the most abundant saturated fatty acids—and elaidic acid, which is the *trans* homolog of oleic acid. Both symmetrical (PEP and SES, where P = palmitic, E = elaidic, and S = stearic acids) and asymmetrical triglycerides were studied (PEE, EPP, SEE, and ESS). The symmetrical diacid triglycerides studied are the *trans* counterparts of two of the three major constituents of cocoa butter (POP and SOS, where O = oleic acid).

Mixed diacid triglycerides that contain elaidic acid are not commercially available. Therefore, we first had to synthesize them. The aim of the present work was to prepare and purify the six aforementioned mixed diacid triglycerides to establish their polymorphism (4,5). Particular attention was given to the purification steps because the polymorphic transitions of triglycerides are known to be strongly influenced by other lipid materials that are coproduced during the different syntheses (6).

## EXPERIMENTAL PROCEDURES

*Reagents for synthesis.* Glycerol used in the synthesis of the symmetrical triglycerides was purchased from Sigma Chemical Co. (St. Louis, MO). Isopropylidene glycerol used for the synthesis of the asymmetrical triglycerides was obtained from Solvay (Brussels, Belgium). Palmitic, stearic and elaidic acids, elaidic anhydride, 1,3-dipalmitin, oxalyl chloride, *p*-toluene sulfonic acid (*p*TSA), 4-dimethylaminopyridine, and pyridine were purchased from Sigma. Sodium acetate and boric acid were obtained from Janssen Chemica (Beerse, Belgium).

*Thin-layer chromatography (TLC).* TLC analyses were

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performed on  $8 \times 4$  cm silica gel plates (Macherey-Nagel, Düren, Germany). The eluent, leading to the best achievable separation of the different lipid classes, consisted of a mixture of petroleum ether [b.p. =  $60\text{--}80^\circ\text{C}$ ]/diethyl ether/formic acid (60:40:1.5, vol/vol/vol). After elution, the plates were dried, sprayed with a 0.2% ethanolic solution of 2,7-dichlorofluorescein, and examined under ultraviolet radiation at 254 nm.

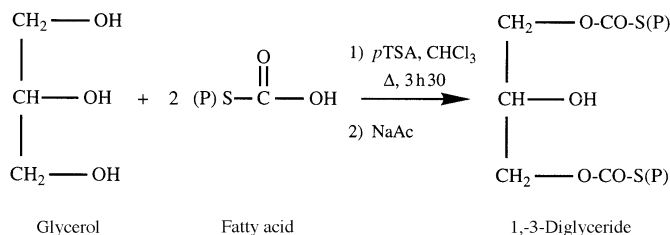
**Gas-liquid chromatography (GLC).** The molar proportion of the acyl residues in the triglycerides was determined by GLC analysis of their corresponding fatty acid methyl esters (FAME) (7) and compared to the "theoretical values." A Hewlett-Packard 5880A chromatograph (Palo Alto, CA), fitted with an on-column injector and a flame-ionization detector (FID) at  $250^\circ\text{C}$ , was used. The operating conditions were as follows:  $25 \text{ m} \times 0.25 \text{ mm}$  CP-WAX 52CB column (Chrompack, Middleburg, The Netherlands) with  $0.2 \mu\text{m}$  film thickness; temperature program from  $55$  to  $150^\circ\text{C}$  at  $30^\circ\text{C}/\text{min}$  and from  $150$  to  $220^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$ ; helium at  $50 \text{ kPa}$  was used as carrier gas. The purity of the synthesized triglycerides was checked by establishing the carbon number profile (CNP) (8,9) on a  $3 \text{ m} \times 0.32 \text{ mm}$  CP-Sil 5CB column (Chrompack)  $0.2 \mu\text{m}$  film thickness; temperature program from  $60$  to  $340^\circ\text{C}$  at  $15^\circ\text{C}/\text{min}$ ; carrier gas helium at  $70 \text{ kPa}$ ; Carlo Erba MEGA 5160 (Milan, Italy), equipped with an on-column injector and a FID at  $350^\circ\text{C}$ . For SES and PEP, the proportion of their positional isomers (i.e., ESS and EPP) was measured by high-performance liquid chro-

mography (HPLC) according to a method previously described (10).

