SHORT COMMUNICATION

Medium-Chain Fatty Acid-Rich Glycerides by Chemical and Lipase-Catalyzed Polyester–Monoester Interchange Reaction

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ABSTRACT: Medium-chain triglycerides (MCT) that contain caprylic acid ($C_{8:0}$) and capric acid ($C_{10:0}$) have immense medicinal and nutritional importance. Coconut oil can be used as a starting raw material for the production of MCT. The process, based on the interchange reaction between triglycerides and methyl esters of medium-chain fatty acids by chemical catalyst (sodium methoxide) or lipase *(Mucor miehei)* catalyst, appears to be technically feasible. Coconut oils with 25–28.3% (w/w) and 22.1–25% (w/w) medium-chain fatty acids have been obtained by chemical and lipase-catalyzed interchange reactions. Coconut olein has also been modified with $C_{8:0}$ and $C_{10:0}$ fatty acids, individually as well as with their mixtures, by chemical and lipase-catalyzed interchange reactions. Coconut olein is a better raw material than coconut oil for production of medium-chain fatty acid-rich triglyceride products by both chemical and lipase-catalyzed processes.
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KEY WORDS: Coconut oil, coconut olein, medium-chain fatty acid, *Mucor miehei.*

Medium-chain triglycerides are mainly utilized as a nutritional supplement for patients who suffer from malabsorption caused by intestinal resection and also as a component for infant feeding formulas (1–4). It is also used as a solvent or carrier of lipophilic nutrients or drugs, such as vitamin K (5) and phospholipids (6).

Commercially, medium-chain glycerides (MCG) are manufactured by direct esterification of medium-chain fatty acids and glycerol at high temperature and high pressure, followed by alkali-refining, washing, molecular distillation, ultrafiltration, and activated carbon treatment for the purification of the product (7).

Recently, Kim and Rhee (8) studied the enzymatic synthesis of MCG by using capric acid and glycerol as substrates in the presence of immobilized lipase *(Mucor miehei)* without any solvent or surfactant. They studied the reaction in detail by considering enzyme activity, method of removal of water, and temperature of reaction, etc. The percentage conversion was close to 90% on the basis of capric acid consumption within 80 h. Kaimal and Saroja (9) have also incorporated 12% caprylic acid ($C_{8:0}$) and 9.7% capric acid ($C_{10:0}$) in coconut oil with the help of *M. miehei* lipase by acidolysis reaction.

The information available on the technology of production of medium-chain triglycerides is meager. There is a need for further investigation on the production aspects of medium-chain fatty acid-rich glycerides from coconut oil and its fraction by processes based on chemical and lipase-catalyzed polyester–monoester interchange reaction.

MATERIALS AND METHODS

Crude coconut oil was purchased from the local market and was purified by alkali-refining and bleaching processes. A 30% (wt/vol) solution of sodium methoxide in dry methanol was prepared in the laboratory and was stored as a stock solution for periodical reaction. Sodium was purchased from E. Merck (Bombay, India) Ltd., and methanol was purchased from S.D. Fin Chemicals (Calcutta, India). *Mucor miehei* lipase was a gift of Novo Industries (Copenhagen, Denmark).

Chemically catalyzed polyester–monoester interchange reaction. The refined, bleached, deodorized coconut oil (30 g, 0.044 mole) was reacted separately with the methyl esters of $C_{8:0}$ (13.5 g, 0.086 mole) and $C_{10:0}$ (15.8 g, 0.085 mole) and with a mixture [$C_{8:0}$ (7.0 g, 0.044 mole) and $C_{10:0}$ (8.2 g, 0.044 mole)] in a 100-mL round-bottom flask. The reactants were continuously stirred with a magnetic stirrer for about 1 h under vacuum (20 mm Hg). The temperature of the mixture was raised to 60°C, and sodium methoxide catalyst (0.2% on weight of charge) was added and stirred again for 45 min under the same vacuum. After the reaction, the catalyst was destroyed by treating with hot distilled water. The product was made free from soap by hot-water washing and centrifugation.

The excess monoesters were removed from the reaction mixture by steam distillation at 180°C and 20 mm Hg for 30 min in all-glass steam distillation equipment. The product was collected after cooling to around 60°C.

