

Evaluation of Physicochemical Properties and Sensory Products of Cocoa Liquor and Dark Chocolate High Polyphenols and Flavanoids

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Abstract

Objectives: This research aims to determine the comparison of cocoa beans without fermentation and cocoa beans fermented dark chocolate products that meet the criteria as a health food based on the content of polyphenols and flavonoids with the aroma and taste that is liked by consumers. **Methods/statistical analysis:** The parameters tested on dark chocolate and cocoa liquor product are melting properties were determined using DSC (*Differential scanning calorimeter*), texture (*TA-Xt Plus Texture Analyzer*), Colour lightness was measured using Hunter method (*Chromameter*), and total levels of polyphenols and flavonoids. In addition, the sensory analysis of aroma and taste using difference from control test methods. Statistical analyses were carried out with Design Expert Stat-Ease Version 11 for response surface methodology (DOE). Panelist data were subjected to analysis of variance (ANOVA) followed by *Duncan's Multiple Range*, with a significance level of 0.05. **Findings:** The results of this study showed that the content of polyphenols and flavonoids on cocoa liquor and the highest dark chocolate respectively amounted to 195.472 mg/g samples and 79.622 mg/g samples while the levels of flavonoid respectively amounted to 206.15 mg/g samples and 113.15 mg/g samples. Best quality produced from cocoa liquor and dark chocolate (100% cocoa beans without fermentation) is the viscosity of 10.49 ± 1.539 poise and 42.166 ± 14.936 poise, texture 5280 g Force/sec, color lightness 22.03 and 27.42, melting point 32.17 °C. Based on the organoleptic test, dark chocolate products with a comparison of cocoa beans without fermentation and cocoa beans fermentation 25%: 75% have a better aroma and taste and more liked by consumers compared to other products. **Applications:** Mixing cocoa beans fermentation and without fermentation in the making of dark chocolate can increase the aroma and taste of dark chocolate, so it not only has

functional properties as a healthy food but also has aroma and flavor that liked by consumers.

Keywords: Cocoa Liquor, Dark Chocolate, Fermentation, Physicochemical Properties, Polyphenols.

1. Introduction

Cocoa is an export commodity that contributes to an increase in foreign exchange. The quality of cocoa beans from Indonesia, especially South Sulawesi and West Sulawesi, is below the quality of the cocoa exporting country in the world. The leading cause of low quality of cocoa beans because the fermentation process is not done correctly. The fermentation process can decrease the content of polyphenols in cocoa beans, but the fermentation process is necessary for the formation of aromas and flavors [1–2]. The phytochemical aspects of cocoa beans are well developed into functional chocolate products that are of economic value such as antioxidant tablets, dark choco, late and instant chocolate drink rich in polyphenols. Some of the benefits of polyphenol compounds in cocoa beans are as antidiabetic, antihypertensive, premature anti-aging as well as anti-cancer possibilities [3–4]. In [5] general, cocoa beans produced by farmers are without fermentation so that the quality as a raw material of processed chocolate food products, including the low category. Some of the disadvantages of cocoa beans produced by farmers include low acidity levels, relatively high slaty seed content, and a distinctive flavor of cocoa that is weak because it does not have a compound aroma precursor. The quality of cocoa beans in the chocolate industry is determined by the compound content of polyphenols, aroma, and flavor. The compound content of chocolate aroma and flavor can be obtained through the complete fermentation process of wet cocoa beans before drying [6].

The optimal fermentation process can produce good quality cocoa beans with desired characteristics [7]. Dark chocolate has antioxidant content that can reduce the formation of free radicals in the body so it is good for health. Dark chocolate contains antioxidant components that play a role in controlling Low-Density Lipoprotein (LDL) levels. Choosing dark chocolate with a cacao mass content of 60–80% will get more nutritional benefits [8–9]. The unfermented cocoa beans contain various compounds of polyphenols, about 60% of the total polyphenols in cocoa beans (raw cocoa-nuts) are the monomers of flavanol (Epikatekin and Catechins) and pro-Cyanidin oligomers (dimmer and dekamer) with a concentration of vary. The concentration of Epikatekin in cocoa bean extract is estimated at 7–10 times higher than that of cocoa liquor [10–11].

Despite the importance of the chocolate market, there are comparatively few studies, which consider the chemical constituents of the finished chocolate product, which is the product of cocoa beans after fermentation, drying process, roasting, winnowing, alkalization, conching, and finally tempering. The majority focus on analytical methods for determining the geographical origin of unfermented cocoa beans and certain fermentation products. Previous research to look at fatty acid profiles [12], volatile compounds [13],

Solid State Magic Angle Spinning (MAS) NMR [14], and Fourier Transform Near-Infrared (FT-NIR) [15] are amongst those reported.

