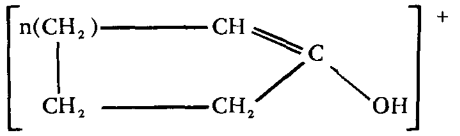
as the corresponding acylium ion $[RCO]^+$ (Fig. 5).

In all cases, a distinct pattern of fragmentation was noted for all the propanediol diesters studied. A base peak corresponding to the ion $[M\text{-}RCOO]^+$ was observed in all the spectra obtained. Another fragmentation typical of propanediol diesters is due to a common ion of the structure:



and giving rise to m/e 84 and 98 corresponding to n of 1 and 2, respectively. Additional peaks of low intensities (287, 315, 341, 343) arising from the loss of the acyl group from the compound and capture of two hydrogens also were found in the spectra (Table II). In general, the pattern of fragmentations obtained in the spectra of propanediol diesters was in agreement with those of ethanediol diesters reported previously (2).

ACKNOWLEDGMENT

J.H. Cornell synthesized the ketones and helped prepare the propanediol diesters.

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[Received July 18, 1980]

Cocoa Butter Substitutes from Mango Fat

B.P. BALIGA and **A.D. SHITOLE**, Research and Development Laboratories, M/s, The Tata Oil Mills Company Limited, Sewri, Bombay, 400 033, India

ABSTRACT

Mango fat obtained by solvent extraction of the kernels of the mango fruit (*Magnifera indica*) has been studied for its suitability in making cocoa butter substitutes. The fat has been fractioned from acetone at low temperatures in one and/or two stages in order to segregate suitable solid fractions having physical properties closer to cocoa butter. The data pertaining to the solidification characteristics and dilatometric behavior of the mango fat, its acetone-fractionated products and their admixtures with cocoa butter in equal proportions have been determined in order to assess their compatibility with cocoa butter. Fractionated mango fat can serve as a good partial substitute for cocoa butter.

INTRODUCTION

Cocoa butter is a unique, naturally occurring fat containing mainly monounsaturated and diunsaturated glycerides in which palmitooleostearin constitutes a single dominant glyceride. Several workers have attempted to prepare cocoa-butter-like products from other fats which have some degree of resemblance to cocoa butter and which could be modified into cocoa-butter-like fats. The various methods tried (1-12) include esterification, (inter-, trans- and directed), hydrogenation (selective or homogeneous), fractionation (dry, with solvent or water containing a surface-active agent) or combination of these in order to have a product with a melting point (mp) around 36 C and a sufficient degree of hardness and brittleness so that the finished product retains its shape at normal room temperatures.

All of these routes, except for fractionation alone, have some obvious disadvantages, such as randomization, isomerization and *trans* acid formation, which preclude exact simulation of a cocoa-butter-like product. Or, if the physical properties are reproduced, the product might be incompatible with cocoa butter when used in blends. Fractionation is considered the most suitable method for segregating glyceride fractions in their natural form/configuration which could have cocoa-butter-like properties, and which could be blended with cocoa butter without adversely affecting the original characteristics of cocoa butter. The preparation of Coberine (12) by solvent fractionation of palm oil is an ideal example of this method.

In India, a number of indigenous fats that are rich in monounsaturated and disunsaturated glycerides and low in linoleic acid content are available which can serve as good starting materials for making cocoa butter substitutes. Examples are sal (*Shorea robusta*), dhupa (*Vateria indica*), kokum (*Garcinia indica*), mowrah (*Bassia latifolia*) and mango (*Magnifera indica*). The reported fatty acid and glyceride compositions of these fats and of cocoa butter are given in Table 1 (14-20). Cocoa butter substitutes have been prepared from sal, kokum and mowrah fats (6-11).

In this study, an attempt has been made to prepare cocoa-butter-like products from mango fat by fractionation.

At least 1,000 varieties of mango are available in India, of which about 25 varieties are commercially important (13). The mango kernels contain 6-15% fat. The composition of the fat varies among sources (Table II, ref. 21). The glyceride composition reported by Pathak et al. (20) shows that the fat contains 14% trisaturated glycerides. The proportion of disaturated to monosaturated glycerides is very low (0.4:1) compared to that of cocoa butter (3.7:1). It is therefore necessary to fractionate the fat in order to segregate a suitable fraction having properties similar to cocoa butter. Some work has been reported in this area (22,23).

