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Characterization of Cocoa Butter Equivalent from Formulated Hard Palm Oil Mid-fraction and Canola Oil Blend

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Abstract. A search for an alternative to cocoa butter (CB) has increased due to premium price, uncertainty in supply and variability in quality problems. The study to find cocoa butter equivalent (CBE) as an alternative to CB from available and high nutritional oils or fats was carried out using enzymatic interesterification method. The objective of this study was to characterize the CBE obtained from hard palm oil mid-fraction (PMF) and canola oil blend using immobilized lipase from *Rhizomucor miehei*. The experiment was performed at hard PMF concentration of 50%, lipase load of 7.2% (based on weight of substrate) and reaction time of 2 hours. The characteristics observed were fatty acid profiles, triacylglycerol (TAG) composition, slip melting point (SMP) and solid fat content (SFC). CBE obtained exhibit higher percentage of linoleic acid (omega 6, 7.98%) and linolenic acid (omega 3, 2.47%) than CB (3.40% of linoleic acid) due to the addition of canola oil. TAG composition was 28.65% of palmitic-oleic-palmitic (POP), 19.52% of palmitic-oleic-stearic (POS), and 3.57% of stearic-oleic-stearic (SOS). SMP value of CBE (46.25°C) was higher than CB (32 – 35°C). The SFC value of CBE was different to CB. It was due to high amount of POP TAG, free fatty acid (FFA) or saturated saturated saturated (StStSt) TAGs in CBE produced and also lack amount of TAGs which has oleic acid at sn 2 position.

1. Introduction

Cocoa butter (CB) is a natural fat that responsible for the flavor, smooth texture, and gloss of the confectionary and chocolate product. It is due to its specific characteristic and unique composition. Moreover, these advantages make CB expensive and highly valued compared to other natural vegetable oils and fats [1,2]. Variability in quality, uncertainty in supply as well as high and fluctuated price has led the industry to find alternatives either for partial replacement or full replacement of CB. One of the alternatives is cocoa butter equivalents (CBEs). CBE is a non-lauric fat, which has similar physicochemical characteristics as CB and can be blended with CB without changing its properties.

CBE could be produced by using enzymatic interesterification method. Enzymatic interesterification is preferable because it offer widely usage of oil and fat [3,4]. Previous research has been using enzymatic interesterification to produce CBE from various mixtures of oil and fat [5-10]. Most of the study mentioned did not measure the fatty acid content in CBE [5-9]. Even though, the fat and oil used contains high nutrition and could improve the nutritional value of CBE. Therefore,



current study tried to combine hard PMF and canola oil to obtain high nutritional CBE by using enzymatic interesterification method. Hard PMF was used due to it has high content of POP and nearly similar melting characteristic to CB [11]. Blending with canola oil was aim to improve the nutritional value of CBE, because it contains oleic acid and a balanced ratio (2:1) of linoleic (omega-6) and linolenic acid (omega-3) [12]. By modifying the oil and fat using enzymatic interesterification, it was expected this technique would not alter the nutritional value. Furthermore, it would improve the commercial benefit of the product.

2. Methods

2.1. Materials

The materials used in this study were Hard PMF (IV 35.3) (Sime Darby Kempas Sdn. Bhd.), canola oil (Lam Soon Edible Oils Sdn. Bhd., lipase RM IM, a sn-1,3 specific immobilized lipase from *Rhizomucor miehei* (RML, EC.3.1.1.3, Sigma-Aldrich) and stearic acid (Qrec).

2.2. Enzymatic Interesterification

Hard PMF was melted and then blended with canola oil using 50% (w/w) ratio. The total reaction mixture was 20 grams. After that, the mixture was blended with stearic acid at 5:4 (w/w). Then, 7.2% (based on weight of substrate) of lipase was added to start the reaction. Reaction condition was 68 – 70°C with mechanical agitation at 200 rpm (Pol-Eko aparatura, EU). After 2 hours, the stirrer was turned off for 1-2 minutes till the enzyme particles sediment. CBE were taken from the top of the mixture and then it stored in the freezer at -18°C before analyzed.

2.3. Analysis of Fatty Acid Profile

Fatty acid profile was analyzed based on Whitaker [13] by using GC (Agilent 6890, Minnesota, USA). The column size was HP-88 60 m x 0.25 mm x 0.20 µm. The detector temperature was programmed at 250°C with detector flow 40 ml/min and carrier pressure 30 psig. The injector temperature was set at 110°C. Hydrogen was used as the carrier gas with nitrogen and compress air as make up gas. The peaks detected by the retention time were identified by comparing with standards under the same condition.

