Polymorphic Changes in Mixtures of Confectionery Fats[1]

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ABSTRACT

The polymorphic behavior of mixtures of cocoa butter and high melting cocoa butter fraction with three types of confectionery fats and mixtures of the confectionery fats with each other were investigated with a differential scanning calorimeter. The confectionery fats were an interesterified-fractionated fat, a hydrogenated-fractionated fat, and a lauric acid fat. The lowered melting point observed in mixtures of confectionery fats with cocoa butter or cocoa butter fraction was related to the proportion of triglycerides dissimilar to the major components in cocoa butter and cocoa butter fraction contained in a particular confectionery fat. The hydrogenated-fractionated fat contained ca. two-thirds 2-oleodisaturated triglycerides similar to the major components of cocoa butter; the interesterified-fractionated fat, ca. one-third 2-oleodisaturated triglycerides. The lauric acid fat contained virtually no triglycerides similar to cocoa butter. The series of mixtures of confectionery fats with cocoa butter and cocoa butter fraction that had the least melting point lowering were those that contained 25% hydrogenated-fractionated fat; the ones that had the greatest lowering of melting point were those that contained 25% lauric acid fat. Mixtures of confectionery fats with cocoa butter possessed considerable amounts of low melting components, whereas similar mixtures with cocoa butter fraction exhibited a narrower melting range and possessed few low melting components. The more highly crystalline confectionery fats can accommodate the addition of fats containing some low melting components. The most compatible of the series of mixtures of confectionery fats with each other was the mixture of interesterified-fractionated fat containing 25% hydrogenated fractionated fat; the least compatible, hydrogenated fractionated fat containing 25% lauric acid fat.

INTRODUCTION

The polymorphic behavior of triglycerides (TGs) has been investigated by various techniques, including dilatometry, capillary melting point determinations, and X-ray diffraction. Rossell (1) used dilatometry to construct isodilatation diagrams to study the interactions of TGs and the fats containing them. Included were studies of blends of triolein with tristearin; blends of a fat rich in saturated acids with a hardened cottonseed fraction rich in elaidic acid; blends of an experimental confectionery fat, shea stearine, and a hydrogenated cottonseed fraction, each with cocoa butter; blends of fats containing the glycerides 1-oleodipalmitin and 2-oleodipalmitin; and blends of two crambe stearines. Wille and Lutton (2) identified six polymorphs of cocoa butter (CB) by X-ray diffraction and determined their respective melting points by the capillary melting point technique. In addition, the polymorphism of 2-oleopalmitostearin (POS), 2-oleodistearin (SOS), a binary system of POS and SOS and a tertiary system approximating the proportion of the major glycerides, POS, SOS, and 1,2-dioleostearin in CB were reported by them. Paulicka (3) determined the phase behavior of three types of CB extenders, two of which were derived from natural fats and the third from hydrogenated-fractionated domestic vegetable oils. Huyghebaert and Hendrickx (4) used melting curves from the differential scanning calorimeter to demonstrate the six polymorphs of CB, thus confirming those demonstrated by Wille and Lutton (2) from X-ray diffraction studies.

The purpose of this investigation was to determine the polymorphic changes occurring in mixtures of confectionery fats of various types. CB and a high melting cocoa butter fraction (CBF) in mixtures with an interesterified-fractionated fat (Fat I), a hydrogenated-fractionated fat (Fat H), and a lauric acid fat (Fat L), as well as mixtures of the non-CB fats with each other, were investigated by differential scanning calorimetry (DSC).

EXPERIMENTAL PROCEDURES

Materials

CB from Hershey Chocolate Corp. (Hershey, PA) was used in this study. The CB was fractionated by crystallization of a 9% solution of CB in acetone at 0 C to yield 80.2% of CBF. The preparation and characterization of Fat I has been described previously and consists of the combined runs 1-4 in Table III (5), later characterized as Fat No. 1 in Table I (6). Hydrogenated cottonseed oil and triolein (iodine value 85.0) were interesterified in a ratio of 7:3. The interesterified product was fractionated by two crystallizations from acetone. Crystallization at 28 C removed the trisaturates, and crystallization of the ensuing filtrate at -1.5 C crystallized the confectionery fat product, leaving the low melting fat in the filtrate. The preparation and characterization of Fat H has been described previously as product HP-8F (7). Cottonseed oil stearine, a by-product in the solvent winterization of cottonseed oil, was partially hydrogenated to reduce the linoleic acid groups to oleic and iso-oleic. The hydrogenated product was fractionally crystallized from commercial hexane (1:1 w/w) at 25 and 17 C to remove most of the trisaturated portion. Fat L was extracted from a commercial pastel coating with *n*-hexane (technical grade, Phillips Petroleum Co., Bartlesville, OK). The fatty acid composition of these fats is given in Table I.

