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Effect of fractional crystallization on the composition and thermal properties of engkabang (*Shorea macrophylla*) seed fat and cocoa butter

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RESUMEN

Efecto de la cristalización fraccionada sobre la composición y propiedades térmicas de grasas de semillas de engkabang *(Shorea macrophylla)* y de manteca de cacao

Se investigan los comportamientos de una cristalización fraccionada de la manteca de cacao (CB) y la grasa de enkabang (EF) en acetona. Las muestras fundidas de CB y EF se mezclaron por separado con acetona en una relación 1:02 (w/v) y se dividen en fracciones sólida y líquida bajo condiciones de temperatura controlada. Las fracciones aisladas se compararon con sus respectivas muestras nativas con respecto a diversos parámetros físico-químicos utilizando métodos químicos estándar, así como técnicas instrumentales, como la cromatografía gas-líquido (GLC), cromatografía líquida de fase inversa de alta resolución (RP-HPLC), y calorimetría de barrido diferencial (DSC). De acuerdo con los resultados, el fraccionamiento tanto de CB como EF bajo condiciones de cristalización asistida con disolvente produjo una fracción sólida mayoritaria y una fracción líquida minoritaria. Ambas fracciones sólidas y líquidas de ambas grasas mostraron muchas similitudes, y pocas diferencias con respecto a su composición y propiedades térmicas. Mientras que las fracciones sólidas pueden ser útiles por su acción de fuerza en una margarina dura y formulaciones cosmética, la fracción líquida sería útil como ingrediente para aplicaciones alimentarias.

PALABRAS CLAVE: Análisis térmico – Cristalización – Estearina de cacao – Grasa de Engkabang – Manteca de cacao.

SUMMARY

Effect of fractional crystallization on composition and thermal properties of engkabang *(Shorea macrophylla)* seed fat and cocoa butter

The fractional crystallization behaviors of cocoa butter (CB) and enkabang fat (EF) in acetone were investigated. Melted samples of CB and EF were mixed separately with acetone in 1:2 a (w/v) ratio and partitioned into solid and liquid fractions under controlled temperature conditions. The isolated fractions were compared to their respective native samples with respect to various physico-chemical parameters using standard chemical methods as well as instrumental techniques such as gas liquid chromatography (GLC), reversed-phase high performance liquid chromatography (RP-HPLC), and differential scanning calorimetry (DSC). According to the results, partitioning of either CB or EF under solvent assisted crystallization conditions yielded a major solid and a minor liquid fraction. The solid and liquid fractions of both fats were found to display many similarities, but few differences with regard to their composition and thermal properties. While the solid fractions may be useful as a hard stock in hard margarine and cosmetic product formulation, the liquid fraction would be useful as an ingredient for food applications.

KEY-WORDS: Cocoa butter – Cocoa stearin – Engkabang fat – Fractional crystallization – Thermal analysis.

1. INTRODUCTION

Hard stocks are hardened fat substances required for industries to formulate various consumer products. In the past, the hydrogenation of liquid vegetable oils was the most popular industrial process to produce hard stocks of various kinds. For instance, the hydrogenation of canola (Eskin *et al.,* 1996), soybean, peanut, and cotton seed oils (de Man, 1990) were useful for producing hard margarines with varying degrees of solid fat content. However, the use of hydrogenation to convert liquid oil to solid fat has become a less attractive option due to the negative health effect of *trans* fatty acids formed during partial hydrogenation (Miskandar and Nor Aini, 2010; Reddy and Jeyarani, 2001). Alternatively, state-of-the art developments in fractional crystallization have paved the way for the production of hard stocks to meet the varying demands of the industry. As of date, considerable progress has been made in the fractionation of semi-solid fats such as palm oil (Che Man *et al.,* 1999), avocado butter (Yanty *et al.,* 2013), milk fat (Campos *et al.,* 2003), lard (Yanty *et al.,* 2011), mee fat (*Madhuca longifolia*) (Marikkar *et al.,* 2010), etc. In spite of their brittle and hard texture, the fractionation of stearic acid-rich fats such as CB, mahua fat (*Madhuca latifolia*), kokum fat (*Garcinia indica*), and phulwara butter (*Madhuca butyracea*) has been feasible to some extent. According to past literature, Devitt and Weyland (1991) patented a process for the fractionation of CB to separate olein and stearin fractions, which were useful for chocolate filling or chocolate coating. Studies on fractional crystallization of *Mahua* fat (Reddy and Jeyarani, 2001) and phulwara butter (Reddy and Prabhakar, 1994) were undertaken to isolate hard stocks to be used as components in the preparation of cocoa butter extenders. However, past investigations on the fractionation behavior of EF, which is the seed fat of *Shorea macrophylla* are still limited. Despite the use of EF for food, therapeutic and cosmetic purposes by the natives of the Borneo in the eastern part of Malaysia, its utilization has not been commercially expanded probably due to the lack of technical information with regard to its properties and potential uses. Although the composition and solidification behavior of EF was reported earlier in a preliminary study (Nesaratnam and Mohd Ali, 1992), the thermal behavior and compositions of its fractionated products were not given in detail. This kind of information would be highly useful when searching for specialty fats to be used as hard butters. Hence, in this study, it was attempted to isolate the hard stock and liquid fraction from EF and CB to assess their thermal properties for uses in food and cosmetic applications.