2.4. Analysis of Triacylglycerol (TAG) Composition

Triacylglycerol (TAG) was analyzed by GC (Agilent 6890 N, Minnesota, USA) [14] equipped with flame ionization detector. The column size was 30 m x 0.25 mm x 1.0 µm. Inlet temperature was programmed at 336°C with detector flow 2 ml/min and carrier pressure 23.8 psig. The injector temperature was set at 360°C. Hydrogen was used as the carrier gas with nitrogen and compress air as make up gas.

2.5. Analysis of Slip Melting Point (SMP)

Slip melting point (SMP) was analyzed based on AOCS official methods Cc 3-25 [15].

2.6. Solid Fat Content (SFC)

Solid fat content (SFC) value was analyzed based on PORIM method [16]. Pulsed nuclear magnetic resonance (pNMR) (Bruker, Karlsruhe, Germany) was used to measure the value.

3. Results and discussion

3.1. Fatty Acid Profile

The fatty acid profiles of initial mixture, CBE, commercial CBE and CB are given in Table 1. It shows that palmitic, stearic and oleic was three major fatty acids in the initial mixture, CBE, commercial CBE, and CB [2]. The CBE contained a higher percentage of palmitic acid and lower percentage of stearic acid than CB and those values were significantly different. Moreover, the percentage of oleic

acid in current CBE was not significantly different to CB. These results were consistent with findings reported by Lipp *et al.* [1].

CBE produced in this study contained higher and significantly different percentage of linoleic acid and linolenic acid than CB and commercial CBE. It means that the nutritional value of CBE was improved due to the canola oil additions. Furthermore, enzymatic interesterification could retain the nutritional value in the final product. It proves that enzymatic interesterification was suitable method to enrich lipids with specific fatty acids in order to improve the nutritional properties of fats and oils or to produce structured lipids in medical foods [17].

Table 1 shows that no significant difference between fatty acid in initial mixture (before interesterification) and CBE (after interesterification). This finding was similar to Li *et al.* [4] research in producing zero trans shortening fats. There were no significant statistical differences between the fatty acid composition of the high oleic sunflower oil and fully hydrogenated soybean oil blend (before interesterification) and enzymatic interesterified products.

Table 1. Fatty acid profiles of initial mixture, CBE and CB

| Fatty acid (% w/w) | Initial mixture (before interesterification) | CBE (after interesterification) | CBE (commercial)* | CB* |
|---------------------------------|----------------------------------------------|---------------------------------|------------------------------|------------------------------|
| Palmitic acid | 38.49±4.55 ^a | 37.26±2.58 ^a | 37.21±15.12 ^a | 26.23±0.38 ^a |
| Stearic acid | 13.85±0.92 ^a | 13.06±0.37 ^a | 25.02±14.82 ^{ab} | 35.76±0.87 ^b |
| Oleic acid | 35.37±1.81 ^a | 34.99±1.26 ^a | 33.29±1.15 ^a | 33.60±0.76 ^a |
| Linoleic acid (Omega-6) | 9.10±1.31^a | 7.98±0.92^a | 2.63±1.01^b | 2.68±0.34^b |
| Linolenic acid (Omega-3) | 2.99±0.69^a | 2.47±0.47^a | - | - |

*Source: Lipp *et al.* [2]

Note : similar code shows that the value is not different ($p > 0.05$)

different code shows that the value is significantly different ($p < 0.05$)

3.2. Triacylglycerol (TAG) Composition

TAG composition of CBE was shown in Table 2. It shows that the content of POS and SOS in the CBE were increased significantly compared to the initial mixture, while the content of POP decreased. It means that acyl exchange occurred between the palmitoyl group from the hard PMF and the stearoyl group from the stearic acid [18]. Soekopitojo *et al.* [18] came with similar findings. They produced CBE from PMF and fully hydrogenated soybean oil (FHSO) mixture. Content of the TAGs target (POS and SOS) in the interesterified blends were increased, whereas the main TAGs of PMF (POP and POO) and TAGs of FHSO (PSS, SSS) were decreased.

Table 2 TAG percentage of initial mixture, CBE, and CB

| TAG [%] | Initial Mixture (before interesterification) | CBE (after interesterification) | CBE (commercial)* | CB* |
|---------|----------------------------------------------|---------------------------------|--------------------------|-------------------------|
| POP | 48.32±0.42 ^a | 28.65±2.00 ^b | 41.58±23.36 ^b | 18.27±0.48 ^c |
| POS | 6.90±0.01 ^a | 19.52±0.96 ^b | 18.41±11.27 ^b | 42.08±0.83 ^c |
| SOS | 0.60±0.01 ^a | 3.57±0.11 ^b | 24.80±15.76 ^c | 26.39±1.26 ^c |

*Source: Lipp *et al.* [2]

Note : similar code shows that the value is not different ($p > 0.05$)

different code shows that the value is significantly different ($p < 0.05$)

According to Lipp *et al.* [2], commercial CBE generally contains higher percentage of POP, lower percentage of POS and similar percentage of SOS than CB. Current study had similar findings. The

CBE obtained had a higher percentage of POP and a lower percentage of POS compared to CB. Those values were significantly different. However, the percentage of SOS in current CBE was significantly lower compared to CB's. It has been observed that stearic acid was a poor acyl donor which was similar to the result of Ciftci *et al.* [6].

