Confectionery Fats. II. Characterization of Products Prepared by Interesterification and Fractionation[1]

WERNER LANDMANN,[2] N.V. LOVEGREN, and R.O. FEUGE, Southern Regional Research Laboratory,[3] New Orleans, Louisiana

Several cocoa butter-like fats, which had been prepared by fractional crystallization of the reaction product obtained on interesterifying highly-hydrogenated cottonseed oil and a triolein product or olive oil, were characterized and compared with cocoa butter.

The fats, as obtained by fractional crystallization from acetone solutions, contained varying amounts of glycerides melting above 37°C., an undesirable feature which caused the fats to thicken too much when used in chocolate type compositions under the same conditions employed with cocoa butter. The higher-melting glycerides could be removed by filtration, or their proportions could be decreased by changing the fractionation temperatures. The fats melted mostly over the same temperature range associated with cocoa butter, and the best of the fats resembled cocoa butter closely over the temperature range 0° to 30°C.

The cocoa butter-like fats resembled cocoa butter in hardness at all test temperatures.

The fats were reasonably compatible with cocoa butter, that is, in mixtures of the two, one did not cause extensive premelting of the other.

According to their cooling curves, the cocoa butter-like fats did not supercool as cocoa butter does. The former contain not only the 2-oleodisaturated glycerides of cocoa butter but also positional isomers of these glycerides. When the fats were molded under the same conditions employed with cocoa butter, linear shrinkage was only about one-third that of cocoa butter.

IN A PRECEDING ARTICLE (9) the preparation of cocoa butter-like fats on a pilot-plant scale was described. In these preparations highly-hydrogenated cottonseed oil (iodine value, 1.8) was randomly interesterified with a triolein product or olive oil, and a cocoa butter-like fraction consisting mostly of oleodisaturated glycerides was obtained by fractional crystallization from acetone. The unwanted by-products could be reused in succeeding runs. The process employed was relatively simple and should be suitable for large-scale commercial use. Some of the characteristics of the products which were obtained are recorded in Table I. Data also are recorded for Fat No. 1a, the preparation of which was not described in the earlier article. Fat No. 1a was obtained by warming a portion of Fat No. 1 to 37°C., keeping it at this temperature for several hours, then filtering out the relatively small proportions of unmelted triglycerides.

The purpose of the present article is to present a further evaluation of the cocoa butter-like fats, particularly with respect to those characteristics which affect performance in confections.

Dilatometric Examination

One of the prized characteristics of cocoa butter is a very short melting-range lying almost entirely between room temperature and body temperature, 37.0°C., which makes it possible for the cocoa butter to be hard and brittle at room temperature yet melt abruptly in the mouth when eaten. This characteristic is attributed to the fact that approximately 80% consists of two closely related glycerides, 2-oleopalmitostearin and 2-oleodistearin. To define quantitatively and compare the melting characteristics of the cocoa butter-like fats and cocoa butter, dilatometric data were obtained. Dilatometers of the gravimetric type with mercury as the confining liquid were used. Previously-described techniques and methods of making the calculations were followed (2,3). Usually the dilatometer was kept at each test temperature for 20 min. before a weighing was made. To obtain data on untempered samples, a "thrust-in" technique was employed (7), that is, whenever necessary, the sample in the dilatometer was melted, resolidified by rapid chilling, and thrust directly into the dilatometer bath at the test temperature. The mercury reservoir on the dilatometer was placed so that mercury was forced into the reservoir as expansion of the sample occurred but could not return as tempering occurred.

The dilatometric curves for the tempered samples of the three fats, Figure 1, indicate that the greater portion of each sample melted over a relatively short temperature-interval. Fat No. 3 possessed the most desirable melting characteristics while those of Fat No. 1 were least desirable. All three contained small amounts of high-melting glycerides, which explains the high melting-points recorded in Table I. The presence of 1% of completely hydrogenated cottonseed oil can raise the melting point of a fat by about 10°. Cocoa butter, Curve B, Figure 2, contains no high-melting glycerides. The cocoa butter was a sample produced by a large manufacturer of chocolate.

