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Fatty-Acid Profiles, Triacylglycerol Compositions, and Crystalline Structures of Bambangan-Seed Fat Extracted Using Different Solvents

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Abstract: Currently, research on the bambangan-fruit seed has become interesting because of its potential application as a cocoa butter alternative. This work aimed to determine the changes in the quality of the extracted bambangan-seed fat (BSF) obtained using hexane, petroleum ether, and ethanol. The extraction solvents affected the total fat content (TFC), physicochemical properties, fatty-acid profile, triacylglycerol composition, and crystalline structure of the extracted BSF. The results showed that BSF has a high content of 1,3-distreoyl-2-oleoyl-glycerol (SOS). The solvent-type significantly ($p < 0.05$) impacts the stearic and oleic acids of the extracts, resulting in apparent changes in the high-melting symmetrical triacylglycerols, such as SOS. Petroleum-ether-extracted BSF has a high stearic acid of 33.40%, followed by that of hexane- and ethanol-extracted BSF at 29.29% and 27.84%, respectively. Moreover, the spherulitic microstructure with needle-like crystals of the extracts also ranges from 30 to 70 µm in diameter. Hexane-extracted BSF illustrated a less-dense, spherulitic, crystalline microstructure with a less-granular centre than those extracted using the other solvents. The results suggested that the quality of the extracted BSF obtained from the nonpolar solvents of hexane and petroleum ether are better than that extracted using ethanol.

Keywords: bambangan; extraction solvents; fatty acid; triacylglycerol; crystalline microstructure

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1. Introduction

Mangifera pajang is an indigenous fruit distributed around the Borneo Islands, such as Kalimantan (Indonesia), Sabah and Sarawak (Malaysia), and Brunei [1]. This fruit is locally known as bambangan and has become a prominent, underutilised fruit with significant economic value. Bambangan trees can grow up to 30 m tall, with a cylindrical bole with smooth, broadly fissured, grey bark [2]. It initially grows widely in the forest and is currently cultivated by the local Kadazan–Dusun people, specifically in Sabah [3]. The cultivation of bambangan fruit in Sabah was reported as having a constant growth of 121.6 to 133.03 metric tons from 2016 to 2020, as the trees are currently being planted in orchards or in the backyards of homes, corresponding to the increasing demand for this fruit [4,5]. Bambangan fruit is larger in size, and it has a thick peel (of a brown colour, with rough skin), fibrous flesh. Each fruit can weigh up to 1.5 kg [6].

The local community prefers mature bambangan fruit for consumption and utilises this fruit in functional food-forms, including juice and processed fruit, and as a health drink, and it can be added to food as a flavouring ingredient. However, the seed is not consumed, but rather disposed of as a waste by-product. This waste by-product has been reported to have significant health benefits, based on the considerable number of antioxidant compounds found in the seed and in the peel [2,4,7]. The seed is made up of 9.8–11% fat, 3.08–4.1% protein, and 38.68–72.9% carbohydrate, indicating that the seed has nutritional potential as a source of protein and carbohydrates [7–11]. Bambangan-seed fat (BSF) is

mainly composed of palmitic (7.29–15.8%), stearic (32.37–40.39%), oleic (39.24–48.05%), and linoleic (4.95–8.11%) fatty acids (FAs), which corresponds to the presence of three main triacylglycerols (TG): SOS, SOO, and POS (8.7–40.70%, 11.20–26.87%, and 11.60–11.93%, respectively) [1,9,12,13]. BSF has also become an interest for researchers due to its similarities with cocoa-butter-like fats: illipe butter, mango-seed fat, kokum butter, sal fat, and shea butter [4,8,10,12,14]. Moreover, BSF is SOS-rich, which makes it applicable as an SOS-rich fat resource to increase the hardness of soft fats, which is desirable in a country with a high climate.

The extraction of BSF can be performed in various ways, including using Soxhlet extraction. Soxhlet extraction is economical, simple, and allows several extractions to be carried out simultaneously with high oil-recovery as compared to the other method [15]. The operational cost is also lower because the solvent can be recovered after the extraction, creating reusable solvents to be used for another extraction process [16]. Soxhlet extraction is an economical method that lowers operational costs by using reusable solvents with higher extraction efficiencies than the other method. Using different solvents in Soxhlet extraction gives variation to the oil-quality parameter and thus could extend the applicability of the oil based on its properties, and it offers the best option for extraction. Moreover, fresh solvents are repeatedly brought into contact with the sample, thus supplanting the equilibrium transfer [17]. The extraction's efficacy depends on the temperature, oil nature, particle size, sample pre-treatment conditions, time, and solvent type [18]. The choice of solvents for the extraction is essential for determining the quality of the extracted fat. Different studies have reported on the ways that extraction solvents influence oil quality, specifically the yield and bioactive compound levels [17,19,20]. The process of the Soxhlet extraction of oil can be performed using ethanol; the polar protic solvents or hexane and petroleum ether; the nonpolar solvents [20].

Hexane is commonly preferred among solvents due to its low-melting properties, high availability, and polarity, which lead to high solubility [21–23]. In comparison, petroleum ether has been used for the extraction of lipophilic compounds, and ethanol has been used because of its low-toxicity properties and high availability, as well as its being bio-based [24,25]. Hexane has been classified as a toxic chemical by the US Environmental Protection Agency because it can react with air pollutants to produce ozone and other environmental pollutants [26]. Hence, it is only permitted in maximum amounts of 5 ppm and 10 ppm in meal and oil, respectively, under the PFA Act of 1954 [27]. Several replacement solvents have been found to extract oil from oilseeds without utilising hexane due to safety, health, and environmental concerns [28,29]. Thus, hexane substitutes, for instance, ethanol, water, petroleum ether, and other potential solvents, have been developed and used for oil extraction [25].

However, the work of comparing the fatty acid (FA) composition, triacylglycerol (TG) content, and crystalline microstructure of BSF, as extracted using different solvents, is still in the early stage. Thus, this study aimed to evaluate the changes in the physicochemical properties (iodine value and Slip melting point), FA and TG compositions, and the crystalline microstructure of the extracted BSF using different solvents, as well as the efficiency of the extraction solvents.

2. Materials and Methods

2.1. Materials

Ripe bambangan fruits were provided by a local farmer in Ranau, Sabah, Malaysia. The following items were acquired from Sigma–Aldrich: acetone, acetonitrile, cyclohexane, ethanol, hexane, n-hexane, methanol, potassium hydroxide, petroleum ether, potassium iodide, sodium thiosulfate, starch indicator, Wijs solution, triacylglycerols, and fatty acid methyl esters standard. The analytical chemicals, reagent-grade chemicals, and extraction solvents used were of the highest possible quality.

