Effect of Liquid Fat on Melting Point and Polymorphic Behavior of Cocoa Butter and a Cocoa Butter Fraction[1]

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ABSTRACT

The polymorphic behavior of cocoa butter and a high-melting fraction of cocoa butter (CBF) was investigated by differential scanning calorimetry. The effect of liquid fat on melting point and polymorphic behavior was established for six mixtures: 83.5% cocoa butter and 16.5% of a low-melting fraction of cocoa butter (CBF-LM), 90% cocoa butter and 10% olive oil, and four mixtures of CBF and olive oil containing 10%, 20%, 30%, and 50% olive oil. Six polymorphs were found for cocoa butter and at least five for CBF. The melting points for cocoa butter and CBF were 35 and 38 C, respectively. Addition of CBF-LM to cocoa butter reduced the observable polymorphs to four and the melting point to 32.5 C. In cocoa butter, 10% olive oil reduced the observable polymorphs to three and the melting point to 31.5 C. Similarly, 10% olive oil in CBF reduced the observable polymorphs to three and the melting point to 37 C. Amounts of 20%, 30%, and 50% olive oil in CBF reduced the polymorphs to two and the final melting point to 34.5, 33, and 32 C, respectively. Possible explanations for the observed polymorphic behavior are advanced. Changes in the rates of tempering of cocoa butter and CBF on addition of various amounts of liquid fat are discussed.

INTRODUCTION

Polymorphism and rates of transition of cocoa butter (CB) and the effect of addition of liquid fat on these characteristics can be studied effectively by differential scanning calorimetry (DSC). Six polymorphs of CB have been identified by X-ray diffraction and other properties, and an attempt was made to relate the polymorphism of CB to the polymorphism of a binary and ternary system of the major triglycerides (TGs) in appropriate proportions (1). These six polymorphs were also confirmed by DSC (2). The polymorphic behavior and thermal properties of CB, especially in relation to the technical problems of tempering, have been examined by X-ray diffraction and DSC (3). X-ray diffraction has also been used to determine the effect of addition of liquid oils or organic solvents on rate of transition of tristearin (4). Differential thermal analysis has been used to examine the effect of the varying degrees of hydrogenation on the polymorphism of soybean oil, the effect of the addition of various amounts of soybean oil to fully hydrogenated soybean oil (5), and the effect of various degrees of hydrogenation on the polymorphism of beef tallow, cottonseed oil, and soybean oil (6).

CB contains ca. 20% TGs that are liquid at room temperature. The composition of CB has been determined by a variety of analytical procedures (7), including countercurrent analysis (8). The purpose of this investigation was to determine the influence of liquid fats on the polymorphic behavior of CB and the high melting fraction of cocoa butter (CBF).

The concept of a mixture of TGs existing as a polymorph, which has been employed by others working with CB, is employed in the present discussion. CB is composed mainly of two compounds, 2-oleopalmitostearin and 2-oleodistearin, which are similar in crystal behavior and which form mixtures that behave like a single compound.

MATERIALS AND METHODS

CB was from the Hershey Chocolate Corp. (Hershey, PA); refined olive oil was from Drew Chemical Corp. (Lindsay, CA). The CB was fractionated by crystallizing a 9% solution of CB in acetone at 0 C into high-melting (CBF) and low-melting (CBF-LM) fractions with yields of 80.2 and 19.8%, respectively. Portions of the CB, olive oil, and the two CB fractions were treated with boron trifluoride-methanol (9) , and the resulting methyl esters were analyzed in a Barber-Colman Model 20 gas chromatograph equipped with a tritium ionization detector and a 15 ft x 1/8 in. stainless steel column packed with 12% stabilized diethyleneglycol succinate on Gas Chrom P, 80-100 mesh. The injection port was held at 270 C, the column at 185 C, and the detector at 200 C. The fatty acid composition of CB, the two CB frac-

lauric acid, methyl palmitate, and ice, whose equilibrium melting-solidification temperatures had previously been determined with a calibrated thermometer.

