Modification of Sal Fat *(Shorea robusta)* and Mowrah Fat *(Madhuca latifolia)* by Methyl Ester-Triglyceride Interchange Reactions

D. K. BHATTACHARYYA and K. BANERJEE,
Applied Chemistry Department, University College of Science and Technology,
92, Acharyya Prafulla Chandra Road, Calcutta 700 009, India

ABSTRACT

Methyl ester-triglyceride interchange reactions provide a convenient route for preparing palmitic and lauric acid-rich Sal fat, and stearic and palmitic acid-rich Mowrah fat, with altered triglyceride compositions and thermal properties. The products are new kinds of plastic fats and may be useful as extenders of cocoa butter, high stability bakery fat, vanaspati (unhydrogenated type), tropical margarine, etc.

INTRODUCTION

Sal *(Shorea robusta)* fat and Mowrah *(Madhuca latifolia)* fat are two major tree-borne seed fats of India. The potential availabilities of Mowrah fat and Sal fat in India are 171,000 tons and 688,000 tons annually, while production is ca. 20-25,000 tons and 23,000 tons, respectively (1, 2). Mowrah fat is softer than cocoa butter; Sal fat is a hard brittle fat and closely resembles cocoa butter. Kane et al. (3) reported the preparation of a cocoa butter substitute from Sal fat by fractionation, using acetone as solvent. Subsequently, work has been initiated for the modification of Sal fat and Mowrah fat by the utilization of an interesterification process based on triglyceride-triglyceride interchange reactions for making edible fat products more like polyunsaturated fatty acid-rich vanaspati, margarine fats, etc., for use in the form of blends with some nontraditional and traditional liquid oils, or alone (4-7).

Only one or two reports of the preparation by acidolysis of palmitic acid-rich Sal fat and Mowrah fat, and also of lauric acid-rich Mowrah fat, are available (8, 9). The preparation of any selective fatty acid-rich Sal fat or Mowrah fat can also be achieved by methyl ester-triglyceride interchange. However, no work has been done on Sal fat and Mowrah fat involving methyl ester-triglycerides interchange reaction. The literature reports the preparation of confectionery fats by interesterifying lauric fat with methyl esters containing $C_{12:0}$ to $C_{18:0}$ fatty acid as carried out by Brown et al. in 1970 (10) and by Schmulinzon et al. (11) in 1971. The reaction mixture was ester-interchanged at temperatures below 140 C in the presence of a small amount of an alkali metal alkoxide as catalyst, followed by fractionation.

The present study aims primarily at preparing palmitic acid-rich Sal fat and stearic acid-rich Mowrah fat by the methyl ester-triglyceride interchange reaction with a view to comparing physical properties such as slip point and dilation, and the chemical composition, with those of the original fats. The study also includes the introduction of lauric acid into Sal fat and the preparation of plastic fats from Mowrah fat by reacting it with methyl palmitate.

The methyl ester-triglyceride interchange reaction was studied with respect to such variables as catalyst amount, molar ratios of the reactants, temperature and reaction time for Sal fat and methyl palmitate. The conditions favoring the reaction have been adopted for the reaction between Sal fat and Mowrah fat with other methyl esters.

EXPERIMENTAL

Materials and Methods

The fats used in the reaction were Sal fat and Mowrah fat supplied by K.N. Oil Industries of Mahasamund, Raipur, Madhya Pradesh, India, the largest producer of these two seed fats. The methyl esters used were prepared from corresponding fatty acids by esterification with methanol in the presence of catalytic amounts of conc sulfuric acid. Methyl palmitate and methyl laurate were found to be 99.5% pure, whereas the methyl stearate contained ca. 10% methyl palmitate. Sodium methoxide catalyst in methanol (30% v/v), prepared according to the standard method, was used in the present study.

