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Isopropanol Fractionation of Coconut Oil into its Olein and Stearin Fractions

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ABSTRACT

The present study deals with the fractionation of coconut oil by using isopropanol as solvent and characterization of the olein and stearin fractions obtained in terms of melting properties, iodine value, saponification value and fatty acid composition. Coconut oil was fractionated with isopropanol (1:3, 1:4 and 1:5 wt/vol) at three temperatures (20°,15° and 10°C). The yields of oleins and stearins were dependent on the volume of solvent and the temperature of fractionation. Thus, 54 to 25% of oleins and 43 to 71% of stearins could be obtained when crystallized from 15°C to 10°C with the varying volume ratio of solvent (1:5 to 1:3 wt/vol.). The olein fractions displayed a distinct variation in the fatty acid compositions. Both Caprylic acid and Capric acid content increased in olein fractions from original coconut oil whereas decreased in corresponding stearin fractions. From the results, it appears that isopropanol is a good solvent to yield relatively higher amounts of medium chain triglycerides (MCT) which may be important from health and economical point of view. Coconut oil can be fractionated from isopropanol at relatively high temperatures in much less time to produce olein and stearin fractions of specific composition and properties.
Keywords: Fractionation, Isopropanol, Coconut Olein, Coconut Stearin, Medium Chain Triglyceride

I. INTRODUCTION

Coconut oil, traditional edible oil in India, has been receiving importance for its medium chain triglycerides content that confers health and nutritional benefits (1). In fact, the use of medium chain triglyceride rich oil or fraction in products like health margarines and in blending with other cooking oils especially in oils with long chain fatty acids demands for development of an appropriate process technology to produce very effectively medium chain triglyceride-rich fraction from coconut oil. The process that appears feasible is the adaptation of the solvent fractionation process.

Fractionation is a process that uses heat to separate a substance into its components. The most widely practiced form of fractionation is that of crystallization wherein a mixture of triglycerides is seperated into two or more different melting fractions based on solubility at a given temperature. Generally under a certain specific conditions the fractionation of coconut oil is done by fractional distillation process, Lanza process by using detergent and by solvent like acetone or hexane to yield olein and stearin fractions (2).

Isopropanol, a bio-renewable solvent, is increasing in importance for vegetable oil extraction, and its use in fractionation of fats is also known (2). Saturated acid-rich glycerides, having short-chain and long-chain acid moieties, are relatively less soluble in isopropanol than the corresponding glycerides with unsaturated fatty acids. As a result, a sharper fractionation is expected between the saturated acid-rich glycerides and the glycerides with unsaturated fatty acids. Also, it has been reported that isopropanol, as compared to hexane, enables fractionation to be conducted at a comparatively high temperature because of its polarity and with a lower volume of solvent. Further, time of crystallization is reported to be reduced and the loss of isopropanol is also less in comparison to n-hexane during recovery by distillation. It is already known that the boiling point of

commercial n-hexane miscella remarkably increases with increase in the oil content of hexane miscella that requires more energy for recovery of hexane. On the other hand, isopropanol may not behave like that of hexane miscella because of its polar nature that may not behave as an ideal solvent for raising the boiling point of isopropanol miscella with the corresponding increase in oil content . Moreover it is stated that isopropanol is more eco-friendly than hexane in view of the fact that isopropanol is a food grade material and also condenses more completely compared to n-hexane (3, 4).

Recent study in Brazil states that daily intake of coconut oil combined with exercise would restore baroreflex sensitivity and reduce oxidative stress, resulting in reduction in Blood pressure (5). The olein fractions are normally more enriched in medium chain triglycerides. Coconut olein yields low calorie and contains high medium chain triglyceride to prevent cholesterol production. Medium chain triglycerides allow fatty acids to be metabolized without use of the carnitine transport system (6). Oxidation of medium chain triglyceride provides 8.3 calories per gram, while long chain triglyceride provides 9.2 calories per gram (7). Medium chain triglycerides are useful in treating disorders that involve impaired or damaged lipid metabolism, including obstructive jaundice, billiary cirrhosis, pancreatitis, cystic fibrosis, celiac disease (8). It is also reported to be useful for feeding newborn infants, both to assist their initial growth and contribute to their physiological development. A mixture of medium chain monoglyceride and diglyceride was found to be an effective solvent for dissolving cholesterol gallstones in humans. (9-12). Stearins are available for use in bakery shortenings, pastry, margarine formulation.

The present study deals with the fractionation of coconut oil by using isopropanol as solvent for the first time in different ratios (1:3, 1:4 and 1:5 wt/vol) at different temperatures (10°C,15°C and 20°C) and characterization of the olein and stearin fractions obtained in terms of melting properties, iodine value, saponification value and fatty acid composition.