The mixtures of CB with olive oil or with CBF-LM, and mixtures of CBF with various amounts of olive oil were weighed in appropriate amounts, melted and mixed well, then quickly solidified and tempered by appropriate means. After tempering, mixtures were weighed into DSC pans to the nearest 0.1 mg. Sample size varied from 8.5 mg for CBF to 14.7 mg for CB. Data obtained from the DSC scans were

TABLE I

Fatty Acid Composition of Cocoa Butter, Cocoa Butter Fractions, and Olive Oil

	Composition (% by wt)			
		Cocoa butter fraction		
Fatty acid	Cocoa butter[a]	High-melting	Low-melting	Olive oil
C_{10}				0.02
C_{12}				0.08
C_{18}	32.1	41.5	18.3	3.8
$C_{18:1}$	36.1	35.2	42.2	72.5
$C_{18:2}$	3.0	0.8	9.9	7.0
$C_{18:3}$			0.5	0.4
C_{20}	0.3	tr	0.9	0.3
$C_{20:1}$			tr	0.3
Iodine value[c]	36.3	31.6	55.9	76.8

[a]Cocoa butter from different lot used for fractionation.
[b]tr = Trace, <0.1, or present but not measured.
[c]Calculated.

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[1] Presented at AOCS meeting, New Orleans, April 1973.

recalculated to a unit wt basis to facilitate comparison. Unless otherwise noted, the scanning rate was 5 C/min. Before heating was started, the sample was cooled with dry ice to -13 to -8.5 C for 30 min or longer. A slow flow of nitrogen gas excluded moisture from the sample area. The α-form was obtained by rapidly cooling the melted sample to ca. -13, then immediately heating it. Higher melting polymorphs were obtained by stepwise tempering at the temperature at which the sample began to melt, then cooling and again bringing up to the temperature at which melting began. Samples that converted slowly were held at the incipient melting temperature for several hr, thus reducing the number of repeat cycles required to obtain polymorphic conversion.

Various criteria were used to determine the polymorphs present in the DSC heating curves. In most instances, samples that started melting at about the same temperature were considered to be a single polymorph. A considerable overlap of peak areas was considered to indicate a single polymorph. In some instances, samples tempered at higher temperatures remained partially liquid. When solidified and remelted, these samples produced a peak for the untempered portion, followed by a peak for the tempered portion. A longer tempering period permitted complete conversion to the higher polymorph in some instances, but not for samples having a high content of liquid fat. The melting point given for the various samples is that temperature at which the highest polymorph had melted completely. The polymorphs referred to in the heating curves are designated at I – VI in order of their decreasing melting points. The curves in the figures were selected from a larger series of curves to illustrate the various polymorphs found.

RESULTS

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 liquid at, or near, room temperature (7). The TG composition of CB is responsible for its unique physical properties. In the DSC heating curves (Fig. 1) scanned at 5 C/min, all six polymorphs of CB 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 that for Curve B, but scanned at 10 C/min, Polymorph VI comprised nearly half of the melted fat, giving the peak near 13 C. These six polymorphs conform fairly closely to those found by Wille and Lutton (1).