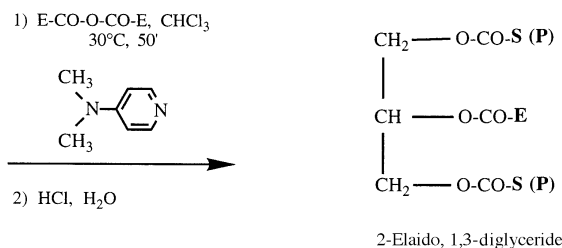
**Differential scanning calorimetry (DSC).** Determination of melting and transition points, as well as enthalpies of fusion ( $\Delta H$ ), were performed on a Perkin-Elmer DSC-7 (Norwalk, CT), assisted by an IBM PS/2 computer and coupled to a TAC 7/3 control instrument (Perkin-Elmer). An intracooler allowed measurements at temperatures below  $0^\circ\text{C}$ . Samples of  $3\text{--}5 \text{ mg}$  were sealed into aluminum pans; a similar empty pan served as reference.

**Crystallographic measurements.** Powder x-ray diffraction (XRD) fraction patterns were recorded on a Philips PW 1710 (Eindhoven, The Netherlands) diffractometer (Cu tube,  $\lambda = 1.54178 \text{ \AA}$ ), which was composed of a camera, equipped with a thermostat unit (Huber HS-60; Offenburg-Elgersweier, Germany; TTK-Anton Paar, Graz, Austria), a temperature control system (Pt 100 probe) and connected to a heating ( $20$  to  $300^\circ\text{C}$ ) and to a cooling device that allowed a minimum temperature of  $-40^\circ\text{C}$ . Gaseous nitrogen flow prevented condensation of water during measurements at low temperatures. The diffractometer was coupled to a Digital Micro-Vax II system (Digital Equipment Corporation, Maynard, MA) that allowed data treatment.

**Synthesis and purification of symmetrical triglycerides (PEP and SES).** The chemical synthesis of symmetrical mixed triglycerides takes place in two steps (Scheme 1). It



Yield: ~12%  
(1,3-distearin)



Yield: ~40%

P =  $\text{CH}_3\text{---}(\text{CH}_2)_{14}\text{---}$

S =  $\text{CH}_3\text{---}(\text{CH}_2)_{16}\text{---}$

E =  $\text{CH}_3\text{---}(\text{CH}_2)_7\text{---CH=CH---}(\text{CH}_2)_7\text{---}$  *trans*

pTSA = *p*-toluene sulfonic acid

SCHEME 1

begins with the preparation of 1,3-diglyceride from glycerol and the corresponding fatty acid in the presence of *p*TSA as a catalyst. We only synthesized 1,3-distearin; 1,3-dipalmitin is commercially available. In the second step, the triglyceride is obtained by acylation of 1,3-distearin or 1,3-dipalmitin with elaidic anhydride in the presence of 4-dimethylaminopyridine.

*Synthesis of 1,3-distearin.* In a 250-mL two-necked round-bottomed flask, topped by a Hartman apparatus, 3.00 g glycerol (0.033 mol), 18.78 g stearic acid (0.066 mol), and 0.5 g *p*TSA (0.0029 mol) are dissolved in 100 mL anhydrous chloroform and reflux-heated for 3.5 h. Afterward, the reaction mixture is cooled and neutralized by 0.50 g sodium acetate (0.006 mol). The content of the round-bottomed flask is transferred into a separatory funnel, and the flask is rinsed out with 50 mL chloroform. The solution is then washed several times with deionized water. The white emulsion at the water/chloroform interface is eliminated with the aqueous phase. The solution is dried over  $\text{MgSO}_4$ , and chloroform is evaporated at 35°C under reduced pressure. It is imperative the reaction takes place in anhydrous conditions to prevent hydrolysis of the formed diglyceride.