II. METHODS AND MATERIAL

Coconut oil (Shalimar Chemical Works Limited) was purchased from local market, Kolkata, India. Isopropanol (A.R Grade) and all chemicals used were MERCK, India.

Fractionation of Coconut oil from Isopropanol:

The coconut oil (100g.) was placed in a 1 L Stoppard conical flask (Borosil) after it was completely melted on a water bath at 50°C. Isopropanol was added in different ratio of 1:5,1:4 and 1:3 (wt/v). Each time the mixture was kept initially at 40°C for 10 min. the beaker was placed in a constant-temperature bath and stirred by a low-speed magnetic stirrer for 1 hour. The crystallization process was done at different temperatures of 20°C, 15°C and 10°C. The solid fraction was separated from the liquid fraction by filtration under vacuum. The fractions were desolventized at 80°C for 1 hour at 10 mm Hg pressure. Both the fractions were weighed and stored in a refrigerator at 4°C for further analysis.

Analytical procedures

Determination of Slip Melting Point

Melting points were determined by the Capillary Tube Method of AOAC (13).

Determination of Iodine Value

Iodine values were determined by the Wijs Method of AOAC (13).

Determination of Saponification Value

Saponification values were determined by the method of AOAC (13).

Fatty acid composition (%wt/wt) of the Coconut oil and its fractions obtained from Isopropanol fractionation

Pure Coconut oil and different fractions were methylated by the simplest KOH catalyzed methanolysis method of Brockerhoff (14). About 40 mg of triglyceride was dissolved in 0.5 ml of diethyl ether and 1ml of 0.5 (N) methanolic KOH solutions was added and shaken. After 10 minutes at room temperature 1ml of 1(N) HCl was added and shaken. The methyl esters were extracted with each 1.0 ml of petroleum ether for three consecutive times. The extracts were evaporated in water bath. The sides of the tube were washed with sufficient GLC grade n-hexane to redissolve the methyl esters for GLC analysis. The gas chromatograph

(Agilent 6890 N) was fitted with a DB Wax capillary column(30 m x 0.32mm x 0.25µm) and FID.N_2 , H_2 and airflow rate were maintained at 1, 30 and 300ml/min respectively. Inlet and detector temperatures were kept at 250ºC and oven temperature was programmed at 70 ºC for 1 min holding time and then increase in temperature from 70ºC to 230ºC at a rate of 5ºC/min then holding time for 5min.

Statistical Analysis

Statistical analysis was performed by using analysis of variance (ANOVA) and the means were compared across groups by Tukey test. All analyses were carried out with the Origin Pro 8 and the significant differences were determined at $p \leq 0.05$.

III. RESULT AND DISCUSSION

Original Coconut oil was characterised in terms of Slip melting point, Iodine value, Saponification value along with fatty acid composition and the results were shown in Table 1. The fractionation of Coconut oil using isopropanol in different volume of solvent ratio (1:3, 1:4 and 1:5 wt/vol.) was carried out at different crystallization temperatures, *viz.* 20°, 15°, and 10°C for each at 1 h only. No fractions were obtained at 20°C temperature but fractionation was observed to be rapid and reproducible at 15°C and 10°C respectively. The yield of olein and stearin fractions obtained as included in the Table 2, depends on the ratio of oil and solvent used, and also on crystallization temperatures.

Table 1: Some analytical characteristics including Fatty acid composition of Coconut oil

	Slip melting point (° C)	Iodine value	Saponification value
Coconut oil	24.40±0.36	8.47±0.32	260.33±4.04

Fatty acid (%w/w)	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2
	3.72± 0.03	4.77± 0.01	51.0 ± 0.02	21.65± 0.03	9.60± 0.03	2.35± 0.01	5.47± 0.01	1.46± 0.02

Results have been expressed as mean ± SD (n=3).

Table 2: Yield %, Slip melting point, Iodine value and Saponification value of Coconut olein and stearin fractions