In this study, acetone fractionation of mango fat in a single stage and in two stages has been done to obtain suitable hard fractions. A detailed evaluation of the physical properties of the individual fractions, original mango fat and their blends with cocoa butter in equal proportions

TABLE I

Fatty Acid and Glyceride Composition of Cocoa Butter and Some Indigenous Fats

	Theobroma cacao[a] (cocoa butter)	*Shorea robusta*[b] (sal fat)	*Vateria indica*[c] (dhupa fat)	*Garcinia indica*[d] (kokum fat)	*Bassia latifolia*[e] (mowrah fat)	*Magnifera indica*[f,g] (mango fat)
Fatty acid (mol %)						
16:0	26.2	4.6	12.2	3.1	24.1	8.4
18:0	34.4	44.2	42.4	56.1	19.3	42.2
20:0	–	6.3	2.7	–	–	2.3
18:1	37.3	42.1	40.5	39.1	43.4	42.4
18:2	2.1	2.8	2.2	1.7	13.2	4.7
Glyceride (mol %)						
SSS	2	1	1	2	1	14
SUS	77	64	73	76	28	24
SUU	21	34	22	20	71	61
UUU	–	1	4	2	–	1
SUS-to-SUU ratio	3.7:1	1.9:1	3.3:1	3.8:1	0.4:1	0.4:1

[a] Hilditch and Stainsby, 1936 (14).
[b] Hilditch and Zaky, 1942 (15).
[c] Baliga and Meara, 1949 (16).
[d] Hilditch and Murti, 1941 (17).
[e] Hilditch and Ichaporia, 1938 (18).
[f] For fatty acid composition, Shitole et al., 1979 (19).
[g] For glyceride composition, Pathak et al., 1946 (20).

has been done in order to assess the compatibility of the mango fractions or the fat as such with cocoa butter.

EXPERIMENTAL

Mango fat was obtained by extraction of the powdered kernels of the Alphonso variety in a Soxhlet extractor with petroleum ether (boiling range 60-80 C). The yield of the fat was 15% on a dry basis. The raw fat with an acid value (AV) of 5.4 was refined with caustic alkali to an AV of 0.2 and subsequently bleached with 1% Tonsil Optimum and 0.2% activated carbon at 100 C for .5 hr. This fat was used for fractionation experiments.

Experiment I

Mango fat (200 g) was dissolved in 1,400 ml of acetone by warming and the solution was then cooled gradually to 10 C. This temperature was maintained for 4 hr. The crystallized fraction was separated from the liquid by filtration under slight vacuum and then washed with 100 ml of cold (10 C) acetone. The two fractions were recovered by desolventization. The solid fraction obtained in 57.2% yield (Table III) was designated fraction I.

Experiment II

Mango fat (250 g) was dissolved in 2,250 ml of acetone by warming and then cooled gradually to 23 C until slight turbidity appeared. The temperature was raised to 26 C, and was maintained for 3 hr. The crystallized fraction was separated from the liquid fraction. The filtrate was further cooled to 5 C in steps and kept there for 3 hr. The second solid fraction was separated from the liquid fraction. The yields of the three fractions and their iodine values (IV) are given in Table IV. The intermediate fraction (43.1%) was designated fraction II.

TABLE II

Range in Fatty Acid Composition of Mango Fats[a]

Fatty acid	mol %
14:0	0.7 – 8.0
16:0	6.0 – 18.0
18:0	24.0 – 49.0
20:0	0.1 – 6.7
18:1	33.0 – 53.0
18:2	0.0 – 13.0

[a] Lakshminarayana, 1977 (21).

Products were prepared by mixing fractions I and II and original mango fat with equal amounts of cocoa butter which was prerefined and bleached in the laboratory. The different products were:

Product I: Fraction I + Cocoa butter
Product II: Fraction II + Cocoa butter
Product III: Mango fat + Cocoa butter

Evaluation of the Samples

Solidification test. The cooling characteristics were determined according to Jensen's solidification test procedure (24).