*Purification of 1,3-distearin.* TLC analysis of the raw product revealed the occurrence of 1,3-diglyceride, 1,2-diglyceride, monoglyceride, and free fatty acid. To isolate 1,3-distearin, the raw product is first purified by crystallization in a 80:20, vol/vol petroleum ether [b.p. = 40–65°C]/distilled ethanol mixture (15 mL/g of raw product). After a night at 6°C, the precipitate is filtered in a constant-temperature Buchner funnel kept at the same temperature. This operation allows elimination of the majority of 1,2-distearin and monostearin. Two or three additional recrystallizations at controlled temperature are necessary to isolate pure 1,3-distearin. For that purpose, the mixture to purify and the crystallization solvent are held at 50°C until complete dissolution. It is then cooled at constant rate (1°C/min). As soon as crystals appear, the temperature of the bath is kept constant, and the solution is filtered at the same temperature. Synthesis of the diglycerides is repeated five times; 2.55 g of 1,3-distearin was recovered. Its purity, checked by gas GLC, was greater than 99% but the yield of the reaction was only on the order of 12%.

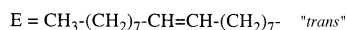
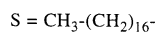
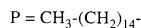
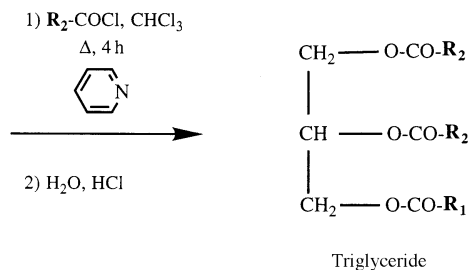
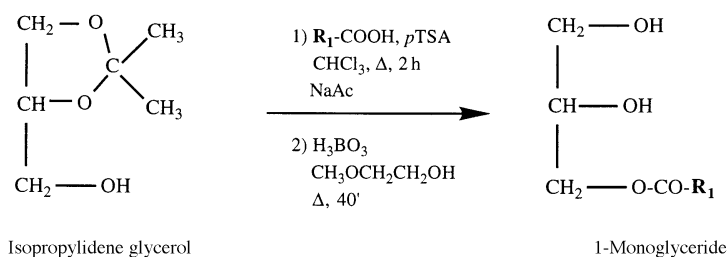
*Synthesis of PEP and SES.* 1,3-Distearin (0.480 g) or 0.437 g 1,3-dipalmitin ( $7.68 \cdot 10^{-4}$  mol) and 0.005 g of 4-dimethylaminopyridine ( $4.1 \cdot 10^{-5}$  mol) are solubilized in 10 mL of anhydrous chloroform (ethanol-free) inside a three-necked round-bottomed flask, which is maintained at 10°C. Elaidic anhydride (0.250 g =  $4.59 \cdot 10^{-4}$  mol) dissolved in 3 mL chloroform is added drop by drop under constant stirring with the help of a dropping funnel. When all of the anhydride has been added, the temperature is raised to 30°C, and the reaction is allowed to proceed for 50 min. Afterward, the catalyst is neutralized with 2 mL HCl (0.5M), and the remaining anhydride is hydrolyzed by 2 mL water. The solution is transferred in a separatory funnel, washed three times with 2 mL saturated  $\text{NaHCO}_3$  solution, and dried over anhydrous  $\text{MgSO}_4$ . The solvent is evaporated at 35°C under reduced pressure.