2.2. Extraction of Bambangan-Seed Fat (BSF) Using Hexane, Petroleum Ether, and Ethanol

Each bambangan seed was separated from the flesh and then cut into small pieces (10 mm × 10 mm × 5 mm) for sample preparation. Next, it was stored in a drying cabinet (48 h at 45 °C) for drying processes. Each dried seed was ground into a powdered form using a grinding mill and kept at −20 °C before the analysis. The extraction was conducted using the AOAC [30] official method of analysis for Soxhlet extraction (Method 945.16), using petroleum ether with slight modifications. A total of 80.0 ± 0.00 g of seed powder was extracted for 8 h at 40 °C using 3 different solvents: hexane, petroleum ether, and ethanol. Ethanol was used as a hexane substitute for oilseed-extraction because of health, safety, and environmental concerns [28,31]. The remaining solvent in the extracted BSF was removed using a rotary evaporator (40 °C) (HEIDOLPH LABORTA 4001) and then filtered in an oven (at 45 °C) to remove any impurities. The total fat content (TFC) for the fat is expressed as the following equation:

$$\text{TFC } (\%) = \frac{Extracted\ crude\ fat\ (\text{g})}{Bambangan\ seed\ powder\ (\text{g})} \times 100 \quad (1)$$

2.3. Physicochemical Properties

The changes in the physicochemical properties, such as the iodine value (IV) and the Slip melting point (SMP), of the extracted BSF were determined according to the AOCS [32] official methods, Cc 3b-92 and Cd 1b-87, respectively. For IV analysis, 0.5 g of melted BSF (at 60 °C) were homogenised with 20 mL of cyclohexane and 25 mL of Wijs solution (iodine solution) and left in the dark for 1 h. Next, 20 mL of 15% KI and 100 mL of distilled water were added to the mixture. A quantity of 0.1 N sodium thiosulfate solution was used to titrate the mixture. After the yellow solution became colourless, 2 mL of the starch indicator was added, and the mixture was titrated until the blue solution became colourless. The following calculation was used to calculate the IVs of the fat samples:

$$\text{IV } (\text{g iodine/g}) = \frac{(Vol\ of\ blank\ titrant - vol\ of\ sample\ titrant) \times Normality\ of\ titrant \times 12.69}{mass\ (\text{g})} \quad (2)$$

The SMP of the hexane-, petroleum-ether-, and ethanol-extracted BSF was determined using an open-ended capillary glass tube. Before analysis, the glass tube was dipped into the fat samples to a depth of 10 mm, and the fat was chilled and solidified in an ice bath. Using a rubber band, the BSF samples were attached to the bottom of the thermometer and then immersed in the glass test tube before being placed in a water bath (10 °C) for analysis. The hot-plate temperature (SP131320-33-V, Thermo Scientific, Shanghai, China) was gradually increased by 1 °C to increase the water-bath temperature until the fat column ascended. When the fat column reached a height of 30 mm, the SMP of the fat samples was determined.

2.4. Profile of FA

The FA content of the extracted BSF was determined using a gas chromatography–flame ionisation detector (6890 N, Agilent, Santa Clara, CA, USA) as described by Norazlina et al. [9]. The FA methyl esters (FAMEs) for the extracted BSF were prepared before being injected into the BPX70 column (30 m × 0.25 µm × I.D. 0.25). A quantity of 0.5 g of BSF was dissolved using 2.5 mL of n-hexane and 0.5 mL of potassium hydroxide in methanol (2 N), vortexed (1 min at 1200 rpm), and left to stand at room temperature. After 10 min, the translucent upper-layer was injected into the GC for analysis. The following condition was used to identify the FAMEs: an initial temperature of 90 °C (hold for 5 min), then raise by 8 °C at a time to 185 °C (hold for 1 min), then raise by 2 °C to reach a final temperature of 250 °C (hold for 5 min). Using split-mode, maintain a temperature of 250 °C for the injector and detector (1:20). The FA profile was determined using the FAMEs standard. The results were presented in % concentrations and compared with the FAME standard.

2.5. TG Content

The TG composition of the extracted BSF was measured according to AOCS [32] official method Ce 5c-93, using high-performance liquid chromatography (HPLC; 1200, Agilent, Mississauga, ON, Canada) equipped with a refractive index detector (RID) with slight adjustments. For sample preparation, 0.1 g of the melted fat samples (at 60 °C) was diluted to 10 mL of mobile-phase solution (acetone: acetonitrile, premixed) to make a 10% solution. The mixture was then filtered through a 0.45 µm PTFE syringe filter (47 mm millipore diameter) and placed into the HPLC vial for analysis. A C18-HPLC column (Kromasil C18, Merck, Germany) was used for the study. An injection volume of 5 µL, a column temperature of 30 °C, a detector temperature of 40 °C, a pressure of 8–9 mPa, and mobile-phase acetone: acetonitrile (70:30, v/v) were utilised in the studies. The results were presented in % concentrations and compared with the TG standard

2.6. Crystalline Structure

The changes in the crystalline structure for the 3 extracted BSFs were observed using polarised light microscopy (DM2500P, Leica, Wetzlar, Germany), a method developed by Narine and Marangoni [33]. The crystalline structure of the fat crystals helps define the texture of a product for use in confectionery because it is directly related to the polymorphic behaviour of a fat [34]. A quantity of 15 µL of melted BSF was placed on the microscopic slide (heated at 80 °C), covered with a coverslip, and then chilled at 4 °C for 1 h. The samples were then incubated at 25 °C for 2 days for proper crystallisation before being observed under a polarised light microscope at 40× magnification.

2.7. Statistical Analysis

The total fat content (TFC) analysis and all other studies were conducted in triplicate, and the results are expressed as means and standard deviations (±). The Tukey test and one-way analysis of variance (ANOVA) were used to find any significant differences in the treatment means. A $p < 0.05$ significance value was used to define the significance level.

3. Results

3.1. Extraction of BSF and Its IV and SMP Properties

Figure 1 shows the differences in the physical appearance of the extracted BSFs obtained using hexane, petroleum ether, and ethanol. BSF extracted using a nonpolar solvent is lighter in colour than is polar-solvent-extracted BSF. The hexane and petroleum-ether extracts showed similar appearances, with a common yellow oil-colour, and they solidified faster than did the ethanol extracts. A similar observation was reported in the extraction of kariya seed oil: nonpolar solvents produced yellow oil extracts, and the polar solvent produced a cloudy, dark-golden oil extract [35]. The variation in the extracted BSF appearances was presumably associated with the acid value and free-fatty-acid content, in which free fatty acid is more soluble in the polar solvent [36]. Therefore, the ethanol-extracted BSF had a darker-golden appearance than the hexane and petroleum-ether extracts.