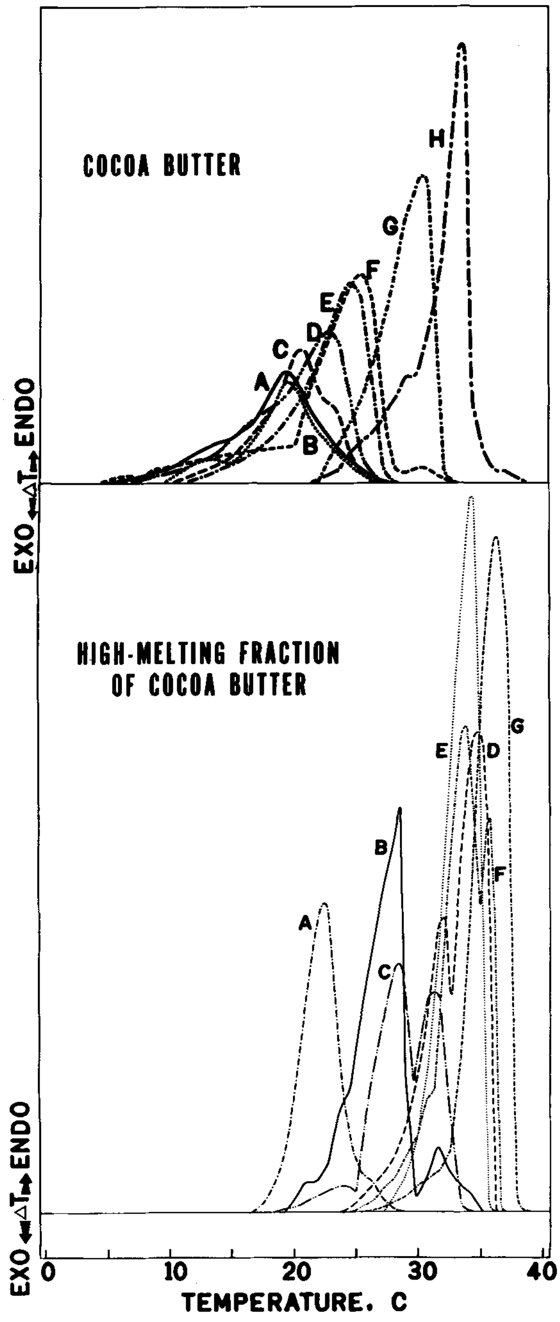

FIG. 1. Differential scanning calorimetric heating curves after various degrees of tempering. **Cocoa butter:** A, untempered; B, untempered, heated rapidly to 5.3 C; C, tempered at -12.4 C, 20 min; D, tempered at 5.3 C, 29 min; E, tempered at 9.7 C, 120 min; F, stepwise tempering at 9.7 C for 30 min, 14.1 C for 85 min, and 18.5 C for 62 min; G, tempered overnight at 22 C; and H, tempered. **High-melting cocoa butter fraction:** 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.

High-Melting Fraction of Cocoa Butter

CBF is primarily a mixture of 2-oleopalmitostearin, 2-oleodistearin, and some 2-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, CBF becomes more crystalline and complex, the melting range becomes shorter, and the heat of fusion increases. The DSC heating curves in Figure 1 (Curves A and C scanned at 5 C/min and the others at 2.5 C/min) reveal at least five polymorphs. Rapid solidification of the melt followed immediately by heating at 5 C/min (Curve A) produced primarily Polymorph V. Mild tempering produced Polymorph IV and some Polymorph III (Curves B and C). More extensive tempering produced some Polymorph III (Curve D) and Polymorph II (Curves D, E, and F). Curve F also indicates the presence of some Polymorph I, but Curve G, obtained with the well tempered sample, is almost entirely Polymorph I. The effect of removing much of the liquid components from CB was to narrow the melting range and to increase both crystallinity

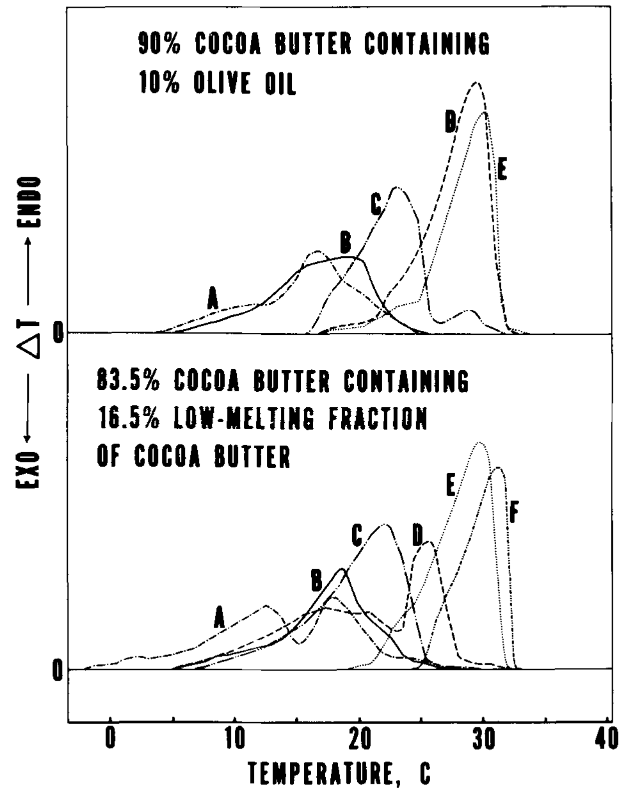

FIG. 2. Differential scanning calorimetric heating curves after various degree of tempering. **Cocoa butter containing 10% olive oil:** A, untempered; B, tempered at -8 C; C, tempered at 14 C; D, tempered overnight at 22 C; and E, tempered. **Cocoa butter containing 16.5% low-melting cocoa butter fraction:** A, untempered; B, tempered at -8 C; C, tempered at 5 C; D, stepwise tempering to 22 C; E, tempered overnight at 22 C; and F, tempered.

and melting point of the product. The lower polymorphs were less stable, and there was increased complexity in the high polymorphs.