This research aims to develop cocoa beans without fermentation as a healthy chocolate product. Cocoa with a high content of polyphenols is a significant health food product of polyphenols. This research is done by producing and evaluating the quality of dark chocolate by varying the amount of concentration of fermented cocoa beans and without fermentation to produce a product rich in polyphenols. Cocoa products obtained will be analyzing the total content of polyphenols and flavonoids, but first conduct an analysis of the total polyphenols and total flavonoids in cocoa liquor before becoming a dark chocolate product. Cocoa liquor is the base of all types of chocolate without any other material added. The purpose of analyzing the content of polyphenols and flavonoids cocoa liquor in advance to compare whether there is a decrease in the levels of polyphenols and flavonoids levels after becoming a dark chocolate product. Mixing cocoa beans fermentation and without fermentation in the making of dark chocolate can increase the aroma and taste of dark chocolate, so it not only has functional properties as a healthy food but also has aroma and flavor that liked by consumers.

2. Material and Methods

2.1. Material

The chocolate samples evaluated in this study were made and kindly supplied by Cocoa varieties Forastero from Soppeng Regency, South Sulawesi, Indonesia. All samples were made of dark chocolate with lecithin from Sigma-Aldrich (St. Louis, MO), cocoa butter from *Mars Symbioscience Company* (Makassar, South Sulawesi, Indonesia), and sugar in this order. All chemicals were of analytical grade, hexane (CAS: 110-54-3), sodium carbonate (CAS: 497-19-8) were supplied by Merck Millipore (Burlington, MA), DPPH (D4313, CAS: 1898-66-4) was from Tokyo Chemical Industry (Tokyo, Japan), Folin Ciocalteau (109001), while aluminum chloride (254134, CAS: 12125-02-9), sodium nitrate (CAS: 7631-99-4), gallic acid (CAS: 149-91-7), and sodium hydroxide (CAS: 1310-73-2) were from Sigma-Aldrich (St. Louis, MO). All samples were made of fermented cocoa beans and cocoa beans without fermentation in this order. Early stages of this research are the manufacture of cocoa liquor with a variation of cocoa nibs fermentation and without fermentation, then continued with the manufacture of dark chocolate. Enrichment ingredients and their addition to plain cocoa liquor and dark chocolate are listed in Tables 1 and 2.

2.2. Methods

2.2.1. Preparation of Cocoa Liquor Products

Fermented cocoa beans are roasted in (roasting machine KL Protech Type Number 043.13P033 capacity 15 kg) at 100–105 °C for 1 h, while the cocoa beans without fermentation are injected at 80 °C for 40 min to form a distinctive aroma and flavor of

chocolate. Minimum roasting machine capacity 8 kg. After the roasting stage is completed, then proceed with cooling up to reach the temperature 40–50 °C. Then samples of cocoa beans were inserted in winnower (nibs separator machine KL Protech Type Number 049.13P043) to separate between nibs and shell (seeds and outer skin). Once separated from the seeds and outer skin, nibs and shells are weighted with a comparison in Table 1. Nibs are then ground using a stone mill (KL Protech Type Number 066.13P063) to destroy nibs that initially shaped coarse solid granular into the cocoa paste (cocoa liquor). Furthermore, cocoa liquor was taken in a ball mill (ball mill mini KL Protech Type Number 041.,13P028) which is useful to smooth the still rough cocoa liquor at 50 °C for 30 h. Cocoa liquor will be analyzed physicochemical content include the analysis of viscosity, the colour, content of polyphenols, and flavonoids.

TABLE 1. Experimental variables and their levels used for response surface methodology (Box Behnken Design) of products cocoa liquor

Trial	Code samples	Fermented cocoa beans (%)	Cocoa beans without fermentation (%)
1	L1	0	100
2	L2	25	75
3	L3	50	50
4	L4	75	25

2.2.2. Preparation of Dark Chocolate Products

The process of dark chocolate begins with the formulation process in Table 2. Chocolate dough is inserted into the ball mill for conching at a temperature of 50 °C for 12 h, so obtained the level of smoothness of dough with a particle size close to 20 microns. The molten chocolate was mixed and kept at 25 °C for 30 min at a speed of 75 rpm. Samples

TABLE 2. Experimental variables and their levels used for response surface methodology (Box Behnken Design) of dark chocolate products

Trial	Code samples	Sugar (%)	Cocoa liquor (%)	Lecithin (%)	Cocoa butter (%)	Vanilla (%)
1	D1 (100% cocoa beans without fermentation)	45.6	45.3	0.5	8.5	0.1
2	D2 (75% cocoa beans without fermentation: 25% fermented cocoa beans)	45.6	45.3	0.5	8.5	0.1
3	D3 (50% cocoa beans without fermentation: 50% fermented cocoa beans)	45.6	45.3	0.5	8.5	0.1
4	D4 (25% cocoa beans without fermentation: 75% fermented cocoa beans)	45.6	45.3	0.5	8.5	0.1

were then quenched to 25 °C and held at that temperature level for 10 min, and then the samples were heated to 30 °C and kept at that temperature for 10 min. Tempering is the process of melting the chocolate, precisely at the temperature required by brown fats to form a perfect crystallization or freezing, so that the results are shiny and dried. Chocolate dough in shape for 15–25 min with a mixed temperature of 30 °C. Throughout the entire conventional tempering process, all the samples were stirred automatically. Finally, after depositing the freshly tempered chocolates (15 °C), they were stored at 5–15 °C and 45% RH for 24 h to improve crystal growth. Then samples were maintained at 5 °C until the analyses.