TABLE I

Fatty Acid Composition of Confectionery Fats

Fatty acid methyl esters	Confectionery fats[a] (% composition)				
	CB	CBF	Fat I	Fat H	Fat L
C_8			0.11		0.07
C_{10}			0.11		2.1
C_{12}			0.8	0.04	41.8
C_{14}			0.7	0.6	24.1
C_{16}	28.6	22.6	17.4	45.2	13.6
$C_{16:1}$	0.08		0.38		
C_{17}	tr[b]		0.15		0.07
$C_{17:1}$			tr		tr
C_{18}	32.1	41.5	48.4	8.6	7.0
$C_{18:1}$	36.0	35.1	29.1	44.5	9.9
$C_{18:2}$	3.0	0.8	2.4	1.0	1.4
$C_{18:3}$			tr		tr
C_{20}	0.24	tr	0.18		tr
$C_{20:1}$			tr		

[a]CB = Cocoa butter, CBF = cocoa butter fraction, Fat I = interesterified-fractionated fat, Fat H = hydrogenated-fractionated fat, Fat L = lauric acid fat. Composition determined by gas liquid chromatrography.

[b]tr = not measured, estimated <0.1%.

[1]Presented at the AOCS Meeting, Mexico City, April 1974.

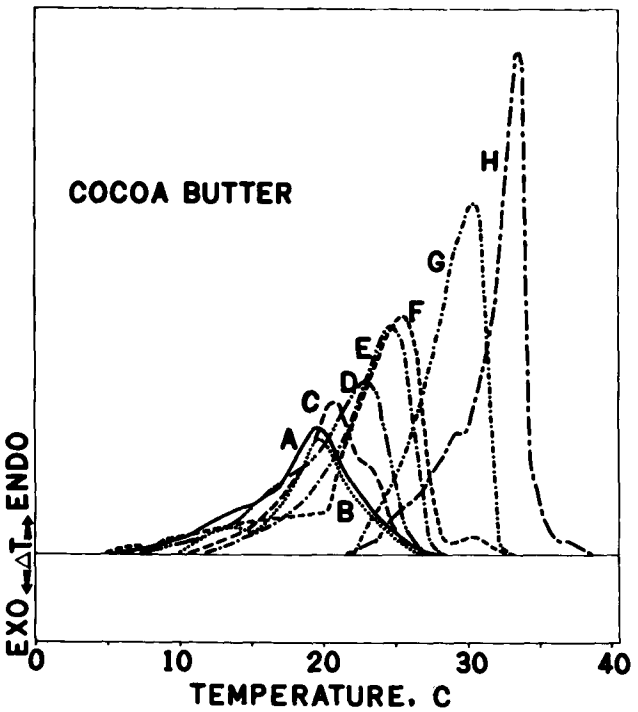

FIG. 1. Differential scanning calorimetric heating curves for cocoa butter, heating rate 5 C/min. A, quick chilled; B, untempered, heated rapidly to 5.3 C; C, tempered 20 min at -12.4 C; D, tempered 29 min at 5.3 C; E. Tempered 120 min at 9.7 C; F, stepwise tempering 30 min at 9.7 C, 85 min at 14.1 C, 62 min at 18.5 C; G, tempered overnight at 22 C; and H, tempered.

Procedures

A Perkin-Elmer DSC-1 differential scanning calorimeter (8) was used. The instrument was calibrated with indium (H_f = 6.79 cal/g). To ensure the accuracy of the temperature readings, the instrument was calibrated by melting samples of palmitic acid, lauric acid, methyl palmitate, and ice. The equilibrium melting-solidifaction temperatures, as determined with an NBS calibrated thermometer, for palmitic acid, lauric acid, methyl palmitate, and water were 62.5, 43.2, 29.4, and 0.0, respectively.

The confectionery fats were weighed in appropriate 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 into place. Sample size varied from 11 to 17 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 rate, and the sample cover was filled with dry ice. To obtain consistent results, all samples were stabilized for 30 min or longer with the slow flow of nitrogen through the sample area chilled with dry ice before starting a scan.

The scanning rate used for heating curves was 5 C/min except for five of the seven CBF curves that were scanned at 2.5 C/min. The polymorphic forms referred to in the heating curves are designated as 1, 2, 3, etc., in decreasing order of their melting points. The highest melting polymorphs were obtained on solvent crystallized or well tempered samples. Well tempered samples were obtained by storage at 22-25 C for at least 2 weeks, or until no further polymorphic change was apparent. In reference to the figures, tempered refers to aged, unmelted for CB, Fat I, Fat H, and Fat L; to solvent crystallized for CBF; and to well tempered for the various mixtures. The low melting polymorphs were obtained on samples quickly chilled from the melt to 10 C to below 0 C, depending on the temperature at which the particular sample crystallized. 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 melting temperature. This cycle was repeated, the temperature at which the sample started to melt being somewhat higher 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 conversion took place. Slowly converting samples were held at the incipient melting temperature for 2 or more hr, thus reducing the number of repeat cycles required to attain a polymorphic conversion. Many samples, however, converted quickly and required a minimum holding time.