Mixture of 90% CB and 10% Olive Oil

DSC heating curves for a mixture of cocoa butter and olive oil after various degrees of tempering are shown in Figure 2. At least three polymorphs can be identified in this mixture. The highest melting polymorph (Polymorph I, mp 31.5 C) is shown in Curve E and was obtained with the tempered sample. Polymorph III was obtained by heating the untempered sample at 5 C/min (Curve A). There is an indication of the presence of a still lower melting polymorph (5-12 C) preceding this major endothermic peak. Tempering at -8 C (Curve B) resulted in a single endothermic peak produced by Polymorphs II and III. Tempering at 14 C (Curve C) resulted in the major portion of the sample being converted to Polymorph II, with a small part to Polymorph I. Tempering overnight at 22 C (Curve D) converted the mixture almost entirely to Polymorph I.

Mixture of 83.5% CB and 16.5% CBF-LM

DSC heating curves for a mixture of CB and CBF-LM after various degrees of tempering are shown in Figure 2. All six polymorphs of CB can be identified in this mixture. Polymorph I (mp 32.5 C) in Curve F was obtained with the tempered sample. Polymorph VI was obtained by heating the untempered sample at 5 C/min (Curve A). A large part of the sample converted to Polymorph V, with some to higher polymorphs. There is evidence of a still lower melting polymorph at 0 – 6 C preceding Polymorph VI. Tempering at -8 C and at 5 C (Curves B and C) formed primarily Polymorphs V and IV, respectively. Stepwise tempering to 22 C (Curve D) resulted in various degrees of tempering of the fat fraction that was liquid below the tempering tem-