2.2.3. Total Phenolic Assay

The total phenolic content of dark chocolate and cocoa liquor was determined by using the Folin-Ciocalteu assay [16]. An aliquot (1 g) of extracts or standard solution of gallic acid (2, 4, 6, 8, 10, and 12 ppm) was added to a 25 ml volumetric flask containing 9 ml of distilled deionized water (ddH₂O). A reagent blank using ddH₂O was prepared. One milliliter of Folin-Ciocalteu phenol reagent was added to the mixture and shaken. After 5 min, 10 ml of 7% Na₂CO₃ solution was added to the mixture. The solution was diluted to volume (25 ml) with ddH₂O and mixed. After incubation for 90 min at room temperature, the absorbance against prepared reagent blank was determined at 750 nm with a UV–Vis Spectrophotometer Lambda 5. The total phenolic content of dark chocolate and cocoa liquor was expressed as mg gallic acid equivalents (GAE)/100 g fresh weight. All samples were analyzed in duplicates.

2.2.4. Total Flavonoid Assay

Total flavonoid content was measured by the aluminum chloride colorimetric assay. An aliquot (0.5 ml) of extracts or standard solution of catechin (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, and 55 ppm) was added to 10 ml volumetric flask containing 4 ml of ddH₂O. To the flask was added 0.3 ml 5% NaNO₂. After 5 min, 0.3 ml 10% AlCl₃ was added. At 6 min, 2 ml 1 M NaOH was added, and the total volume was made up to 10 ml with ddH₂O. The solution was mixed well, and the observance was measured against prepared reagent blank at 510 nm. The total flavonoid content of dark chocolate and cocoa liquor was expressed as mg catechin equivalents (CE)/100 g fresh mass. Samples were analyzed in duplicates.

2.2.5. Colour Analysis of Food Products

Colour lightness of the dark chocolate and cocoa liquor samples was measured using Hunter method (as L, a, and b value) in triplicate with a Minolta Chroma CR-400 (Minolta Co, Osaka, Japan). The parameter of the value L, a, and b sample will be visible, where the value of L is the lightness, the value (+) on a indicates the red color and the value (–) on a show green color, the value (+) in the b indicates the yellow color and the value (–) on the b indicates the blue color. It is then measured on the chart to know the color specifications [17].

2.2.6. Determination of Viscosity

The viscosity of the melted dark chocolate and cocoa liquor samples was obtained by fitting shear stress and shear rate values using the Casson fitting model, Using a Viscometer (*DV1 Digital Viscometer Brookfield*). The spindle tool used is the 64 spindles, at a speed of 10 rpm with a temperature of 50 °C for 1 min. Friction between the spindle surface and the sample fluid determines the viscosity level [18].

2.2.7. Determination of Melting Properties

Melting properties of dark chocolate and cocoa liquor samples were determined using differential scanning calorimeter (DSC) DSC-60 Plus Series Shimadzu for this aim. Samples (approximately 4 mg) were loaded into 40 ml capacity pans and sealed with hermetic lid using a sample press. The corresponding parameters representing melting profile of the samples, onset temperature (T_{onset} where melting of the samples started), peak temperature (T_{peak} where the highest rate of the melting was observed), end temperature (T_{end} where the samples melted completely) and ΔH (energy required for complete melting of the samples) were calculated from the thermograms obtained after heating the pans from 23 to 50 °C at 3°C/min heating rate performed by N₂ stream [19].

2.2.8. Texture Profile Analysis (TPA) of Dark Chocolate and Cocoa Liquor

Determination of textural properties of molten chocolates was evaluated using a TA-XT Plus Texture Analyzer (Stable Micro Systems, Godalming, Surrey, England) with back extrusion rig and a 35 mm diameter compression disk attached to an extension bar using 50 kg load cell. Samples melted at 50 °C for 75 min were quickly transferred to a standard back extrusion container (50 mm diameter) and work done in back extruding 100 ml chocolate determined to measure force in compression. Two replications per sample test of 5.0 mm/s above sample surface, penetrating 30 mm, then returning to the start position. Mean values were used to obtain a force–time curve (XT.RA Dimension, Exponent 32 software; Stable Micro Systems) calculating as texture parameters: 1. Firmness = maximum compression force in extrusion thrust into the sample (g); 2. Index of viscosity = area of curve negative region during probe withdrawal (gs). The hardness of solid tempered dark chocolate and cocoa liquor was measured using the Texture Analyzer with a penetration probe (needle P/2) attached to an extension bar, a 50 kg load, cell and a platform. Maximum penetration force through a sample (80 × 20 mm, depth 8 mm) was determined with eight replications at a speed of 1.0 mm/s, test of 2.0 mm/s, post-speed of 10.0 mm/s, penetrating 5 mm at 20 °C, converting mean values into hardness data using XT.RA Dimension, Exponent 32 software (Stable Micro Systems, Godalming, UK) [20–21].