Purification of Fat

The gummy material of Sal fat was removed by degumming with phosphoric acid. The fat was mixed with 85% phosphoric acid (1% by the weight of the fat) at 55-60 C for 30 min with constant stirring. The gummy material separated on standing for 1 hr and was removed by centrifugation. Sal fat and Mowrah fat were next refined to acid value 0.05-0.1 and bleached to make them peroxide-free according to the standard procedure (12). The refined and dried fat was then bleached by mixing with 2.5% Tonsil and heating under vacuum at ca. 85-90 C for 45 min. The refined fat was then obtained by hot filtration under vacuum.

Interesterification

The interesterification procedure was based on Brown et al.'s experimental method (10) and the methyl ester-triglyceride interchange reaction was carried out by heating refined and bleached fat and methyl ester in suitable molar proportions in the presence of catalyst at different temperatures in an inert atmosphere of nitrogen for a definite period. The catalyst was destroyed with phosphoric acid and the salt and excess acid removed with a hot water wash.

The products were isolated by removing methyl esters, which include both those derived from fat and the excess of unreacted methyl esters, by high vacuum distillation at 2-4 mm pressure of mercury and a temperature varying from ca. 120 to 200 C. The residual triglyceride fraction was bleached.

Slip Point

The slip points of the prepared fats were determined after proper stabilization at 15 ± 1 C for 16 hr by following AOCS procedure Cc 3-25 (13).

Dilatometry

The dilatation was performed on selected samples melting at 35-52 C according to the procedure given by Hannewizk et al. (14). Before dilatation measurements, the samples were stabilized at 15 ± 1 C for 16 hr and the readings were noted at temperatures of 10, 15, 20, 25, 30, 37, 40 and 45 C, respectively.

Fatty Acid Composition

The samples after high vacuum distillation contained traces of methyl esters detected by thin layer chromatography. The methyl esters were removed by silicic acid column chromatography by eluting the column first with a 99:1 hexane/diethyl ether solvent mixture. Finally the pure triglyceride was eluted by 150 mL of 95:5 hexane/diethyl ether solvent mixture. The methyl esters of the pure triglyceride fractions were prepared by the method of Luddy et al. (15). The fatty acid compositions were determined by gas liquid chromatography.

Glyceride Composition

The glyceride compositions of selected samples were determined by Coleman's enzymatic hydrolysis method (16) and glyceride compositions of remaining interesterified products were calculated by random distribution theory (17). The melting points of some of the interesterified products were ca. 50 C. The lipolysis results of Sal fat and Mowrah fat at 37.5 C and 50 C were found to be identical. Hence the lipase hydrolysis of the products having slip points above 40 C was done at 50 C and results so obtained were compared with those calculated from random theory.

RESULTS AND DISCUSSION

The extent of incorporation of palmitic acid in Sal fat by the methyl ester-triglyceride reaction is controlled by the amount of catalyst used, concentration of reactants, and temperature. Sodium methoxide is very effective, as indicated by the incorporation of palmitic acid in Sal fat (Table I). The amount of palmitic acid in Sal fat is increased from 12 to 28% when the concentration of methoxide catalyst is increased from 0.2 to 0.4% at the same temperature. Above 0.4% catalyst concentration, the amount of incorporation of palmitic acid declines from 28 to 21%. The extent of palmitic acid incorporation in Sal fat is largely controlled by the molar ratios of Sal fat and methyl palmitate. Table I shows that only 6-7% of palmitic acid is introduced into Sal fat by using 1:0.5 and 1:1 Sal fat and methyl palmitate mixtures, but between 1:2, 1:3 and 1:4 molar proportions of the reactants the incorporation of palmitic acid into Sal fat is as high as 18-23% when treated with 0.4% by weight of sodium methoxide catalyst at ca. 140 C.