The TFC, IV, and SMP properties of the extracted BSFs are shown in Table 1. The solvents selected, such as hexane and petroleum ether for the current study, are typically used to extract oil from plant kernels [17], while ethanol is considered a green solvent in chemical extraction because of its low toxicity. Among the extraction solvents, hexane produced a high TFC, followed by the petroleum-ether and ethanol extracts. It can be seen that the hexane had a higher level of efficiency for extracting the BSF. The solutes and solvent interactions, boiling temperature, and solvent polarity might be the prominent factors that influenced the BSF's yield, extraction efficacy, and composition [17]. The hexane's low-polarity properties caused rapid molecule-transfer between the solvents, thus leading to a high TFC in the hexane-extracted BSF as compared to the petroleum-ether- and ethanol-extracted BSFs [37]. The presence of the antioxidant compounds and other extract compounds, soluble primarily in polar solvents, presumably led to the low yield of TFC

in the ethanol-extracted BSF. The extraction yield for the 3 extracts was comparable to the reported fat content of mango seed fat, with values of 5.73–7.74% in a previous study [38]. On the other hand, the extracted BSFs' physicochemical properties, such as the IV and the SMP, also showed variation in their values.

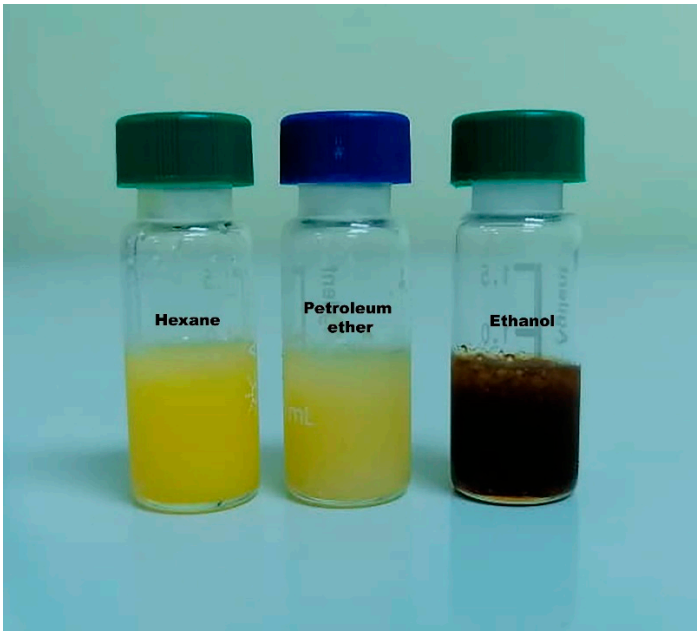


Figure 1. Physical appearance of the extracted BSFs using hexane, petroleum ether, and ethanol.

As seen in Table 1, petroleum-ether-extracted BSF has the lowest IV, followed by the hexane- and ethanol-extracted BSFs. The IV is used to determine the unsaturation levels and the stability of oil for industrial applications [39]. A low IV in the petroleum-extracted BSF indicates that it is prone to better resist oxidation, and it has a higher quality and longer shelf-life than the other two extracts. This behaviour is supported by the results of our previous study, in which the petroleum-ether extracts with low IVs showed a low acidity, with a value of 3.74 mg KOH/g, and had better thermal profiles than the ethanol extracts, with a 7.41 mg KOH/g acid value [40]. The changes in the IV also are associated with the FA composition. A low unsaturation value indicates a low presence of unsaturated FA (UFA); thus, petroleum-ether extracts have more saturated FA (SFA) than hexane and ethanol extracts. The extraction solvents also influence the SMP for the extracted BSFs. The petroleum-ether-extracted BSF showed high SMP values followed by the hexane and ethanol extracts. The low IVs in the petroleum-ether extracts indicate more SFAs and a higher melting-point-TG content than the other solvents; thus, the SMP is higher. The trends in the efficacy of the extraction solvents and the changes in the physicochemical properties for the extracted BSF align with the results reported by Kittiphom and Sutasinee [17] and Jedidi et al. [20].

Table 1. Physicochemical properties of BSFs extracted from hexane, petroleum ether and ethanol.

Physicochemical Properties	Hexane	Petroleum Ether	Ethanol	Bambangan-Seed Fat [9,12]	Mango-Seed Fat [39–41]
Total fat content (%)	7.70 ± 0.00 ^{a}	6.40 ± 0.10 ^{b}	2.21 ± 0.01 ^{c}	-	5.73–7.74
Iodine value (g iodine/g)	56.40 ± 0.00 ^{b}	52.96 ± 0.00 ^{c}	59.84 ± 0.00 ^{a}	50.3–53.5	40.9–44.36
Slip melting point (°C)	31.57 ± 0.51 ^{c}	31.40 ± 0.52 ^{b}	28.4 0 ± 0.5 1 ^{a}	32.0–32.2	30.03–35.7

Values are the mean ± standard deviation of three replicates; means with a different letter (a, b, or c, with a showing the highest value) within a column are significantly different ($p < 0.05$) as measured by the Tukey test.

3.2. Characterisation of FA Profiles in BSF Extracts

Vegetable fats and oils are beneficial for industrial and food purposes, and their quality is closely related to their FA composition [20]. As shown in Table 2, significant ($p < 0.05$) changes in the FA profiles of the 3 extracts were influenced by the solvents used. Obvious changes can be seen in the extracts' stearic and oleic acid compositions. About 52.32–59.70% of the BSFs' FA composition was dominated by the UFA, primarily oleic (43.90–48.31%), with a significant presence of linoleic (8.04–9.72%) acid. This result explains the high unsaturation value of all extracts, especially the ethanol-extracted BSF. The extracts obtained in this study showed softer properties with high UFA compositions as compared to the BSF reported in the previous study [1], in which 56.19% of the FA composition was saturated. The variation obtained in this study was presumably correlated with the geographical latitude, thus showing variation in their compositions. The composition and quality of the fat may vary depending on the fruit's growth condition. According to Varnham [42], the type of a plant, the environment, and the degree to which the seeds ripen determine the FA and the unsaponifiable components of oilseeds. The bambangan fruit used in the study was ripening but over-softening due to transportation and storage, which made the fruit spoil, resulting in variations in the quality parameter.

Table 2. Fatty-acid composition of BSF extracted from hexane, petroleum ether, and ethanol.