2. MATERIALS AND METHODS

2.1. Materials

Dried seeds of engkabang (*Shorea macrophylla*) were collected from three different locations in the Sarawak region of Malaysia. Three samples of prime processed CB *(Theobroma cacao*) were purchased from the Malaysian Cocoa Board. All chemicals used in this experiment were either analytical or HPLC grade unless otherwise specified.

2.2. Oil extraction

The extraction of oil from finely ground samples of Engkabang seeds was carried out using the soxhlet extraction method with petroleum ether (40-60 °C) (AOAC, 2007). The extracted oil samples were kept in an oven at 60 °C for 1 h to expel solvent before storing at –20 °C. Before analysis, the oil samples were removed from frozen storage, and left static at room temperature for 1 h and then warmed at 60 °C until they became completely molten.

2.3. Fractional crystallization of CB and engkabang fat

One hundred gram portions of the melted samples of EF and CB were mixed separately with acetone in a 1:2 (w/v) ratio. The solutions were boiled at 60 °C until they became uniformly dissolved, and then were left at 5 ± 1 °C for 1 h to crystallize. The precipitated fats were filtered off to give high-melting fractions called cocoa stearin (CBS) and engkabang stearin (EBS). The filtered mother-liquors were recrystallized at 25 ± 1 °C for 24 h to allow the remaining solid to precipitate. After removing the precipitate, the mother-liquors were evaporated under reduced pressure to yield liquid fractions known as cocoa olein (CBO) and engkabang olein (EFO) (Yanty *et al,* 2013; Marikkar *et al,* 2010).

2.4. Determination of slip melting point (SMP) and iodine value (IV)

SMP and IV of the fat samples were determined according to the AOCS method Cc.3.25, and AOCS method Cd Id-92, respectively (AOCS, 1999).

2.5. Determination of fatty acid composition

Fatty acid methyl esters (FAME) were prepared by dissolving a 50 mg portion of oil in 0.8 ml of hexane and adding a 0.2 ml portion of 1M solution of sodium methoxide (PORIM, 1995). This mixture was then analyzed on a gas chromatograph (Agillent Technologies, Singapore) fitted with an FID detector. All the instrumental conditions were as described in the previous report of Yanty *et al.* (2012). The identification of the peaks of the samples was done with reference to a chromatographic profile containing FAME standards (Supelco, Bellefonte, PA). The percentage of fatty acids was calculated as the ratio of the partial area to the total peak area.

2.6. Determination of TAG composition

The TAG composition was determined using a Waters Model 510 liquid chromatography equipped with a differential refractometer Model 410 as the detector (Waters Associates, Milford, MA). All the instrumental conditions including the type of column were as described in a previous report by Yanty *et al.,* (2012). The identification of the TAG peaks of the samples was done using a set of TAG standards purchased from Sigma-Aldrich (Deisehofen, Germany) and in accordance with the TAG profiles of cocoa butter (Yanty *et al.*, 2012), and *Madhuca longifolia* seed fat (Marikkar *et al.*, 2010) reported previously.

2.7. Thermal analysis by differential scanning calorimetry (DSC)

Thermal analysis was carried out on a Mettler Toledo differential scanning calorimeter (DSC 823 Model) equipped with a thermal analysis data station (STARe software, Version 9.0x, Schwerzenbach, Switzerland). All the instrumental conditions including the sampling procedure were as described in the previous report by Yanty *et al.,* (2012). The onset (°C) is the temperature where the extrapolated leading edge of the endotherm intersects with the baseline. The value of each DSC parameter used in this work was obtained as illustrated in Tan and Che Man (1999).