3.3 Slip Melting Point (SMP) and Solid Fat Content (SFC)

The SMP value of CBE was significantly higher (46.25°C) than CB (32-35°C). This condition could resolve the stability issues of CB at high temperature [22]. Higher melting profile would be advantageous for some application in coating fats [5]. The presence of saturated-saturated-saturated (StStSt), unsaturated-unsaturated-unsaturated (UUU), saturated-unsaturated-saturated (StUSt), and saturated-unsaturated-unsaturated (StUU) TAG content in fat were the main cause of high SMP value of CBE [20]. Since the SMP value alone could not reflect the melting profile of CBE, the measure of SFC was needed.

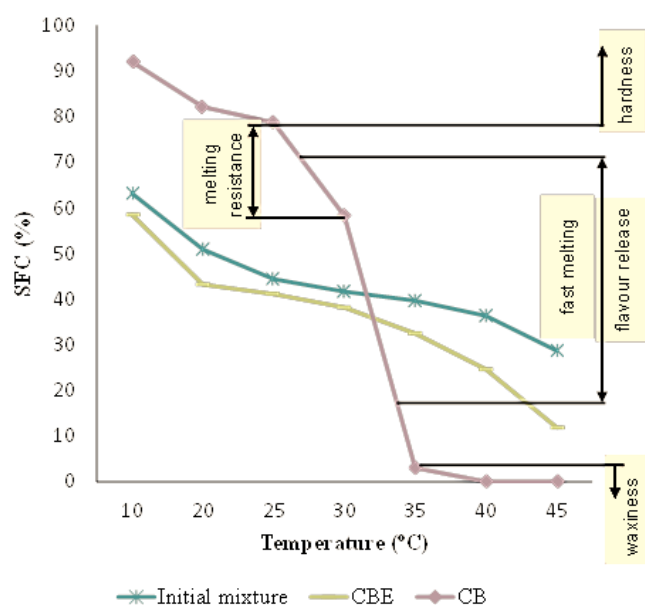


Figure 1. Trends of SFC value of initial mixture (before interesterification), CBE, and CB [1] as measured by pNMR

The SFC value shows the amount of solid fat present in a fat [19]. The trends of SFC value of CB was shown in Figure 1 and characterized by three typical zones [21]. SFC value below room temperature (25°C) shows the hardness of CBE, whereas the melting resistance is shown in SFC value between 25°C and 30°C. Figure 1 shows that initial mixture and CBE had lower melting resistance than CB. It indicated that both of fats were softer than CB. It was due to high amount of POP TAG in initial mixture (48.32%) and CBE (28.65%), while CB contain high amount of SOS TAG (26.39%). According to De Clerq [19], SOS melts at higher temperatures compared to POP.

SFC value between 25°C until 33°C shows the steepness melting profile of CB [21]. It was mostly affected by the presence of oleic acid at sn-2 position [21]. This melting profile contributes to the flavor release and cooling sensation in the mouth [19]. As shown in Figure 1, CBE did not show the steepness. It was due to lower amount of TAGs (51.74%) which has oleic acid at sn-2 position (POP, POS, and SOS) than CB (77.6% - 92.8%).

After 33°C, the SFC value of CB was close to 0%. Nevertheless, the SFC value of CBE at above 33°C was higher than CB. High SFC value at temperatures above 37°C (body temperature) is not desirable because it causes a waxy mouth feel [22, 23]. High amount of free fatty acid (FFA) or StStSt

TAGs might be the cause of it. To solve this problem, fractionation is needed to remove FFA and StStSt TAGs content in CBE [8].

4. Conclusion

The CBE produced in this study contained a higher percentage of palmitic acid, a lower percentage of stearic acid and nearly similar percentage of oleic acid than CB's. However, the percentage of linoleic and linolenic acid were higher than CB. Furthermore, CBE contains a higher percentage of POP, a lower percentage of POS and SOS. The SMP value of CBE was higher than CB and shows different melting profile to CB's. It was due to high amount of POP TAG, free fatty acid (FFA) or StStSt TAGs and lack amount of TAGs which has oleic acid at sn 2 position.

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