TABLE I

Data on Cocoa Butter-Like Fats[a]

Fat No.	Yield, %	Iodine value	Free fatty acid, as oleic	Softening point, °C.	Melting point, °C.	*trans* Isomers,[b] %	Linoleate, %
1	35.0[c]	27.2	0.22	50.0	57.1	4.3	1.6
1a[d]	......	29.1	......	33.5[e]	34.8[e]	......	......
2	30.0	26.3	0.28	42.1	47.0	4.8	1.5
3[f]	24.0	27.5	0.32	43.5	49.0	2.5	2.0

[a] Analytical methods of American Oil Chemists' Society (1) were used, unless noted otherwise.

[b] Calculated as trielaidin (4).

[c] Approximate value.

[d] Obtained by warming Fat No. 1 to 37.0°C. and filtering out solid glycerides.

[e] After tempering for 4 days at 26°C.

[f] Olive oil used in the preparation of this fat. Triolein product used in the preparation of Fats No. 1 and 2.

Percentages of solids at various temperatures were calculated and are recorded in Table II. From these

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[1] Presented at the 51st Annual Meeting, American Oil Chemists' Society, Dallas, Tex., April 4–6, 1960.

[2] Fellow, National Confectioners Association.

[3] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

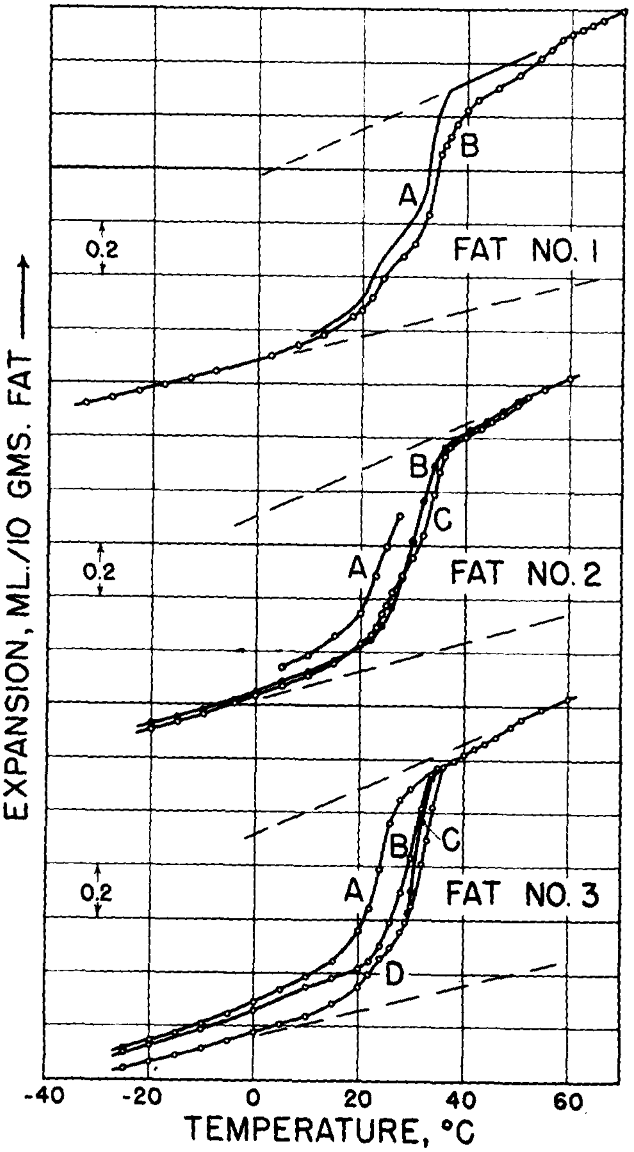

FIG. 1. Dilatometric curves of the cocoa butter-like fats. Fat No. 1: A, theoretical curve of well-tempered form after removal of the 20.0% of solids melting above 37.0°C.; B, well-tempered form. Fat No. 2: A, quick-chilled sample (curve obtained by "thrust-in" technique); B, tempered for 2.5 hrs. at 26°C.; and C, tempered for 6 weeks at 26°C. Fat No. 3: A, quick-chilled sample (curve obtained by "thrust-in" technique); B, tempered for 1.5 hrs. at 26°C.; C, tempered for 1.5 days at 26°C.; and D, tempered for 28 days at 26°C.

