Effect of 2-Oleodipalmitin and 2-Elaidodipalmitin on Polymorphic Behavior of Cocoa Butter[1]

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ABSTRACT

The polymorphic behavior of cocoa butter mixed with 2-oleodipalmitin (POP) or 2-elaidodipalmitin (PEP) was investigated with a differential scanning calorimeter. Six mixtures of cocoa butter containing 10, 25, and 50% POP and 10, 25, and 50% PEP were used. Each of the three cocoa butter-POP mixtures exhibited at least four polymorphic forms. The low-melting form was obtained by quick chilling; the intermediate, by tempering for several hours just below the melting range; and the high-melting, by raising the temperature slowly to 25 C then holding there overnight or longer. In the cocoa butter-POP mixtures, only the low-melting form appeared to be more stable than the corresponding form for pure POP or cocoa butter. In addition to increased stability of the unstable low form, the rate of conversion from the intermediate to the high form, normally quite slow, increased in the cocoa butter-POP mixtures. Typical melting point lowering occurred when POP was added. POP was quite compatible with cocoa butter, the tempered mixture melting as a single compound; and the melting curves were fairly sharp. The three cocoa butter-PEP mixtures appeared to be incompatible. The cocoa butter and PEP behaved like a mixture of two fats, each of which melted independently.

INTRODUCTION

Probably over half of the total fats and oils used annually by the domestic confectionery industry consist of cocoa butter-like fats, the so-called "hard butters." The cocoa butter-like fats are prepared primarily from lauric acid oils, but a few are prepared from oleic-linoleic acid oils. Although these lauric acid fats have a price advantage, their physical properties are not ideal for the intended uses.

Paulicka (1) determined the phase behavior of three types of cocoa butter extenders, two of which were derived from natural fats and the third from hydrogenated-fractionated domestic vegetable oils. Using a differential scanning calorimeter, Lovergren et al. (2) determined the polymorphic behavior of cocoa butter and of a high-melting cocoa butter fraction with three types of confectionery fats and mixtures of the confectionery fats with each other. The confectionery fats used were an interesterified-fractionated fat, a hydrogenated-fractionated fat, and a lauric acid fat.

Cocoa butter-like fats can be prepared readily from the stearine obtained as a byproduct in the solvent winterization of cottonseed oil (3). Partial hydrogenation and fractional crystallization gave a cocoa butter-like fat that consisted primarily of 2-oleodipalmitin (POP) with varying amounts of 2-elaidodipalmitin (PEP).

The purpose of this investigation was to determine the effect of POP and PEP on the melting characteristics and polymorphic behavior of cocoa butter in mixtures of varying proportions under varying tempering conditions.

MATERIALS AND METHODS

Cocoa butter from Hershey Chocolate Corp., Hershey, PA, was used in this study. The syntheses of POP and PEP were described previously (4) and their respective purities were 99.7% and 98.5%.

A Perkin-Elmer DSC-1 differential scanning calorimeter (5) was used. The instrument was calibrated with indium (H_f = 6.79 cal/g). 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. The calibration temperatures were determined under the same conditions that were used for the fat samples. Melting points were determined for the four standard samples at heating rates of 2.5, 5, and 10 C/min. The experimental heating curve readings were converted to centigrade by use of the appropriate temperature calibration curve.

Cocoa butter and POP or PEP were weighed in suitable amounts for the various mixtures, melted and mixed well, then quickly solidified and tempered by appropriate means. After tempering, the fat samples or mixtures were weighed into DSC pans to the nearest 0.1 mg and the covers crimped in place. Sample size varied from 11 to 18 mg. An empty covered sample pan was used as reference. After the sample and reference pans were placed in the DSC-1, the low temperature Dewar flask sample cover was put in place and the sample area flushed with nitrogen. The nitrogen flow was then adjusted to a very slow flow rate and the sample cover was filled with dry ice. To obtain consistent results, all samples were stabilized for 30 min or longer in the dry ice-chilled sample area before starting a scan.

