Cocoa Butter-Like Fats from Fractionated Cottonseed Oil: II. Properties

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ABSTRACT

Previously it was reported that the stearine obtained as a byproduct in the solvent winterization of cottonseed oil is a good starting material for the preparation of cocoa butter-like fats by way of hydrogenation and fractionation. The composition, physical properties, and compatability with cocoa butter have been determined for some of these fats. While the products contained triglyceride species other than those in cocoa butter, the major components were similar in that they were 2-oleodisaturated glycerides. The cocoa butter-like fats underwent slow polymorphic transformations, but made confectionery coatings remarkably resistant to bloom. Cooling curves resembled those of cocoa butter. Hardness was related to melting point; those fats melting below 35 C were softer than cocoa butter at room temperature, but fats melting above 35 C could be made to resemble cocoa butter in hardness. Adding cocoa butter to the cocoa butter-like fats had little effect on the softening point. X-Ray diffraction studies of 1:1 mixtures gave no evidence of mixed crystal formation; the long spacings resembled those of mechanical mixtures. In some other mixtures, certain short spacings became more pronounced.

INTRODUCTION

In a previous report (1), it was shown that cocoa butter-like fats can be prepared readily from the stearine obtained as a byproduct in the solvent winterization of cottonseed oil. This stearine, which consists of about two parts 1,3-disaturated (mostly 1,3-dipalmito) triglycerides and one part 1-monosaturated (mostly 1-palmito) triglycerides of oleic and linoleic acids, is partially hydrogenated to reduce the linoleic acid groups to oleic and iso-oleic; and some of these together with some of the original oleic acid groups are hydrogenated to stearic. The hydrogenated product is fractionally crystallized to remove most of the trisaturated portion and leave a cocoa butter-like fat in yields up to 70%.

By the procedure mentioned, a variety of products can be made by changing the degree of hydrogenation, the selectivity of the hydrogenation reaction, and the conditions (solvent, temperature, time, etc.) under which the fractionation is conducted. The better products would be expected to contain relatively little linoleic acid and to contain a very large proportion of 2- "oleo" -disaturated glycerides of palmitic and stearic acids. Cocoa butter consists of ca. 60% 2-oleopalmitostearin and 20% 2-oleodistearin, the remainder being largely dioleopalmitin and dioleostearin (2,3). The cocoa butter-like fats under discussion contain a relatively large proportion of palmitic acid, and 2- "oleo" -dipalmitin undoubtedly is the component present in greatest proportion.

The purpose of the present report is to further describe the composition of some of these cocoa butter-like fats and to present in more detail their physical properties, alone and in combination with cocoa butter.

Preparation of Cocoa Butter-Like Fats

Cocoa butter-like fats HP-3F and HP-5F described below are among the fats mentioned in an earlier report (1). The stearine used as starting material (560 g of stearine A) was dissolved in heptane 1:1 w/w, and the hydrogenation was conducted in a 2 liter, laboratory hydrogenation apparatus (Pressure Reaction Apparatus, Series 4500, Parr Instrument Co.) at ca. 84 C and a hydrogen pressure of 22 psig. For product HP-3F a zirconium-promoted nickel catalyst, no. G-70 manufactured by the Chemical Products Div., Chemetron Corp., was used at a level of 0.25% nickel, based on the weight of the stearine. For product HP-5F a Raney nickel catalyst prepared in the laboratory (4) was employed at a level of 3.6% nickel. Hydrogenations for products HP-3 and HP-5 were stopped at iodine values of 29.3 and 33.8, respectively. Each of the reaction products was dissolved in commercial hexane 1:1 w/w, cooled to 20 C over a 22 hr period and filtered to remove the unwanted, trisaturated fraction. Yields of HP-3F and HP-5F, corrected for filtrate remaining in the cake, were 68.6% and 55.0%, respectively. Additional properties of the products are recorded in Table I.