RESULTS AND DISCUSSION

Cocoa Butter

CB is primarily a mixture of 2-oleopalmitostearin, 2-oleodistearin, and some 2-oleodipalmitin, along with lesser amounts of dioleo-, linoleo-, and other TGs that are liquid at or near room temperature (9). The particular TG composition of CB is responsible for its unique physical properties. Six polymorphs have been recognized in CB. In the DSC heating curves (Fig. 1), scanned at 5 C/min, all six polymorphs are illustrated. 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 I: Curve H (peak 33.5 C)
Polymorph II: Curve G (peak 30 C)
Polymorph III: Curves E and F (peak 25 C)
Polymorph IV: Curve D and part of C (peak 23 C)
Polymorph V: Curves A, B, and part of C (peak 20 C)
Polymorph VI: Curve B (peak 13 C)

In a run similar to Curve B, scanned at 10 C/min, Polymorph VI comprised nearly half of the melted fat with the peak near 13 C. These six polymorphs correspond to those found by Wille and Lutton (2) and were also confirmed by X-ray diffraction spectra.

High Melting Fraction of Cocoa Butter

CBF is primarily a mixture of 2-oleopalmitostearin, 2-oleodistearin, and some oleodipalmitin but has virtually no components that are liquid at room temperature. With the removal of the moderating influence of the more liquid components of CB, the high melting fraction becomes highly crystalline, with a narrow melting range, a high endothermic value, and a rather complex crystalline structure. In the DSC heating curves (Fig. 2), in which Curves A and C were scanned at 5 C/min and the others at 2.5 C/min, at least five polymorphs are illustrated. Curve A consists primarily of Polymorph V, produced by rapid solidification of the melt followed immediately by melting at 5 C/min. Mild tempering conditions produced Polymorph IV and some Polymorph III in Curves B and C. Much more extensive tempering produced some Polymorph III in Curve D and Polymorph II in Curves D, E, and F. Curve F also has some Polymorph I whereas Curve G, the well tempered sample, is almost entirely Polymorph I. Removal of much of the liquid component from CB narrowed the melting range and increased the melting point and the crystallinity of the prod-

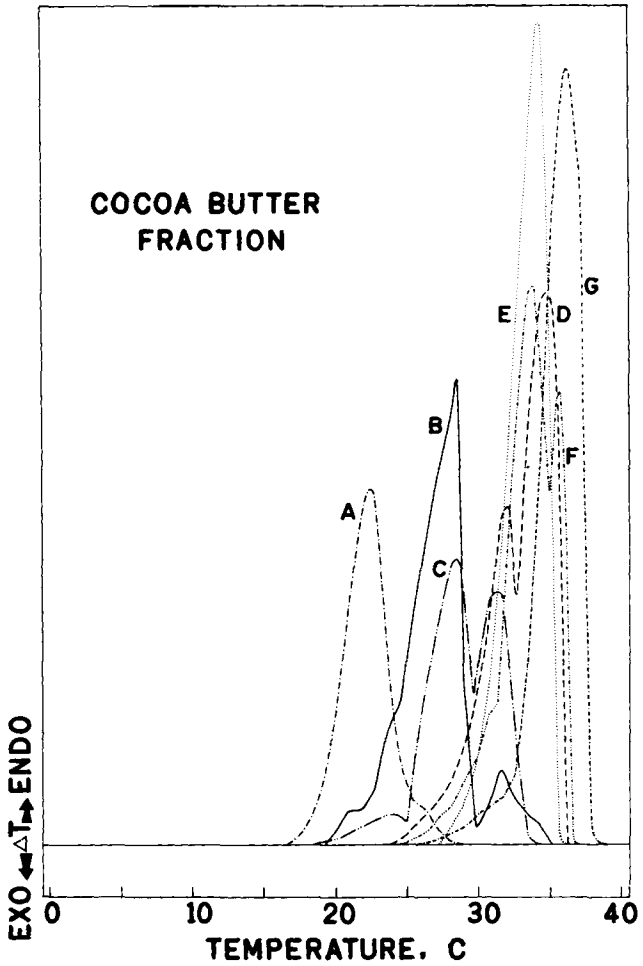

FIG. 2. Differential scanning calorimetric heating curves for the high melting cocoa butter fraction, heating rate 5 C/min for A and C, 2.5 C/min for others. A, untempered; B, tempered overnight at 22 C; C, stepwise tempering to 28 C; D, stepwise tempering to 28 C, weekend tempering at 22 C, stepwise tempering to 31 C; E, tempered 4.5 days at 22 C; F, stepwise tempering to 30 C; and G, tempered.

uct. The lower polymorphs are less stable, and there is increased complexity in the higher polymorphs.