The scanning rates used for heating curves were 1.25, 2.5, 5, and 10 C/min for POP; 1.25 5, 10, and 20 C/min for PEP; and 5 C/min for cocoa butter, the cocoa butter-POP mixtures, and the cocoa butter-PEP mixtures. Samples were cooled to ca. -13 C before heating was started. The low-melting form was obtained by rapidly cooling a melted sample to ca. -13 C, then immediately heating it. 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 consists 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. On repetition of cycle, the temperature at which the sample started to melt increased each time, until the sample had 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 the conversion took place. Slowly converting samples were held at the incipient melting temperature for 2 or more hr, thus reducing the number of cycles required to attain a polymorphic conversion. Well-tempered samples were obtained by storage at 22-25 C for at least 2 wk, or until no further polymorphic change was apparent. In reference to Figures 3, 4, and 5, tempered refers to aged, unmelted for cocoa butter, and to well tempered for the various mixtures. The polymorphic forms referred to when discussing the heating curves are designated as 1, 2, 3, etc., in order of their decreasing melting points.

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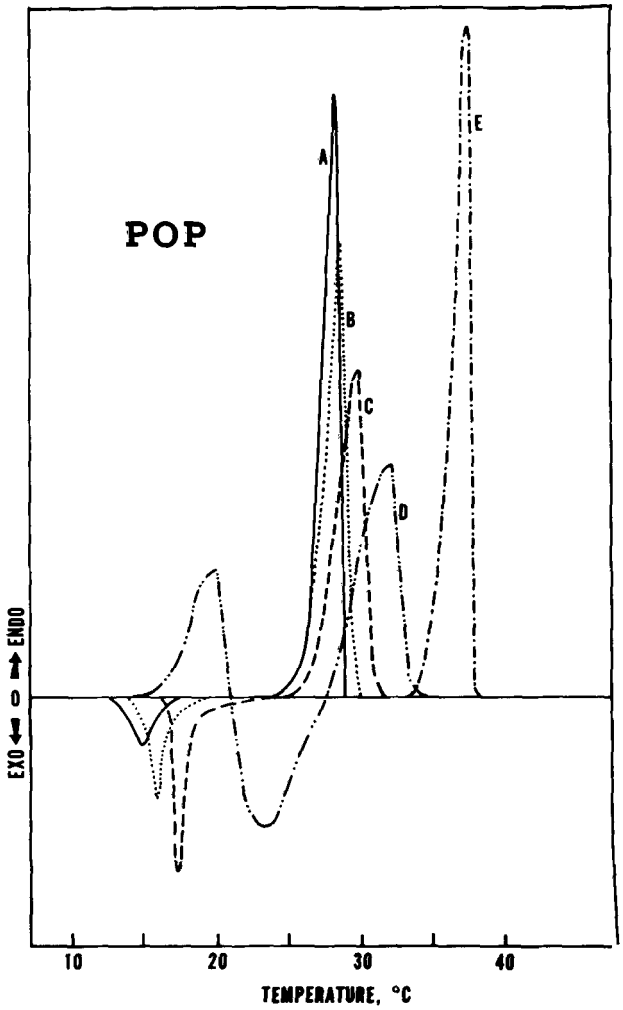

FIG. 1. DSC heating curves for 2-oleodipalmitin (POP) (vertical scale, half height). Quick chilled, heating rate; A, 1.25 C/min; B, 2.5 C/min; C, 5 C/min; D, 10 C/min; and E. solvent crystallized (Form 1), heating rate 1.25 C/min.