Solid fat index. The solid fat index (SFI) of the samples at various temperatures was determined by using (a) vol-

TABLE III

Single-Stage Acetone Fractionation of Mango Fat

Fraction	Yield (%)	Iodine value
Solid[a]	57.2	34.7
Liquid	42.8	67.8
Original fat	–	48.7

[a] Designated as fraction I.

TABLE IV

Two-Stage Acetone Fractionation of Mango Fat

Fraction	Yield (%)	Iodine value
1st solid (hardest)	17.8	34.2
2nd solid (intermediate)[a]	43.1	38.8
Liquid	39.1	67.1
Original fat	–	48.7

[a] Designated fraction II.

TABLE V

Characteristics of Cocoa Butter, Mango Fat, Mango Fractions and Blended Products

Characteristic	Cocoa butter	Mango fat	Fraction I	Fraction II	Product I	Product II	Product III
Iodine value	34.5	48.7	34.7	38.8	34.4	37.1	41.4
Slip point (C)	35.5	35.7	38.6	37.2	37.3	36.3	36.6
Saponification value	196.5	191.0	190.7	190.8	193.6	194.0	193.3
Solidification test							
Min temp. (C)	22.5	21.2	26.8	26.0	25.4	24.1	23.2
Max temp. (C)	29.0	30.6	36.1	34.7	33.3	31.8	29.2
Rise in temp. (C)	6.5	9.4	9.3	8.7	7.9	7.7	6.0

TABLE VI

Solid Fat Index of Cocoa Butter, Mango Fat, Mango Fractions and Blended Products

	Cocoa Butter		Mango Fat		Fraction I		Fraction II		Product I[c]		Product II[d]		Product III[e]	
Temp. (C)	N[a]	D[b]	N	D	N	D	N	D	N	D	N	D	N	D
25	78.4	83.5	49.3	54.0	82.8	101.0	74.0	79.0	79.2	89.0	74.0	80.0	61.7	64.5
30	69.4	64.0	43.7	44.0	80.4	99.0	70.0	75.5	72.8	78.0	65.7	64.0	51.5	44.0
33	29.5	24.0	29.9	28.0	72.7	88.0	68.3	63.5	55.4	56.0	42.7	41.0	32.6	24.0
36	1.6	2.0	8.6	5.0	53.9	62.0	32.4	30.0	25.4	24.0	12.8	13.5	6.6	tr
37	0.0	0.0	1.5	tr	40.3	39.0	18.7	16.0	15.0	9.0	5.5	4.0	0.0	0.0
39	–	–	0.0	0.0	19.3	13.0	3.0	tr	3.3	tr	0.0	0.0	–	–
40	–	–	–	–	0.0	0.0	0.0	0.0	0.0	0.0	–	–	–	–

[a] N: by NMR.

[b] D: by dilatometry.

[c] Product I: fraction I + cocoa butter (50:50).

[d] Product II: fraction II + cocoa butter (50:50).

[e] Product III: mango fat + cocoa butter (50:50).

umetric dilatometer and (b) Newport NMR Analyzer. The samples for both determinations were tempered as described in the next section. This was necessary to have the samples in their highest-melting polymorphic state (25,26).

Tempering procedure. The melted samples were chilled in a water bath at 0 C for 1 hr. The temperature of the bath was gradually raised to 28 C over 10-12 hr. The samples were kept at this temperature for 10 days. The temperature of the bath was next lowered to 20 C and maintained for 2 days, and was then kept at 7 C for 2 days; finally it was held at 0 C overnight before starting the readings.

After taking the reading at 0 C, the readings at the subsequent higher temperatures were taken in steps of 3 C up to a maximum of 60 C. The samples were maintained at each temperature until there was no further volume expansion, indicated when the reading remained constant.

For the determination of SFI by NMR Analyzer, olive oil was used as a standard.

Slip point. The slip points (SP) were determined by the open tube capillary method on samples thoroughly tempered as already mentioned.

The other analyses were done according to standard AOCS procedures.