Interesterified-Fractionated Fat

Fat I essentially consists of monounsaturated disaturated TGs with the unsaturated fatty acid in any of the three positions on the glycerol molecule, whereas CB has the unsaturated fatty acid primarily in the 2-position.

Fat I is as crystalline as CB and has similar melting range. The polymorphism is less complex than that of either CB or CBF. In the DSC heating curves (Fig. 3), which were scanned at 2.5 C/min, four polymorphs are illustrated. Conversion from Polymorph 4 to Polymorph 2 was fairly rapid. Curve A consists primarily of Polymorph 4, produced by melting the untempered sample. Tempering 30 min at 23 C (Curbe B) converted most of Polymorph IV to Polymorph III, with a small amount of Polymorph II also being present. After tempering overnight at 22 C (Curve C), Fat I is essentially converted to Polymorph II. The well tempered sample (Curve D) consists of Polymorph I with a moderate amount of Polymorph III, which could be due to incomplete conversion or to segregation.

Hydrogenated-Fractionated Fat

Fat H essentially consists of monounsaturated disaturated TGs with the unsaturated fatty acid primarily in the 2-position. Ca. 25% of the unsaturated fatty acids is the high melting elaidic acid produced during hydrogenation.

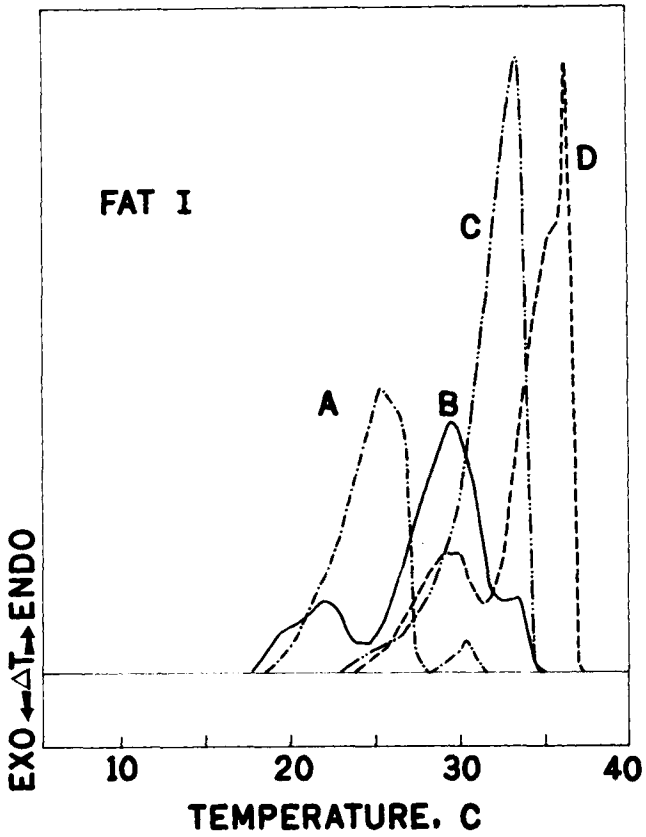

FIG. 3. Differential scanning calorimetric heating curves for the interesterified-fractionated fat (Fat I), heating rate 2.5 C/min. A, untempered; B, tempered 30 min at 23 C; C, tempered overnight at 22 C; and D, tempered.

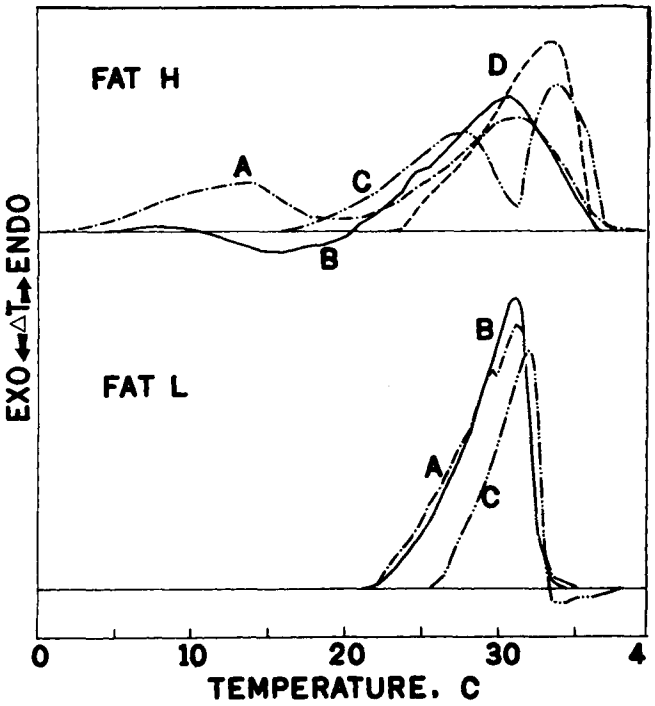

FIG. 4. Differential scanning calorimetric heating curves after various degrees of tempering. Hydrogenated-fractionated fat (Fat H), heating rate 10 C/min for A, 5 C/min for others: A, tempered 2 min at 1 C; B, untempered; C, stepwise tempering to 29 C; and D, tempered overnight at 22 C. Lauric acid fat (Fat L), heating rate 2.5 C/min: A, untempered; B, tempered overnight at 22 C; and C, tempered.