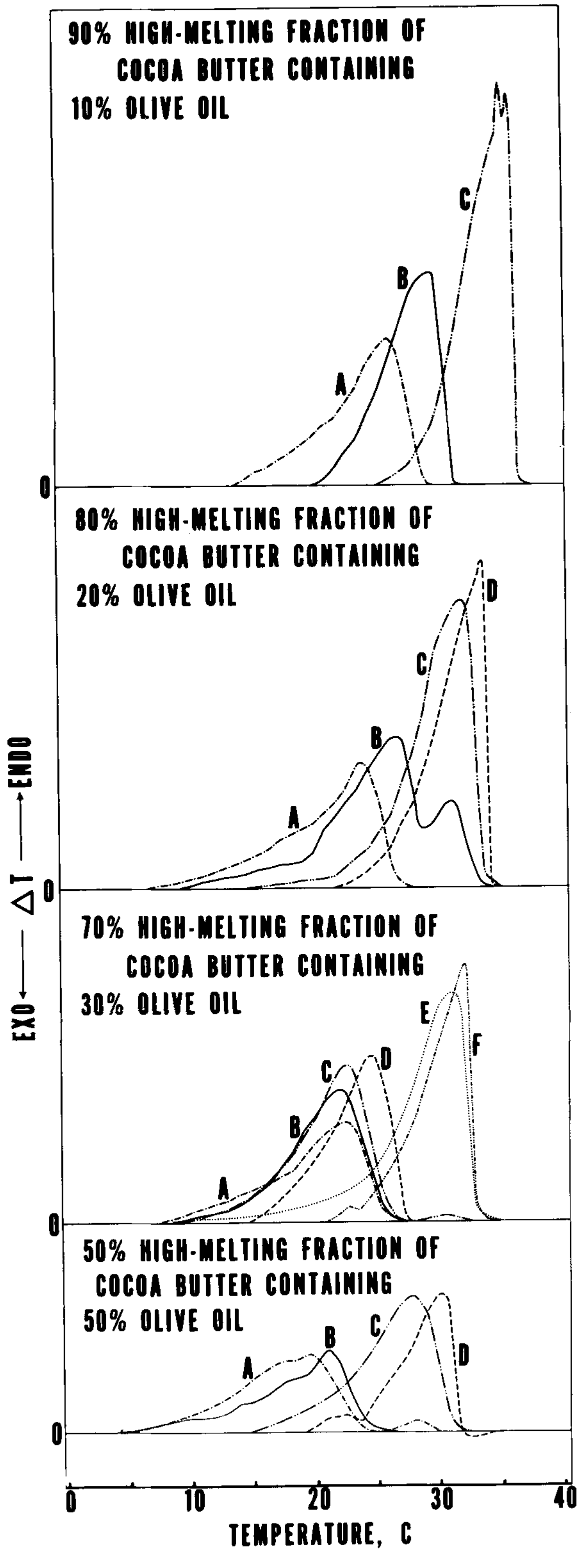

FIG. 3. Differential scanning calorimetric heating curves for the high-melting cocoa butter fraction containing various amounts of olive oil after various degrees of tempering. **10% Olive oil:** A, tempered at -13 C; B, stepwise tempering to 20 C; and C, tempered. **20% Olive oil:** A, untempered; B, stepwise tempering to 18 C; C, tempered overnight at 22 C; and D, tempered. **30% Olive oil:** A, tempered at -13 C; B, cooling rate 5 C/min, tempered at -13 C; C, tempered at -8 C; D, tempered at 14 C; E, tempered overnight at 22 C; and F, tempered. **50% Olive oil:** A, tempered at -13 C; B, cooling rate 5 C/min to -13 C; C, stepwise tempering to 14 C; and D, tempered.

perature to Polymorphs IV and V, whereas the solid portion of the fat converted to Polymorph III. Curve E was produced mostly by Polymorph II and lesser amounts of Polymorphs I and III.

Mixtures of CBF and Olive Oil

Three polymorphs can be identified in the DSC heating curves for the mixture of 90% CBF–10% olive oil after various degrees of tempering (Fig. 3). Polymorph I (mp 37 C), shown in Curve C, was obtained when the tempered sample was scanned at 2.5 C/min. The configuration of the original sample is responsible for the double peak. Polymorph III was obtained by tempering at -13 C and heating at 5 C/min (Curve A). Stepwise tempering to 20 C (Curve B) resulted in conversion to Polymorph II.

Two polymorphs can be identified in the DSC heating curves for the mixture of 80% CBF–20% olive oil after various degrees of tempering (Fig. 3). Polymorph I (mp 34.5 C) is shown in Curves B, C, and D. Tempering overnight at 22 C gave Polymorph I (Curve C), whereas stepwise tempering to 18 C resulted in partial conversion to Polymorph I (Curve B). Polymorph II, obtained by heating the untempered sample at 5 C/min (Curve A), has a broad melting range.

Two polymorphs also can be identified in the DSC heating curves for the mixture of 70% CBF–30% olive oil after various degrees of tempering (Fig. 3). Polymorph I (mp 33 C) is shown in Curves E and F. The tempered sample (Curve F) appeared to have a small amount of Polymorph II. When the sample was tempered overnight at 22 C (Curve E), a larger amount of Polymorph II formed, and the melting range of Polymorph II then extended over a range of > 15 degrees. Polymorph II was also obtained by tempering at -13 C, by cooling the melt at 5 C/min, tempering again at -13 C, then at -8 C (Curves A, B, and C). These tempering conditions resulted in a progressively more orderly alignment of the crystal structure, thus requiring an increasing amount of calories during melting. With tempering at 14 C (Curve D), Polymorph II started to melt at ca. 15 C, 7 or 8 degrees higher than in Curves A, B, and C. The shape of the lower temperature section of Curve A and the change in the temperature at which the sample melted in Curve D indicate that a lower melting polymorph may exist.