Product HP-8F was a composite of several hydrogenation and fractionation runs. Five hydrogenations were made in a stainless steel, dead-end type hydrogenator described previously (5). The hydrogenator, which had a capacity of 3.25 gal, was charged with ca. 12 lb of stearine B, and the zirconium-promoted nickel catalyst was added (0.25% nickel on a stearine basis); the reaction was conducted

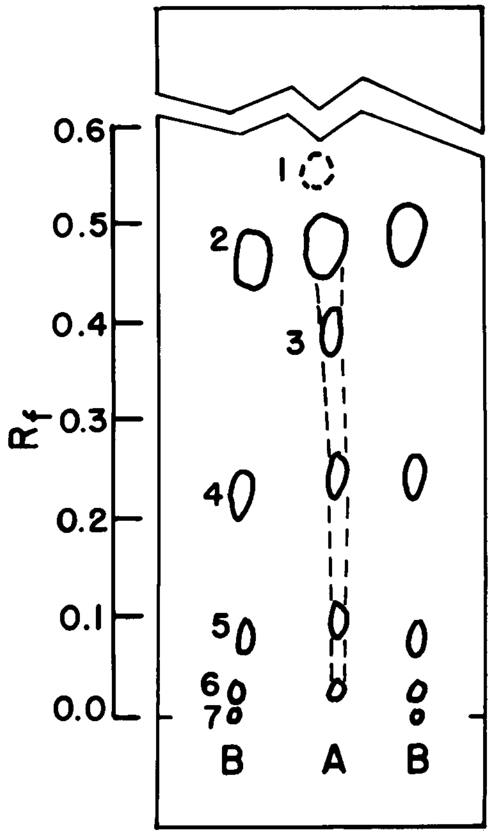

FIG. 1. Thin layer chromatographs of cocoa butter-like fat HP-8F (A) and cocoa butter A (B).

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TABLE I

Analytical Data on the Cocoa Butter-Like Fats and Cocoa Butter

Property	HP-3F	HP-5F	HP-8F	HP-9-1	HP-9-2	Cocoa butter A[a]	Cocoa butter B[b]
Iodine value	37.9	53.6	42.0	37.3	38.4	37.1	35.8
Trans isomers, %[c]	11.6	5.4	11.6	12.6	12.1	0.0	0.0
Fatty acid composition, %[d]							
Myristate	0.3	0.2		0.6	0.6	—	—
Palmitate	44.1	44.8		44.5	43.8	25	26.1
Stearate	9.0	7.4		10.3	10.1	31	31.0
Oleate[e]	45.2	25.6		44.6	45.5	40	38.7
Linoleate	1.4	21.9		0.0	0.0	4	4.2
Liquid content, %[f]							
10 C	2	6	10	9	9	10	11
15 C	3	8	15	12	12	12	15
20 C	3	24	21	15	16	14	21
25 C	10	56	31	21	24	19	38
30 C	32	74	66	43	54	34	63
35 C	60	88	98	76	87	94	100
40 C	90	98	—	97	100	—	—
50 C	100	100	—	—	—	—	—

[a] Commercial product.

[b] Sample of Prime West African.

[c] Calculated as trielaidin.

[d] Calculated on a methyl ester basis.

[e] Includes iso-oleates.

[f] Well tempered samples.

between 88 and 92 C at a hydrogen pressure between 16 and 20 psig. The iodine values of the reaction products ranged between 30.3 and 32.3 (average, 31.3). Content of *trans* isomers was 10.6%. The five products (total weight, 60.8 lb) were mixed and then divided into three batches. Each batch was dissolved in commercial hexane 1:1 w/w, cooled to room temperature (25 C) and filtered to remove the crystals formed. The latter were washed with hexane, and the washings were added to the filtrates. After removal of the hexane from the filtrates, the residual fats were melted, mixed, subdivided into 8 lb portions, and tempered. Each tempered portion was leached for 16 hr with an equal weight of hexane at 16-17 C (1). The hexane slurries were filtered but not washed, and the cocoa butter-like fat HP-8F was separated from the filtrates; the overall yield was 46%. Fat HP-8F was given a mild deodorization before being analyzed (Table I).