2.8. Determination of solid fat content

A solid fat content (SFC) measurement of samples was carried out using a Bruker Minispec (Model Mq 20) pulse Nuclear Magnetic Resonance (pNMR) spectrometer (Karlsruhe, Germany) according to AOCS (1999). All the instrumental conditions including the sampling procedure were as described in the previous report by Yanty *et al.* (2012).

2.9. Statistical analysis

In all analyses, three replicates were used and the results were expressed as the mean value ± standard deviation. The data were statistically analyzed by one-way analysis of variance (ANOVA), using Tukey's Test of MINITAB (version 15) statistical package at a 0.05 probability level.

3. RESULTS AND DISCUSSION

3.1. The slip melting point and iodine value

The SMP and IV of the two fats and their fractions are compared as shown in Table 1. The SMP and IV of CB were 35.65 and 34.0, respectively, which are within the ranges specified by the MCB (2000) guidelines. In the case of EF, SMP and IV were 37.25 and 30.5, respectively. These were closely similar to those reported previously for EF (Nesaratnam and Mohd Ali, 1992). Upon fractionation, the SMP of the hard stocks were found to increase slightly with the concurrent reductions in their IV. In the case of liquid fractions, changes in the values of SMP and IV occurred inversely with respect to the native samples. As the SMP value of CBS is below the physiological temperature, it can still be directly used in edible applications such as fat components in the confectionery industry. On the other hand, the SMP value of EFS is found to exceed the physiological temperature. However, its value is within the range of the commercially available palm sterine that may be useful as a raw material for the preparation of either hard margarine or commercial shortenings (Miskandar and Nor Aini, 2010). Apart from this, the increasing melting temperature of hard stock would be a useful property for the fat ingredients in lipsticks. The SMP and IV of liquid fractions (CBO/EFO) were significantly ($p < 0.01$) lower than those of the native samples. These fractions may not be directly comparable to the properties of palm olein derived from palm oil since their SMP values were remarkably higher than those of the liquid edible oils. Instead, they could be used in fat blend preparations suitable for the manufacturing of soft margarine (Miskandar and Nor Aini, 2010).

3.2. Fatty acid composition

The fatty acid (FA) profiles of EF/ CB and their fractions are compared in Table 2. Both CB and EF were found to possess oleic, stearic, and palmitic as their major FA comprising more than 96% of the total. In both fats, stearic acid (37.91-47.83 %) was the most dominant fatty acid followed by oleic (31.83-32.49%) and palmitic (16.92-26.34%) acids. When compared to CB, higher proportions of stearic acid and lower amounts of oleic and palmitic acids were found in EF. Because of this, the IV of EF was significantly lower than that of CB. In both fats, linoleic (1.00-2.75%) and arachidic (1.17-2.10%) acids were found in very minute amounts. These results are in accordance with the findings reported in previous studies (Nesaratnam and Mohd Ali, 1992). The characteristic fatty acid distributional pattern of the two native samples was found to change by fractionation as there were considerable deviations in the fatty acid profiles of the solid and liquid fractions (Table 2). In both fats, the saturated fatty acid (SFA) contents of low-melting fractions decreased with a concurrent increase in the USFA content. Naturally, with the reduction of more steric acid, the liquid phases of both fats were to become more enriched with oleic acid (Table 2). On the other hand, the SFA and USFA contents of the two high-melting fractions of both plant fats are found to undergo only slight differences. For instance, the changes taking place in the stearic and oleic acid contents of the high-melting fractions is merely around 1-2%. This is, in fact, quite different from

Table 1

Yield, iodine value, and slip melting points of fractions derived from cocoa butter and engkabang fat[1]

Sample Code	IV ± SD	SMP ± SD (°C)	Yield (%, W/W)
CB	34.00 ± 1.41	35.65 ± 0.06	–
CBS	32.50 ± 0.71	36.45 ± 0.35	94.5
CBO	43.15 ± 0.50	26.75 ± 0.35	5.5
EF	30.50 ± 0.71	37.25 ± 0.45	–
EFS	28.10 ± 0.57	38.5 ± 0.35	96.0
EFO	44.75 ± 0.64	25.50 ± 0.71	4.0

[1] Abbreviations: CBS, cocoa stearin; CB, cocoa butter; CBO, cocoa olein, EFS, engkabang stearin; EF, engkabang fat; EFO, engkabang olein.