Two polymorphs for Fat H are evident in the DSC heating curves (Fig. 4). The conversion from Polymorph II to

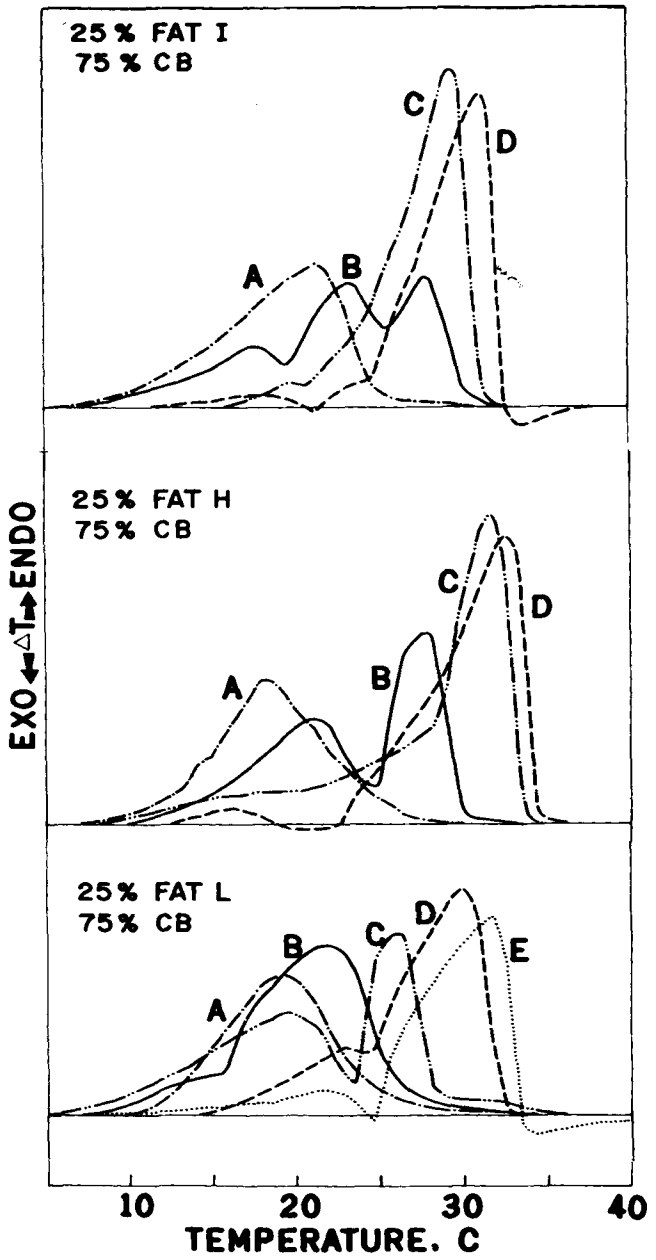

FIG. 5. Differential scanning calorimetric heating curves after various degrees of tempering, heating rate 5 C/min. Cocoa butter (CB) with 25% interesterified-fractionated fat (Fat I): A, tempered 20 min at -3 C; B, stepwise tempering to 18 C, tempered 1 hr at 18 C; C, tempered overnight at 22 C; and D, tempered. CB with 25% hydrogenated-fractionated fat (Fat H): A, untempered; B, tempered 2 min at 14 C, 70 min at 20 C, 80 min at 23 C; C, tempered overnight at 22 C; and D, tempered. CB with 25% lauric acid fat (Fat L): A, untempered; B, tempered 5 min at 11 C, 8 min at 14 C; C, stepwise tempering to 21 C, tempered 15 min at 21 C; D, tempered overnight at 22 C; and E, tempered.

Polymorph I was fairly rapid. Curve A, scanned at 10 C/min after 2 min tempering at 1 C, consists of Polymorph II with the major portion of the fat converting to Polymorph I. An untempered sample scanned at 5 C/min (Curve B) converted almost entirely during heating to Polymorph I; a negligible amount of Polymorph II remained unchanged. Stepwise Tempering to 29 C (Curve C) promoted conversion to Polymorph I but also segregated the fat into high and low melting components. When Fat H (Curve D) was tempered at 22 C overnight, the sample converted to Polymorph I.