2.2.9. Sensory Evaluation of Dark Chocolate

We are using sensory analysis methods, Difference from Control Test. The panelist is presented with 1 (one) Control sample (R) and 7 (seven) samples as a test, and 1 Control sample is treated as a blind control test sample. A panel of skilled evaluators assessed the

samples with a 9-point scale (1- Very, very good taste of R, 2- Very better taste of R, 3- flavors better than R, 4- Taste somewhat better than R, 5- Taste as good as R, 6- Taste somewhat worse than R, 7- Taste worse than R, 8- Taste very worse than R, and 9- Awful taste of R), by 31 trained panelists selected from post-graduate students and staff of the Department Chemical Engineering, Politeknik Negeri Ujung Pandang.

2.2.10. Statistical Analysis

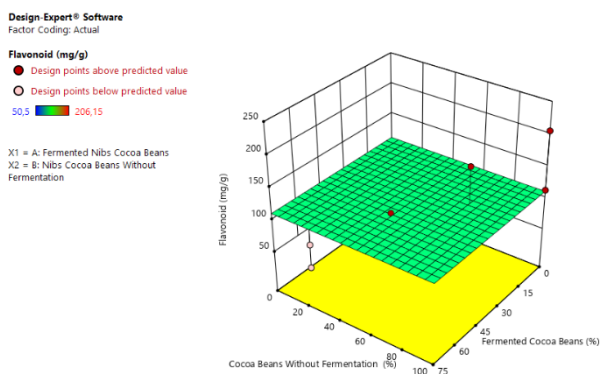
Statistical analyses were carried out with Design Expert Stat-Ease Version 11 (Stat-EaseInstitute Inc Minneapolis., 2019) for response surface methodology (DOE). Panelist data were subjected to analysis of variance (ANOVA) followed by *Duncan's Multiple Range*, with a significance level of 0.05. All analysis was performed using the statistical program Statistical Package for the Social Sciences (SPSS) version 17.0 (International Business Machines Corporation, New York, NY).

3. Results and Discussion

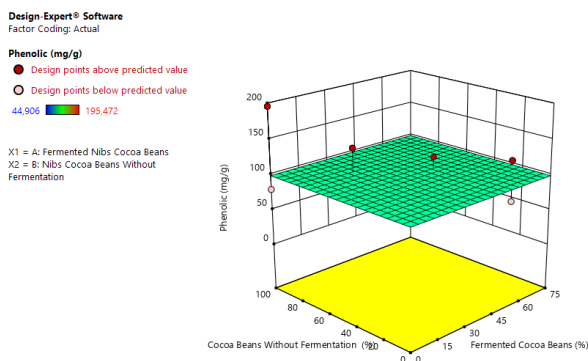
3.1. Identification Total Phenolic and Flavonoid

The products in this research are cocoa liquor and dark chocolate made from cocoa beans with a variation of the number of cocoa beans without fermentation and fermented cocoa beans. Dark chocolate is a product that is rich in polyphenols and flavonoids with cocoa mass (liquor), about 70%. Variation of the number of cocoa beans without more significant fermentation of fermented cocoa beans. Cocoa liquor samples produced from 100% of cocoa beans without fermentation show the highest levels of high polyphenols and flavonoid, while cocoa liquor samples from 25% cocoa beans without fermentation and 75% of fermented cocoa beans demonstrate the total levels of polyphenols, due to the fermentation process that can lower the levels of polyphenols and flavonoid in the product. In cocoa liquor products, sample L1 with the highest content of polyphenols and flavanoids of 195.472 mg/g samples and 206.15 mg/g samples (Figure 1). While on the sample, dark chocolate code D1 total content of polyphenols and the highest flavonoids of 79.622 mg/g samples and 113.15 mg/g samples (Figure 2). The total levels of polyphenols and flavonoids in dark chocolate samples (D1–D4 code) are reduced by increasing the number of fermented cocoa beans. The fermentation process can decrease the content of polyphenols and flavonoids, which are directly proportional to the increasing number of fermented cocoa beans [22–23].

The decrease in the content of polyphenols during fermentation is caused by the diffusion of polyphenols that come out of the seed chip. During cocoa beans fermentation, polyphenols are subjected to biochemical modifications through oxidation and polymerization and binding with protein, hence decreasing their solubility and astringency effect. At the same time, anthocyanins are hydrolyzed to produce anthocyanidins, galactose and arabinose; beside dimerisation of leucocyanidins and exudation of the flavonoids from the bean. Subsequently, during drying, the amount of polyphenols are substantially reduced mainly by enzymatic browning [24–25]. Polyphenols are oxidized by polyphenols



