Thermal Properties of 2-Oleodipalmitin and 2-Elaidodipalmitin and Some of Their Mixtures[1]

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ABSTRACT

The polymorphism of 2-oleodipalmitin (POP), 2-elaidodipalmitin (PEP), and five of their mixtures was investigated by differential scanning calorimetry (DSC). The heat of fusion (ΔH_f), heat of crystallization (ΔH_c), and heat of transition (ΔH_t) were determined. Rapid conversion to higher polymorphs, partial melting during conversion, and the overlapping of polymorphic forms precluded accurate determination of some caloric values. Four of five previously identified polymorphs of POP and all four polymorphs of PEP were identified by DSC. Five POP: PEP mixtures containing 8, 16, 25, 50, and 75% PEP, respectively, were examined. The presence of PEP in POP increased the stability of the lower POP polymorphs and, in concentrations as low as 8%, also increased the conversion rate of the higher POP polymorphs. In these heating curves, POP forms 5, 4, and 3, and a higher melting fraction that consisted of higher polymorphs of POP, polymorphs of PEP, and probably mixed crystals were evident. The ΔH_f values for the tempered mixtures are lower, and the ΔH_c values for the mixtures are higher than the calculated values. Heating and cooling curves and calorimetric data tables for POP, PEP, and their five mixtures are included.

INTRODUCTION

The polymorphic behavior of pure mixed triglycerides and their mixtures have been investigated by various techniques including dilatometry (1,2), capillary melting points (3-6), phase behavior (7,8), X-ray diffraction patterns (9-11), differential thermal analysis (DTA) (11), and other methods (4,12,13). Although these techniques have provided much insight into polymorphism, certain aspects of the polymorphic behavior of triglycerides and their mixtures are unclear.

The differential scanning calorimeter (DSC) (14) provides a technique whereby a pure triglyceride can be examined under dynamic thermal conditions, thus providing direct calorimetric data, rather than the indirect thermometric data provided by DTA. Because of the instrument's sensitivity, various thermal events such as the transition from one polymorphic form to another, with or without partial melting, and the melting of particular polymorphs can be detected and quantitated as a direct caloric measurement as these events take place. Mixtures of polymorphic forms can be detected, and various tempering techniques can be evaluated for their effectiveness in bringing about desired polymorphic changes. When binary mixtures consisting of known proportions of pure triglycerides are examined by DSC, the effect of one triglyceride on the polymorphic behavior of the other, as well as the effect of the various proportions of the components in the mixtures, can be determined.

The exothermic and endothermic changes that take place with a particular triglyceride or mixture at a given heating or cooling rate can be measured in cal/g. To duplicate on a large scale a tempering technique developed by DSC, a knowledge of the amount of heat absorbed or desorbed is necessary to properly compensate for these thermal changes. The caloric data from DSC can be used to calculate the heating and cooling requirements for large-scale operations.

Lovegren et al. (15) recently examined the polymorphic behavior of 2-oleodipalmitin (POP), 2-elaidodipalmitin (PEP), and some of their mixtures by means of melting points, dilatometry, and X-ray diffraction. No detailed study, however, has been made of the polymorphic behavior of these two triglycerides and their mixtures by thermal analysis. Moran (2) studied the phase behavior of some palmito-oleo triglyceride systems by DTA and determined the heat of fusion (ΔH_f) of 2-oleodipalmitin, but made no study of the various polymorphic forms of transitions.

In this study, high purity POP and PEP and samples of some of their mixtures were examined by DSC to identify the polymorphs and polymorphic changes and to measure the calories involved in fusion, transitions, and crystallization.

MATERIALS AND METHODS

A Perkin-Elmer DSC-1 differential scanning calorimeter calibrated with indium (ΔH_f = 6.79 cal/g) was used. To ensure accuracy of the temperature readings, the instrument was calibrated by melting samples of palmitic acid, lauric acid, methyl palmitate, and ice. The equilibrium melting-solidification temperatures, as determined with a NBS calibrated thermometer, for palmitic acid, lauric acid, methyl palmitate, and water were 62.5, 43.2, 29.4, and 0.0 C, respectively.