*Purification of the triglycerides.* A TLC analysis showed the presence in the raw product of triglyceride, free fatty acid, 1,3-diglyceride, and traces of ethyl elaidate. This latter is a by-product of the reaction. Its presence is due to traces of ethanol remaining in chloroform (stabilizer). The triglyceride is purified by column chromatography. The glass column (15 × 1.4 cm) is packed with Machery-Nagel G60 silica gel (70–230 mesh) at 5% humidity. *n*-Hexane/diethyl ether mixtures are used for the elution. For the purification of SES, the elution with 85 mL of *n*-hexane/diethyl ether (9:1, vol/vol) allows the separation of ethyl elaidate. SES is then eluted with 85 mL of *n*-hexane/diethyl ether (8:2, vol/vol). For PEP, 75 mL of the same eluents are used. The final step of the purification procedure consists in recrystallization in an ethanol/diethyl ether mixture (7:3 vol/vol; 100 mL/g of purified triglyceride) to eliminate possible residual colloidal silica. Five syntheses of SES and PEP were carried out. After purification, we recovered 1.06 g of SES and 0.99 g of PEP. The yield of the reaction (acylation of 1,3-diglyceride by elaidic anhydride) is about 40%. The GLC analyses of SES and PEP as a function of the carbon number reveal purities superior to 99% (99.5% for SES and 99.6% for PEP). The FAME molar ratios (molar percentage of elaidic acid/molar percentage of stearic or palmitic acid: E/S and E/P), determined by GLC, were 0.489 and 0.495 for E/S and E/P, respectively. They are in line with the theoretical ideal value of 0.500. The “isomeric” purity was checked by HPLC of the epoxidated triglycerides (10), allowing quantitation of the symmetrical and asymmetrical isomers. The purity of PEP was 99.7%, and that of SES attained 96.3%. The impurity has not yet been identified.

*Synthesis and purification of asymmetrical triglycerides (PEE, EPP, SEE, and ESS).* The synthesis of asymmetrical mixed triglycerides is also a two-step reaction (Scheme 2). The first step consists in the preparation of the 1-monoglyceride, i.e., 1-monoelaidin, from isopropylidene glycerol and elaidic acid; 1-monopalmitin and 1-monostearin are commercially available. In a second step, the triglyceride is obtained by esterification of monoelaidin by stearoyl (for ESS) or palmitoyl chloride (for EPP), or by acylation with the elaidoyl chloride of monostearin (for SEE) or monopalmitin (for PEE). The chlorides have been previously synthesized from the corresponding fatty acid and oxalyl chloride.

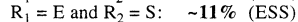
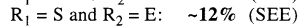
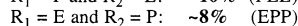
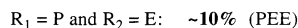
*Synthesis of fatty acid chlorides.* Palmitic (5.00 g = 0.019 mol), stearic (0.018 mol), or elaidic acid (0.018 mol) is dissolved in 25 mL of anhydrous benzene. Oxalyl chloride (3.5 g = 0.028 mol) is then added, drop by drop, to this mixture, which is continuously stirred. The reaction takes place at room temperature for 3 d. Progress of the synthesis is followed by infrared spectroscopy: disappearance of the C=O absorption band of the free fatty acid (1720  $\text{cm}^{-1}$ ) and appearance of the band characteristic of the carbonyl group of an acid chloride (1800  $\text{cm}^{-1}$ ).

*Synthesis of 1-monoelaidin.* In a 250-mL two-necked round-bottomed flask, topped by a Hartman apparatus, 5.00 g isopropylidene glycerol (0.038 mol) (11), 10.17 g elaidic acid (0.036 mol), and 0.30 g *p*TSA (0.0019 mol) are dissolved in 30 mL anhydrous chloroform and reflux-heated for 2 h. The mix-



*p*TSA = *p*-toluene sulfonic acid

#### Yield:



### SCHEME 2

ture is then cooled, and the excess *p*TSA is neutralized by adding 0.3 g sodium acetate (0.0036 mol). The solution is washed with deionized water, the aqueous phase is decanted, and the rest of the solution is dried over  $\text{MgSO}_4$ ; chloroform is then evaporated under reduced pressure. 2-Methoxyethanol (60 mL) and 20 g boric acid are then added to the product, and this mixture is reflux-heated for 40 min. After reaction, the mixture is dissolved in 300 mL diethyl ether, rinsed out with deionized water, and dried over  $\text{MgSO}_4$ . The solvent is finally evaporated at 40°C under reduced pressure.

**Purification of 1-monoelaidin.** According to TLC analysis, the raw product is a mixture of monoglycerides, diglycerides, and elaidic acid. Two crystallizations, in a diethyl ether/hexane mixture (80:20, vol/vol) are necessary to isolate 1-monoelaidin. The first one is performed at  $-18^\circ\text{C}$  for 2 h with 20 mL solvent/g product, while the second is made overnight at  $6^\circ\text{C}$  in 15 mL solvent/g product. About 1.5 g of 1-monoelaidin were obtained per synthesis; the yield of the reaction was approximately 11%.