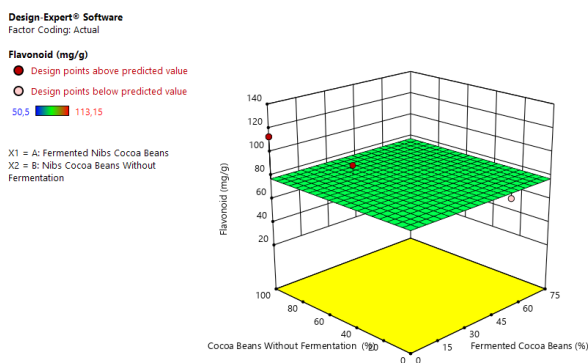
(a)



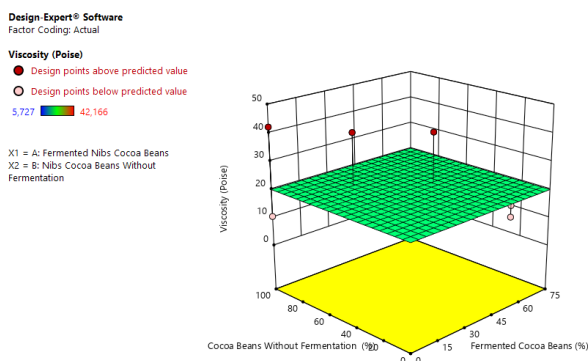
(b)

FIGURE 1. Response surface plot for the effect of process cocoa beans without fermentation and fermented cocoa beans (a), flavonoid, and (b) phenolic of cocoa liquor.

oxidase forming quinone and diquinone followed by polymerization and the formation of insoluble pigment compounds with high molecular weights. In addition, reactions with proteins also contribute to the decrease in the total content of polyphenols. This research shows that the total levels of polyphenols and flavonoids in cocoa liquor are higher than after being dark chocolate products. This is due to the process of processing from cocoa liquor to dark chocolate has passed several processes of heating (conching) so as to reduce levels of polyphenols and flavonoids. The more stages of processing involving the heating process, the more content of the loss of polyphenols and flavonoids [26–27]. Dark chocolate products produced in this research have high levels of polyphenols and flavonoids so that it can meet the criteria as a health food based on the content of polyphenols and Flavonoidnya. Dark chocolate products can increase the concentration of high-density lipoprotein (HDL) cholesterol, thereby lowering a person to be exposed to cardiovascular diseases. The total phenolic content of the beans and cocoa products is very influenced by the interaction of genetic factors with their surroundings. In the period before the harvest (pre-harvest) total phenolic content influenced by the interaction of genetic



(a)



(b)

FIGURE 2. Response surface plot for the effect of process cocoa beans without fermentation and fermented cocoa beans (a), flavonoid, and (b) phenolic of dark chocolate.

factors (genotype/varieties/clone) with environmental factors biophysics or agronomist (aquaculture). Later in the period of post-harvest, the components of the post-harvest interact each other with processing factors (the process of fruit storage, fermentation, drying, and roasting) to influence polyphenol content [28].

3.2. Color Analysis of Food Products

Color cocoa liquor and milk chocolate products are defined with the color system Munsell (L, a, b). The value L^* , a^* , and b^* is calculated using the Chromameter instrument Minolta CR-400. The basic principle of this tool is the interaction between the diffuse light energy and the atom or molecule of the object being analyzed. In the Munsell Color System, where L indicates the lightness that has a value range of 0 (dark/black) to 100 (light/white), a and b indicate the chroma coordinates, where a indicates the color green (a negative) to red (a positive), b for the color blue (b negative) to yellow (b positive). HUE values indicate the actual sample color, while the C value indicates the color, sharpness of the sample [29]. Colour analysis results with the Munsell method can be seen in Table 3.

TABLE 3. Result color measurement of cocoa liquor and dark chocolate product with Chromameter Minolta CR-400

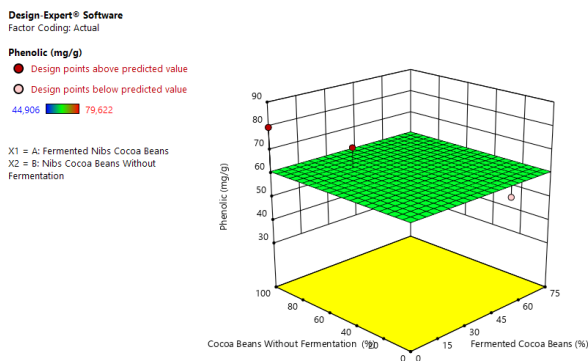
No	Sample	Value					Color
		L*	a*	b*	Hue	C	
1	L1	22.03	+3.63	+3.11	71	11.42	Orange (YR)
2	L2	23.09	+4.34	+5.20	88	22.93	Orange (YR)
3	L3	24.73	+4.56	4.69	80	21.39	Orange (YR)
4	L4	27.89	+5.91	+5.50	75	32.58	Orange (YR)
5	D1	27.42	+7.47	+5.93	67	45.48	Orange (YR)
6	D2	28.65	+6.27	+7.35	86	46.66	Orange (YR)
7	D3	29.91	+7.94	+6.92	72	55.46	Orange (YR)
8	D4	30.42	+9.38	+11.46	88	109.65	Orange (YR)

Legend: Sample L1/D1 (100% cocoa beans without fermentation), sample L2/D2 (25% of fermented cocoa beans: 75% without fermentation), sample L3/D3 (50% of fermented cocoa beans: 50% of without fermentation), sample L4/D4 (75% of fermented cocoa beans: 25% of without fermentation).