Synthesis and purification of POP and PEP used in this study were described previously (15). The purities of POP and PEP were 99.7 and 98.5%, respectively, as determined by gas liquid chromatography. Analysis by thin layer chromatography on Absorbosil-1, developed with 1,2-dichloroethane for polar compounds, or made up with 1.5 vol 16.7% silver nitrate and developed with 0.8% methanol in chloroform for positional isomers, revealed no evidence of free fatty acids, monoglycerides, or diglycerides, nor the migration of the palmitic acid from the 1- and 3-positions on the glycerol molecule during synthesis of the POP and PEP.

About 10-15 mg of the triglycerides to be examined by DSC were weighed into aluminum sample pans, and the covers crimped into place. An empty covered sample pan was used as reference. After the sample and reference pans were placed in the DSC-1, the low-temperature sample cover was put in place, the sample area was flushed with nitrogen, after which adjustment was made to a very slow flow rate, and the sample cover was filled with dry ice. To obtain consistent results, all runs were made with the slow

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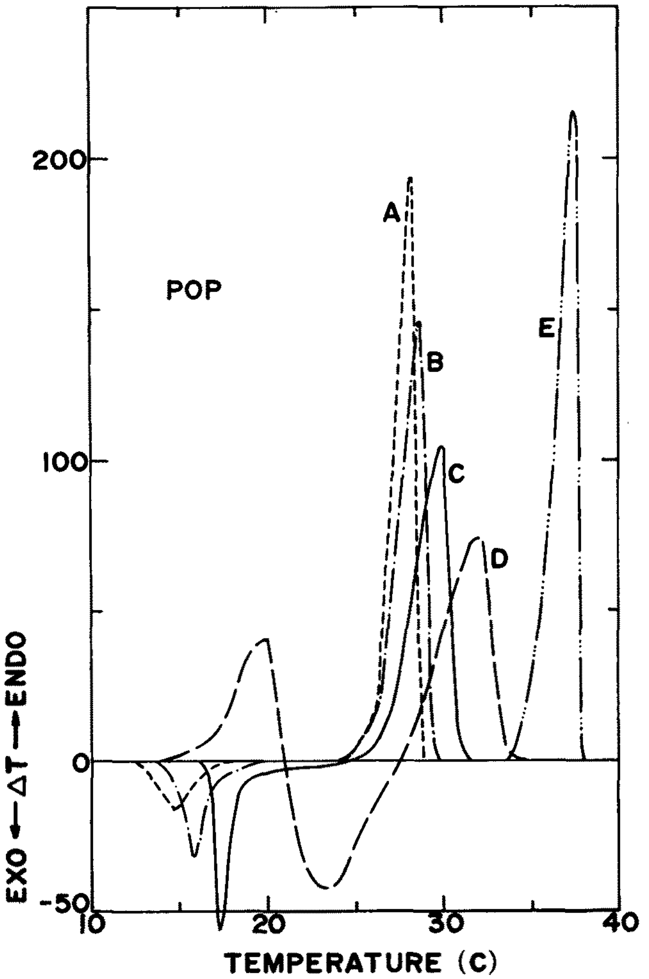

FIG. 1. Differential scanning calorimetry heating curves for 2-oleodipalmitin (POP). Quick chilled, heating rate, A, 1.25 C/min; B, 2.5 C/min; C, 5 C/min; D, 10 C/min; and E, solvent-crystallized (Form 1), heating rate 1.25 C/min.