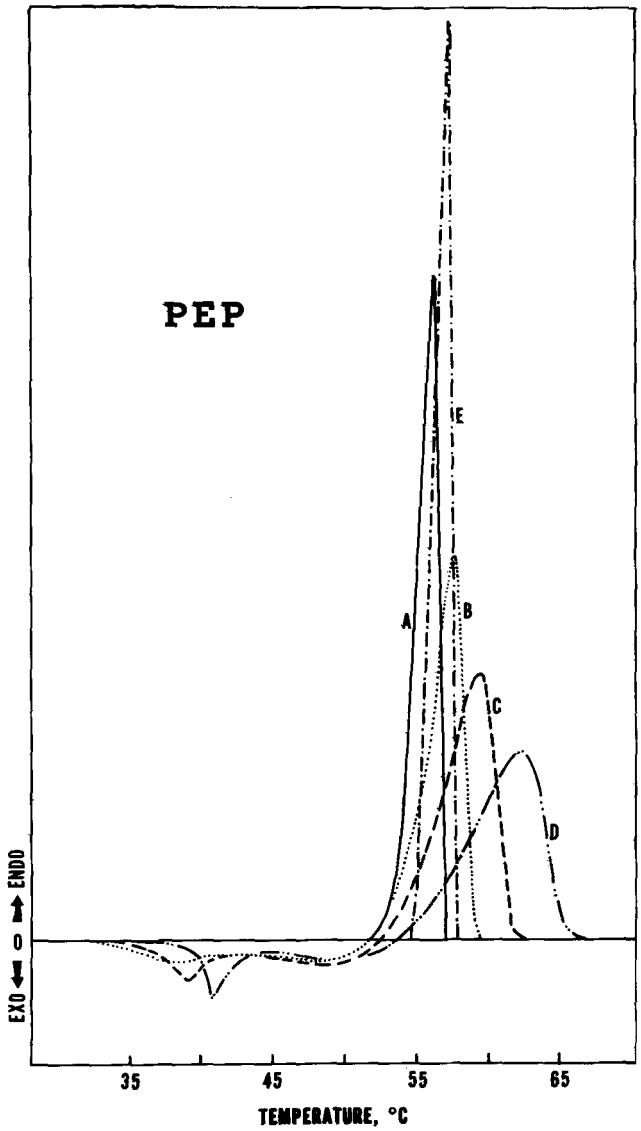

FIG. 2. DSC heating curves for 2-oelaidodipalmitin (PEP) (vertical scale, half height). Quick chilled, heating rate; A, 1.25 C/min; B, 5 C/min; C, 10 C/min; D, 20 C/min; and E, solvent crystallized (Form 1), heating rate 1.25 C/min.

RESULTS AND DISCUSSION

The thermal changes that take place during heating are shown in the heating curves in Figures 1 through 5. (All figures have the same temperature scale but the vertical scale of Figures 1 and 2 are half height). Selected curves were chosen to illustrate the various polymorphs found. 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 polymorphs are insufficiently stable to melt completely before conversion to a higher polymorph. When a partial melting of a polymorph is accompanied by a conversion or transition to a higher polymorph, both endothermic and exothermic changes are represented in the endothermic peak. The peak area in such a case is a measure of the heat absorbed during melting, less the heat given off during the transition and crystallization to a higher polymorph. When a polymorph melts completely and then crystallizes to a higher polymorphic form, the endothermic peak area is the measure of the ΔH_f for that particular polymorph. The exothermic changes appear below the baseline, and the area of the exothermic peak that follows the melting of the polymorph is the measure of the ΔH_t for the transition and crystallization to a higher melting polymorph. In some instances, the transition from a lower to a higher melting polymorph takes place without melting. In this case, only an exothermic change takes place and the exothermic peak area below the baseline is the measure of ΔH_t.

Various criteria were used to determine the different polymorphs present in the DSC heating curves. In most instances, peaks that started melting at about the same temperature were attributed to a single polymorph, as well as where there was a considerable overlap of peak areas. In some instances, samples tempered at higher temperatures had a peak representing the untempered portion followed by the peak for the tempered portion. A longer tempering period permitted complete conversion to the higher polymorph in some instances.

2-Oleodipalmitin, 2-Elaidodipalmitin, and Cocoa Butter

The polymorphic behavior of 2-oleodipalmitin (POP) and 2-elaidodipalmitin (PEP) has been described previously (4,6). Except for Polymorph 4, which is too transient, four of the five polymorphs of POP can be identified by DSC. Reproducible DSC melting curves were not obtained for Polymorph 2, the melting range of which varied from ca. 33 C to just below 37 C and depended on the proportion of other polymorphs present. The DSC heating curves for POP are shown in Figure 1. Curves A, B, and C, with heating rates of 1.25, 2.5 and 5 C/min, respectively, are essentially