Table 2
Basic physico-chemical characteristics and fatty acid compositions (%) of cocoa butter and engkabang fat and their fractions[1]

	Fatty acid (%)						
	C 16:0	**C 18:0**	**C 18:1**	**C 18:2**	**C 20:0**	**SFA**	**USFA**
CBS	26.21 ± 0.16^{b}	38.76 ± 0.37^{c}	31.97 ± 0.28^{c}	2.46 ± 0.04^{d}	0.60 ± 0.14^{d}	65.57	34.43
CB	26.34 ± 0.14^{b}	37.91 ± 0.14^{d}	31.83 ± 0.28^{c}	2.75 ± 0.06^{c}	1.17 ± 0.01^{c}	65.42	34.58
CBO	29.97 ± 0.19^{a}	23.99 ± 0.04^{e}	40.12 ± 0.05^{b}	5.92 ± 0.00^{b}	–	53.96	46.04
EFS	16.92 ± 0.22^{d}	49.12 ± 0.04^{a}	30.92 ± 0.04^{c}	1.00 ± 0.01^{e}	2.04 ± 0.01^{b}	68.08	31.92
EF	16.58 ± 0.35^{d}	47.83 ± 0.13^{b}	32.49 ± 0.06^{c}	1.00 ± 0.02^{e}	2.10 ± 0.01^{a}	66.51	33.49
EFO	21.48 ± 0.13^{c}	24.87 ± 0.01^{e}	44.29 ± 0.03^{a}	8.26 ± 0.01^{a}	1.10 ± 0.00^{c}	47.45	52.55

[1] Each value in the table represents the mean of three replicates. Means within each column bearing different superscripts are significantly ($p < 0.05$) different.
Abbreviations: SFA, saturated fatty acid; USFA, unsaturated fatty acid. For other abbreviations see Table 1.

the fractionation behavior of palm oil (Che Man *et al.,* 1999) and mee fat (Marikkar *et al.,* 2010) as reported previously. It is because palm oil and mee fat were composed of TAG molecular species with widely differing melting properties.

3.3. TAG composition

Comparative TAG profiles of CB/EF and their fractions are presented in Table 3. As a common feature, the TAG profiles of EF and CB were found to possess POP, POS, and SOS as their major TAG molecular species comprising 88 – 92% of the total. While CB was found to have POS (40.78%) as the most dominant TAG followed by SOS (29.35%) and POP (18.08%), EF was found to possess SOS (49.98%) as the most dominant TAG followed by POS (35.58%) and POP (7.27%). The observed difference in the TAG distributional patterns of CB and EF were in accordance with the findings reported in previous studies (Nesaratnam and Mohd Ali, 1992). The characteristic TAG distributional patterns of the two native fats were found to be changed by fractionation since the TAG profiles of the liquid and solid fractions obtained after fractionation show considerable deviations from those of the native samples (Table 3). In the liquid fractions of both plant fats, the TAG molecular species namely SOO, POO and another unknown TAG experienced increments while TAG species such as POS and SOS have undergone decreases. While the liquid fraction of EF showed an increase in the proportion of POP, that of CB displayed a decline. The relative increase in the proportion of di-unsaturated and tri-unsaturated TAG molecules would have led to the increase in the oleic acid contents and IV of the two liquid fractions as shown in Tables 1 and 2. In the solid fractions of both fat, the TAG species POS experienced increments while the TAG species SOS experienced reductions. Meanwhile marginal changes were also observed in the proportions of TAG species such as OOO, SOS, etc. (Table 3).

3.4. Thermal characteristics

DSC cooling characteristics. The DSC cooling curves of CB and EF with their fractions are presented in Figures 1 and 2, respectively. The cooling profile of CB was found to have a single exothermic thermal transition at 13.45 °C with a shoulder peak appearing at 18.70 °C. This is similar to the cooling profile of CB reported previously (Yanty et al., 2012). As explained in our previous report, the thermal profile of CB with single thermal transition is a unique feature when compared to those of palm oil (Yanty et al., 2012), and mee fat (Marikkar et al., 2010), which displayed two well-separated thermal transitions to represent high-melting (> 0) (HMG) and low-melting (< 0) (LMG) groups of TAG molecules. This could be due to the co-crystallization of TAG molecular species with similar melting points (Yanty et al., 2012; Tan and Che Man, 2000). Although the cooling profile of EF was also found to have a single exothermic thermal transition at 16.35 °C, it has two minute thermal transitions at 5.0 °C and 8.55 °C. This could be mostly due to TAG compositional differences between CB and EF as discussed before (Table 3). In fact, this difference in the crystallization behavior of these two plant fats may have some influence on their fractionation products under identical conditions.