**Synthesis of PEE, SEE, EPP, and ESS.** Triglyceride PEE (or SEE) is obtained by reaction between 1-monopalmitin (or 1-monostearin) and elaidoyl chloride. EPP (or ESS) is synthesized from 1-monoelaidin and palmitoyl (or stearoyl) chloride. In a 1000-mL two-necked round-bottomed flask, topped

by a condenser, 1.00 g 1-monopalmitin (0.0030 mol), 1-monostearin (0.0028 mol), or 1-monoelaidin (0.0028 mol) and 0.66 g pyridine ( $8.3 \cdot 10^{-5}$  mol) are dissolved in 50 mL anhydrous chloroform. By a separatory funnel, 2.55 g of elaidoyl (0.007 mol) or stearoyl (0.007 mol) chloride or 1.16 g palmitoyl chloride (0.0045 mol) is then added drop by drop. The mixture is reflux-heated for 4 h. After reaction, the mixture is dissolved into 500 mL petroleum ether [b.p. =  $40\text{--}65^\circ\text{C}$ ]/diethyl ether (50:50, vol/vol). The excess chloride is neutralized by adding 150 mL distilled water, and pyridine is neutralized by a 1% aqueous hydrochloric acid solution. The organic phase is decanted and dried over anhydrous  $\text{MgSO}_4$ . The solvent is finally evaporated under reduced pressure at 40°C.

**Purification of PEE, SEE, EPP, and ESS.** TLC analyses revealed that the raw product is a mixture of triglycerides, diglycerides, monoglycerides, and free fatty acids. Two purification steps are necessary to isolate the triglycerides. A first crystallization, which allows elimination of the residual fatty acids, is performed in an ethanol/diethyl ether mixture (80:20, vol/vol; 100 mL/g of raw product). The triglyceride is then purified by adsorption chromatography. The glass column (15 × 1.4 cm) is packed with G60 silica gel (70–230 mesh) at 5% humidity. A benzene/hexane mixture (50:50,

vol/vol) is used as eluent. This solvent mixture (100 mL) is used to elute the fatty acids, mono- and diglycerides. Afterward, benzene (300 mL) is used to elute the triglycerides. The recovered product is finally recrystallized in an ethanol/diethyl ether mixture as specified above. Yields of 0.185 g PEE (or 0.289 g SEE) and 0.250 g EPP (or 0.281 g of ESS) are obtained per synthesis after purification. Although the global yields of synthesis are low (around 10%), highly purified triglycerides are obtained. Indeed, the CNP recorded for the different molecules indicate purities superior to 99%, while the FAME mole% ratios are close to the theoretical values: 2.000 [for SEE (2.014) and PEE (1.984)] and 0.500 [for ESS (0.503) and EPP (0.501)]. For ESS and SEE these values are presented as mole% methyl elaidate/mole% methyl stearate; for EPP and PEE, mole% methyl elaidate/mole% methyl palmitate.

## RESULTS AND DISCUSSION

*Physicochemical characterization of the synthesized triglycerides.* The thermal behavior as well as the polymorphism of the pure synthesized compounds (i.e., the ability to crystallize in different crystal forms) was studied by means of DSC and powder XRD at variable temperature. To point out both stable and metastable polymorphic forms, the samples were conditioned according to a thermal treatment called dynamic process. The dynamic process consisted of a three-step procedure: complete melting of the triglycerides at temperatures at least 20°C above their melting point, quenching to -40°C at 50°C/min, and heating at constant rate (5°C/min) until complete fusion.