Cocoa butter-like fats HP-9-1 and HP-9-2 were derived from a single hydrogenation product, prepared by using the same materials and conditions employed in the preparation of fat HP-8F, except that the hydrogenation was conducted at 95 C and stopped at an iodine value of 24.2. The hydrogenation product was dissolved in commercial hexane 1:1 w/w, crystallized at room temperature, and the fat from the filtrate was recovered. This fat was divided into several portions, and after thorough tempering some portions were leached at 22.6 C and others at 19.4 C with commercial hexane 1:1 w/w to obtain cocoa butter-like fats HP-9-1 and HP-9-2, respectively. The overall yields (calculated for a complete separation of the hexane solution and solids) were 43.9% for HP-9-1 and 37.7% for HP-9-2.

Composition

On the basis of analyses made previously (1), the cottonseed oil stearines A and B, used as starting materials, contained ca. 57 mol % palmitoyl groups, and the fatty acid

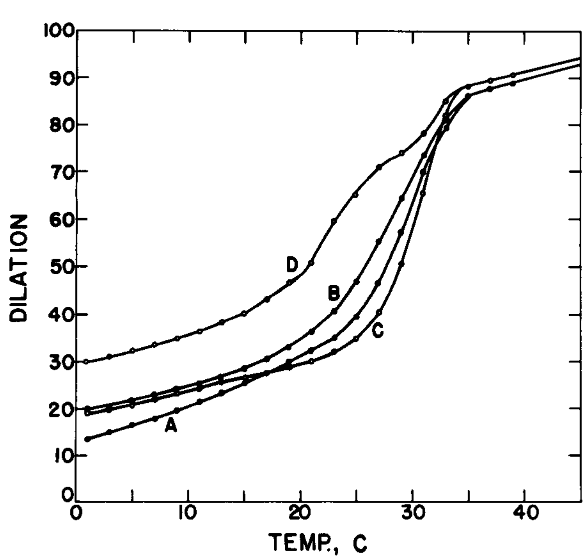

FIG. 2. Dilatometric curves of tempered (A) and untempered (B) cocoa butter-like fat HP-8F and of tempered (C) and untempered (D) cocoa butter A.

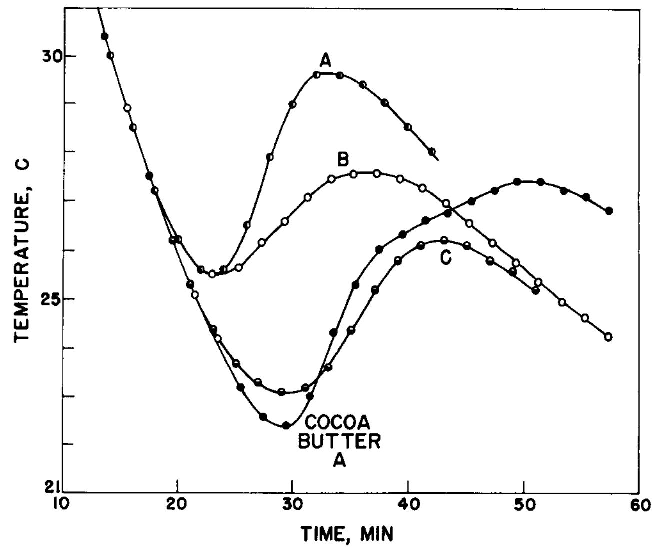

FIG. 3. Cooling curves of cocoa butter A, cocoa butter-like fat HP-3F (A), and cocoa butter-like fats similar to HP-3F but from stearine hydrogenated to iodine values of 36.2 (B) and 40.9 (C).