DISCUSSION

The sample of mango fat under study had an SP of 35.7 C, which is very close to that of cocoa butter (Table V). The high content of trisaturated glycerides in mango fat may be responsible for boosting the SP of mango fat to the level of cocoa butter. However, the main requirement for a cocoa butter substitute is the SFI pattern between 30 and 36-37 C. At 30 C, the SFI should be above 60 and at 36-37 C, it should be zero or nearly zero. The sample of mango fat gave an SFI of 44 only at 30 C, indicating a softer consistency at this temperature (Table VI). The dilatation curve for mango fat also shows a sudden volume change in the temperature range 10-20 C, which indicates the melting of part of its glycerides (Fig. 1).

Fraction I, from which the liquid fraction was removed, does not show this sudden change in volume. The SFI at 30 C is over 80 (Table VI) which becomes 40 at 37 C. The SP of this fraction also is high, i.e., 38.6 C, indicating the presence of high-melting glycerides (Table V).

The dilatation curve of fraction II, from which the low-

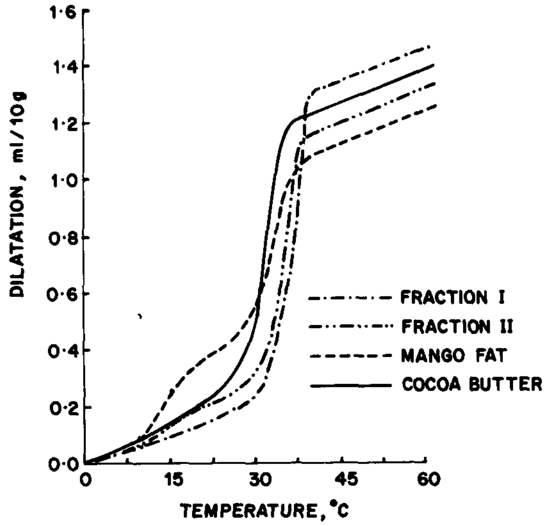

FIG 1. Volume expansion taking place at various temperatures during melting of the fat samples.

melting and high-melting fractions have been removed by two-stage acetone crystallization, is closer to the curve of cocoa butter than fraction I. It has a lower SP (37.2 C) than that of fraction I (38.6 C). The SFI pattern of fraction II (Table VI) shows higher SFI values than the values of cocoa butter at temperatures above 30 C, indicating a somewhat harder consistency.

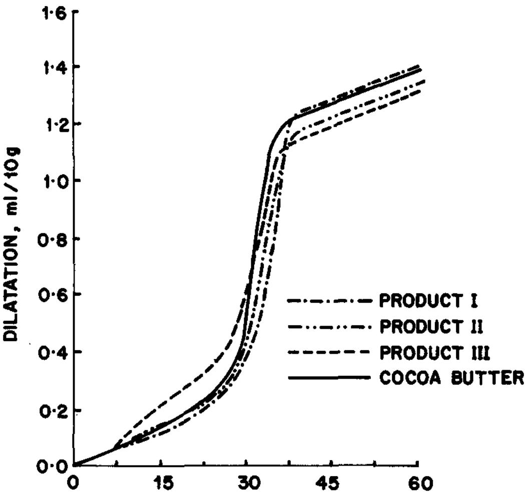

FIG. 2. Volume expansion taking place at various temperatures during melting of the fat samples.