DSC heating curves for the mixture of 50% CBF–50% olive oil after various degrees of tempering are shown in Figure 3. Two polymorphs can be identified. Polymorph I (mp 32 C) is shown in Curves C and D. The tempered sample (Curve D) appeared to have segregated to some extent during tempering at room temperature, and a small amount of premelting occurred. The small exothermic peak following the main melting peak for Polymorph I probably resulted from the mixing of the two dissimilar components. This situation was encountered in several other tempered mixtures of fats. The time interval in the other tempering procedures used was insufficient to allow segregation. With tempering at -13 C (Curve A), most of the sample remained as Polymorph II, with a small amount of conversion to Polymorph I. The irregular conformation of the peak for Polymorph II (Curves A and B) may be caused by poor alignment of crystals in the presence of liquid fat. Cooling the melt at 5 C/min, then remelting at 5 C/min (Curve B), produced Polymorph II, with no conversion to Polymorph I. The slower rate of cooling appeared to effect a more orderly alignment of the crystals than did rapid cooling of the melt followed by tempering at -13 C (Curve A), and a larger proportion of the mixture melts at a higher temperature. Stepwise tempering to 14 C converted the mixture to Polymorph I, but the melting range was greater than that of the tempered sample (Curve D). This melting range could probably be shortened by stepwise tempering to ca. 20 C. Tempering to a still higher temperature would produce a heating curve similar to Curve D, in which part of the sample melted during tempering and resolidified during cooling. Essentially, the sample then segregates and the major portion converts to Polymorph I, while the minor portion remains primarily in a lower polymorphic form.

TABLE II

Solidification Temperatures of Cocoa Butter, High-Melting Fraction of Cocoa Butter, and Their Mixtures with Liquid Fat

Product[a]	Solidification temperature (C)[b] 1st peak[c]	2nd peak[c]	3rd peak[d]
CB	20	14	-1.7
90% CB + 10% olive oil	21	13	-2.2
83.5% CB + 16.5% CBF-LM	20.5	13	-2.2
CBF	21	16	5.8
90% CBF + 10% olive oil	22.5	16	1.4
80% CBF + 20% olive oil	17.5	10.4	-1.5
70% CBF + 30% olive oil	16	9	ND[e]
50% CBF + 50% olive oil	15	7.6	ND

[a] CB = cocoa butter; CBF = high-melting cocoa butter fraction; CBF-LM = low-melting cocoa butter fraction.

[b] Differential scanning calorimetric cooling rate, 5 C/min.

[c] Beginning of solidification.

[d] Middle of solidification; peak too flat to determine temperature at which solidification begins.

[e] Not determined.

Solidification Properties

Cooling curves (cooling rate 5 C/min) were determined for CB, a mixture of CB with 10% olive oil, a mixture of CB with a 16.5% CBF-LM, CBF, and mixture of CBF with 10, 20, 30, and 50% olive oil. During solidification, all samples crystallized in three phases. Initially, a small amount of the sample crystallized, followed by the bulk of the sample, then a small amount crystallized at a lower temperature. The temperatures at which the first and second phases started to crystallize and the middle of the temperature range during which the third phase crystallized are listed in Table II.

A mixture of 90% CB-10% olive oil or 83.5% CB–16.5% CBF-LM, when melted and cooled, first crystallized to a limited extent in the high-melting phase, but crystallization started 0.5-1.0 degrees above that for the corresponding phase in CB and occurred over a somewhat longer temperature interval. The bulk of the mixture crystallized at a lower temperature in a low-melting phase. The energy released during crystallization was less than that of CB alone; however, the decrease was greater than that expected for the proportions of liquid present in the mixtures.

The mixtures of CBF containing 10, 20, 30, and 50% olive oil produced the same pattern of crystallization found when liquid fat was added to CB. With the addition of 20% or more of olive oil to CBF, the temperature at which the high-melting phase started to crystallize was markedly lower than that of CBF alone. The temperature range for crystallization of the first, or high-melting phase, increased, and crystallization of the sample in this phase increased with additional olive oil. The bulk of the sample, which crystallized in the second phase, started crystallization at successively lower temperatures as the content of liquid oil increased, and the energy released during this crystallization was considerably less in proportion to the amount of liquid fat added. The mixture containing 50% olive oil produced very flat DSC peaks, and the energy released was far below that which would be expected.

DISCUSSION

Natural fats usually contain a large number of TG species; thus, the transition from the less ordered crystal structure to the more ordered structure of the stable crystal is often slow. Crystals formed in natural fats frequently contain disparate molecules. The rate at which conversion to the stable polymorph occurs in such fats is related to mobility within the crystal structure. Mobility is associated with the plastic properties of the fat itself and, in the presence of liquid fat, with the solubility of the solid fat. Addition of liquid fat, such as olive oil or CBF-LM, to CB or CBF reduced the number of stable polymorphs in the mixtures due to the ease of conversion to more stable forms. Addition of liquid fat to CB and to CBF simplified the polymorphic behavior of these mixtures, and conversion to the stable crystal progressed more rapidly. Less energy was required for melting, as was evident on comparison of the peak area of CB of CBF to those of their mixtures with liquid fat. With the addition of liquid fat, the peak areas decreased to below that expected for the proportion of liquid fat present in the mixtures.