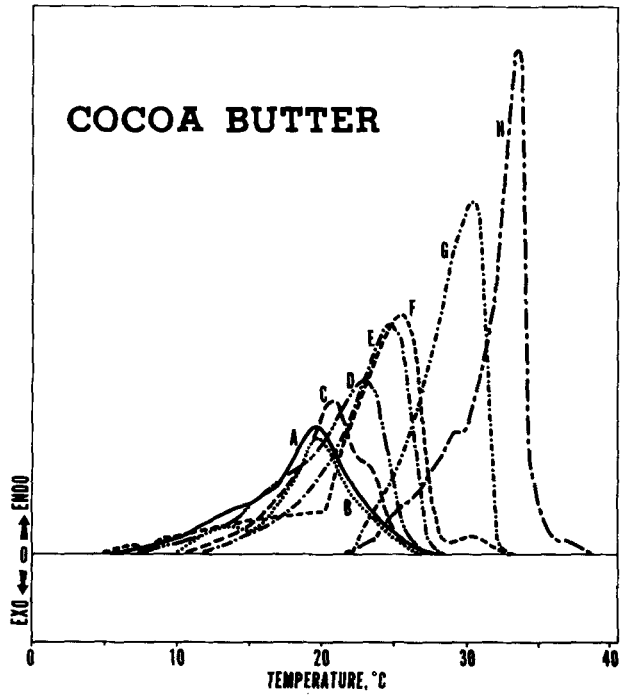

FIG. 3. DSC heating curves for cocoa butter, heating rate 5 C/min. A, quick chilled; B, quick chilled, heated rapidly to 5.3 C; C, tempered at -12.4 C, 20 min; D, tempered 5.3 C, 29 min; E, tempered at 9.7 C, 120 min; F, stepwise tempering at 9.7 C, 30 min; 14.1 C, 85 min; 18.5 C, 62 min; G, tempered overnight at 22 C; H, tempered (unmelted).

the same except for peak displacement due to temperature lag. During heating, conversion of Polymorph 5 to Polymorph 3, without melting, took place at ca. 13-18 C followed by melting of Polymorph 3 at ca. 25-33 C (Curves A, B, and C). Curve D, at a heating rate of 10 C/min, showed partial melting of Polymorph 5 at ca. 17-21 C, crystallization and conversion to Polymorph 3 at ca. 21-28 C, and the melting of Polymorph 3 at ca. 28-33 C. The melting curve of Polymorph 1, illustrated in Curve E, was obtained at a heating rate of 1.25 C/min on a solvent-crystallized sample of POP with melting at ca. 37 C.

The DSC heating curves for PEP are shown in Figure 2. All four polymorphs of PEP can be identified by DSC. Curves A, B, C, and D, with heating rates of 1.25, 5, 10, and 20 C/min, are essentially the same except for peak displacement due to temperature lag. During heating, Polymorph 4 converted to Polymorph 3 at ca. 33-43 C, and then to Polymorph 2 at ca. 40-51 C, followed by melting of Polymorph 2 at ca. 56 C. The melting curve of Polymorph 1, illustrated in Curve E, was obtained at a heating rate of 1.25 C/min on a solvent-crystallized sample of PEP with melting at ca. 57 C.

Caloric data for 2-oleodipalmitin and 2-elaidodipalmitin are reported by Lovegren et al. (6).

The polymorphic behavior of cocoa butter has also been previously described (2) and 6 polymorphs have been identified by DSC. The DSC heating curves are shown in Figure 3, scanned at 5 C/min. Various tempering conditions were required to obtain the different polymorphs, ranging from rapid solidification followed by immediate remelting for Curve A to the well aged, unmelted sample for Curve H. The six polymorphs are illustrated in the following heating curves:

Polymorph 1, Curve H (peak 33.5 C)
Polymorph 2, Curve G (peak 30 C)
Polymorph 3, Curves E and F (peak 25 C)
Polymorph 4, Curve D and part of C (peak 23 C)