The temperature has a significant influence upon the introduction of plamitic acid in Sal fat. Table I indicates that the additional incorporation of palmitic acid is ca. 18% at 60 C and up to 28% at 120 C, but at 140 C it declines to 21%. It is interesting that within 5 min, ca. 23% of palmitic acid can be introduced into Sal fat under favorable reaction conditions (Table II). With extension of the reaction period, more palmitic acid gradually enters, up to a maximum of 27-28% of palmitic acid, within 30-60 min. This points out that ca. 120 C is an optimum temperature for

TABLE I

Effect of Catalyst Amount, Reactant Amount and Temperature on the Composition of Fatty Acids and Triglycerides of Sal fat when Interesterified with Methyl Palmitate for 1 hr

Reactants	Sodium methoxide catalyst (% w/w)	Temperature (± 2 C)	Slip point (C)	Fatty acids (% w/w)						Glyceride (% mol)			
				16:0	18:0	18:1	18:2	20:0	18:3	S_3	S_2U	SU_2	U_3
Sal	—	—	28.0	7.6	42.6	37.0	3.5	8.0	1.3	3.4	68.2	25.9	2.5
Sal + MP[a]													
1:3	0.2	120	38.0	19.8	37.7	32.8	2.2	6.5	1.0	27.8	44.5	23.6	4.1
1:3	0.3	120	40.0	22.8	36.7	32.9	1.1	5.5	1.0	29.1	44.5	22.6	3.8
1:3	0.4	120	51.0	35.9	28.5	29.1	0.4	4.9	1.2	35.1	44.2	18.1	2.6
1:3	0.6	120	44.0	28.3	34.6	29.2	0.6	6.2	1.1	33.7	44.2	19.3	2.8
Sal + MP													
1:0.5	0.4	140	49.0	13.1	38.2	37.0	2.6	7.9	1.2	21.1	42.5	29.6	6.8
1:1	0.4	140	49.0	14.2	37.2	36.9	2.6	7.9	1.2	20.3	45.1	28.6	6.0
1:2	0.4	140	50.5	25.3	35.1	30.3	2.1	6.6	0.6	30.6	44.4	21.5	3.5
1:3	0.4	140	51.0	28.4	34.0	31.2	0.4	5.7	0.3	33.5	43.9	19.7	2.9
1:4	0.4	140	50.5	30.2	34.3	31.1	0.6	3.3	0.5	33.8	44.5	18.9	2.8
Sal + MP													
1:3	0.4	100	48.5	31.7	34.0	26.2	1.3	6.1	0.7	32.1	44.6	20.2	3.1
1:3	0.4	60	49.0	25.6	37.7	30.1	1.3	5.0	0.3	33.6	44.1	19.6	2.7

[a] MP = methyl palmitate.

TABLE IV

Slip Point, Fatty Acid and Glyceride Composition of the Product Obtained by Methyl Ester-Triglyceride Interchange Reaction of Mowrah Fat and Methyl Stearate and Palmitate in 1:3 Molar Ratio in Presence of 0.4% Sodium Methoxide (30% w/v) as Catalyst for 1 hr

Analysis					
Reaction temperature (± 2 C)	100	120	100	120	
Reactants	MS[a] + Mowrah	MS + Mowrah	MP[b] + Mowrah	MP + Mowrah	Original Mowrah
Slip point (C)	39	40	34	38	25
Fatty acid (% w/w)					
16:0	24.4	26.2	33.9	36.3	20.0
18:0	32.5	34.9	20.6	19.8	20.4
18:1	35.7	34.3	39.3	38.2	44.6
18:2	6.9	4.4	5.7	5.2	14.5
20:0	0.5	0.2	0.5	0.5	0.5
Glyceride composition (% mol) (calculated from random distribution)					
S_3	19.8	24.0	18.5	19.9	2.0[c]
S_2U	42.5	43.9	41.9	42.5	38.5
SU_2	30.5	26.7	31.7	30.4	45.1
U_3	7.2	5.4	7.9	7.2	14.4

[a] MS = methyl stearate.

[b] MP = methyl palmitate.

[c] Calculated by pancreatic lipase hydrolysis.

between Mowrah fat and methyl stearate and ca. 10.5% of palmitic acid can be introduced within 5 min.

The slip points of stearic and palmitic acid-rich Mowrah fat products are found to be much higher than that of original fat. The rise in slip points is due to the amount of fatty acid introduced and also depends on the nature of fatty acid displaced from Mowrah fat. The SFI values of stearic acid-rich Mowrah fat products are higher than in original fat, while the SFI values of palmitic acid-rich Mowrah fat are lower than in original fat (Fig. 1). This is due to the difference in the glyceride composition between the products and original Mowrah fat.