The cooling profiles of liquid (CBO) and solid (CBS) fractions derived from CB are represented in Figure 1 by curves (A) and (C), respectively. The cooling profiles of liquid (EFO) and solid (EFS) fractions derived from EF are represented in Figure 2 by curves (D) and (E), respectively. Clearly, the fat derivatives demonstrated thermal features that were distinctly different from those of their respective native samples. While CBS was found to display a sharp major exothermic thermal transition at 15.0 °C, with two minor thermal transitions at 21.15 °C and 2.8 °C, CBO was found to display a broad thermal transition with its peak maximum at 7.3 °C. In the fractionation of EF, the solid fraction

Table 3
TAG composition of cocoa butter and engkabang fat and their fractions[1]

TAG	CBS	CB	CBO	EFS	EF	EFO
PLL	0.21 ± 0.04^{c}	0.27 ± 0.05^{b}	2.14 ± 0.10^{a}	–	–	0.29 ± 0.12^{b}
OOL	–	–	3.39 ± 0.01^{a}	–	–	0.44 ± 0.01^{b}
POL	0.56 ± 0.10^{c}	0.85 ± 0.11^{b}	1.89 ± 0.12^{a}	–	–	1.74 ± 0.22^{a}
PPL	1.11 ± 0.05^{c}	1.55 ± 0.08^{b}	3.26 ± 0.16^{a}	0.14 ± 0.01^{d}	0.15 ± 0.00^{d}	3.12 ± 0.12^{a}
OOO	1.87 ± 0.07^{c}	0.69 ± 0.06^{d}	2.38 ± 0.03^{b}	0.36 ± 0.01^{e}	0.12 ± 0.01^{f}	3.27 ± 0.01^{a}
POO	2.26 ± 0.03^{c}	2.27 ± 0.05^{c}	22.88 ± 0.02^{a}	0.41 ± 0.01^{e}	0.68 ± 0.01^{d}	15.99 ± 0.01^{b}
POP	16.51 ± 0.01^{b}	18.08 ± 0.01^{a}	3.84 ± 0.01^{d}	7.33 ± 0.03^{c}	7.27 ± 0.04^{c}	16.53 ± 0.04^{b}
StOO	2.48 ± 0.04^{d}	2.98 ± 0.10^{c}	28.08 ± 0.03^{b}	1.28 ± 0.01^{f}	1.38 ± 0.01^{e}	29.66 ± 0.05^{a}
POSt	43.23 ± 0.04^{a}	40.78 ± 0.10^{b}	5.49 ± 0.06^{f}	38.20 ± 0.08^{c}	35.58 ± 0.07^{d}	12.28 ± 0.03^{e}
PPSt	0.21 ± 0.01^{f}	0.41 ± 0.01^{b}	0.35 ± 0.01^{c}	0.23 ± 0.02^{e}	0.28 ± 0.01^{d}	0.98 ± 0.04^{a}
OOA	–	–	1.60 ± 0.11^{b}	–	–	1.70 ± 0.08^{b}
StOSt	29.55 ± 0.10^{c}	29.35 ± 0.12^{c}	0.92 ± 0.01^{e}	47.76 ± 0.05^{b}	49.98 ± 0.13^{a}	2.65 ± 0.01^{d}
StStSt	–	1.05 ± 0.21^{a}	–	0.36 ± 0.01^{b}	0.33 ± 0.02^{b}	–
StOA	0.98 ± 0.06^{b}	1.11 ± 0.08^{b}	–	3.69 ± 0.11^{a}	3.82 ± 0.12^{a}	–
Unknown	1.03	0.61	23.78	0.24	0.41	11.35
UUU	1.87	0.69	5.77	0.36	0.12	3.71
UUS	5.51	6.37	56.59	1.69	2.06	49.38
USS	91.38	90.87	13.51	97.12	96.80	34.58
SSS	0.21	1.46	0.35	0.59	0.61	0.98

[1] Each value in the table represents the mean of two replicates. Means within each row bearing different superscripts are significantly ($p < 0.05$) different. Abbreviations: O, oleic; P, palmitic; L, linoleic; St, stearic; U, unsaturated; S, saturated. For other abbreviations see Table 1.