Composition (%)	Hexane	Petroleum Ether	Ethanol	Bambangan-Seed Fat [1,9,12]	Mango-Seed Fat [12–38]
$C_{16:0}$ (Palmitic)	8.24 ± 0.00 ^{b}	9.32 ± 0.00 ^{a}	8.67 ± 0.00 ^{b}	8.35–14.91	4.9–14.91
$C_{16:1}$ (Palmitoleic)	0.32 ± 0.00 ^{a}	0.17 ±0.00 ^{b}	0.06 ± 0.00 ^{c}	-	-
$C_{18:0}$ (Stearic)	29.29 ± 0.00 ^{b}	33.40 ± 0.00 ^{a}	27.84 ± 0.00 ^{c}	36.35–40.39	24.2–47.6
$C_{18:1}$ (Oleic)	46.94 ± 0.00 ^{b}	43.90 ± 0.00 ^{c}	48.31 ± 0.00 ^{a}	39.24–44.5	37.0–58.6
$C_{18:2}$ (Linoleic)	8.51 ± 0.00 ^{b}	8.04 ± 0.00 ^{c}	9.72 ± 0.00 ^{a}	4.95–5.4	3.7–10.4
$C_{18:3}$ (Linolenic)	0.37 ± 0.00 ^{b}	0.38 ± 0.00 ^{c}	0.48 ± 0.00 ^{a}	0.3–0.37	0.4–1.2
C_{20} (Arachidic)	1.87 ± 0.00 ^{a}	1.77 ± 0.00 ^{b}	1.67 ± 0.00 ^{c}	-	-
$C_{20:1}$ (Eicosenoic acid)	0.23 ± 0.00 ^{a}	0.18 ± 0.00 ^{c}	0.21 ± 0.00 ^{b}	-	-
C_{22} (Behenic acid)	0.36 ± 0.00 ^{a}	0.31 ± 0.00 ^{b}	0.30 ± 0.00 ^{c}	-	-

Values are the mean ± standard deviation of 3 replicates; means with a different letter (a, b, or c, with a showing the highest value) within a column are significantly different ($p < 0.05$) as measured by the Tukey test.

Additionally, the temperature also significantly impacts the content of FA, particularly the UFA [43]. On the other hand, the results obtained in this study are in agreement with the FA profiles of BSF extracted by Jahurul et al. [12] and Norazlina et al. [9] and the mango-seed fat extracted by Jahurul et al. [44] and Munchiri, Mahungu, and Gituanja [45]. The SFA and UFA for the reported BSF and mango-seed fat ranged from 44.7 to 44.8% and from 29.1 to 58.6%, from 49.2 to 50.2%, and from 41.1 to 70.2%, respectively. Petroleum-ether-extracted BSF has higher quantities of palmitic and stearic acids, followed by the hexane and ethanol extracts. This shows that petroleum-ether-extracted BSF is harder than the other two extracts. In contrast, ethanol extracts have more oleic acid than do hexane and petroleum-ether extracts. The changes in the FA composition for the 3 extracts can be supported by Kittiphom & Sutasinee [17], who reported similar changes in the extraction of mango-seed oil using hexane (palmitic: 8.97%, stearic: 37.37%, oleic: 43.77%, and linoleic: 6.78%), petroleum ether (palmitic: 8.73%, stearic: 37.70%, oleic: 44.75%, and linoleic: 5.67%) and ethanol (palmitic: 8.50%, stearic: 38.50%, oleic: 43.45%, and linoleic: 6.48%).

Moreover, BSF produced by the Soxhlet extraction in this study exhibited an FA-type similar to commercial cocoa butter (CB) (palmitic: 24.5–33.7%, stearic: 33.3–40.2%, oleic:

26.3–36.5%, and linoleic: 1.7–3.56% acids) reported by Gunstone [46], Sonwai et al. [47], Kadivar et al. [48], and Norazura, Sivaruby, and Noor Lida [49], indicating that the extracts are applicable as potential CB alternatives.

3.3. TG Profiles

The TG fat composition is essential for determining the potential application of the extracts, as well as providing information on the polymorphic behaviour. Table 3 summarises the TG content for all extracts, where it can be seen that the TG content was significantly ($p < 0.05$) affected by the extraction solvents. All extracts were dominated by SOS (30.22–44.29%), SOO (20.19–24.18%), and POS (9.57–12.48%) with a significant presence of OOO (5.18–7.09%), POP (2.44–3.83 %), SSS (1.25–3.40%), OLO (2.90–4.56%), and POL (3.16–3.65%). Based on these values, 39.79–56.77% of the composition is high-melting TG (POS and SOS), thus explaining the solidification process of BSF at an ambient temperature. Petroleum-ether-extracted BSF (56.77%) has a high content of high-melting TG, followed by hexane (48.54%) and ethanol (39.79%). This behaviour results in the high SMP value of petroleum-ether extracts, and it increases the hardness of the fat. The variation in the high-melting composition of the extracts was associated with the solubility of the low-melting TG; low-melting TG is more soluble in a polar solvent [50]. Therefore, the ethanol extracts have more low-melting TG than the other extracts.

In addition, the high-melting TG in the hexane extracts is closer to 50% of the TG composition, thus showing a comparable SMP with the petroleum-ether-extracted BSF. The unsaturation value of the hexane extracts is comparable to the petroleum-ether extracts due to the comparable FA and TG compositions. Therefore, this indicates that the quality of the hexane extracts is comparable to that of the petroleum-ether extracts. The relation between the high-melting TG and the SMP obtained in this study also agrees with the melting point of the POS (23.50–43.0 °C) and SOS (19.50–35.50 °C), as reported by a previous study [51–53]. The TG content in the study is also in line with the TG profiles of the reported BSFs and mango-seed fats [8,12,13,34,54–58]. The BSF extracted using different solvents also showed a noticeable amount of OLL, PLL, OLO, POL, PLP, and SSS, as in a previous study [12].