data it is evident that 61% of Fat No. 1 melted between 20° and 35°C. Over this same range the percentages of melting of Fat No. 2, Fat No. 3, and cocoa butter were 70, 77, and 89%, respectively.

The differences among the three cocoa butter-like fats can be attributed primarily to differences in the temperature ranges over which the three fats were collected and their contents of iso-oleic acid-containing glycerides. Fat No. 3 was collected over the narrowest range, 17° to 1°C. It also contained the lowest content of *trans* isomers.

Under the conditions of fractionation which were employed, some high-melting glycerides remained dissolved in the solutions of acetone and oleodisaturated glycerides. However, after the acetone was removed, these glycerides did not dissolve readily in the main body of the cocoa butter-like fats. The high-melting glycerides could be removed by filtering at 37°C. though this was a relatively slow process. Fat No. 1a is such a product.

TABLE II

Liquid Content of Cocoa Butter and Cocoa Butter-Like Fats

Temperature		Liquid Content, %						
		Cocoa butter		Fat No. 1, tempered	Fat No. 2, tempered	Fat No. 3		1 to 1 mixture of cocoa butter and Fat No. 3, temp'd
°C.	°F.	Tempered	Untempered			Tempered	Untempered	
0	32	0.6	......	2.9	2.7	2.1	6.1	0.9
5	41	1.9	1.3	3.6	4.0	3.1	9.0	2.2
10	50	4.1	3.8	5.7	6.0	3.6	12.6	4.4
15	59	6.8	10.0	8.7	8.0	5.1	16.6	15.4
20	68	10.8	19.6	13.8	12.7	10.6	28.3	29.6
25	77	16.7	61.4	29.3	29.3	22.7	67.0	34.0
30	86	36.1	98.2	39.0	48.0	40.3	90.4	51.9
....	90.5	......	......	49.5	......	......	......	......
....	93.4	100.0	......	......	......	......	......	......
35	95	......	......	74.4	83.0	88.0	95.1	95.4
....	98.6	......	......	80.0	......	......	......	......
40	104	......	......	88.2	93.6	96.0	95.7	97.7
45	113	......	......	92.3	95.5	97.2	97.0	99.4
....	114.8	......	......	......	......	......	......	100.0
50	122	......	......	93.4	98.8	100.0	100.0	......
....	126	......	......	......	100.0	......	......	......
55	131	......	......	96.8	......	......	......	......
....	136.4	......	......	100.0	......	......	......	......

When quickly solidified, the cocoa butter-like fats exhibited a tendency to crystallize to some extent in unstable polymorphic forms. Curves A for Fats No. 2 and 3, Figure 1, show that quick chilling produced mixtures which started to melt at lower temperatures than do the same mixtures after tempering. In this respect they resembled cocoa butter (Curve A, Figure 2). However there was a difference. The lower-melting polymorphs of the components of cocoa butter were much more stable. Curve A for cocoa butter, Figure 2, was obtained without the use of the "thrust-in" technique. Several weeks of tempering at 26°C.