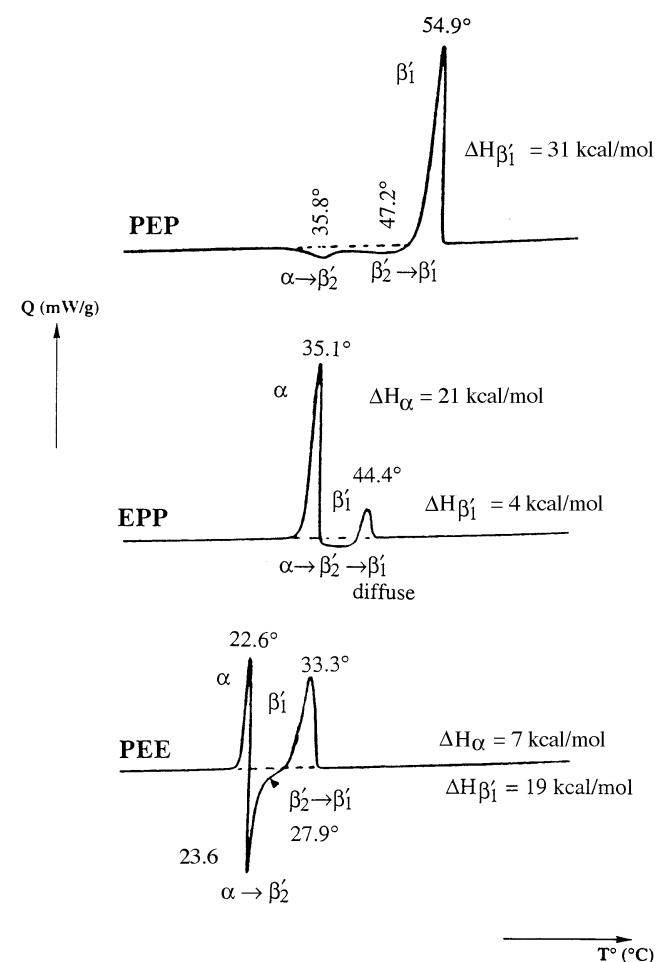
*Description of palmito-elaidic triglycerides (PEP, EPP, and PEE).* After complete melting and rapid cooling, PEP crystallizes in the  $\alpha$  form. During heating at constant rate, this form transforms in  $\beta'_2$  form and finally melts under  $\beta'_1$  form. For EPP, the less stable form identified, according to the same thermal treatment, is the  $\alpha$  form as well. However, during heating, the  $\alpha$  form melts and recrystallizes in the  $\beta'_2$  form, which quickly evolves toward the  $\beta'_1$  form. As far as PEE is concerned, the same three polymorphic forms are indicated. All palmito-elaidic triglycerides studied present three polymorphic forms:  $\alpha$ ,  $\beta'_2$  and  $\beta'_1$ , which crystallize in double chainlength packing. Crystallographic data of both symmetrical and asymmetrical triglycerides, PEP, EPP and PEE, are summarized in Table 1. In addition, at low temperature, the diffraction line corresponding to the  $\alpha$  form of each triglyceride is broadened, suggesting the presence of a sub- $\alpha$  form. A  $\beta$  form was never isolated, neither by dynamic process nor after long stabilization times of the  $\beta'_1$  form. The  $\beta' \rightarrow \beta$  transition is probably hindered by an important interpenetration of the palmitic and elaidic hydrocarbon chains at the methyl-end group planes. Therefore, the  $\beta'_1$  form is the thermodynamically stable form of all those triglycerides. The DSC curves provide different melting and transition temperatures as well as the enthalpy of fusion of the polymorphic forms (Fig. 1). A symmetric arrangement of the hydrocarbon chains around the glycerol moiety induces better

**TABLE 1**  
Crystallographic Data [short ( $\text{\AA}$ ) and long ( $\text{\AA}$ ) spacings] of PEP, EPP, and PEE Obtained After a Dynamic Process<sup>a</sup>

		$\alpha$ -2	$\beta'_2$ -2	$\beta'_1$ -2
PEP	SS	4.2 (strong)	4.2 (very strong) 3.9 (medium)	4.4 (medium) 4.2 (very strong) 4.1 (medium)
	LS <sup>b</sup>	48	47	44
	SS	4.2 (very strong)	4.3 (very strong) 3.9 (medium)	4.4 (weak) 4.3 (strong) 4.2 (weak) 3.9 (strong)
EPP	LS <sup>b</sup>	48	46	44
	SS	4.2 (very strong)	4.2 (strong) 3.9 (medium)	4.4 (weak) 4.2 (strong) 4.1 (weak) 3.9 (strong)
	LS <sup>b</sup>	49	47	45

<sup>a</sup>SS = short spacings; LS = long spacings.