Sal fat has less palmitic and oleic acid but a higher percentage of stearic acid when compared to cocoa butter, along with high proportion of arachidic acid, whereas Mowrah fat contains less stearic acid but more oleic and linoleic acids than cocoa butter. Also, a comparison of glyceride composition reveals that Sal fat has a lower percentage of GS_2U and a higher percentage of GS_3, while Mowrah fat has a lower percentage of GS_2U and higher percentage of GSU_2 and GU_3 than cocoa butter. In spite of these differences in the fatty acid and glyceride compositions, Sal fat and Mowrah fat have been gaining importance as potential fats for the preparation of cocoa butter substitutes.

Glyceride compositions calculated from random distribution and by actual determination by lipase-hydrolysis of some selected interesterified samples of Sal fat and Mowrah fat indicate that GS_3 percentage increases sharply along with GS_2U, while GSU_2 and GU_3 decrease, when compared to the original Sal fat and Mowrah fat (Table V). Glyceride compositions of products calculated from lipase hydroly-

TABLE V

Fatty Acid Composition of 2-Monoglyceride and Glyceride Composition of Some of the Interesterified Sal Fat and Mowrah Fat Products by Pancreatic Lipase Hydrolysis

		Fatty acid composition (% mol)					Glyceride composition (% mol)			
Fat		12:0	16:0	18:0	18:1	20:0	S_3	S_2U	SU_2	U_3
Sal	MG	–	0.6	4.4	94.7	0.3	3.4	68.2	25.9	2.5
	TG	–	7.1	44.8	42.5	5.6				
Sal:MP 1:3 at 120 C	MG	–	33.4	29.1	37.2	0.3	35.4	44.0	18.1	2.5
	TG	–	38.4	27.5	29.8	4.3				
Sal:MP 1:3 at 80 C	MG	–	28.3	27.4	34.4	9.9	39.9	42.7	15.6	1.8
	TG	–	28.8	39.9	26.1	5.2				
Sal:MP 1:3 at 100 C	MG	–	26.3	39.8	25.0	8.9	32.1	44.6	20.2	3.1
	TG	–	34.1	28.5	31.3	6.1				
Sal:ML 1:3 at 120 C	MG	25.6	10.7	32.9	30.8	–	30.8	44.4	21.4	3.4
	TG	35.0	5.0	27.5	32.5	–				
Mowrah	MG	–	3.2	2.2	60.6	34.0	2.0	38.5	45.1	14.4
	TG	–	22.1	20.3	43.8	13.8				
Mowrah:MP 1:3 at 120 C	MG	–	32.6	20.0	42.9	4.5	19.6	42.9	30.4	7.1
	TG	–	38.9	19.4	36.8	4.9				
Mowrah:MS 1:3 at 120 C	MG	–	25.8	37.6	33.1	3.5	24.0	43.9	26.7	5.4
	TG	–	28.3	33.8	33.6	4.3				

MP = methyl palmitate, ML = methyl laurate, MS = methyl stearate, MG = monoglyceride, TG = triglyceride.

TABLE II

Rate of Incorporation of Palmitic Acid in Sal Fat and Palmitic Acid and Stearic Acid in Mowrah Fat by Methyl Ester-Triglyceride Interchange Reaction of Fat with Methyl Ester in 1:3 Molar Ratio at Temperature of 120 ± 2 C in Presence of 0.4% Sodium Methoxide Catalyst (30% w/v in Methanol)