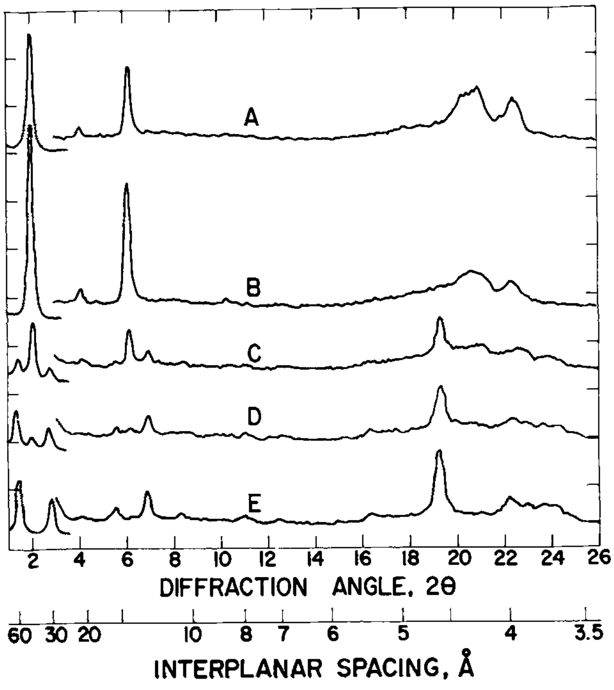

FIG. 4. X-Ray diffraction patterns of cocoa butter-like fat HP-8F (A), cocoa butter A (E), and mixtures of the two containing 25% cocoa butter (B), 50% cocoa butter (C), and 75% cocoa butter (D). All samples were tempered.

groups in the 2 position analyzed ca. 90 mol % unsaturated (practically all linoleic and oleic). These stearines, after selective hydrogenation under conditions that practically eliminated the linoleoyl group and produced low proportions of *trans*-isomers, would be expected to be richest in 2-"oleo" -dipalmitin (POP), the "oleo" or O including oleic acid and its *cis*-isomers. Other types expected to be found in relatively high concentrations would be 2- "elaido" -dipalmitin (PEP), where "elaido" or E includes elaidic acid and its *trans*-isomers the several di("oleo" or "elaido") palmitins, and various palmitostearins. The hydrogenation product from which cocoa butter-like fat HP-3F was prepared contained 21% trisaturated glycerides by weight (1). Fractionation of the hydrogenated products to yield cocoa butter-like fats would be expected to change markedly the relative proportions of the different triglycerides.

Because 1-oleo-disaturated glycerides exhibit polymorphic behavior quite different from that of 2-oleo-disaturated glycerides and because cocoa butter contains ca. 80% of the latter, the importance of the 2- "oleo" -disaturated glyceride in the cocoa butter-like fats is obvious. Fat HP-3F was subjected to a lipase hydrolysis under conditions that removed virtually all of the fatty acid groups in the 1 and 3 positions (6). The residual monoglycerides were treated to obtain the methyl ester of the fatty acid groups present, and the esters were analyzed by gas-liquid chromatography; results are shown in Table II. Obviously, the acyl groups in the 2 position are to a very large extent unsaturated, as desired.

TABLE II

Gas Liquid Chromatographic Analysis of Methyl Esters

Type of ester	Amount found, wt %
Saturated	
Myristate	0.2
Palmitate	2.7
Stearate	4.9
Unsaturated	
Palmitoleate	0.2
"Oleate-elaidate"	91.3
Linoleate	0.7

An estimate of the types and proportions of the various triglycerides in the cocoa butter-like fats can be obtained by thin layer chromatographic analysis using a silicic acid-silver nitrate plate (7). The results of such an analysis should be six separate spots on the plate, and perhaps some streaking between the spots because the cocoa butter-like fats would be expected to contain, in addition to the major triglycerides, small quantities of many others. Employing the frequently used convention for representing triglycerides and letting O represent oleic acid and its isomers; E, elaidic acid and its isomers; P, palmitic acid; S, stearic acid; and L, linoleic acid, the more important groups of triglycerides and the order in which they might be expected to appear on the chromatographic plate can be represented as follows: PSP, SSP; PEP, ESP, SEP; POP, POS, OSP, EEP(?); EOP, OEP; OOP; and OLP.

Subsequently a thin layer chromatographic analysis was made of product HP-8F and a sample of cocoa butter using the silicic acid-silver nitrate technique of Barrett et al. (7), except that benzene was used as the developing solvent. The results are represented in Figure 1.