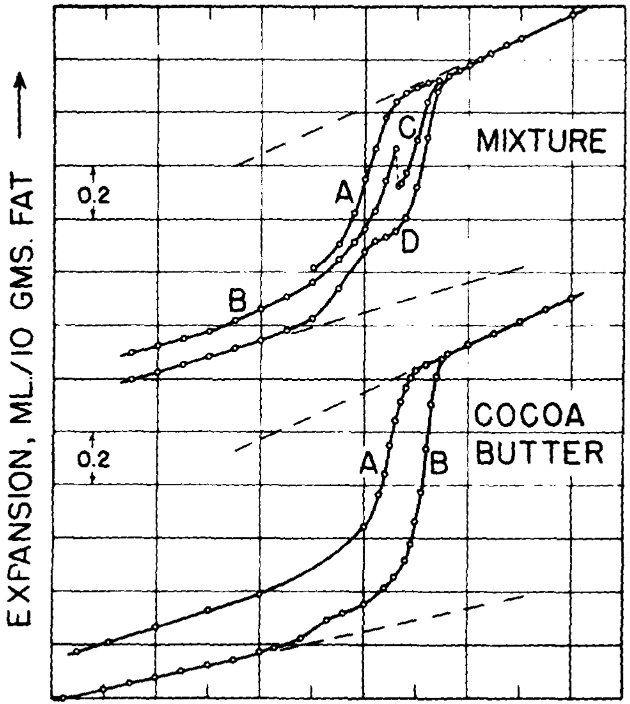

FIG. 2. Dilatometric curves of cocoa butter and a 1:1 mixture by weight of cocoa butter and Fat No. 3. Mixture: A, quick-chilled sample (curve obtained by "thrust-in" technique); B, quick-chilled sample; C, tempered for 16 hrs. at 26°C.; and D, tempered for 5 weeks at 26°C. Cocoa butter: A, quick-chilled sample; and B, tempered for several weeks at 26°C.

were necessary to convert cocoa butter as represented by Curve A into cocoa butter as represented by Curve B. On the other hand, the curve for Fat No. 2, Figure 1, could be changed from A to B by tempering for just 1.5 hrs. at 26°C. The slight additional change to Curve C could be obtained by tempering for less than 5.5 days. These were, of course, minimum tempering-times. Similar data were obtained with Fat No. 3.

On comparing Curves A through D for the 1:1 mixture of Fat No. 3 and cocoa butter with the curves for cocoa butter, Figure 2, and on comparing the corresponding data in Table II, it is evident that the two fats are not completely compatible. Each depresses the melting-point of the other. This situation is to be expected because Fat No. 3 contains not only 2-oleopalmitostearin and 2-oleodistearin, the main components of cocoa butter, but also the positional isomers of these components.

The 1:1 mixture tempers faster than does cocoa butter alone. Curves B and C for the mixture actually represent one run made over a period of two days. Curve B was obtained the first day. Then the dilatometer was stored over-night (16 hrs.) at 26°C., and Curve C was obtained the following day.

Cooling Curves

Information on the solidification characteristics of Fat No. 3 and cocoa butter was obtained by determining their cooling curves. A 75-g. sample was heated well above its melting-point and placed in a test tube measuring 10 x 3.5 cm.; a wire-loop stirrer and a thermometer were inserted; and the assembly was immersed in an air bath at 16°C. The sample was stirred at a rate of six strokes per minute until solidification occurred. Temperature readings were taken once per minute. The cooling curves that were obtained are recorded in Figure 3.

The cocoa butter behaved as expected. It supercooled appreciably and, when crystallization started, it was rapid enough to raise the temperature of the mass by several degrees. Fat No. 3, on the other hand, did not supercool to noticeable extent. Seed crystals formed early in the cooling process, and, as cooling continued, more and more crystals formed. Even when 15-g. samples of Fat No. 3 were used and the temperature of the air bath was reduced to 10°C., supercooling was not found.