CB converted very slowly to the stable polymorph. Addition of 10% olive oil to CB markedly affected the rate of conversion and reduced the number of polymorphs present from the six found in CB alone to three in the mixture. On standing overnight at room temperature (ca. 22 C), CB containing 10% olive oil converted essentially to the highest polymorph. Stepwise tempering of this mixture was not faborable to conversion, producing only a small amount of conversion. Addition of 16.5% CBF-LM had much less effect on the conversion rate but expanded the melting range more than did the addition of 10% olive oil. There was no reduction in the number of identifiable polymorphs when the CBF-LM was added, but no more than four polymorphs could be identified when 10% olive oil was added.

CBF converted slowly to the stable polymorph. The endothermic and exothermic changes required considerably more energy than they did for either the CB or any of the various mixtures containing liquid fat. CBF behaved in a polymorphically complex manner, exhibiting five polymorphs. Addition of liquid fat (olive oil) simplified the polymorphic behavior; on adding 10% olive oil, the number of polymorphs was reduced from five to three, and 20% olive oil further reduced the number to two. Various amounts of olive oil added to CBF reduced the energy required for the endothermic and exothermic changes below that expected for the proportions present in the composition of the mixtures.

It is to be expected that addition of similar amounts of CBF-LM or of olive oil to CB would affect the polymorphic characteristics of CB to different degrees. CBF-LM had an iodine value of ca. 56 and a saturated fatty acid content of ca. 46%. The fraction was primarily liquid ar room temperature (22-24 C) but contained a small amount of crystallized fat. Also, some TGs in CBF-LM so closely resemble TGs in CBF that mixed crystal formation with the latter would be expected. Olive oil, on the other hand, has an iodine value of ca. 77, a saturated fatty acid content of ca. 19%, an oleic acid content of ca. 72%, and is completely liquid at room temperature. The TG composition of olive oil is such that the addition of a given amount to CB could provide greater mobility of the molecules within the crystal structure than that provided by addition of an equal amount of CBF-LM.

In several of the heating curves of well tempered samples, the heat of fusion was smaller than that of the corresponding sample when less well tempered. This phonomenon was found only in samples that had been tempered over a long period of time, usually having been stored at room temperature. For example, the area under Curve E, Figure 2 (90% CB-10% olive oil), is smaller than that under Curve D; and the area under Curve F, Figure 2 (83.5% CB–16.5% CBF-LM), is smaller than the area under Curve E. In Figure 3, Curve F (70% CBF–30% olive oil) and Curve D (50% CBF-50% olive oil) are further examples of a decrease in heat of fusion on extensive tempering.

These observations can be explained by mixed crystal formation. Rapid solidification of the fat mixture from the melt resulted in formation of a relatively homogenous solid in which normally liquid fat entered the crystal matrix at a molecular level. After limited tempering, the entire mixture acted as a homogenous solid, and the sample melted as a single solid phase. Extensive tempering, however, destroyed the relatively homogenous solid. The higher melting TGs segregated into a smaller amount of higher melting solid phase, and the lower melting TGs coalesced and segregated into a phase liquid at or near room temperature. This was a slow process, although marked variations in room temperature accelerated the segregation. When such a sample was melted during a DSC scan, only the solid phase adsorbed appreciable energy during melting, resulting in a lower caloric absorption for the sample.

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ERRATUM

Moulton Actual Chairman of Fats and Oils Symposium

In the January issue of *JAOCS* (53:27), Associate Editor G.C. Cavanagh was mistakenly credited with chairmanship of the New Processing of Fats and Oils Symposium presented at the 66th Annual Meeting in Dallas and published in part in that issue. In fact, the chairman of the symposium, to whom we extend our sincere apologies, was Karl J. Moulton of the Northern Regional Research Laboratory (ARS, USDA) in Peoria, IL.