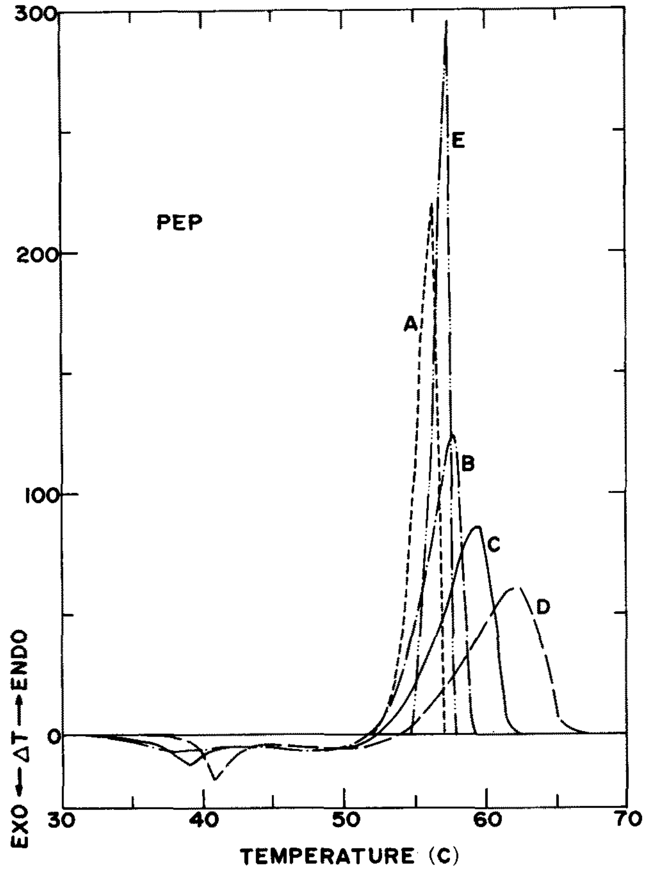

FIG. 2. Differential scanning calorimetry heating curves for 2-elaidodipalmitin (PEP). Quick chilled, heating rate, A, 1.25 C/min; B, 5 C/min; C, 10 C/min; D, 20 C/min; and E, solvent-crystallized (Form 1), heating rate 1.25 C/min.

nitrogen flow through the sample area for 30 min or longer accompanied by dry ice cooling.

The five POP:PEP mixtures used in this study were prepared by weighing appropriate quantities of the two components. The actual percentages for PEP in the mixtures were 7.9 (8), 15.9 (16), 25.0 (25), 50.3 (50), and 75.2 (75), but the number in parenthesis will be used when referring to a mixture of a given composition. Each mixture was melted and mixed well to ensure homogeneity, then solidified rapidly in ice water. After being tempered at room temperature (ca. 22 C), the solidified mixtures were weighed.

The ΔH_f values for POP and PEP were obtained on solvent-crystallized samples, which are in the highest melting polymorphic form. The ΔH_f values for the five POP:PEP mixtures were obtained on the samples after tempering at room temperature. The ΔH_c values were obtained on samples in which the thermal history had been erased by melting. The ΔH_t values were obtained by heating a sample that had been quickly solidified from the melt. Under the operating conditions used, the transitions were solid to solid except for POP at a heating rate of 10 C/min (Fig. 1, Curve D), in which a partial melting preceded the transition to a higher polymorph. The ΔH_f values for the low melting polymorphs were obtained on samples quickly chilled to 10 C from the melt in instances where the particular polymorph melted, either wholly or partially, before or during converison to a higher polymorph. The ΔH_f values for the higher melting polymorphs were obtained after a slow, stepwise tempering of the sample in the DSC-1 following solidification from the melt. This stepwise tempering process consisted of (a) heating the sample until melting just starts, (b) holding the sample at this temperature to allow time for conversion to a higher polymorph, and (c) cooling the sample 4-10 C below the holding temperature. This cycle was repeated, the temperature at which the sample started to melt being somewhat higher each time, until the sample had been converted to a particular polymorph. The number of times the cycle had to be repeated depended on the degree of stability of the lower polymorphs and the ease with which conversion took place. Samples that converted slowly were held at the incipient melting temperature for several hours, thus reducing the number of repeat cycles required to obtain a polymorphic conversion. The polymorphic forms are designated in this study as 1, 2, 3, etc., in decreasing order of their melting points.

To obtain a good baseline for measuring caloric data, the sample was heated at a rate of 5 C/min or higher. At heating rates below 5 C/min, the temperature lag is small but the baselines is difficult to determine in some instances. The slower heating rates are useful for determining the melting temperature; the temperature lag in heating rates higher than 2.5 C/min is measurable and reproducible.

RESULTS AND DISCUSSION

Thermal changes that take place during heating of POP, PEP, and mixtures of the two are shown in the heating curves in Figures 1, 2, and 3. The endothermic changes appear above the baseline, and the peak area is a direct caloric measure of the heat absorbed during the melting of a particular polymorph. Some of the lower melting poly-