Utilization of High-Melting Palm Stearin in Lipase-Catalyzed Interesterification with Liquid Oils

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ABSTRACT: Palm stearin with a melting point (m.p.) of 49.8°C was fractionated from acetone to produce a low-melting palm stearin (m.p. = 35°C) and a higher-melting palm stearin (HMPS, m.p. = 58°C) fraction. HMPS was modified by interesterification with 60% (by weight) of individual liquid oils from sunflower, soybean, and rice bran by means of *Mucor miehei* lipase. The interesterified products were evaluated for m.p., solid fat content, and carbon number glyceride composition. When HMPS was interesterified individually with sunflower, soybean or rice bran at the 60% level, the m.p. of the interesterified products were 37.5, 38.9, and 39.6°C, respectively. The solid fat content of the interesterified products were 30–35 at 10°C, 17–19 at 20°C, and 6–10 at 30°C, respectively. The carbon number glyceride compositions also changed significantly. C_{48} and C_{54} glycerides decreased remarkably with a corresponding increase of the C_{50} and C_{52} glycerides. All these interesterified products were suitable for use as *trans* acid-free and polyunsaturated fatty acid-rich shortening and margarine fat bases.
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KEY WORDS: High-melting palm stearin, low-melting palm stearin, *Mucor miehei* lipase, palm stearin.

Palm stearins, produced in commerce from palm oil by fractionation, have limited use due to their high melting points. A great deal of work has already been done in utilizing palm stearin by interesterification and by blending in mixtures with liquid oils (1). Nutritional quality of these interesterified products (2) and blended products (3) has also been evaluated.

Palm stearin can be further fractionated (4) to produce a low-melting palm stearin (LMPS) and a higher-melting palm stearin (HMPS). The LMPS fraction of melting point 35°C will be more useful than palm stearin as such. The HMPS fraction with melting point of about 58°C cannot be used as such in fat-based edible products due to its high melting point. However, HMPS can be used after some modification by lipase–catalyzed interesterification with other liquid oils.

The present study aims at utilizing HMPS by lipase-catalyzed interesterification with individual liquid oils, such as from sunflower, soybean and rice bran, to produce fatty materials suitable for the production of *trans*-free shortening and margarine.

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MATERIALS AND METHODS

Refined, bleached, and deodorized (RBD) palm stearin was provided by PORIM (Kuala Lumpur, Malaysia). RBD sunflower oil was supplied by ITC (Agro-Tech) Ltd. (Hyderabad, India); RBD soybean oil and rice bran oil were supplied by K.N. Oil Industries (Raipur, India). 1,3-Specific *Mucor miehei* lipase was a kind gift of NOVO Industry (A/S Copenhagen, Denmark). Except otherwise specified, all other chemicals and solvents (A.R. Grade) were purchased from S.D. Fine Chemicals (Calcutta, India).

Fractionation of palm stearin. Palm stearin was fractionated from acetone (5 mL/g palm stearin) at 35°C for 3 h to get 19% by weight of HMPS and 81% by weight of LMPS. These two fractions were collected after removal of acetone.

Lipase-catalyzed interesterification reaction. About 50 g of total fat mixture was placed in a 100-mL round-bottom flask with 5 g (10% w/w on total fat charge) of immobilized 1,3-specific *M. miehei* lipase (lipase contains 10% w/w water) and stirred at 60°C ± 2°C with a magnetic stirrer under a vacuum of 2 mm Hg for 5 h. After the reaction, the product mixture was isolated by filtration, and the free fatty acids formed during the reaction (about 1.5% w/w) were then neutralized by a standard mixed-solvent refining process (5).

Analytical procedures. Melting points were determined by the method of the Indian Standard Institution (6).

Solid fat content (SFC) was determined with a pulsed nuclear magnetic resonance (NMR) spectrophotometer (Minispec PC 120; Bruker, Germany) by following standard procedures (7).

Fatty acid composition (8) and carbon number triglyceride composition (9) of fats and oils were determined by gas–liquid chromatography.