Apparently product HP-8F contained such a small amount of trisaturated glycerides that no well defined spot was found. Spot no. 1 on the pate is believed to be the PEP group of triglycerides, and they were present in very small amount. Spot no. 2 was the largest and darkest by far, and was estimated to contain 75% of the total glycerides, both in the case of cocoa butter and cocoa butter-like fat HP-8F. Spot no. 2 undoubtedly represented the POP group of fat HP-8F and the 2-oleo-disaturated glycerides of cocoa butter. Spot no. 3 can with some certainty be said to represent the EOP and OEP glycerides. Spot no. 4 was the second largest on the chromatograms of both HP-8F and cocoa butter, representing the OOP glycerides and the dioleo-saturated glycerides, respectively. Spots 5 and 6 probably were produced by linoleic acid-containing glycerides. The small spot at the origin for cocoa butter, spot no. 7, was probably produced by phosphatides or free fatty acids.

Physical Properties

Dilatomeric curves obtained with the cocoa butter-like fats using a previously published technique (8) were typical of those for HP-8F (Fig. 2), which indicates that slow polymorphic transformations occur after the fats are rapidly solifified from the melt. Therefore they need to be

TABLE III

Hardness Index of Cocoa Butter and Cocoa Butter-Like Fats

Temperature C	Cocoa butter A	Cocoa butter-like fats				
		HP-3F	HP-5F	HP-8F	HP-9-1	HP-9-2
16	30.6	17.1	3.4	9.2	34.5	25.6
18	25.5	15.1	2.5	6.8	26.7	19.8
21	17.8	13.1	1.7	3.8	16.7	12.5
24	10.0	10.1	—	1.7	9.8	7.1
27	3.6	7.2	—	—	3.5	1.6
30	—	2.7	—	—	—	—

TABLE IV

Softening Point of Mixtures of Cocoa Butter A and Cocoa Butter-Like Fat HP-3F

Tempering time, days	Cocoa butter in mixture, %				
	100	90	80	70	50
1	32.2	32.1	32.3	32.6	34.0
7	32.7	32.5	32.8	33.4	34.9

tempered somewhat like cocoa butter, when used in confections. Such tempering or transformation to the more stable and higher melting polymorphs is ordinarily accomplished by heating and cooling of the fat at about its melting point, while simultaneously mixing seed crystals into the mass. However the heat treatment required for good performance of the cocoa butter-like fats would not be expected to be as critical as in the case of cocoa butter. When fat HP-8F was melted to destroy all seed crystals and quickly solidified, it contained only about one-third more liquid fat at 25 C than did a well tempered sample. Under the same conditions untempered cocoa butter contains about three times as much liquid fat as does a tempered sample.

Cooling curves obtained with cocoa butter, HP-3F, and two samples similar to HP-3F (except that the stearine used as starting material was hydrogenated to different iodine values) give further evidence that the crystallization behavior of the cocoa butter-like fat resembles that of cocoa butter. The curves obtained by a commonly used procedure (3) and reproduced in Figure 3 are proof that the fats supercool and exhibit a marked rise in temperature during the solidification process. The latter characteristic is helpful in obtaining the proper polymorphic transformations during the molding of chocolate-type confections.

As is evident from Table I, the cocoa butter-like fats can be made to resemble cocoa butter with respect to the percentage of fat melted at given temperatures. It should be noted that the two samples of cocoa butter have somewhat different melting characteristics.

One of the properties of cocoa butter-like fats most difficult to obtain is a hardness comparable to that of cocoa butter at room temperature. The results of hardness tests made by a modified Brinell method (9) on well-tempered samples are recorded in Table III.

Fat HP-3F has a hardness equal to that of cocoa butter at the most important temperatures, 20-27 C. Below this range it is softer, and above this range it is harder. However this desirable hardness is attained at the expense of the melting properties (Table I). Fat HP-8F, on the other hand, melts at ca. 35 C but is relatively soft at room temperature. Fats HP-9-1 and HP-9-2, which have a relatively high ratio of mono- to diunsaturated triglycerides, possess the best combination of hardness and melting characteristics. Fat HP-5F is, of course, not a satisfactory product. It was included merely to show the effect of a large proportion of linoleic acid.