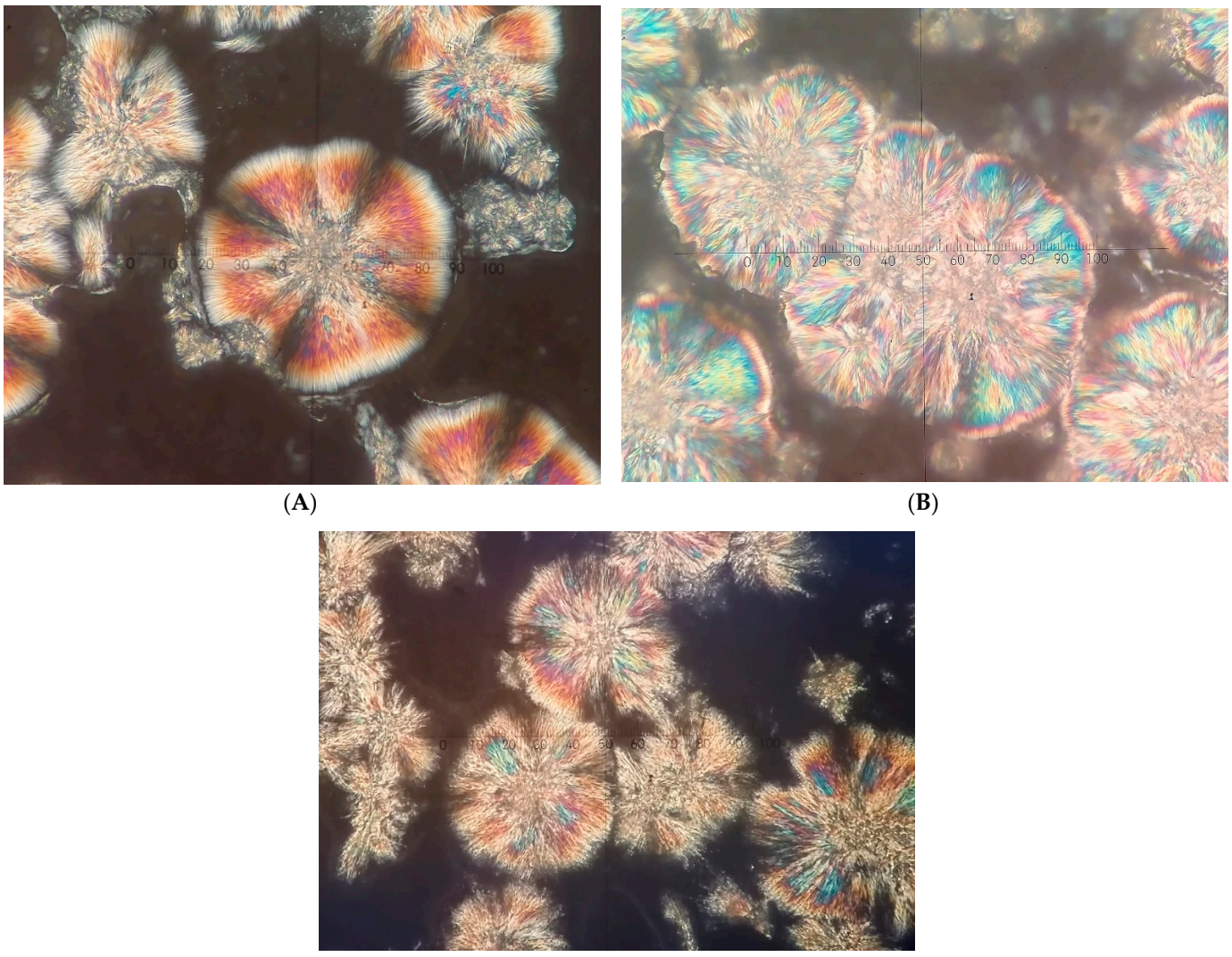
Table 3. Triacyglycerol content of BSF extracted from hexane, petroleum ether, and ethanol.

Composition (%)	Hexane	Petroleum Ether	Ethanol	Bambangan-Seed Fat [8,12,13]	Mango-Seed Fat [41,53–57]
OLL	1.80 ± 0.00 ^{b}	1.34 ± 0.00 ^{c}	2.07 ± 0.00 ^{a}	Traceable	Traceable
PLL	1.19 ± 0.00 ^{b}	0.71 ± 0.00 ^{c}	1.42 ± 0.00 ^{a}	Traceable	Traceable
OLO	3.83 ± 0.00 ^{b}	2.90 ± 0.00 ^{c}	4.56 ± 0.00 ^{a}	Traceable	Traceable
POL	3.02 ± 0.00 ^{c}	3.16 ± 0.00 ^{b}	3.65 ± 0.00 ^{a}	Traceable	Traceable
PLP	1.27 ± 0.00 ^{b}	0.98 ± 0.00 ^{c}	1.56 ± 0.00 ^{a}	Traceable	Traceable
OOO	6.57 ± 0.00 ^{b}	5.18 ± 0.00 ^{c}	7.09 ± 0.00 ^{a}	3.6–5.89	2.5–5.7
POO	2.68 ± 0.00 ^{a}	2.30 ± 0.00 ^{b}	2.18 ± 0.00 ^{c}	3.8–4.57	2.4–10.8
POP	3.83 ± 0.00 ^{a}	2.95 ± 0.00 ^{b}	2.44 ± 0.00 ^{c}	0.75–5.90	1.3–8.9
SOO	23.84 ± 0.00 ^{b}	20.19 ± 0.00 ^{c}	24.18 ± 0.00 ^{a}	11.20–26.88	5.7–30.8
POS	11.78 ± 0.00 ^{b}	12.48 ± 0.00 ^{a}	9.57 ± 0.00 ^{c}	11.35–11.94	5.7–14.8
SOS	36.79 ± 0.00 ^{b}	44.29 ± 0.00 ^{a}	30.22 ± 0.00 ^{c}	28.67–40.71	14.3–51.6
SSS	3.40 ± 0.00 ^{b}	3.52 ± 0.00 ^{a}	1.25 ± 0.00 ^{c}	Traceable	Traceable

Values are the mean ± standard deviation of three replicates; means with a different letter (a, b, or c, with a showing the highest value) within a column are significantly different ($p < 0.05$) as measured by the Tukey test.

3.4. Crystalline Microstructure

Figure 2 shows the crystalline microphotograph of BSFs extracted using hexane, petroleum ether, and ethanol. All fat structures showed spherulite crystals, consisting of needle-like crystals branching outwards with a diameter of 40–70 µm. This structure is commonly associated with the β polymorphic form of a CB [59]. Such a crystalline structure is desirable for making chocolate and confectionery products. The crystalline structure of the extracted BSFs was significantly changed after exposure to the extraction solvents. Petroleum-ether- and ethanol-extracted BSFs showed a compact cluster of fat crystal compared to the hexane-extracted BSF. The spherulite structure of the petroleum-ether-extracted BSF was disrupted after exposure to the solvent, making the structure oval and compact. The ethanol-extracted BSF showed a smaller crystal structure than the hexane-extracted BSF. These findings are similar to the microphotograph reported by Norazlina et al. [9] The changes in the crystalline microstructure (polymorphism, distribution size, size, surface of a structure, and shape) occurred because of the variety in the textural properties of fat and the TG composition [60]. The crystalline microstructure was also potentially influenced by the different FA and TG contents [9], resulting in the difference in the crystallisation state.



(**A**) (**B**)

(**C**)

Figure 2. Crystalline microstructure of (**A**) hexane-, (**B**) petroleum-ether-, and (**C**) ethanol-extracted BSF.

Moreover, the saturation-degree of the fat also affected the crystalline microstructure [52]. The unsaturated ethanol-extracted BSF has crystals with a small, densely packed centre, a loose and scattered structure similar to the crystalline microstructure of the mango-seed fat (Thai cultivar) reported by Sonwai and Ponprachanuvut [38]. On the other hand, hexane-extracted BSF exhibited a loosely scattered, spherulite structure similar to that of CB, as reported by Asep et al. [61], thus suggesting that hexane-extracted BSF is similar to CB-like fats and may be applicable as CB alternative.

4. Discussion

This study analysed the FA profiles, TG compositions, and the crystalline microstructures of BSFs obtained using different extraction solvents. To achieve this goal, three different organic solvents were used to obtain the best extraction solvents. Interestingly, the findings showed the solvents affect the composition of the BSF, in which the BSFs extracted using nonpolar solvents (hexane and petroleum ether) are of better quality than those extracted using the polar solvent. Besides that, a previous study also reported that the seed oils extracted using the nonpolar solvents have a high-quality parameter [17,19,20]. The results showed that the characteristics of the extracted BSFs in this study are also in agreement with the reported properties of the BSF reported by Azrina et al. [1], Jahurul et al. [12], and Norazlina et al. [9,13], but the TFC is very low. The unsaturation value (59.84 g iodine/g), UFA (more than 50%) content, and the low-melting TG (33.45%) were high in the ethanol-extracted BSF.