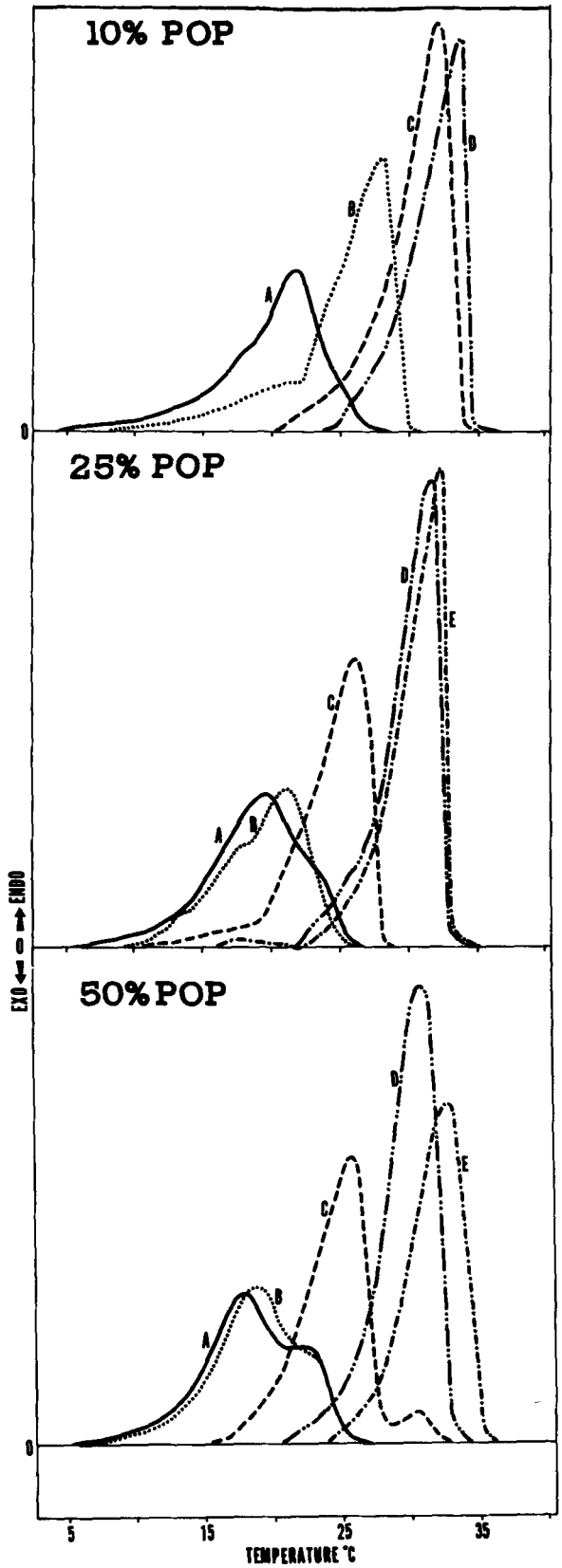

FIG. 4. DSC heating curves for 2-oleodipalmitin (POP): cocoa butter mixtures, heating rate 5 C/min, **10% POP:** A, cooling rate 5 C/min B, cooling rate 5 C/min, stepwise tempering at 16.7 C, 3 min; 18.5 C, 80 min; 20.3 C, 28 min; C, tempered overnight at 22 C; and D, tempered 9 days at 22 C. **25% POP:** A, cooling rate 5 C/min; B, quick chilled; C, cooling rate 10 C/min; stepwise tempering at 14.1 C, 4 min; 16.7 C, 45 min; D, tempered overnight at 22 C; and E, tempered 7 days at 22 C. **50% POP:** A, quick chilled; B, cooling rate 5 C/min; C, tempered at 14.1 C, 110 min; D, tempered overnight at 22 C; and E, tempered 4 days at 22 C.