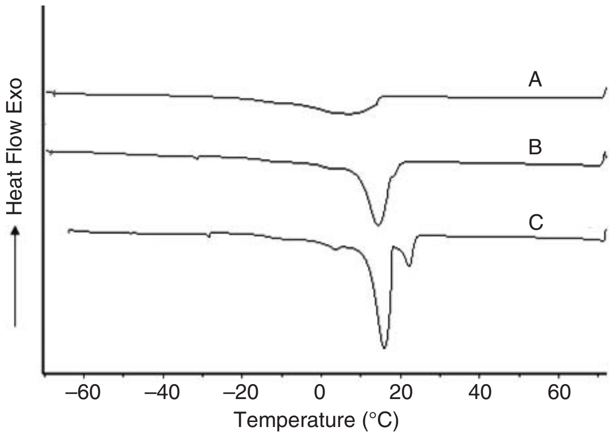

Figure 1
DSC cooling curves of cocoa olein (*curve-A*), cocoa butter (*curve-B*), and cocoa stearin (*curve-C*).

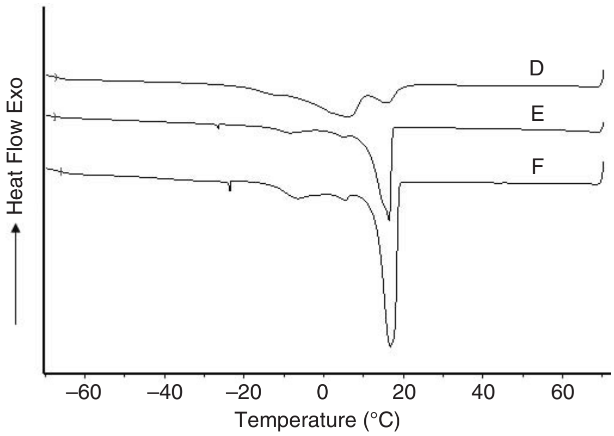

Figure 2
DSC cooling curves of engkabang olein (*curve-D*), engkabang fat (*curve-E*), and engkabang stearin (*curve-F*).

(EFS) showed a major sharp transition at 17.15 °C with two minor thermal transitions at 5.7 °C and –5.2 °C and its liquid fraction (EFO) showed a broad thermal transition with a duplex maximum at 15.8 °C and 5.7 °C. Apart from the changing pattern of the thermal transitions, there were significant shifts in the onset of crystallization of these fat derivatives with respect to the DSC parameters of the native samples. While the onset of crystallization of both high-melting fractions (CBS and EFS) shifted to higher temperatures, the onset of crystallization of low-melting fractions (CBO and EFO) was found to decrease. These changes in thermodynamic parameters could be attributed to the changing fatty acid and TAG compositions of these fat derivatives. According to the data presented in Tables 2 and 3, there were significant ($p < 0.05$) increases in the proportions of USFA and di-unsaturated TAG molecules in CBO and EFO. Certainly, increasing degree of unsaturation would cause a decrease in the thermal transition temperatures (Tan and Che Man, 2000). Likewise, increasing di-saturated and tri-saturated TAG molecular proportions has already been noticed for CBS and EFS (Table 3). For comparison and confirmation purposes, there is hardly any report giving the detailed compositional changes of the fractions of CB and EF. However, similar compositional changes have been reported in the fractionation of plant fats such as avocado butter (Yanty *et al.,* 2013), mee fat (Marikkar *et al.,* 2010). etc.

DSC melting characteristics. The DSC heating curves of CB and EF with their fractions are presented in Fig. 3 and Fig. 4, respectively. The heating profile of CB is found to have a single exothermic thermal transition at 21.1 °C with the endset at 24.95 °C. Overall, this is similar to the cooling profile of CB reported previously (Yanty *et al.,* 2012). On the other hand, the heating profile of EF was found to have a major transition at 26.60 °C and a minute transition at 33.65 °C with the endset at 35.25 °C. The availability of data on the DSC thermal characteristic of EF is scanty for any comparison purpose. The observed differences in their heating profiles were mainly due to the differences in their TAG distribution (Table 3). In addition, both of these fats did not display two well-separated endothermic transitions in high (> 0 °C) and low (< 0 °C) temperature regions of their heating curves as seen previously. These two fats not having major TAG species in a widely distributed temperature range could be attributed to this. This may have some effect on the heating profiles of their fractionations isolated under similar temperature conditions.