<sup>b</sup>Mean reticular distance calculated from odd diffraction orders  $n = 1$  and  $n = 3$ . P, palmitic; E, elaidic.



**FIG. 1.** Differential scanning calorimetry curves of PEP, EPP, and PEE (P = palmitic, E = elaidic) recorded according to the dynamic process. Melting and transition temperatures: °C—Enthalpies of fusion ( $\Delta H$ ): kcal/mol.

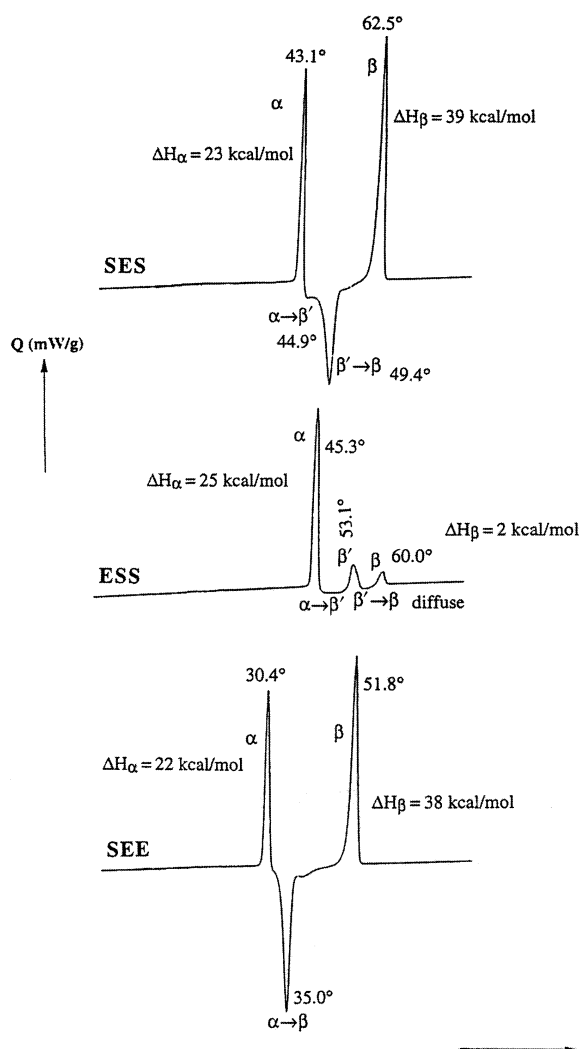
**TABLE 2**  
**Crystallographic Data [short (Å) and long (Å) spacings] of SES, ESS, and SEE Obtained After a Dynamic Process**

		sub- $\alpha$ -2	$\alpha$ -2	$\beta'_2$ -2	$\beta'_1$ -2	$\beta$ -2
SES	SS	4.1 (strong)	4.2 (very strong)	4.25 (medium) 4.0 (weak)		4.6 (strong) 3.9 (medium) 3.8 (medium)
	LS <sup>b</sup>	56	55	54		48
ESS	SS	4.1 (strong)	4.2 (very strong)	4.3 (weak) <sup>c</sup> 4.0 (medium) <sup>c</sup>	4.4 (very weak) 4.3 (very strong) 4.1 (very weak) 3.9 (strong)	5.3 (medium) 4.6 (very strong) 3.9 (strong) 3.7 (strong)
	LS	51	52	47	47	45
SEE	SS	4.1 (strong)	4.2 (very strong)			5.3 (weak) 4.6 (very strong) 3.9 (strong) 3.6 (strong)
	LS	46	49			44

<sup>a</sup>SS = short spacings; LS = long spacings.