Lauric Acid Fat

The lauric acid fat (Fat L) in Figure 4 consists of about two-thirds trisaturated and one-third disaturated TGs. Fat L is crystalline and has a moderately narrow melting range. Only one polymorph was observed in the three DSC heating curves of the untempered (Curve A), tempered overnight (Curve B), and tempered (Curve C) samples.

Cocoa Butter-Confectionery Fat Mixtures

DSC melting curves for mixtures of 25% of each of the three confectionery fats with 75% CB are illustrated in Figure 5. All scans were made at 5 C/min. The addition of confectionery fats to CB simplified the polymorphism of CB, and there was some tendency to stabilize the lower melting polymorphs in each instance.

Fat I in CB has the narrowest melting range of the three mixtures, although the TGs in Fat I are less similar to CB than are those of Fat H. The more crystalline properties of Fat I appear to compensate for the more compatible properties of Fat H. In Curve B, tempering at 18 C caused some segregation of the liquid portion, producing the dip near that temperature in the DSC scan.

Fat H in CB lowered the melting point the least. The TG composition of Fat H is more like that of CB than of Fat I and Fat L. The dip in Curve B is due to tempering at 22 C.

Fat L in CB was the least compatible of the mixtures and was also the least similar to CB in TG composition. The Fat L-CB mixture has a broad melting range and contained a considerable amount of low melting components.

Cocoa Butter Fraction-Confectionery Fat Mixtures

DSC melting curves for the mixture of 25% of each of the three confectionery fats with 75% high melting CBF are illustrated in Figure 6. All scans were made a 5 C/min. The addition of confectionery fats to CBF simplified the polymorphism of the CBF. The melting range of each of these mixtures was narrower and the structure more crystalline than was the corresponding mixture with CB. Removal of the liquid components from CB appeared to promote better compatibility with other fats.

Fat I in CBF lowered the melting point somewhat more than did Fat H. There was not as much simplification of polymorphism and slightly less compatibility than that with Fat H. In Curve C, tempering at 20 C produced the dip near that temperature in the DSC scan.

Fat H in CBF lowered the melting point least and was the most compatible of the three confectionery fats. There was also marked simplification of polymorphism. CB can tolerate a certain amount of components that are normally liquid at room temperature, and it derives some of its desirable properties from the inclusion of this liquid fat. The better compatibility of Fat H with CBF may be due in part to the larger amount of the liquid components present in Fat H, as well as to the similarity of their TG components. Fat I and Fat L had very little liquid component at room temperature, but Fat H had some.

Fat L in CBF was the least compatible of the three confectionery fats. The Fat L-CBF mixture had a broad melting range, and a considerable amount of low melting components was present. In Curve C, tempering at 19 C produced the dip near that temperature in the DSC scan.

Confectionery Fat Mixtures

DSC melting curves for the two mixtures of Fat I with Fat H, and mixtures of 25% Fat L with 75% Fat I, and 75% Fat H are illustrated in Figure 7. All scans were made at 5 C/min.

The mixture of 25% Fat H with 75% Fat I was quite compatible and crystalline. The addition of Fat H lowered the melting point somewhat and increased the melting range of Fat I. However, both melting point and range of the tempered mixture were satisfactory.