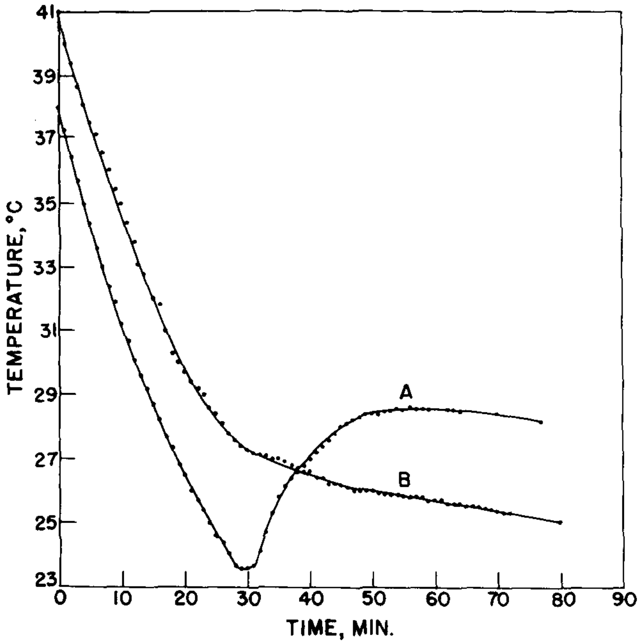

FIG. 3. Cooling curves: A, cocoa butter; and B, Fat No. 3.

Though the glycerides of Fat No. 3 melted predominately over the same short temperature-interval associated with cocoa butter, Fat No. 3 did contain more components, some of which were quite easily transformed from lower- to higher-melting polymorphs. Solidification and polymorphic transformation were relatively continuous processes in this case. This probably explains the fact that Fat No. 3 on solidification did not shrink away from the walls of the container as does cocoa butter. The latter behaves more or less as a single compound. Crystallization is not only sudden, but the heat of crystallization, when suddenly released, should aid in tempering the cocoa butter to a higher-melting and denser polymorph. As the mass cools from the relatively-high temperature, shrinkage should be further enhanced.

Insufficient shrinkage away from the walls of a container or mold is, of course, a disadvantage in some instances. But the conditions which are responsible for this should be desirable in another respect. Fat No. 3, when compared with cocoa butter, should possess a decreased tendency to bloom and should hold its gloss better.

Hardness

As mentioned above, one of the desirable characteristics of cocoa butter is its hardness at room temperature. Actually this hardness varies markedly with small changes in ambient temperatures, but qualitatively cocoa butter always appears to be hard. Hardness indices, determined for both cocoa butter and Fat No. 2, are recorded in Table III. Apparently there was no real difference between the two. They were equivalent after three days of tempering and after five months of storage at room temperature.

TABLE III

Hardness of Cocoa Butter and Fat No. 2[a]

Temperature, °C.	Hardness Index	
	Cocoa butter	Fat No. 2
16.6	26.1	27.1
20.0	20.0	22.1
22.8	11.8	14.3
26.0	6.0	7.4
19.7	16.6[b]	14.5[b]

[a] Samples heated above melting temperature, molded, held for 15 min. at 5°C., and stored at room temperature for 3 days. Tests made with a modified Brineli instrument and technique (8).

[b] Same samples after five months at room temperature.

Softening Points

Open-tube melting points (softening points) were determined for mixtures of cocoa butter with Fat No. 2 and Fat No. 3. Tests were made with both well- and poorly-tempered mixtures. The data obtained are recorded in Figure 4. The addition of relatively small amounts of cocoa butter-like fats to cocoa butter depressed the softening-point of the latter. With well-tempered samples the maximum depression was less than 1.5° and occurred with compositions containing about 20% cocoa butter-like fats. With poorly-tempered samples the maximum depression was somewhat greater and occurred in mixtures containing about 30% cocoa butter-like fats. These observations conform with the claim of Verkade (10) that clear melting-point depressions are encountered when one oleopalmitostearin is mixed with another. The depressions in softening point indicated in Figure 4 can be regarded as relatively minor, probably less than those produced by milk fats and other confectionery fats currently used with cocoa butter. Some mixtures of glycerides can produce effects greater than those shown. For example, a product consisting essentially of oleodipalmitins, when mixed with cocoa butter, has been found to depress the softening-point by more than 5° (5).