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TABLE 1
Chemical Modification of Coconut Oil by Polyester–Monoester Interchange Reaction

Fat/products	Methyl ester of fatty acids	Fatty acid composition (% w/w)								
		$C_{6:0}$	$C_{8:0}$	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
Coconut oil (original)	—	0.9	4.9	6.2	50.3	19.2	8.3	1.3	6.3	2.6
Coconut oil (modified)	$C_{8:0}$	0.8	23.3	5.0	41.5	17.8	6.7	1.1	4.2	1.2
Coconut oil (modified)	$C_{10:0}$	1.0	3.8	21.3	39.1	18.8	7.1	1.4	5.1	2.4

Lipase-catalyzed polyester-monoester interchange reaction. Lipase-catalyzed polyester-monoester interchange was carried out with the same amount of substrates used in the chemically catalyzed reaction in a 100-mL round-bottom flask and 10% w/w (on total reactants) *M. miehei* lipase (lipase initially contains 10% w/w water) at 60°C and at 20 mm Hg for 5 h, based on the earlier study (10) where the interchange reaction was complete in 5 h. After the reaction, the product mixture was separated by filtration under vacuum.

From the product mixture, the excess methyl ester was removed by steam distillation as mentioned earlier.

Analytical methods. Fatty acid compositions of the fats were determined by following a standard procedure (11).

RESULTS AND DISCUSSION

The fatty acid compositions of the original coconut oil and its modified products, obtained by interchange with methyl caprylate and methyl caprate with the aid of a chemical catalyst (0.2% sodium methoxide), are shown in Table 1. Original coconut oil contains 11.1% medium-chain fatty acids (4.9% caprylic and 6.2% capric). Upon interesterification with methyl caprylate, the content of medium-chain fatty acids in coconut oil becomes 28.3% (23.3% caprylic and 5.0% capric) for increase of medium-chain fatty acids by 17.1%. In fact, 18.4% caprylic acid was incorporated in the oil by the displacement of mainly lauric acid. Methyl caprate upon chemical interesterification incorporates as much as 15.1% capric acid in coconut oil. The total content of medium-chain fatty acids becomes 25.1%, which means an increase in the original content of medium-chain fatty acids by 14.1%.

Caprylic acid and capric acid can also be incorporated in coconut oil by 1,3-specific *M. miehei* lipase. Table 2 shows that coconut oil, after enzymatic interesterification with methyl caprylate, was changed in the content of medium-chain fatty acids. Thus, the proportion of medium-chain fatty acids increases by 13.9%, and capric acid also increased in the modified coconut oil from 6.2 to 18%. There has been a corresponding decrease in the proportion of mainly lauric ($C_{12:0}$) acid.

Kaimal and Saroja (9) report on the incorporation of 12% caprylic acid and 9.7% capric acid in coconut oil by enzymatic acidolysis reaction. The present study points out that coconut oil with 22.1–25.0% medium-chain fatty acids can be easily obtained by conducting microbial lipase-catalyzed polyester–monoester interchange in place of acidolysis.

Coconut oil was fractionated from acetone (1:3, wt/vol) at 8°C for 3 h to a liquid fraction, known as coconut olein (yield 84%), and a solid fraction, known as coconut stearin (yield 16%). Coconut olein has a slip melting point of 22.9°C and is typically composed of (% w/w) $C_{6:0}$ (1.1); $C_{8:0}$ (5.4); $C_{10:0}$ (6.8); $C_{12:0}$ (48.2); $C_{14:0}$ (18.1); $C_{16:0}$ (7.8); $C_{18:0}$ (1.4); $C_{18:1}$ (7.8), and $C_{18:2}$ (3.5). Coconut stearin has a slip point of 30.1°C and contains (% w/w) $C_{6:0}$ (0.4); $C_{8:0}$ (2.2); $C_{10:0}$ (3.1); $C_{12:0}$ (57.3); $C_{14:0}$ (23.9); $C_{16:0}$ (10.9); $C_{18:0}$ (0.7); $C_{18:1}$ (7.8), and $C_{18:2}$ (0.7). It can be utilized in biscuit and chocolate production (12).