The mixture of 25% Fat I with 75% Fat H gave a

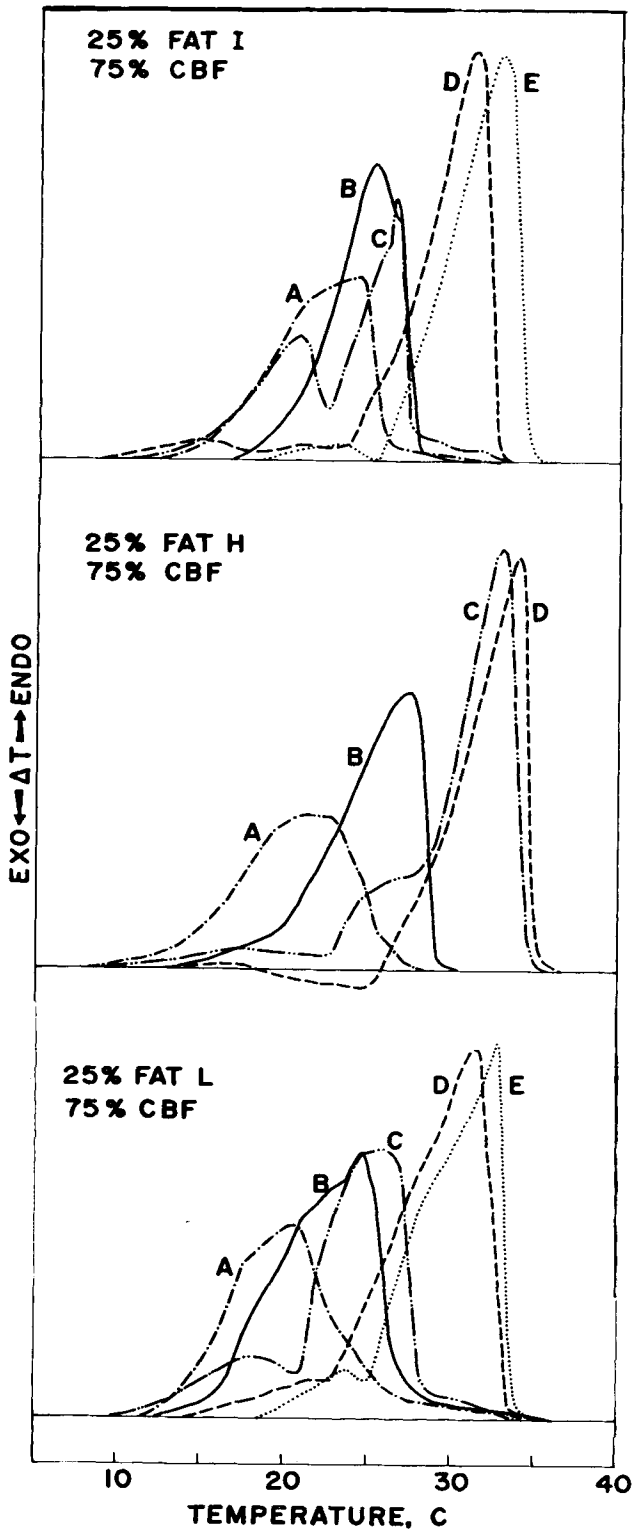

FIG. 6. Differential scanning calorimetric heating curves after various degrees of tempering, heating rate 5 C/min. Cocoa butter fraction (CBF) with 25% interesterified-fractionated fat (Fat I): A, untempered; B, tempered 95 min at 14 C; C tempered 12 min at 14 C, 13 min at 18 C, 39 min at 20 C; D, tempered overnight at 22 C; and E, tempered. CBF with 25% hydrogenated-fractionated fat (Fat H): A, tempered 17 min at -12.5 C; B, tempered 12 min at 14 C, 31 min at 18 C; C, tempered overnight at 22 C; and D, tempered. CBF with 25% lauric acid fat (Fat L): A, untempered; B, tempered 40 min at 14 C; C, tempered 115 min at 14 C, 41 min at 17 C, 46 min at 19 C; D, tempered overnight at 22 C; and E, tempered.