The oil's lower solubility could explain the differences in the extracted BSF's quality parameters, such as the TFC, in the polar solvents compared to the nonpolar solvents. The extracted BSF in the polar solvent was mainly disturbed by another component, such as the antioxidant-extract compounds and free fatty acids, which were co-extracted during the extraction process; thus, a low TFC was obtained in the ethanol oil-extracts. The final results, such as the oil yield, FA profile, and the physicochemical qualities, were significantly influenced by the solvents used for extraction, which have been previously reviewed [61,62]. In fact, hexane and petroleum ether, commonly used as the extraction solvents for lipid-extraction in seed oils [22,25], are supposed to have similar properties. However, these solvents showed significant differences in the properties of the extracted BSF.

Although petroleum-ether-extracted BSF shows high-quality parameters; it has a low unsaturation value, a high SFA, and a high-melting TG composition, the extracts' crystalline microstructure is dense and oval and has a low yield. Concerning the TFC, FA, and TG compositions and the crystalline microstructure, hexane seems to be the most efficient among the extraction solvents studied, with a TFC of 7.7%. Still, it has a low POP (3.83%) and POS (11.78%) content and a high SOO (23.83%) level, which could result in the softening effect. The toxicity of the hexane solvents could also become a concern, such that the solvents' traces should be analysed and not exceed the permitted maximum amount in edible oil, as mentioned above. Nevertheless, petroleum ether is an alternative solvent choice known to have less toxicity than hexane, and it could also be used as an extraction solvent as it has comparable properties with hexane-extracted BSF but with a significantly lower yield.

5. Conclusions

This report is the first study to explore how different organic solvents affect the composition of BSF. This work successfully performed BSF extraction using polar (ethanol) and nonpolar (hexane and petroleum-ether) solvents. The changes in the physicochemical properties, FA and TG compositions, and the crystalline structures of the BSFs extracted from different solvents are presented in this report. The results suggest that the hexane-extracted BSF had better overall fat quality, including a high TFC and IV and SMP values comparable to the petroleum-ether extracts. Although petroleum-ether-extracted BSF has a stearic-acid content similar to that of CB, the FA profiles are close to those of the hexane-extracted BSF. Both extracts showed FA-types similar to those of CB, and only the hexane

extracts exhibited a similarly less-dense crystalline structure. Therefore, hexane-extracted BSF is applicable as a CB alternative due to its similarities with CB. Therefore, hexane is suitable for the extraction of BSF. This research is beneficial for providing the solvent's choice information for BSF extraction and speciality-fat production.

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References

1. Azrina, A.; Aznira, A.R.; Khoo, H.E. Chemical properties and fatty acid composition of *Mangifera pajang* and *Mangifera indica* kernel fats. *Malays. J. Nutr.* **2015**, *21*, 355–363.
2. Tangah, J.; Bajau, F.E.; Jilimin, W.; Chan, H.T.; Wong, S.K.; Chan, E.W.C. Phytochemistry and pharmacology of *Mangifera pajang*: An iconic fruit of Sabah, Malaysia. *Syst. Rev. Pharm.* **2017**, *8*, 86–91. [CrossRef]
3. Abu Bakar, M.F.; Mohamed, M.; Rahmat, A.F.; Fry, J.R. Bambangan (*Mangifera pajang*) seed kernel: Antioxidant properties and anti-cancer effects. In *Nuts and Seed in Health and Disease Prevention*; Elsevier Inc.: Amsterdam, The Netherlands, 2011; pp. 183–187.
4. Jahurul, M.H.A.; Zaidul, I.S.M.; Beh, L.; Sharifudin, M.S.; Siddiquee, S.; Hasmadi, M.; Jinap, S. Valuable components of bambangan fruit (*Mangifera pajang*) and its co-products: A review. *Food Res. Int.* **2018**, *115*, 105–115. [CrossRef] [PubMed]
5. Department of Agriculture. *Fruits Crops by State and Type Malaysia: Department of Agriculture*; Department of Agriculture: Kuala Lumpur, Malaysia, 2020; pp. 7–177.
6. Bakar, M.F.A.; Fry, J.F. A review on underutilised indigenous bambangan (*Mangifera pajang*) fruit as a potential novel source for functional food and medicine. *J. Med. Plants Res.* **2013**, *7*, 3292–3297.
7. Abu Bakar, M.F.; Mohamed, M.; Rahmat, A.; Fry, J. Phytochemicals and antioxidant activity of different parts of bambangan (*Mangifera pajang*) and tarap (*Artocarpus odoratissimus*). *Food Chem.* **2009**, *113*, 479–483. [CrossRef]
8. Jahurul, M.H.A.; Ping, L.L.; Sharifudin, M.S.; Hasmadi, M.; Mansoor, A.H.; Lee, J.S.; Noorakmar, B.W.; Amir, H.M.S.; Jinap, S.; Mohd Omar, A.K.; et al. Thermal properties, triglycerides and crystal morphology of bambangan (*Mangifera pajang*) kernel fat and palm stearin blends as cocoa butter alternatives. *LWT-Food Sci. Technol.* **2019**, *107*, 64–71. [CrossRef]
9. Norazlina, M.R.; Jahurul, M.H.A.; Hasmadi, M.; Sharifudin, M.S.; Patricia, M.; Mansoor, A.H.; Lee, J.S. Characteristics of bambangan kernel fat fractions produced by solvent fractionation and their potential industrial applications. *J. Food Proces. Preserv.* **2020**, *44*, e14446. [CrossRef]
10. Jahurul, M.H.A.; Soon, Y.; Sharifudin, M.S.; Hasmadi, M.; Mansoor, A.H.; Zaidul, I.S.M. Optimization of fat yield of bambangan (*Mangifera pajang*) kernel using response surface methodology and its antioxidant activities. *J. Food Meas. Charact.* **2018**, *12*, 1427–1438. [CrossRef]
11. Haron, H.; Said, M. Determination of the nutrient and anti-nutrient contents in seed of *Mangifera pajang* kostermans. *Malays. J. Health Sci.* **2004**, *2*, 1–11.
12. Jahurul, M.H.A.; Soon, Y.; Shaarani Sharifudin, M.; Hasmadi, M.; Mansoor, A.H.; Zaidul, I.S.M. Bambangan (*Mangifera pajang)* kernel fat: A potential new source of cocoa butter alternatives. *Int J. Food Sci. Technol.* **2018**, *53*, 1687–1697. [CrossRef]
13. Norazlina, M.R.; Jahurul, M.H.A.; Hasmadi, M.; Sharifudin, M.S.; Patricia, M.; Lee, J.S.; Amir, H.M.S.; Noorakmar, A.W.; Riman, I. Effects of fractionation technique on triacylglycerols, melting and crystallisation and the polymorphic behavior of bambangan kernel fat as cocoa butter improver. *LWT-Food Sci. Technol.* **2020**, *129*, 109558. [CrossRef]
14. Al-Sheraji, S.H.; Ismail, A.; Manap, M.Y.; Mustafa, S.; Yusof, R.M. Viability and activity of bifidobacteria during refrigerated storage of yoghurt containing *Mangifera pajang* fibrous polysaccharides. *J. Food Sci.* **2012**, *77*, 624–630. [CrossRef]
15. Oladipo, B.; Betiku, E. Process optimisation of solvent extraction of seed oil from *Moringa oleifera*: An appraisal of quantitative and qualitative process variables on oil quality using D-optimal design. *Biocatal. Agric. Biol.* **2019**, *20*, 101187. [CrossRef]
16. Handa, S.S. An overview of extraction techniques for medicinal and aromatic plants. In *Extraction Technologies for Medicinal and Aromatic Plants*; Handa, S.S., Khanuja, S.P.S., Longo, G., Rakesh, D.D., Eds.; International Centre for Science and High Technology: Trieste, Italy, 2008.
17. Kittiphoom, S.; Sutasinee, S. Mango seed kernel oil and its physicochemical properties. *Int. Food Res. J.* **2013**, *20*, 1145–1149.
18. Mani, S.; Jaya, S.; Vadivambal, R. Optimization of solvent extraction of moringa (*Moringa oleifera*) seed kernel oil using response surface methodology. *Food Bioprod. Process.* **2007**, *85*, 328–335. [CrossRef]
19. Stevanato, N.; da Silva, C. Radish seed oil: Ultrasound-assisted extraction using ethanol as solvent and assessment of its potential for ester production. *Ind. Crops Prod.* **2019**, *132*, 283–291. [CrossRef]