<sup>b</sup>Mean reticular distance calculated from odd diffraction orders  $n = 1$  and  $n = 3$ .

<sup>c</sup>Obtained by cooling from the melt at 42°C.



**FIG. 2.** Differential scanning calorimetry curves of SES, ESS, and SEE (S = stearic, E = elaidic) recorded according to the dynamic process. Melting and transition temperatures: °C—enthalpies of fusion ( $\Delta H$ ): kcal/mol.

stability of the  $\beta'_1$  crystalline lattice than an asymmetric one (higher melting temperature and  $\Delta H$  of fusion). Moreover, the  $\alpha \rightarrow \beta'$  transition of PEP takes place in the solid state, while this transition is preceded by melting of the  $\alpha$  form (liquid  $\alpha = L\alpha$ ) for EPP and PEE.

*Description of stearo-elaidic triglycerides (SES, ESS, and SEE).* After melting and quenching, SES, ESS and SEE crystallize in a sub- $\alpha$  form (X-ray pattern characterized by a broadened diffraction line at 4.1 Å). During constant heating, this form successively transforms into  $\alpha$ ,  $\beta'$  and  $\beta$  forms. However, the  $\beta'$  form is only observed for SES and ESS. Indeed, it was not possible to isolate the  $\beta'$  variety for SEE as for EEE (12). All polymorphic forms of the three triglycerides adopt a double chainlength packing. The crystallographic data are presented in Table 2. Thermal data, i.e., melting and transition temperatures, as well as enthalpies of fusion, are summarized in Figure 2. It appears that (like palmito-elaidic compounds) a better stability of the most stable form (in this case  $\beta$ ) is obtained when the arrangement of the hydrocarbon chains around the glycerol is symmetric (higher melting points and  $\Delta H$  of fusion). Moreover, as for EPP, the stability of the  $\beta$  form of ESS is low. A particularity of the  $\beta' \rightarrow \beta$  transition of ESS is that it is preceded by melting of the  $\beta'$  form (liquid state called  $L_{\beta'}$ ). As mentioned for EPP and PEE, the  $\alpha \rightarrow \beta'$  transition of the three stearo-elaidic compounds takes place *via* a liquid state called  $L_{\alpha}$ . For SEE, this unstable liquid phase directly transforms in a  $\beta$  form.

In conclusion, the polymorphic behavior of high-purity palmito- and stearo-elaidic triglycerides can be summarized as follows:

- PEP:**  $\alpha$ -2  $\rightarrow$   $\beta'_2$ -2  $\rightarrow$   $\beta'_1$ -2 [1]  
**EPP and PEE:**  $\alpha$ -2  $\rightarrow$   $L\alpha$   $\rightarrow$   $\beta'_2$ -2  $\rightarrow$   $\beta'_1$ -2 [2]  
**SES:** sub- $\alpha$ -2  $\rightarrow$   $\alpha$ -2  $\rightarrow$   $L\alpha$   $\rightarrow$   $\beta'_2$ -2  $\rightarrow$   $\beta$ -2 [3]  
**ESS:** sub- $\alpha$ -2  $\rightarrow$   $\alpha$ -2  $\rightarrow$   $L\alpha$   $\rightarrow$   $\beta'_2$ -2  $\rightarrow$   $\beta'_1$ -2  $\rightarrow$   $\beta$ -2 [4]  
**SEE:** sub- $\alpha$ -2  $\rightarrow$   $\alpha$ -2  $\rightarrow$   $L\alpha$   $\rightarrow$   $\beta$ -2 [5]

All palmito-elaidic compounds are stable in a  $\beta'$  polymorphic form, whereas stearo-elaidic triglycerides are  $\beta$ -stable. The six triglycerides studied crystallize according to a double chainlength longitudinal packing. For these palmito- and stearo-elaidic series, a symmetric arrangement of the hydrocarbon chains around the glycerol induces better stability of the stable polymorphic form than an asymmetric one. Except for PEP, all  $\alpha \rightarrow \beta'$  (or  $\alpha \rightarrow \beta$  for SEE) transitions take place via a liquid state called  $L\alpha$ .

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