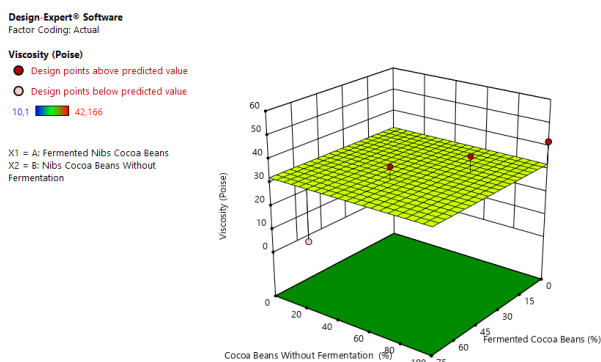
The values of L*, a*, and b* cocoa liquor samples (codes L1, L2, L3, and L4) that the value of L (lightness) samples of L1, L2, L3, and L4, respectively were 22.03, 23.09, 24.73, and 27.89. The decrease in the L value causes the lightness of the cocoa liquor sample to be darker. Furthermore, the value of a* and b* cocoa liquor samples each increased from +3.63 (L1) to +5.91 (L4) and from +3.11 to +5.50. Oxidation of the epicatechin compounds in the seeds during the fermentation and drying process determines the characteristic of brown colour in the fermented cocoa beans as the raw material of chocolate. Polyphenols content contributes to bitterness, astringency, color (a* and b*), flavor, smell, and oxidative stability [30–31]. Fermented cocoa beans have a more brown colour, can provide better colour and aroma when compared to cocoa without fermentation. The intensity of cocoa color during the fermentation process is increased compared to the cocoa beans without fermentation that produce a darker color, but between the sample L1 until the sample L4 and the sample D1 until the sample D4 color intensity is not much different (smaller differences). Some factors that can affect the product colour are the composition of raw materials and production processes, where fermented cocoa beans will change the characteristics of seeds through the chemical reaction process.

3.3. Viscosity

The manufacture of chocolate products begins with grinding nibs into cocoa liquor as a semi-productive in the liquid phase. One parameter that determines the characteristics of chocolate products is the viscosity of cocoa liquor. Figure 3 shows the response surface plot on the viscosity value of cocoa liquor and dark chocolate resulting from a comparison of the fermented cocoa nibs composition and without fermentation. Cocoa liquor viscosity value is directly proportional to the concentration variation of each sample. The L1 sample has the highest viscosity value of 10.49 ± 1.539 poises and the lowest of the L4 sample is 5.727 ± 0.072 poises. From a sample L1 to a sample of L4, the viscosity value began to decline with a decrease in the concentration of cocoa beans without fermentation. At the dark chocolate, the highest viscosity value of the sample D1 is 42.166 ± 14.396 poise and



(a)



(b)

FIGURE 3. The response surface plot for the effect of process cocoa beans without fermentation and fermented cocoa beans on the viscosity (a), cocoa liquor, and (b) dark chocolate.

the lowest in the D4 sample is 10.1 ± 1.414 poises. Similar to the sample L1 up to the L4 sample, its viscosity value from the sample D1 until the D4 sample began to decline with a decrease in the amount of cocoa concentration without fermentation. This is due to decreased seeds without fermentation occurs a decrease in the amount of fat so that the viscosity value is low (Table 4).

Cocoa beans without fermentation have a fat content that is still less than fermented cocoa beans. Decreasing the number of cocoa beans without fermentation causes a decrease in the amount of fat, thereby increasing the viscosity value. The phospholipid content in cocoa butter affects viscosity. The viscosity is reduced by the rise of phospholipids in cocoa butter. Coarse fat content (crude fat) fermented cocoa beans amount $22 \pm 0.10\%$ and cocoa beans without fermentation of $6 \pm 0.07\%$ [32].

Fermented cocoa beans will decrease the content of fat, raw materials such as proteins, polyphenols and carbohydrates that decompose so that the relative fat levels will increase [33–34]. Cocoa fats can decrease the viscosity value of chocolate products, the increase in fat content in the product will reduce its viscosity value [35]. Processing of the product into

TABLE 4. The viscosity of cocoa liquor and dark chocolate

Products	Sample	Viscosity value (Poise)
Cocoa liquor	L1	10.49 ± 1.539
	L2	9.49 ± 1.414
	L3	6.655 ± 0.068
	L4	5.727 ± 0.072
Dark chocolate	D1	42.166 ± 14.936
	D2	39.133 ± 14.068
	D3	38.15 ± 16.062
	D4	10.1 ± 1.414