RESULTS AND DISCUSSION

The melting point and fatty acid composition of palm stearin and its two fractions (HMPS and LMPS) are shown in

TABLE 1
Melting Point and Fatty Acid Composition of Palm Stearin, Its Fractions, and Liquid Oils

Fractions	Melting point (°C)	Fatty acid composition (% w/w)						
		$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
Palm stearin (original)	49.8	0.4	1.1	53.9	3.6	33.7	7.3	—
High-melting palm stearin	58.8	0.8	2.5	79.7	3.1	10.4	3.4	—
Low-melting palm stearin	34.8	—	1.4	46.8	4.0	39.5	8.3	—
Sunflower oil	—	—	—	6.5	3.5	31.1	58.1	—
Soybean oil	—	—	—	11.2	3.1	24.2	54.3	7.2
Rice bran oil	—	—	—	24.1	1.6	43.4	30.9	—

Table 1, and their carbon number glyceride compositions are included in Table 2. In the HMPS fraction, C_{48} glyceride increased to 73.6%, C_{50} decreased to 16%, and C_{52} to only 0.7%. The high melting point of the HMPS fraction is due to concentration of most of the saturated glycerides as tripalmitin (PPP). In the LMPS fraction, C_{48} glyceride has decreased to 19.4% with a corresponding increase of both C_{50} and C_{52} glycerides to 59.1% and 17.5%, respectively.

During interesterification of HMPS with different liquid oils, the melting point of the products gradually decreased with time (Fig. 1) and reached an equilibrium after 5 h. The enzymatic interesterification with *M. miehei* lipase took 5 h to complete.

HMPS could be modified in terms of its physical properties and composition with 1,3-specific lipase in admixture with liquid oils from sunflower, soybean, and rice bran. The melting point of the interesterified products (Table 3) decreased with increased use of liquid oils in the blends in an analogous manner with the original blends. When MHPS was interesterified individually with sunflower, soybean and rice bran oil at a 60% level, the corresponding melting points of the products were 37.5, 38.9, and 39.6°C, respectively. The high melting point of the interesterified product of HMPS (40%) and rice bran oil (60%), compared to the soybean and or sunflower oil blends, was due to a higher amount of saturated fatty acids in rice bran oil (Table 1: rice bran = 25.7%, soybean = 14.3% and sunflower = 10.0%).

SFC of the interesterified products (Table 3) indicated significant values, *viz.,* 30–35 at 10°C, 17–19 at 20°C, and 6–10 at 30°C.

TABLE 2
Carbon Number Triglyceride Composition of Palm Stearin and Its Fractions

Fractions	Carbon number triglycerides (% w/w)				
	C_{46}	C_{48}	C_{50}	C_{52}	C_{54}
Palm stearin (original)	3.7	31.6	41.3	13.8	1.6
High-melting palm stearin	9.7	73.6	16.0	0.7	—
Low-melting palm stearin	2.2	19.4	59.1	17.5	1.8

A significant change in carbon number glyceride composition of the blends and the corresponding products could be seen (Table 4). In all interesterified products, C_{48} and C_{54} glycerides decreased remarkably with a corresponding increase of the C_{50} and C_{52} glycerides compared to the blends. The decrease in the melting points of the blends by interesterification was due to the decrease in the content of trisaturated glycerides G_{S_3}, mainly PPP, and to the concomitant formation of G_{S_2U} and G_{U_3} glycerides (U = unsaturated fatty acid).

The HMPS fraction (m.p.—58.8°C), rich in saturated fatty acids (about 83%), could be processed by lipase-catalyzed interesterification reaction with sunflower, soybean, and rice bran oil to make plastic fats for potential use as *trans* acid-free and polyunsaturated fatty acid-rich shortening and margarine fat bases.

TABLE 3
Lipase-Catalyzed Interesterification of High-Melting Palm Stearin (HMPS) with Some Liquid Oils: Melting Point and Solid Fat Content [SFC by nuclear magnetic resonance (NMR)]

Products[a]	Melting point (°C)	Solid fat content (SFC by NMR) (°C)		
		10	20	30
HMPS (70) + SFO (30)	50.4 (57.1)	—	—	—
HMPS (50) + SFO (50)	42.5 (55.8)	—	—	—
HMPS (40) + SFO (60)	37.5 (53.1)	35.2	18.4	9.2
HMPS (40) + SBO (60)	38.9 (54.6)	36.2	19.6	10.7
HMPS (40) + RBO (60)	39.6 (54.1)	30.2	17.3	5.5

[a]SFO, sunflower oil; SBO, soybean oil; RBO, rice bran oil.
[b]Parentheses represent the values of the corresponding blends before interesterification.