The curve (A) in Fig. 3 representing the high-melting fraction CBS was slightly different from that of the native CB sample. It is found to possess a single exothermic thermal transition at 19.05 °C with the endset at 30.65 °C. Possessing a shoulder peak at 27.85 °C and a higher end-set were features which differentiate it from the native sample. On the other hand, the low-melting fraction CBO, which is represented by curve (C) in Figure 3 differed drastically from the native CB sample in many respects. It had its major thermal transition in the lower temperature region at 7.2 °C and a minor broad transition with a peak maximum at 16.9 °C. The observed shifting of its thermal transition to the low temperature region could be directly connected to its TAG composition. With respect to the native CB sample, there was a drastic increase in the di-unsaturated TAG molecules (POO and SOO) with the concurrent decrease in di-saturated TAG molecules (POS and SSO) (Table 3).

As shown in Figure 4, the heating profiles of the high-and low-melting fractions of EF are represented by the DSC curves D (EFS) and F (EFO), respectively. Clearly, there were significant differences in the heating profiles of the two fractions with respect to the native sample. The curve D representing EFS displayed a narrow melting range with a sharp thermal transition at 27.05 °C with the end-set at 37.50 °C. The slight increases in the DSC thermodynamic parameters could be related to the increasing proportion of TAG molecules esterified with palmitic and stearic acids. According to the data presented in Table 3, the amount of POS in the EFS fraction has gone up by 2.62%. On the other hand, the heating curve displayed by EFO was completely different from those of either EF or EFS. For instance, the shifting of the peak maximum of thermal transitions toward the low temperature region was a noteworthy feature. Generally, a lowering of the transition temperatures is directly related to the increasing degree of unsaturation caused by TAG compositional changes (Tan and Che Man, 2000). As already pointed out, the unsaturated fatty acid content of EFO has gone up by 19.05% because of the increase in the proportion of di-unsaturated (OOS + OOP + PLO) TAG molecular species (49.38%) in EFO. It is a common phenomenon that the migration of more saturated TAG molecules into the solid phase would cause an elevation of unsaturated TAG molecules in the liquid phase.

Solidification behavior. The SFC profiles of CB and EF are compared with those of their fractions as shown in Figure 5. The SFC values of CB and EF at 0 °C were 93.24% and 93.18%, respectively.

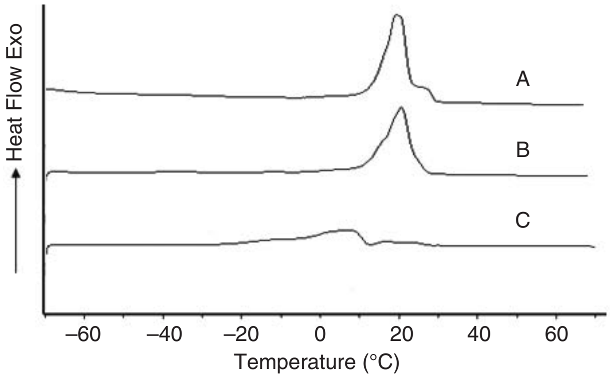

Figure 3
DSC heating curves of cocoa stearin (*curve-A*), cocoa butter (*curve-B*), and cocoa olein (*curve-C*).

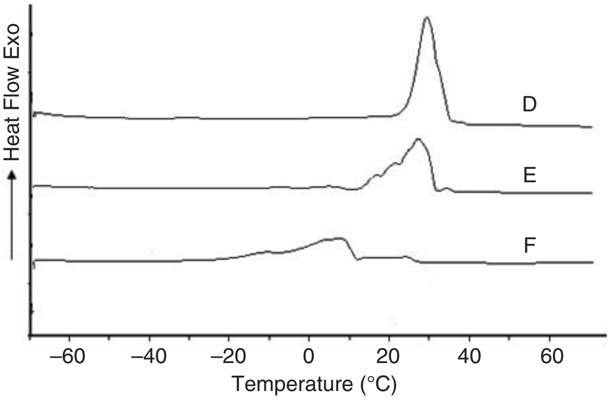

Figure 4
DSC heating curves of engkabang stearin (*curve-D*), engkabang fat (*curve-E*), and engkabang olein (*curve-F*).