Legend: Sample L1/D1 (100% cocoa beans without fermentation), sample L2/D2 (25% of fermented cocoa beans: 75% without fermentation), sample L3/D3 (50% of fermented cocoa beans: 50% of without fermentation), sample L4/D4 (75% of fermented cocoa beans: 25% of without fermentation).

a dark chocolate viscosity value will increase due to the addition of different ingredients (lecithin, sugar, and cocoa butter) so that the viscosity can increase. Viscosity can affect the material added. The more types of materials added to the chocolate the higher the viscosity. The viscosity of a fluid is a trait that indicates large and small prisoners in the fluid against friction. Friction between spindle surfaces on a device with fluid determines the viscosity of the fluid level [36]. Flavor parameters of chocolate products in the mouth one of them is influenced by viscosity. Some research suggests that high viscosity chocolate products have *amouth-feel pasty* and are related to particle size, composition, and process strategy. Measurement of physical product properties aims to maintain quality control of necessary materials and processing processes [37–38].

3.4. Determination of Melting Properties

DSC is a thermal analysis used to measure the difference in heat flow between samples and references measured as temperature functions [20]. The main application of the DSC is to study phase transitions, such as smelting, glass transitions, or exothermic decomposition. This transition involves changes in energy or changes in heat capacity that the DSC can detect with great sensitivity. Based on Figures 4–5, samples D1 shows the *endothermic peak process* with a melting point of 32.17 °C. This process shows that cocoa butter melted perfectly. Cocoa butter (*cocoa fat*) is a mixture of triglycerides that are composed of a POST (Palmitate-oleate-stearate) of 38.0%–43.8%, POP (Palmitate-oleate-stearate) of 16.8%–19.0% and SOS (Stearate-oleate-stearate) of 22.8%–30% melted perfectly at the temperature of 32–35 °C. The high melting point occurs in the temperature of 35 °C, where the chocolate will melt completely. The initial melting point is the temperature when the first drip occurs fat, while the final melting point is the temperature when the whole fat has been melted perfected [35]. The lowest melting point on the D4 sample of 31.73 °C and the highest melting point is on the D2 (Figures 6–7) sample of 32.68 °C. The melting point of each sample indicates a relatively small difference.

Storage conditions and tempering process can change the crystal structure in cocoa butter and affect the melting point. The tempering process is a process to regulate the bond

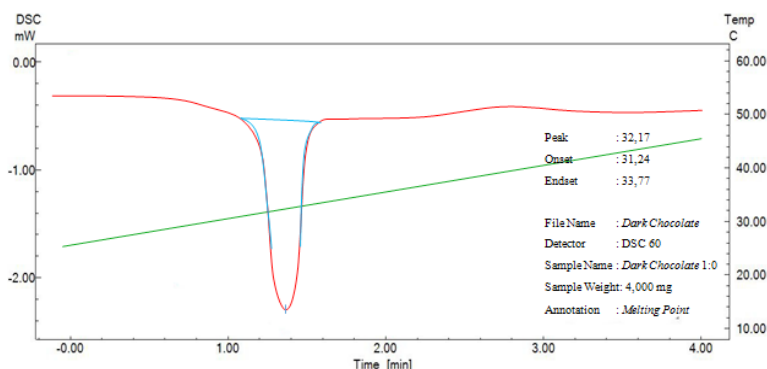


FIGURE 4. DSC curve sample D1 (100% cocoa beans without fermentation).

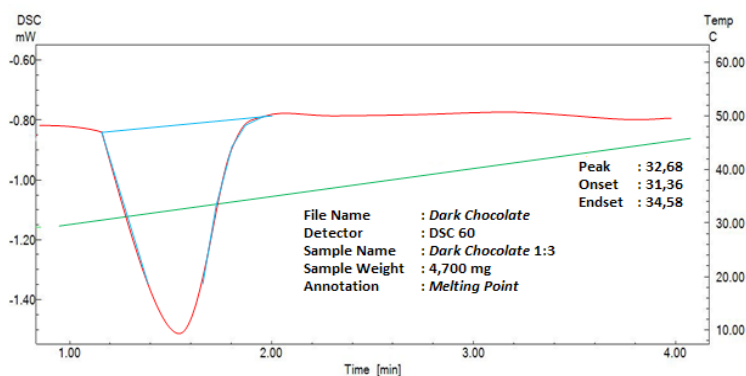


FIGURE 5. DSC curve sample D2 (cocoa beans without fermentation 75%; cocoa beans fermentation 25%).

of crystals in cocoa fat. After the heating process, the bonding structure of each of them regardless corresponds to the type of fatty crystals and forms the bonds of polymorphism α , β , and β' . The form of β is the most desirable form by the cocoa industry because it has a melting point of 29.5–36 °C and is most stable at room temperature. The crystals in cocoa can form γ , α , β , and β' with a melting point is the same as 16.9–18 °C, 22–24 °C, 24–29.4 °C and 29.5–36 °C. In the sample D1 until the D4 sample, the melting point ranges from 31.73 °C–32.68 °C. From the melting point range, a sample D1 to a sample of D4 is included in the type of fatty crystals of a β polymorphism bond because it has a stable 29.5–36 °C melting point at room temperature. The cocoa butter in chocolate products has six different crystal structure [36–39]. Table 5 shows a melting point for six chocolate structures dark chocolate products (sample code D1, D2, D3, and D4) show a type V crystal structure with good texture and stability influences. Based on research conducted by Rothkopf & Danzl (2015), the filling lipids can function as an activator for diffusion processes with the formation of fat bloom as a consequence. Filling lipids can merge with chocolate during production or storage. However, in most studies concerning crystallization or migration cocoa butter and hazelnut oil were analyzed, investigations on chocolate are rare. To cover