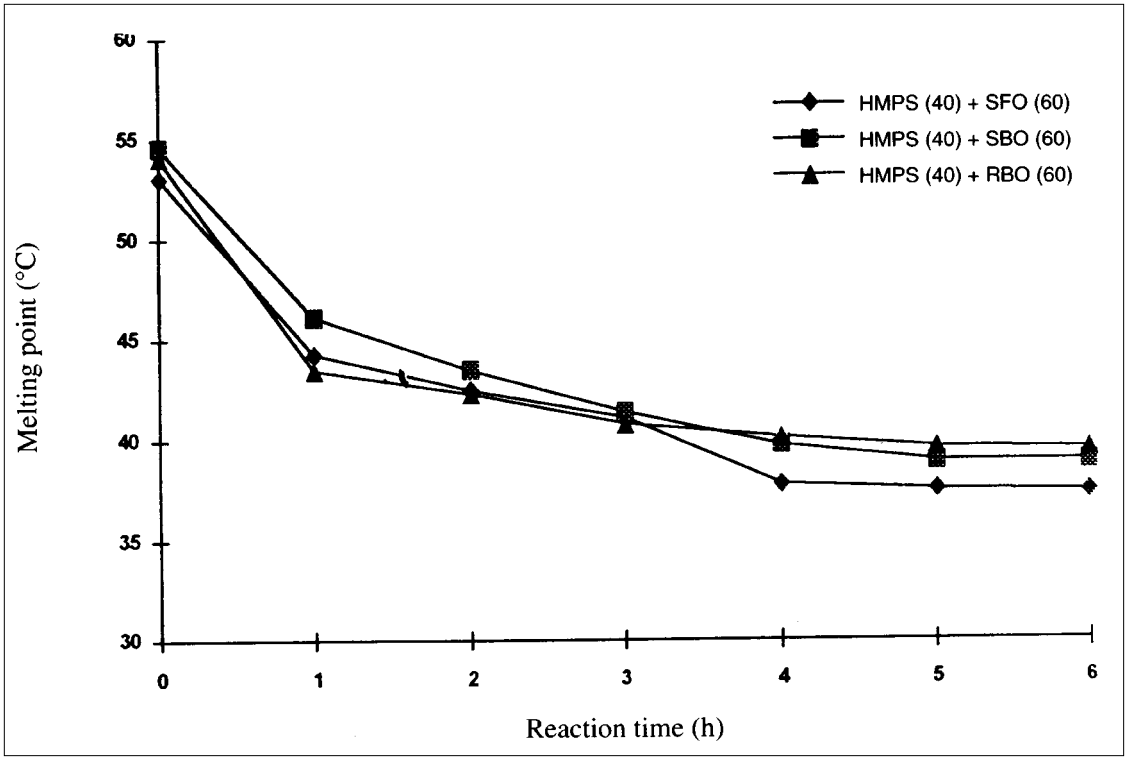

FIG. 1. Reaction time vs. melting point of lipase-catalyzed interesterification of high-melting palm stearin (HMPS) with liquid oils: lipase, *Mucor miehei* (10% w/w, on oil charge); temperature, 60°C; pressure, 2 mm of Hg; SFO, sunflower oil; SBO, soybean oil; RBO, rice bran oil.

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TABLE 4
Lipase-Catalyzed Interesterification of HMPS with Some Liquid Oils: Carbon Number Triglyceride Composition

	Carbon number triglycerides (% w/w)[b]				
Products[a]	C_{46}	C_{48}	C_{50}	C_{52}	C_{54}
HMPS (40) + SFO (60)	4.9 (3.9)	12.8 (29.4)	40.8 (9.3)	25.3 (10.6)	16.2 (46.8)
HMPS (40) + SBO (60)	3.1 (3.5)	15.6 (28.6)	44.1 (13.8)	29.5 (25.2)	7.7 (28.9)
HMPS (40) + RBO (6)	2.1 (3.6)	6.1 (29.9)	52.3 (21.8)	35.2 (31.2)	4.3 (13.5)

[a]See Table 3 for abbreviations.
[b]Parentheses represent the values of the corresponding blends before interesterification.

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