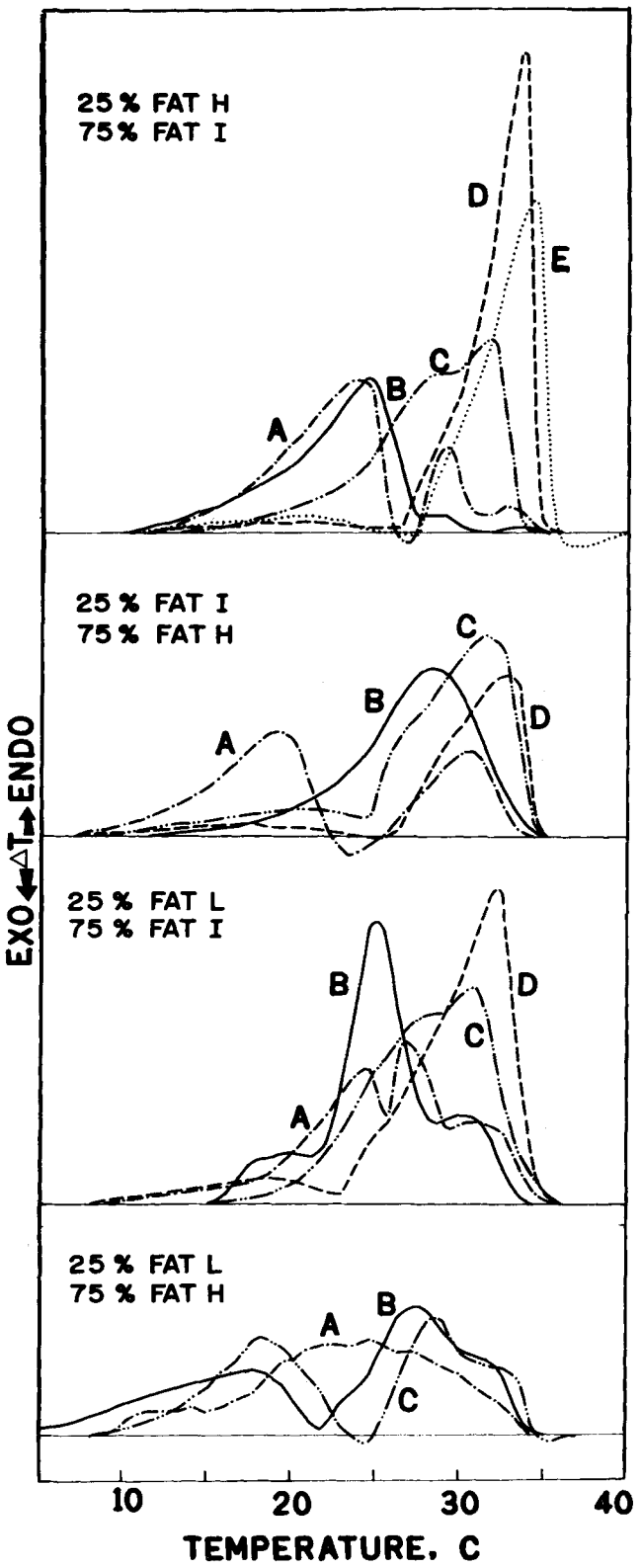

FIG. 7. Differential scanning calorimetric heating curves after various degrees of tempering, heating rate 5 C/min. Interesterified-fractionated fat (Fat I) with 25% hydrogenated-fractionated fat (Fat H): A, tempered 30 min at 10 C; B, untempered; C, tempered 54 min at 14 C; D, tempered overnight at 22 C; and E, tempered. Fat H with 25% Fat I: A, tempered 2 min at -12.5 C; B, tempered 6 min at 10 C, 5 min at 14 C; C, tempered overnight at 22 C; and D, tempered. Fat I with 25% lauric acid fat (Fat L): A, untempered; B, tempered; C, tempered 96 min at 14 C; and D, tempered overnight at 22 C. Fat H with 25% Fat L: A, untempered; B, tempered over weekend at 22 C; and C, tempered.

product having too broad a melting range, and there was slightly more melting point depression. The mixture was considerably less crystalline than that of the 25% Fat H with 75% Fat I mixture.

The mixture of 25% Fat L with 75% Fat I gave a

markedly crystalline product, but the melting range was too broad and there was some lowering of the melting point. In Curve D, tempering at 22 C produced the dip near that temperature in the DSC scan.

The mixture of 25% Fat L with 75% Fat H was incompatible, inasmuch as the product during tempering separated into high and low melting components.

General

In several of the heating curves of well tempered samples, an exothermic area was observed after melting was completed. Also, the area of the heat of fusion in these samples, as well as that of several other samples not having this exothermic area, was smaller than that of the sample when less tempered. This phenomenon was found only in samples that had been tempered over a long period of time, usually having been stored at room temperature. Examples of smaller areas of fusion with exotherms after complete melting are Figure 4, Fat L, Curve C; Figure 5, 25% Fat I with 75% CB, Curve D, and 25% Fat L with 75% CB, Curve E; Figure 7, 25% Fat H with 75% Fat I, Curve E. An example of smaller area of fusion is Figure 7, 25% Fat I with 75% Fat H, Curve D. The TG compositions of natural fats and products made from natural fats are complex and varied, and hydrogenation introduces geometrical isomers, adding to the complexities. A possible explanation of these observations is that in each of these instances there is sufficient variety in the TG 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 any liquid fat present 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. The well tempered sample of CB, Figure 1, Curve H, showed no evidence of melting below 22 C, although ca. 20% of the CB is liquid at that temperature when separated from the higher melting component of CB. However, in contrast to CB, a well tempered sample of the fats or fat samples cited above changed from a homogeneous mixture of TGs into a segregated one having a solid and a liquid phase. The low melting components, which are liquid at or near room temperature, gradually migrate and coalesce, and segregation develops. This is a slow process, although marked variations in room temperature will accelerate the segregation. The fats and fat mixtures in which segregation occurs are those that are less able to incorporate the liquid TGs within the crystal matrix. When such a sample is melted during a DCS scan, only the solid phase adsorbs appreciable energy for melting, resulting in a lower caloric value for the sample. When there are marked differences in the TG composition of the solid and liquid phases, a mixing as the solid melts and, in this case, an exothermic reaction is initiated and continues for several min after melting is complete until the liquid fat mixture is homogeneous. This exothermic reaction also contributes to the lower caloric value during melting and is seen in the DSC scan in the exothermic area following the endothermic peak. In Figure 7, 25% Fat I with 75% Fat H, Curve D, the TGs in the two phases are sufficiently similar so there is little or no cooling effect during mixing of the two liquid phases. When such a sample is melted during a DSC heating scan, only the solid phase adsorbs energy for melting, resulting in a lower caloric value than for the sample tempered over a short period of time.

No simple way was found to assign numberical values for the measurement of compatibility of these confectionery fat mixtures. DSC is useful, however, for screening the compatibility of mixtures of fats. Those exhibiting two separate melting ranges are totally incompatible. The relative compatibility of those mixtures having a single melting range can be evaluated by the changes in melting range and crystallinity of the respective components as measured by DSC procedures. Insight is also provided into favorable tempering conditions for confectionery fats or fat mixtures.

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