	oil:solvent (wt/v)	olein(15°C)	stearin(15°C)	olein(10°C)	stearin(10°C)
Yield (%w/w)	1:3	29.02± 0.42^a	70.97± 0.42^c	26.27± 0.26^a	73.72± 0.26^c
	1:4	44.35± 0.22^b	55.64± 0.22^b	40.30± 0.26^b	59.70± 0.26^b
	1:5	54.34± 0.43^c	45.65± 0.43^a	48.63± 0.31^c	51.36± 0.31^a
Melting point (°C)	1:3	20.63± 0.15^a	28.33± 0.58^c	19.16± 0.15^a	28.66± 0.29^c
	1:4	22.66± 0.58^b	27.66± 0.29^b	21.70± 0.26^b	27.93± 0.12^b
	1:5	25.40± 0.17^c	27.00± 0.10^a	23.83± 0.29^c	27.73± 0.25^a
Iodine value	1:3	8.70± 0.17^a	6.20± 0.26^a	8.96± 0.06^b	5.99± 0.27^a
	1:4	11.00± 0.43^c	5.31± 0.73^a	13.42± 0.42^c	7.35± 0.69^c
	1:5	8.90± 0.26^b	6.02± 0.32^a	8.90± 0.26^a	6.02± 0.33^b
Saponification value	1:3	281.33± 3.51^c	256.00± 4.00^a	284.33±1.15^c	254.33±2.08^b
	1:4	272.33± 3.79^b	258.66± 3.51^a	283.00±2.00^b	251.66±2.08^a
	1:5	264.33± 3.21^b	257.33± 1.15^a	273.00±2.00^a	259.66± 1.53^c

Results have been expressed as mean ± SD (n=3).
For all data in Table 2, Mean Values having different superscript letter in columns are significantly different ($p<0.05$). Values having same superscript letter in columns are not significantly different ($p<0.05$).

The yield of olein fractions increases with the corresponding decrease in stearin fractions at constant temperature, as the volume of solvent increases from 1:3 to 1:5 wt/vol. This may be explained by the fact that the solubility of some of the triglycerides comprising saturated fatty acids of chain length longer than the medium chain fatty acid increases in isopropanol and olein is best separated with the higher volume of solvent (1:5 wt/vol.). The olein obtained from 1:3 wt/vol. is suitable from health point of view but 1:4 wt/vol. is considered to be better from both health and cost aspects based on the fatty acid composition that contains more Capric and Caprylic acids. Crystallization at both 15°C and 10°C temperature at constant ratio of oil and solvent shows decreasing amount of olein fractions with the subsequent increase in the corresponding stearin fractions with varying temperature from 15°C to 10°C.

The melting point of olein fractions increases and corresponding stearin fractions decreases at constant temperature with the increasing volume of solvent from 1:3 to 1:5 wt/vol. In decreasing the crystallization temperature from 15°C to 10°C, melting point of olein fractions decreases and corresponding stearin fractions increases due to increased amounts of the saturated acids of higher molecular size than the medium chain triglycerides in the fractions.

The iodine value of fractions of coconut oil as shown in table 2 shows that the olein fraction has the higher amount of iodine value than the corresponding stearin fraction at constant temperature but the values have varied with different ratio of oil and solvent (1:3, 1:4 and 1:5 wt/vol.). The iodine value increases with olein fraction but decreases with stearin with lowering the crystallization temperature from 15°C to 10°C. The iodine value of olein fractions increases as expected and the highest was observed with 1:4 wt/vol. ratio at constant temperature, which may be explained by the fact that the unsaturated fatty acid containing glycerides concentrated relatively more in olein fraction while the saturated fatty acids containing glycerides concentrated in the stearin fractions.

The determination of saponification value of coconut oil's fractions were made and the values were indicated in table 2.The olein fraction obtained at 15°C using oil and Isopropanol in 1:3wt/v ratio has the saponification value of 281and the corresponding stearin fraction has the saponification value of 256 as the short chain saturated fatty acid containing glycerides were concentrated relatively more in olein fraction than the respective stearin fraction containing the long chain saturated fatty acid containing glycerides.

Table 3: Fatty acid composition (%w/w) of Coconut olein and stearin fractions obtained at 15°C with varying oil:solvent (wt/v)ratios:

Fatty acids (%w/w)	olein (15°C)fractions			stearin(15°C)fractions		
	1:3	1:4	1:5	1:3	1:4	1:5
8:0	3.94± 0.14^{b}	3.25± 0.05^{a}	6.25± 0.05^{c}	2.34± 0.14^{a}	4.13± 0.03^{c}	2.92± 0.03^{b}
10:0	4.41± 0.01^{a}	4.72± 0.03^{b}	5.43± 0.05^{c}	4.05± 0.09^{a}	4.66± 0.09^{c}	4.20± 0.04^{b}
12:0	47.45± 0.33^{a}	47.5± 0.20^{a}	47.92± 0.11^{a}	43.53± 0.06^{a}	48.97± 0.10^{c}	46.81± 0.12^{b}
14:0	23.47± 0.06^{c}	17.28± 0.07^{a}	18.69± 0.09^{b}	22.55± 0.09^{b}	23.40± 0.02^{c}	21.82± 0.03^{a}
16:0	11.31± 0.10^{b}	13.73± 0.15^{c}	8.51± 0.01^{a}	13.86± 0.04^{c}	9.40± 0.01^{a}	9.86± 0.09^{b}
18:0	2.26± 0.14^{a}	2.40± 0.01^{b}	2.73± 0.01^{c}	5.63± 0.05^{c}	2.92± 0.03^{b}	2.74± 0.05^{a}
18:1	5.07± 0.06^{a}	9.52± 0.02^{c}	7.90± 0.02^{b}	6.40± 0.01^{b}	5.19± 0.16^{a}	6.75± 0.05^{c}
18:2	2.19± 0.07^{b}	1.6± 0.01^{a}	2.57± 0.07^{c}	1.64± 0.07^{b}	1.33± 0.05^{a}	4.90± 0.05^{c}