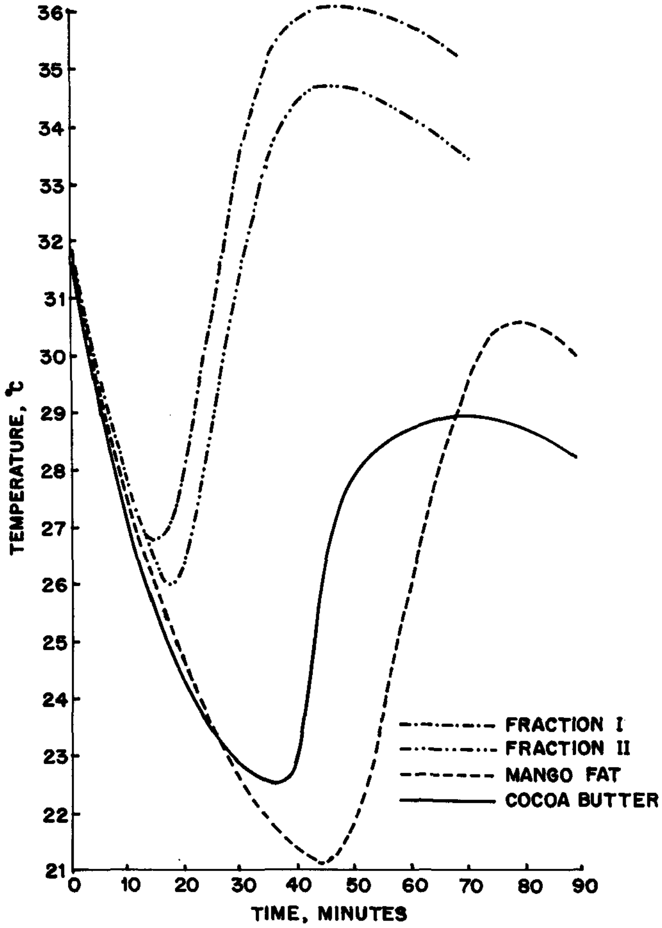

FIG. 3. Temperature changes with respect to time during Jensen's solidification test for fraction I, fraction II, mango fat, cocoa butter.

Products I and II, which are blends of fractions I and II and cocoa butter, show improvement in their SFI values and are closer to the SFI values of cocoa butter. The dilatation curves of products I and II and that of cocoa butter show a similar pattern (Fig. 2). This indicates that the mango fractions and cocoa butter are compatible and could be blended successfully. Simple blending of mango fat and cocoa butter (product III), however, does not show much improvement over the SFI values of unblended mango fat. The dilatation curve of this blend also is different from the curve of cocoa butter.

The solidification curve of mango fat (Fig. 3) is wider than that of cocoa butter, indicating that the rate of solidification of mango fat is slower than that of cocoa butter. However, the minimal temperature reached in the mango fat is lower and the subsequent rise in temperature upon solidification is higher than that of cocoa butter (Table V). This is mainly a result of two factors: (a) there is a considerable amount of liquid portion in mango fat which prevents early solidification of the fat; and (b) stearic acid glycerides are predominant in mango fat compared to palmitic-stearic glycerides in cocoa butter and are responsible for the high rise in temperature.

Fraction I, from which the liquid portion has been eliminated, shows rapid solidification accompanied by a high rise in temperature (Fig. 3). Fraction II, from which the low-melting as well as the high-melting fractions have been removed, shows improved solidification characteristics in comparison to those of fraction I. The minimal temperature reached in fractions I and II is somewhat higher than that for cocoa butter.

The blended products I and II (Fig. 4) gave solidification curves which are between the curves of cocoa butter and the original fractions (Fig. 3), indicating compatibility of

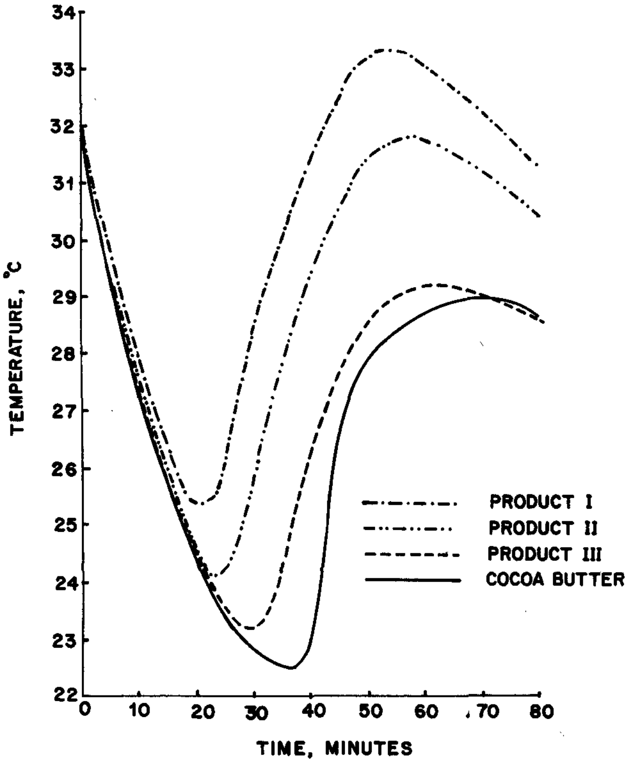

FIG. 4. Temperature changes with respect to time during Jensen's solidification test for product I, product II, product III, cocoa butter.