20. Jedidi, B.; Mokbli, S.; Sbihi, H.M.; Nehdi, I.A.; Younes, M.R.; Al-Resayes, S.I. Effect of extraction solvents on fatty acid composition and physicochemical properties of *Tecoma stans* seed oils. *J. King Saud Uni. Sci.* **2020**, *32*, 2468–2473. [CrossRef]
21. Liu, S.X.; Mamidipally, P.K. Quality comparison of rice bran oil extracted with d-limonene and hexane. *Cereal Chem.* **2005**, *82*, 209–215. [CrossRef]
22. Danlami, J.M.; Arsad, A.; Zaini, M.A.A.; Sulaiman, H. A comparative study of various oil extraction techniques from plants. *Rev. Chem. Eng.* **2014**, *30*, 605–626. [CrossRef]
23. Mujdalipah, S.; Sasmita, A.H.; Amalia, I.K.; Suryani, A. Separation of glycerolysis product using hexane. In *IOP Conference Series: Materials Science and Engineering*; IOP Publishing: Bandung, Indonesia, 2016.
24. Perrier, A.; Delsart, C.; Boussetta, N.; Grimi, N.; Citeau, M.; Vorobiev, E. Effect of ultrasound and green solvents addition on the oil extraction efficiency from rapeseed flakes. *Ultrasonics Sonochem.* **2017**, *39*, 58–65. [CrossRef]
25. Feng, W.; Li, M.; Hao, Z.; Zhang, J. Analytical Methods of Isolation and Identification. In *Phytochemicals in Human Health*; Rao, V., Mans, D., Rao, L., Eds.; IntechOpen: London, UK, 2019.
26. Hanmoungjai, P.Y.L.E.; Pyle, D.L.; Niranjan, K. Enzymatic process for extracting oil and protein from rice bran. *J. Am. Oil Chem. Soc.* **2001**, *78*, 817–821. [CrossRef]
27. Sawada, M.M.; Venâncio, L.L.; Toda, T.A.; Rodrigues, C.E. Effects of different alcoholic extraction conditions on soybean oil yield, fatty acid composition and protein solubility of defatted meal. *Food Res. Int.* **2014**, *62*, 662–670. [CrossRef]
28. Ahmadi Kamazani, N.; Mortazavi, S.A.; Ebrahimi Tajabadi, M.; Hasani, M.; Ghotbi, M. The Effect of Different Solvent Systems on Some Chemical Properties of Pistachio Nut Oil Contaminated with Aflatoxin. *J. Food Biosci. Technol.* **2015**, *5*, 1–13.
29. Kumar, S.J.; Prasad, S.R.; Banarjee, R.; Agarwal, D.K.; Kulkarni, K.S.; Ramesh, K.V. Green solvents and technologies for oil extraction from oil seeds. *Chem. Cent. J.* **2017**, *11*, 9. [CrossRef]
30. AOAC Official Method of Analysis. *Method 945.16, Oil in Cereal Adjuncts*, 18th ed.; AOAC International: Gaithersburg, MD, USA, 2005.
31. Abdolshahi, A.; Majd, M.H.; Rad, J.S.; Taheri, M.; Shabani, A.; Da Silva, J.A.T. Choice of solvents extraction technique affects fatty acid composition of pistachio (*Pistacia vera* L.) oil. *J. Food Sci. Technol.* **2015**, *52*, 2422–2427. [CrossRef]
32. American Oil Chemists' Society. *Official Methods and Recommended Practices of the American Oils Chemists' Society*, 5th ed.; American Oil Chemists' Society: Champaign, IL, USA, 2003.
33. Narine, S.S.; Marangoni, A.G. The difference between cocoa butter and Salatrim lies in the microstructure of the fat crystal network. *J. Am Oil Chem. Soc.* **1999**, *76*, 7–13. [CrossRef]
34. Rios, R.V.; Pessanha, M.D.F.; Almeida, P.F.; de Viana, C.L.; Lannes, S.C. Applications of fats in some food products. *Food Sci. Technol.* **2014**, *34*, 3–15. [CrossRef]
35. Okeleye, A.A.; Betiku, E. Kariya (*Hildegardia barteri*) seedd oil extrcation: Comparative evaluatin of solvents, modeling and optimisation techniques. *Chem. Eng. Commun.* **2019**, *206*, 1181–1198. [CrossRef]
36. Bhatnagar, A.S.; Krishna, A.G.G. Effect of extraction solvent on oil and bioactives composition of commercial Indian niger (*Guizotia abyssinica* (Lf) class.) seed. *J. Am. Oil Chem.* **2013**, *90*, 1203–1212. [CrossRef]
37. Yang, X.; Lyu, H.; Chen, K.; Zhu, X.; Zhang, S.; Chen, J. Selective extraction of oil from hydrothermal liquefaction of *Salix psammophila* by organic solvents with different polarities through multistep extraction separation. *BioResources* **2014**, *9*, 5219–5233. [CrossRef]
38. Sonwai, S.; Ponprachanuvut, P. Studies of fatty acid composition, physicochemical and thermal properties and crystallisation behaviour of mango kernel fats from various Thai varieties. *J. Oleo Sci.* **2014**, *63*, 661–669. [CrossRef] [PubMed]
39. Xu, Y.X.; Hanna, M.A.; Josiah, S.J. Hybrid hazelnut characteristics and its potential oleochemical application. *Ind. Crops Prod.* **2007**, *26*, 69–76. [CrossRef]
40. Norazlina, M.R.; Tan, Y.S.; Hasmadi, M.; Jahurul, M.H.A. Effect of solvent pre-treatment on the physicochemical, thermal profiles and morphological behavior of *Mangifera pajang* seed fat. *Heliyon* **2021**, *7*, e08073. [CrossRef] [PubMed]
41. Lieb, V.M.; Schuster, L.K.; Kronmüller, A.; Schmarr, H.G.; Carle, R.; Steingass, C.B. Fatty acids, triacylglycerols, and thermal behaviour of various mango (*Mangifera indica* L.) kernel fats. *Food Res. Int.* **2018**, *116*, 527–537. [CrossRef]
42. Varnham, A. *Seed Oil: Biological Properties: Health Benefits and Commercial Applications*; Nova Science Publisher Inc.: New York, NY, USA, 2015.
43. Hou, G.; Ablett, G.R.; Pauls, K.P.; Rajcan, I. Environmental effects on fatty acid levels in soybean seed oil. *J. Am. Oil Chem. Soc.* **2006**, *83*, 759–763. [CrossRef]
44. Jahurul, M.H.; Zaidul, I.S.; Norulaini, N.N.; Sahena, F.; Jaffri, J.M.; Omar, A.M. Supercritical carbon dioxide extraction and studies of mango seed kernel for cocoa butter analogy fats. *CyTA-J. Food.* **2014**, *12*, 97–103. [CrossRef]
45. Munchiri, D.R.; Mahungu, S.M.; Gituanja, S.N. Studies on mango (*Mangifera indica* L.) kernel fat of some Kenyan varieties in Meru. *J. Am. Oil Chem. Soc.* **2012**, *89*, 1567–1575. [CrossRef]
46. Gunstone, F.D. *Vegetable Oils in Food Technology Composition, Properties and Use*; Willy-Blackwell: New York, NY, USA, 2011; pp. 291–343.
47. Sonwai, S.; Kaphuekngam, P.; Flood, A. Blending of mango kernel fat and palm oil mid-fraction yo obtain cocoa butter equivalent. *J. Food Sci. Technol.* **2014**, *51*, 2357–2369. [CrossRef]
48. Kadivar, S.; De Clercq, N.; Mokbul, M.; Dewettinck, K. Infulence of enzymatically produced sunflower oil based cocoa butter equivalents on the phase behavior of cocoa butter and quality of dark chocolate. *LWT-Food Sci. Technol.* **2016**, *66*, 48–55. [CrossRef]