Analysis	Time of reaction (min)						Time of reaction (min)		
	5	15	30	5	15	30	5	15	30
Reactant	Sal fat + MP[a]			Mowrah fat + MS[b]			Mowrah fat + MP		
Slip point	50.0	50.0	50.5	39.0	39.5	40.0	36.0	36.5	37.0
Fatty acids (% w/w)									
16:0	30.7	32.0	34.6	24.5	24.9	25.2	30.5	33.0	34.4
18:0	32.7	31.9	29.5	32.2	32.8	33.7	20.4	20.1	20.1
18:1	29.9	29.5	29.2	35.2	35.2	35.0	42.2	40.8	39.7
18:2	0.3	0.4	0.4	7.9	6.9	5.9	6.0	5.5	5.3
20:0	5.3	5.0	5.1	0.2	0.2	0.2	0.9	0.6	0.5
18:3	1.1	1.2	1.2	—	—	—	—	—	—
Glyceride (% mol) (calculated from random distribution									
S_3	34.7	34.9	35.7	19.2	20.2	21.5	19.0	18.7	19.6
S_2U	43.7	43.4	43.9	42.3	42.8	43.2	42.2	42.1	42.4
SU_2	18.9	19.5	17.9	31.0	29.9	28.9	31.1	31.4	30.6
U_3	2.7	2.2	2.5	7.5	7.1	6.4	7.7	7.8	7.4

[a] MP = methyl palmitate.

[b] MS = methyl stearate.

methyl ester-triglyceride reaction of Sal fat with methyl palmitate.

The fatty acid composition of reaction products reveals that the incorporation of palmitic acid always occurs at the expense of stearic, oleic, arachidic acid and other acids of Sal fat, depending on the process variables like catalyst amount, reaction temperature, molar ratio of the reactants and reaction time. It is also evident from Table III that the incorporation of 25-27% of lauric acid into Sal fat is best achieved by the methyl ester-triglyceride reaction at ca. 100 C and 120 C, respectively, with 0.4% catalyst in 1 hr. The incorporation of lauric acid occurs at the expense of all the acids in Sal fat.

The slip points of the reaction products after methyl ester-triglyceride reaction of Sal fat are observed to be much higher than that of the original Sal fat (Tables I-III).

TABLE III

Fatty Acids and Triglyceride Compositions and Slip Points of the Products Obtained by Methyl Ester-Triglyceride Reaction of Sal Fat and Methyl Laurate (1:3 molar proportion) for 1 hr with Sodium Methoxide Catalyst (0.4 g/100 g)

Analysis	Reaction temperature (± 2 C)	
	100	120
Slip point (C)	35	42
Fatty acids (% w/w)		
12:0	25.3	27.2
16:0	6.6	5.3
18:0	32.0	31.1
18:1	31.9	32.5
18:2	3.4	3.5
20:0	0.5	0.4
18:3	0.3	—
Glyceride (% mol) (calculated from random distribution)		
S_3	30.2	30.8
S_2U	44.4	44.4
SU_2	21.8	21.4
U_3	3.6	3.4

The rise of slip points depends on the amount of fatty acid introduced and also on the nature of fatty acids displaced from Sal fat. The SFI values as observed for various palmitic rich Sal fat are much lower than that of the original Sal fat (Fig. 1).

The introduction of palmitic acid and stearic acid in Mowrah fat is controlled by the temperature and the time of reaction. Table IV indicates that the incorporation of stearic acid is ca. 12% at ca. 100 C while it increases up to 14.5% at ca. 120 C in presence of 0.4% sodium methoxide in 1 hr and 14-16% incorporation of palmitic acid has occurred at temperatures of 100 C and 120 C, respectively. Table II shows that within 5 min, ca. 12% of stearic acid can be introduced into Mowrah fat at ca. 120 C, and with extension of reaction time more fatty acid can be introduced. The rate of incorporation of palmitic acid in Mowrah fat at ca. 120 C is very similar to the reaction