Results have been expressed as mean ± SD (n=3).

For all data in Table 3, Mean Values having different superscript letter in rows are significantly different ($p<0.05$). (for olein and stearin separately)

Table 4: Fatty acid composition (%w/w) of Coconut olein and stearin fractions obtained at 10°C with varying oil:solvent (wt/v)ratios:

Fatty acids (%w/w)	olein (10°C) fractions			stearin(10°C) fractions		
	1:3	1:4	1:5	1:3	1:4	1:5
8:0	1.76 ± 0.02^{b}	4.73 ± 0.04^{c}	1.36 ± 0.25^{a}	1.49 ± 0.03^{b}	1.85 ± 0.01^{c}	1.47 ± 0.02^{a}
10:0	4.38 ± 0.03^{b}	5.47 ± 0.04^{c}	4.19 ± 0.02^{a}	4.83 ± 0.02^{c}	4.12 ± 0.07^{b}	3.79 ± 0.59^{a}
12:0	48.44 ± 0.10^{b}	47.48 ± 0.07^{a}	52.01 ± 0.07^{c}	51.98 ± 0.02^{c}	48.42 ± 0.13^{b}	46.48 ± 0.03^{a}
14:0	21.94 ± 0.07^{c}	17.98 ± 0.05^{a}	20.51 ± 0.22^{b}	23.43 ± 0.06^{b}	23.71 ± 0.12^{c}	22.08 ± 0.14^{a}
16:0	9.71 ± 0.02^{c}	8.59 ± 0.02^{a}	8.63 ± 0.05^{b}	9.30 ± 0.06^{a}	10.17 ± 0.29^{b}	13.62 ± 0.21^{c}
18:0	3.00 ± 0.05^{c}	2.93 ± 0.02^{b}	2.56 ± 0.06^{a}	2.79 ± 0.02^{a}	3.14 ± 0.24^{b}	3.27 ± 0.03^{c}
18:1	8.43 ± 0.05^{a}	9.73 ± 0.05^{c}	8.47 ± 0.03^{b}	4.92 ± 0.03^{a}	6.78 ± 0.05^{b}	7.19 ± 0.02^{c}
18:2	2.34 ± 0.10^{b}	3.06 ± 0.10^{c}	2.27 ± 0.07^{a}	1.26 ± 0.02^{a}	1.81 ± 0.02^{b}	2.10 ± 0.17^{c}

Results have been expressed as mean ± SD (n=3).
For all data in Table 4, Mean Values having different superscript letter in columns are significantly different ($p<0.05$) (for olein and stearin separately).

The olein fractions displayed a distinct variation in the fatty acid compositions (shown in Table 3 and Table 4). Both Caprylic acid ($C_{8:0}$) and Capric acid ($C_{10:0}$) content increased in olein fractions compared to original coconut oil whereas decreased in corresponding stearin fractions. The concentration of short chain saturated fatty acids was found to be increased in olein fraction with the decrease in temperature during crystallization from 15°C to 10°C, but the concentrations were found to be decreased in olein fraction as the volume of solvent increased during crystallization from 1:3wt/vol. to 1:5 wt/vol.

IV. CONCLUSION

The fractionation of coconut oil from isopropanol as a solvent was done at different temperatures (10°,15° and 20°C) with different volume of solvent ratio (1:3,1:4 and 1:5 wt/vol.). The crystallization was quite prompt as isopropanol had readily formed crystals while fractionating coconut oil. It is evident from the study that coconut oil can be fractionated with the help of a bio-renewable polar solvent like isopropanol to readily produce oleins rich in medium chain fatty acids and stearin fractions. The olein fractions thus obtained can be used to formulate different food products especially spread like products enriched in medium chain fatty acids. Isopropanol as a fractionating solvent in comparison with acetone and hexane is quite promising from industrial point of view as the recovery of isopropanol was very much convenient, temperature required for crystallization was relatively high and time involved also was much less.

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