49. Norazura, A.M.H.; Sivaruby, K.; Noor Lida, H.M.D. Blended palm fractions as confectioenry fats: A preliminary study. *J. Oil Palm Res.* **2020**, *33*, 360–380. [CrossRef]
50. Kang, K.K.; Kim, S.; Kim, I.H.; Lee, C.; Kim, B.H. Selective enrichment of symmetric monounsaturated triacylglycerols from palm stearin by double solvent fractionation. *LWT-Food Sci. Technol.* **2013**, *51*, 242–252. [CrossRef]
51. Arishima, T.; Sagi, N.; Mori, H.; Sato, K. Polymorphism of POS. I. Occurrence and polymorphic transformation. *J. Am. Oil Chem.* **1991**, *68*, 710–715. [CrossRef]
52. Koyona, T.; Hachiya, I.; Sato, K. Phase behavior of mixed system of SOS and OSO. *J. Phys. Chem.* **1992**, *96*, 10514–10520. [CrossRef]
53. Minato, A.; Ueno, S.; Yano, J.; Smith, K.; Seto, H.; Amemiya, Y.; Sato, K. Thermal and structural properties of sn-1,3-dipalmitoyl-2-oleoylglycerol and sn-1,3-dioleoyl-2-palmitoylglycerol binary mixtures examined with synchroton radiation X-Ray diffraction. *J. Am. Oil. Chem.* **1997**, *74*, 1213–1220. [CrossRef]
54. Jin, J.; Mu, H.; Wang, Y.; Pembe, W.; Liu, Y.; Huang, J.; Jin, Q.; Wang, X. Production of high-melting symmetrical monounsaturated triacylglycerol-rich fats from mango kernel fat by acetone fractionation. *J. Am. Oil Chem. Soc.* **2016**, *94*, 201–213. [CrossRef]
55. Kaphuekngam, P.; Flood, A.; Sonwai, S. Production of cocoa butter equivalent from mango seed almond fat and palm oil midfraction. *J. Food Agro-Ind.* **2009**, *2*, 441–447.
56. Lidefelt, J.O. *Handbook of Vegetable Oils and Fats*, 2nd ed.; Aarhus Karlshamn: Karlshmn, Sweden, 2007.
57. Halcopek, M.; Lisa, M.; Jandera, P.; Kabatova, N. Quantitation of triacylglycerols in plant oils using HPLC with APCI-MS, evaporative light-scattering and UV detection. *J. Sep. Sci.* **2005**, *28*, 1315–1333.
58. Ramel, P.R.; Campos, R.; Marangoni, A.G. Effect of shear and cooling rate on the crystallisation behavior and structure of cocoa butter: Shear applied during the early stages of nucleation. *Cryst. Growth Des.* **2017**, *18*, 1002–1011. [CrossRef]
59. Çiftçi, O.N.; Fadiloğlu, S.; Göğüş, F. Conversion of olive pamoce oil to cocoa butter-like fat in a packed-bed enzyme reactor. *Biores. Technol.* **2009**, *100*, 324–329. [CrossRef]
60. Salvatore, M.M.; Elvetico, A.; Gallo, M.; Salvatore, F.; DellaGreca, M.; Naviglio, D.; Andolfi, A. Fatty acids from *Ganoderma lucidum* Spores: Extraction, identification and quantification. *Appl. Sci.* **2020**, *10*, 3907. [CrossRef]
61. Asep, E.; Jinap, S.; Tan, T.J.; Russly, A.; Harcharan, S.; Nazimah, S. The effects of particle size, fermentation and roasting of cocoa nibs on supercritical fluid extraction of cocoa butter. *J. Food Eng.* **2008**, *85*, 450–458. [CrossRef]
62. Ajala, S.O.; Betiku, E. Yellow oleander seed oil extraction modeling and process parameters optimisation: Performance evaluation of artificial neural network and response surface methodology. *J. Food Process. Preserv.* **2015**, *39*, 1466–1474. [CrossRef]