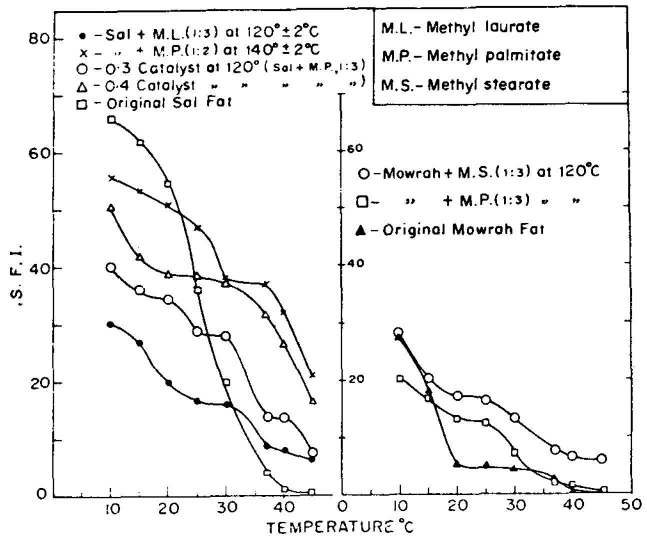

FIG. 1. Solid fat index vs temperature of Sal fat and Mowrah fat after modification by methyl ester-triglyceride interchange.

sis agree with the values calculated from random distribution (Table V).

Palmitic acid-rich Sal fat and stearic and palmitic acid-rich Mowrah fat may be useful for making high stability bakery fat, a new kind of vanaspati, tropical margarines, confectionery fats and other food fats.

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[Received August 13, 1982]

Iso-Solid Diagrams of Fat Blends from Thermal Analysis Data

P. LAMBELET[1] and A. RAEMY, Nestlé Research Department,
CH-1814 La Tour-de-Peilz, Switzerland

ABSTRACT

The use of spline interpolation between solid fat index (SFI) values obtained from calorimetric experiments to determine iso-solid data is described. Computer programs control both the sampling of the data from the calorimeter and the calculation of iso-solid values. This approach allows us to plot iso-solid diagrams fully automatically. Examples for cocoa butter/milk fat mixtures are given.

INTRODUCTION

For a range of mixtures of two components such as fat blends, iso-solid diagrams define curves indicating the temperatures at which constant solid to liquid ratios can be found as a function of the mixture composition.

Iso-solid diagrams are practical for illustrating the behavior of two constituent systems. In the case of fats, they are useful for determining factors relating to melting or crystallization behavior as well as to determine the fat compatability (1). Thus, iso-solid diagrams help fat technologists to choose the appropriate fat blend needed for a particular formulation.

The solid to liquid ratio in a fat or in a fat blend (solid fat index or SFI) can be determined by several methods: dilatometry (2), wide-line (3) or pulsed (4) nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC) (5) or densitometry (6).

Constructing iso-solid diagrams manually from data obtained with one of the abovementioned techniques is tedious and time-consuming, due to the fact that each point of the diagram must be calculated by interpolation between the experimental SFI values. Recently, Timms (7) described a partially automatic method based on a quadratic interpolation between the experimental SFI values determined by NMR, which facilitates this task.

We report below a fully automatic method for calculating iso-solid diagrams from DSC data, based on the rather sophisticated spline interpolation. An iso-solid diagram of cocoa butter/milk fat mixtures is shown.

MATERIALS AND METHODS

Materials

Cocoa butter (CB) was supplied by De Zaan (Zaandan, Netherlands). Milk fat fraction (MFF) was prepared by Corman (Goe, Belgium) by milk fat dry fractionation at melting point 41 C.

Principle of the Method

The SFI depends on the fat temperature. SFI values can therefore be expressed as a function of the temperature. This function is calculated by sequentially integrating the DSC melting curve and normalizing the values obtained by the total surface englobed by the DSC curve (8) (see Fig. 1).

$$\mathrm{SFI}\,(T) = \frac{\int_{T_0}^{T} H\,(T)\,dT}{\int_{T_0}^{T_1} H\,(T)\,dT} \qquad [1]$$

In order to calculate iso-solid diagram of a system of two fats A and B, SFI curves are determined for a series of mixtures representing, say, 10% composition intervals. A convenient SFI value, e.g., 20%, is then chosen and the temperature at which each mixture has this SFI value is calculated by interpolation and reported against sample composition (see Fig. 2).

This procedure is repeated for a series of SFI values, and in this way a set of iso-solid lines is obtained.

Data Acquisition

Data acquisition from the differential scanning calorimeter (Mettler TA 2000B) was carried out using a Hewlett-

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[1] To whom correspondence should be addressed.