Numerous tests were made with cocoa butter-like fats HP-8F, HP-9-1 and HP-9-2 to establish the amount of linear contraction on solidification in molds. Contractions were greatest when well tempered samples were heated to the point of incipient melting, poured into molds and cooled immediately to 8-15 C. Under these conditions the linear contraction was 1.0-1.2%, and it occurred within 10-20 min after cooling was begun. Cocoa butter under similar conditions contracted ca. 2%.

Experimental, chocolate-type coatings were made with the cocoa butter-like fats, including HP-8F. These coatings were made with a cocoa powder, and no cocoa butter was added. The most satisfactory results were obtained on heating the coating to a few degrees above the melting point of the fat, pouring the mixture into molds and chilling in the refrigerator (5 C). This procedure yielded pieces having good contraction, fine texture and good gloss. No bloom developed even after several months' storage at room temperature, during which time the temperature varied a number of degrees.

Compatibility with Cocoa Butter

The fact that the addition of a relatively small amount of one fat to another generally depresses the melting point of the fat present in the greatest proportion and increases its plastic range is of particular importance with cocoa butter. This phenomenon, usually referred to as incompatibility, impairs the prized characteristics of cocoa butter, namely, hardness at room temperature and a very short melting range. The compatibility of HP-3F with cocoa butter A was tested using the standard softening point test (AOCS Method Cc 3-25), except that the mixtures were tempered for 1 and 7 days. The results obtained are recorded in Table IV.

Based on these tests, the cocoa butter-like fat was highly compatible. The maximum softening point depression was only one- or two-tenths of a degree. Some commercial hard butters give a depression 10-15 times as great.

As a further evaluation of compatibility, mixtures of fat HP-8F and cocoa butter A were examined dilatometrically, and the percentage of fat melted at various temperatures was calculated. The results obtained (Table V) indicate that the two fats were fairly compatible.

When the cocoa butter-like fat HP-8F was used in confectionery coating compositions containing added cocoa butter A, the coatings were deemed unduly soft. Neither aging nor intense mechanical working followed by a partial remelting and then a resolidification, which greatly accelerates polymorphic transformations, increased the hardness significantly. Hardness tests on well tempered mixtures of cocoa butter and HP-8F yielded results indicating some interactions may have occurred, but the hardness of the

TABLE V

Melting Characteristics of Mixtures of Cocoa Butter-Like Fat HP-8F and Cocoa Butter A

Temperature, C	Liquid content, %[a]				
	HP-8F	75% HP-8F, 25% CB	50% HP-8F, 50% CB	25% HP-8F, 75% CB	Cocoa butter A
5	6	5	3	4	6
10	10	7	6	8	10
15	15	13	15	14	12
20	21	27	23	22	14
25	31	35	30	29	19
30	66	72	64	54	34
35	98	99	99	100	94

[a] Well tempered samples.

mixtures at a given temperature was always intermediate between the hardness of the components when tested separately. In other words, there was no positive evidence of new crystal types being formed when the fats were mixed.

The possibility of mixed crystal formation was investigated further by obtaining and comparing X-ray diffraction patterns of fat HP-8F, cocoa butter A and mixtures of these two. Several of the diffraction patterns (taken with Cu Kα radiation) are reproduced in Figure 4.

Different long spacings were found for cocoa butter and fat HP-8F, as expected. In the mixtures only these long spacings appear. The absence of new long spacings indicates no new mixed crystals were formed. The proportion of each component in a mixture, as estimated from the long-spacing region of the X-ray diffraction pattern, is usually in agreement with the actual proportion which was mixed. With some mixtures new short spacings appear, indicating that certain polymorphic forms have become more prominent on mixing the fats. This again might be expected because fat HP-8F contains glycerides identical to those found in cocoa butter as well as new glycerides. Therefore any mixed crystals that might form on mixing the new glycerides of HP-8F with cocoa butter are already present to some extent in HP-8F.

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