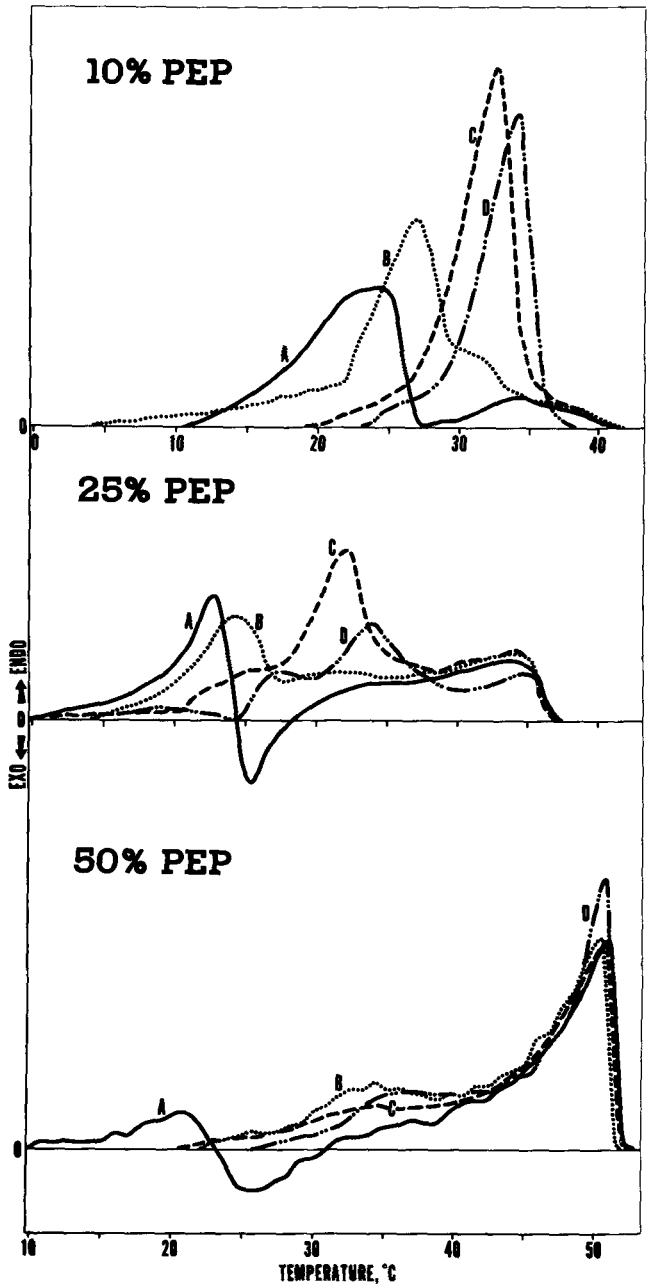

FIG. 5. DSC heating curves for 2-elaidodipalmitin (PEP): cocoa butter mixtures, heating rate 5 C/min. **10% PEP,** A, cooling rate 5 C/min; B, stepwise tempering at 14.1 C, 2 min; 18.5 C, 30 min; 20.3 C, 16 min; C, tempered overnight at 22 C; and D, tempered 3 days at 22 C. **25% PEP:** A, cooling rate 10 C/min; B, tempered at 14.1 C, 34 min; C, tempered overnight at 22 C; and D, tempered 2 days at 22 C. **50% PEP:** A, cooling rate 10 C/min; B, tempered overnight at 22 C; C, stepwise tempering at 11.4 C, 12 min; 18.5 C, 132 min; and D, tempered 1 day at 22 C.

Polymorph 5, Curves A, B, and part of C (peak 20 C)
Polymorph 6, Curve B (peak 13 C)

2-Oleodipalmitin-Cocoa Butter Mixtures

The DSC heating curves for the various mixtures of cocoa butter containing 10, 25, and 50% POP after varying degrees of tempering are shown in Figure 4. The scanning rate for all curves was 5 C/min.

In all three mixtures, the quickly solidified, untempered samples melted in the general temperature range of a similarly treated sample of cocoa butter. The melting point lowering is typical of that which occurs with mixtures of fats (7). Cocoa butter appeared to stabilize the low-melting polymorph of POP, whose melting is indicated only at a scanning rate of 10 C/min for POP alone. In the mixtures, a lower polymorph of POP is indicated on the back of Curves A and B of the 25 and 50% POP mixtures at ca. 23 C. There is some melting point lowering of the cocoa butter with the addition of POP. However, POP is quite compatible with cocoa butter, and the melting point lowering is greatest with the addition of 25% POP whereas there is negligible lowering with the addition of 50% POP. In all three mixtures of cocoa butter and POP, the tempered sample melted as a single compound, indicating good compatibility. The melting range of the mixtures was narrowest with the addition of 25% POP whereas the addition of 10 and 50% POP resulted in somewhat broader melting ranges. The addition of POP somewhat simplified the polymorphism of the cocoa butter, reducing the number of polymorphs from six to four or five. Except for the stabilization of the low-melting polymorph of POP, the addition of POP did not appreciably affect the rate of tempering of the mixtures in relation to the tempering of cocoa butter alone. Complete conversion to the highest-melting polymorph (Polymorph 1) was readily obtained in the POP-cocoa butter mixtures; a well-aged sample of cocoa butter contains a small portion of Polymorph 2 and some Polymorph 3.