the fractions with cocoa butter. The curve of the blend of mango fat and cocoa butter (product III) is closer to the curve of cocoa butter alone, but it lies on the other side and not in between the curves of the individual fats. Thus, mango fat is not fully compatible with cocoa butter. The deficiencies of the mango fat as such are compensated to some extent by the presence of cocoa butter.

Product II, in most respects, appears to be closer to cocoa butter than product I. However, the higher-melting product I may be more suitable in countries where atmospheric temperatures are higher than 30 C. This study indicates that fractionated mango fat can give solid fractions which may be successfully used as partial replacements for cocoa butter.

Because of the wide variation in the compositions of the fats from different mango varieties, however, the yields of the solid fractions having cocoa-butter-like properties are expected to vary considerably.

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[Received May 1, 1980]

Associative Structures of Polyglycerol Esters in Food Emulsions[1]

W. HEMKER, Durkee Foods, Division of SCM Corp.,
Dwight P. Joyce Research Center, Strongsville, OH

ABSTRACT

Liquid crystalline types and the crystalline gel state of the commercially available tri- and octaglycerol esters are identified. The behavior of crystalline and liquid crystalline forms of these polyglycerol esters were studied in water dispersions, soybean oil and water emulsions, and in food emulsions. Triglycerol monoesters, primarily a mixed ester composition of palmitate and oleate, show hexagonal liquid crystalline activity as well as limited regions of stable α crystalline gels. Octaglycerol monostearate and monooleate primarily exhibit hexagonal liquid crystalline behavior which (below their Krafft point) form stable α-gels. A relationship between the associative structures and functional performance of these polyglycerol esters in food emulsions is presented.

INTRODUCTION

Polyglycerol esters (PGE) are versatile nonionic surfactants used primarily as food emulsifiers. They are composed of a mixture of predominantly linear glycerol polymers esterified with fatty acids or interesterified with triglycerides (1,2). Varying polymer length, type and degree of esterification of the PGE provides the basis for utility in product application by enabling the ester to match a desired hydrophilic-lipophilic balance (HLB) (1,3). Nevertheless, applications and acceptance have been limited, primarily because of PGE functional variability, inexplicable from the calculated HLB value.

Anomalies in the HLB approach are apparent when surfactant concentration, emulsion temperature and rela-

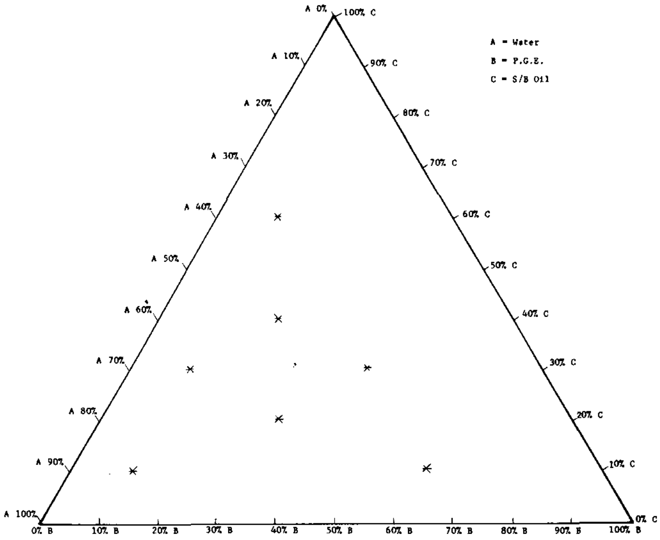

FIG. 1. Original data points.

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[1] Presented at the ISF-AOCS World Congress, April 1980, New York.