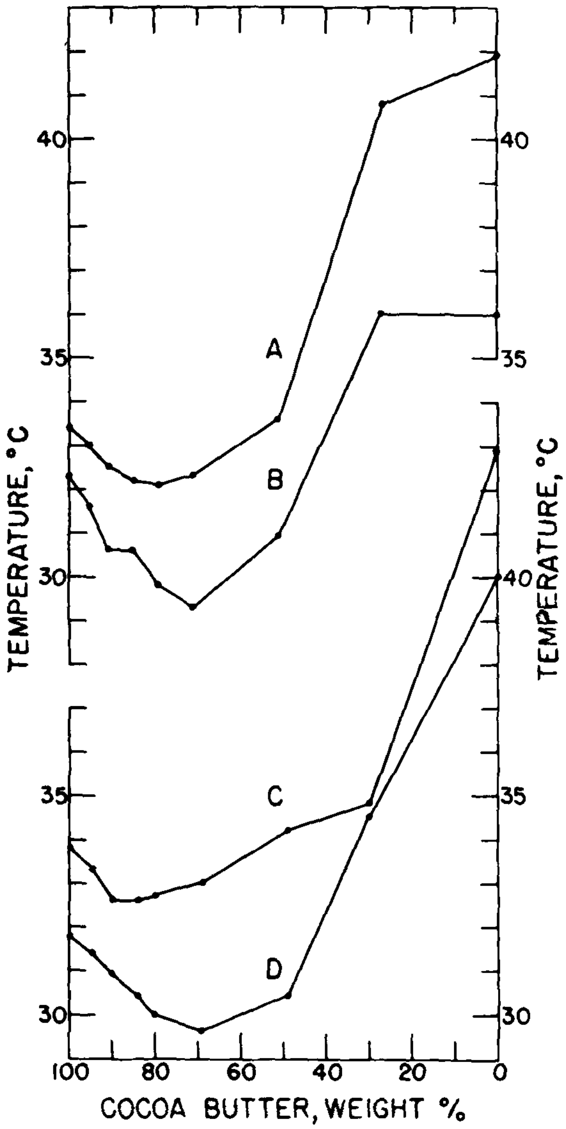

Fig. 4. Softening points of mixtures of cocoa butter and cocoa butter-like fats: A, Fat No. 2, mixtures tempered for 25 days at 26°C.; B, Fat No. 2, mixtures of heat cycled several times between 5° and 26°C. and then tempered for 16 hrs. at 26°C.; C, Fat No. 3, mixtures tempered for 29 days at 26°C.; and D, Fat No. 3, mixtures tempered for 5 days at 26°C.

Performance in Coating Compositions

Each of the fats represented in Table I was sent to a manufacturer of chocolate-coating compositions, and in some instances small samples were sent to manufacturers of confectionery fats. Fat No. 1 was found to produce coating compositions with poor eating qualities; however the addition of emulsifiers was found to make them quite palatable. The eating qualities of coating compositions containing Fats 1a, 2, and 3 were found to be better, primarily because these fats contained less solids at body temperature.

The presence of glycerides melting above about 100°F.(37.8°C.) was found objectionable in another respect. Coating compositions made with fats containing high-melting glycerides could not be worked satisfactorily at about 92°F.(33.3°C.), the temperature commonly used for chocolate compositions. However one confectioner expressed the opinion that the presence of small proportions of high-melting glycerides would be beneficial in some applications. In an earlier report (6) it was shown that the presence of such high-melting glycerides can improve the performance of chocolate at summer temperatures. If necessary, small proportions of high-melting glycerides can be removed by an additional filtration during the preparation of the cocoa butter-like fats.

Possibly the most difficult problem to overcome will be the lack of sufficient contraction on molding. According to preliminary tests, molding Fat No. 3 under conditions employed in the manufacture of chocolate results in a linear contraction equal to about one-third that for cocoa butter. This can be a disadvantage if the confections are to be molded. On the other hand, the factors responsible for poor contraction should make the cocoa butter-like fats more resistant to bloom.

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