The dips in Curve B, (10% POP at 22 C) and in Curve C (25% POP at 19 C) are the result of tempering just below the respective temperatures. Some segregation takes place and part of the sample remains liquid at the tempering temperature. When the sample was cooled after tempering, the liquid portion crystallized in a low polymorphic form and melted at a temperature below that of the tempered portion during heating. In the heating curve of the well-tempered 50% POP-cocoa butter mixture, Figure 4, Curve E, the area of the heat of fusion was smaller than that of the less tempered sample, Curve D. This phenomenon was found only in samples that had been tempered over a long period of time, usually those stored at room temperature, and is also seen to a lesser extent in Curve D of the 10% POP-cocoa butter mixture. Probably, in each of these mixtures there is a sufficient variety in the triglyceride composition that a degree of incompatibility exists. Rapid solidification of a fat or fat mixture from the melt results in a homogeneous solid that incorporates remaining liquid fat within the crystal matrix at perhaps a molecular or near molecular basis. In turn, with a short tempering period, the entire mixture acts as a solid and the sample melts as a single solid phase. On standing, the low-melting components, which are liquid at or near room temperature, gradually migrate, coalesce, and segregate. This is a slow process although marked variations in room temperature will accelerate the segregation. A well tempered sample consists of a solid and a liquid phase. Segregation occurs in those mixtures less able to incorporate the liquid triglycerides within the crystal matrix.

2-Elaidodipalmitin-Cocoa Butter Mixtures

The DSC heating curves for the various mixtures of cocoa butter containing 10, 25, and 50% PEP after varying degrees of tempering are shown in Figure 5. The scanning rate for all curves was 5 C/min.

Cocoa butter can accomodate up to 10% PEP within the crystal structure with little change in the melting range or melting point. The bulk of the mixture, however, melted over a somewhat broader range than did cocoa butter alone. PEP had a seeding effect and promoted conversion of the low-melting polymorphs of cocoa butter to the higher-melting polymorphs. It also reduced the number of polymorphs in cocoa butter from six to four.

The 25% PEP-cocoa butter mixture melted as a mixture of two dissimilar compounds over a range of ca. 15-47 C. The presence of PEP promoted rapid conversion of cocoa butter to the higher polymorphs. When the PEP-cocoa but-

ter mixture melted, the melted cocoa butter behaved as a solvent for the crystallized PEP, and the PEP had completely dissolved in the melted fat when the scan reached 47 C. In Curve D, some PEP appeared to be incorporated in the cocoa butter crystals and resulted in a broad melting range of 25-40 C, with the remaining PEP progressively dissolving in the melted fat over the range of 40-47 C. In Curves C and D, the bulk of the cocoa butter is present in the highest polymorph.

In the 50% PEP-cocoa butter mixture, the behavior was similar to the 25% PEP-cocoa butter mixture in that it melted as a mixture of two dissimilar compounds with a melting range of 20-25 to ca. 53 C. In Curve A, the untempered sample rapidly converted to the higher-melting polymorphs of cocoa butter and PEP. The melting point of the PEP is somewhat depressed by the melted cocoa butter at the higher temperatures in the heating scan. In Curves B, C, and D, the cocoa butter is in the highest polymorph. In all curves, the PEP portion rapidly converted to higher-melting polymorphs.

The liquid fraction and the lower melting temperatures of the cocoa butter facilitate the conversion of the higher-melting PEP to the higher-melting polymorphs. The dip in Curve B, 10% PEP at 22 C is the result of tempering at 20.3 C and is discussed above.

Hydrogenated confectionery fats, such as those prepared from cottonseed oil winterization stearine, containing primarily 2-oleodipalmitin with varying amounts of 2-elaidodipalmitin, are quite compatible with cocoa butter providing that the 2-elaidodipalmitin content of the cocoa butter-confectionery fat mixture does not exceed 10%.

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