The extent of incorporation of caprylic acid and capric acid in coconut olein by chemically interesterifying with methyl caprylate or methyl caprate, individually or with the proper mixture, has been included in Table 3. Caprylate-modified coconut olein contains 30.4% medium-chain fatty acids and consists of 24.3% caprylic acid and 6.1% capric acid. The reaction with methyl caprate yields a product of coconut olein with 32.4% medium-chain fatty acids (5.6% caprylic and 26.9% capric acid).

Coconut olein can also be made into a product that contains 21.9% medium-chain fatty acids with the incorporation of 9.8% caprylic acid and 12.1% capric acid when it is chemically interesterified with a mixture (1:1 molar ratio) of methyl caprylate and methyl caprate.

The effect of lipase *(M. miehei)*-catalyzed interesterification of coconut olein with methyl caprylate or methyl caprate or their mixture on the content of medium-chain fatty acids is

TABLE 2
Lipase-Catalyzed Modification of Coconut Oil by Polyester–Monoester Interchange Reaction

Fat/products	Methyl ester of fatty acids	Fatty acid composition (% w/w)								
		$C_{6:0}$	$C_{8:0}$	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
Coconut oil (original)	—	0.9	4.9	6.2	50.3	19.2	8.3	1.3	6.3	2.6
Coconut oil (modified)	$C_{8:0}$	0.9	17.9	7.1	38.4	19.1	6.7	2.0	5.8	2.1
Coconut oil (modified)	$C_{10:0}$	1.3	4.1	18.0	41.3	18.5	6.8	1.1	6.1	2.8

TABLE 3
Chemical Modification of Coconut Olein by Polyester–Monoester Interchange Reaction

Fat/products	Methyl ester of fatty acids	Fatty acid composition (% w/w)								
		$C_{6:0}$	$C_{8:0}$	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
Coconut olein (original)	—	1.0	5.4	6.8	48.2	18.1	7.8	1.4	7.8	3.5
Coconut olein (modified)	$C_{8:0}$	0.8	24.3	6.1	34.6	16.1	6.3	1.2	7.2	3.4
Coconut olein (modified)	$C_{10:0}$	2.0	5.6	26.9	35.6	15.3	4.9	1.0	5.8	2.9
Coconut olein (modified)	$C_{8:0}$ + $C_{10:0}$ (1:1)	1.3	9.8	12.1	34.2	19.9	8.1	2.5	9.8	2.3

TABLE 4
Lipase-Catalyzed Modification of Coconut Olein by Polyester–Monoester Interchange Reaction

Fat/products	Methyl ester of fatty acids	Fatty acid composition (% w/w)								
		$C_{6:0}$	$C_{8:0}$	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
Coconut olein (original)	—	1.0	5.4	6.8	48.2	18.1	7.8	1.4	7.8	3.5
Coconut olein (modified)	$C_{8:0}$	1.1	18.3	6.2	38.9	17.4	5.8	1.0	8.1	3.2
Coconut olein (modified)	$C_{10:0}$	1.3	4.4	16.3	42.2	17.1	5.2	1.3	9.5	2.7
Coconut olein (modified)	$C_{8:0}$ + $C_{10:0}$ (1:1)	1.6	13.2	9.8	40.9	16.5	6.2	1.3	7.4	3.1

shown in Table 4. Coconut olein contains 24.5% medium-chain fatty acids after reaction with methyl caprylate and has 18.3% caprylic acid and 6.2% capric acid. Coconut olein, after enzymatic interesterification with methyl caprate, produces a product that has 20.7% medium-chain fatty acids, consisting of 4.4% caprylic acid and 16.3% capric acid. After lipase-catalyzed reaction with a methyl caprylate and methyl caprate mixture, coconut olein forms a product that contains 23% by weight of medium-chain fatty acids.

The products obtained by lipase-catalyzed interesterification of coconut olein with methyl esters of caprylic acid, capric acid, and their mixture contain 20.7–24.5% medium-chain fatty acids, 38.9–42.2% lauric acid, and 10.5–12.2% unsaturated fatty acids.

A comparison between the two catalyst systems for interesterification reveals that medium-chain fatty acids ($C_{8:0}$ and $C_{10:0}$) were incorporated, when used individually, in a much greater amount in coconut olein with the aid of the chemical catalyst. This is due to the fact that the chemical catalyst favors complete random reaction in comparison with the lipase *(M. miehei),* which incorporates fatty acids selectively in the 1,3-positions.

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