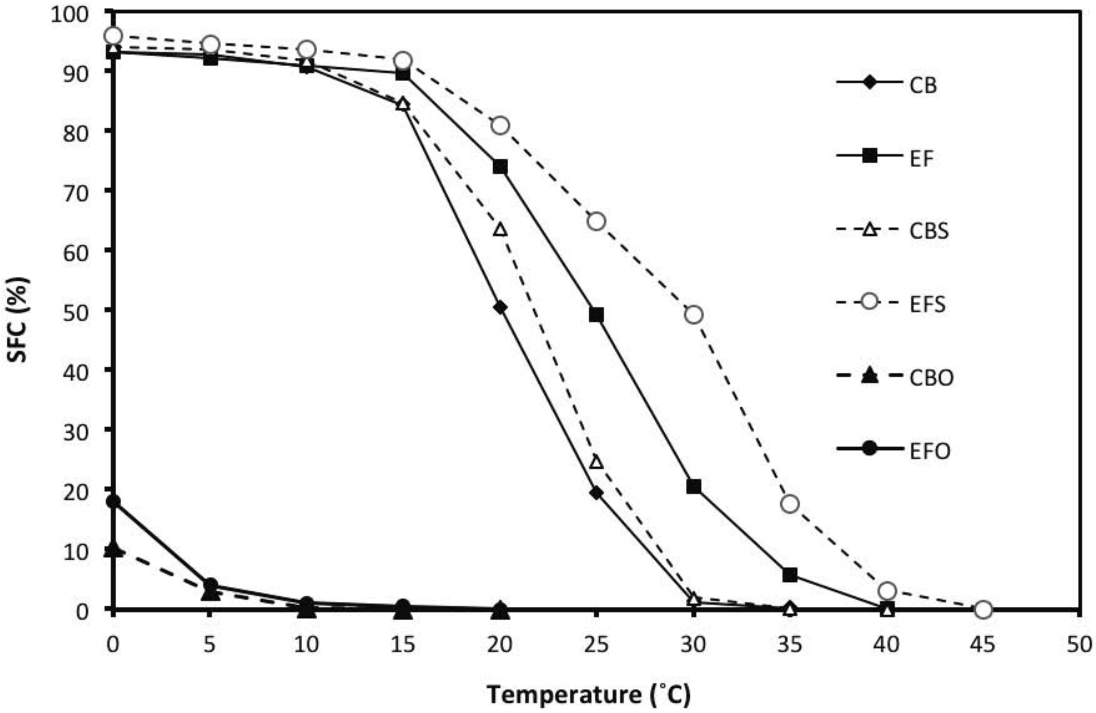

Figure 5
Solid fat content (SFC) profiles of cocoa butter (CB), engkabang fat (EF), and their fractionated products.

In between 0 to 10 °C, both of these fats had similar SFC profiles. However, they were found to differ in their solidification behavior between 10-40 °C. EF always showed a higher SFC value within this temperature range. The observed dissimilarities in the SFC values of these two fats in the range of 10-40 °C could be due to the distribution of TAG molecular species in them. For instance, when EF was found to possess higher proportions of di-saturated TAG species (USS), CB was found to have higher amounts of di-unsaturated TAG species (UUS). Because of these TAG compositional differences, both of these fats were found to display some differences in their fractionation behavior. Within the 10-40 °C temperature range, the SFC curves of the solid fraction of EF always displayed higher values when compared to the solid fraction of CB. Meanwhile, the SFC curves of the liquid fraction of EF showed higher values when compared to the liquid fraction of CB between 0-5 °C. These differences would have important implications in the quality attributes of the products when they are used as ingredients in formulations.

4. CONCLUSIONS

This study demonstrates the feasibility of fractionating stearic acid-rich plant fat such as EF and CB into a major solid and a minor liquid fraction. The fractions were found to experience significant changes in composition as well as thermal properties. While the hard stocks obtained by partitioning were found to become enriched with more saturated TAG molecular species, the liquid fraction were observed to become enriched with more unsaturated TAG molecular species. Because of the improvement in thermal properties, hard stocks may be useful in margarine production and cosmetic product formulations. As a result of the improvement in the unsaturated to saturated fatty acid ratio of liquid fractions, they would be useful as an ingredient in food applications.

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