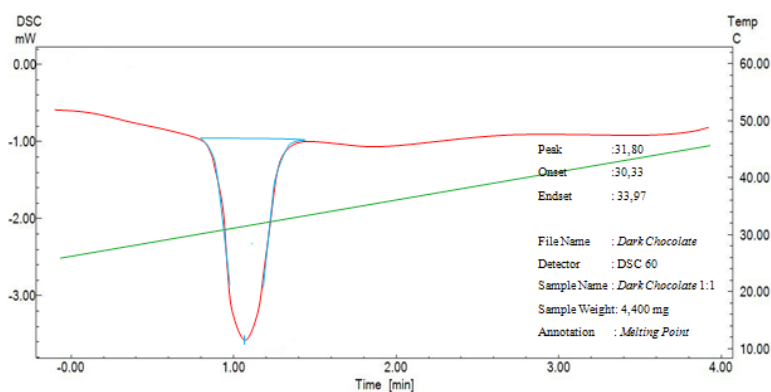


FIGURE 6. DSC curve sample D2 (cocoa beans without fermentation 50%: cocoa beans fermentation 50%).

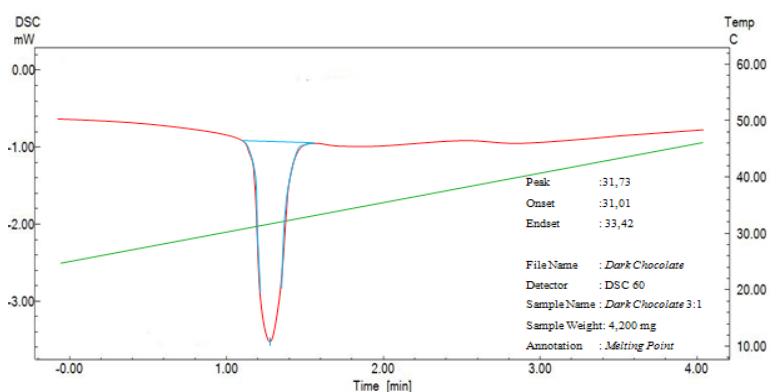


FIGURE 7. DSC curve sample D4 (cocoa beans without fermentation 25%: cocoa beans without fermentation 75%).

TABLE 5. Chocolate crystal type

Crystal	Melting point	Description
I	13.1 °C	<i>Soft, Crumbly, melts too easily</i>
II	17.1 °C	<i>Soft, Crumbly, melts too easily</i>
III	22.4 °C	<i>The firm, poor snap, melts too easily</i>
IV	26.4 °C	<i>The firm, good snap, melts too easily</i>
V	30.7 °C	<i>The glossy, firm, best snap, melts near body temperature</i>
VI	33.8 °C	<i>Hard, takes weeks to form</i>

a broad variety of fillings, dark chocolate was blended with hazelnut oil, butterfat, and coconut oil and crystallization was analyzed. All investigated lipids reduced the solid fat content to the same extend. However, crystallization behavior of the blended samples differed. Hazelnut oil accelerated crystallization rate and did not affect crystallization time, while butterfat reduced crystallization rate and time. The effect of coconut oil addition

was in between those of hazelnut oil and butterfat. Nucleation and crystal growth rate, which affect the crystallization speed, have been shown to be affected by the type of filling lipid. Additionally, there is evidence that crystal transformation during crystallization is also affected by filling lipids. © 2015 WILEY-VCH Verlag GmbH, "author":[{"dropping-particle":",", "family":"Rothkopf", "given":"Isabell", "non-dropping-particle":",", "parse-names":false, "suffix":","}], [{"dropping-particle":",", "family":"Danzl", "given":"Wolfgang", "non-dropping-particle":",", "parse-names":false, "suffix":","}], "container-title":"European Journal of Lipid Science and Technology", "id":"ITEM-1", "issued":{"date-parts":[["2015"]]}, "title":"Changes in chocolate crystallization are influenced by type and amount of introduced filling lipids", "type":"article-journal", "uris":["http://www.mendeley.com/documents/?uuid=6ea9e1d4-f3f9-449a-92ea-98a36d190904"]}], "mendeley":{"formatted Citation":"[40]", "manualFormatting":"Rothkopf & Danzl (2015, shows that high-quality chocolate, in general, has a V crystal type with a rather harsh texture. The V and VI crystal structures with a more tightly-structured arrangement cause a sharp texture difference.

3.5. Texture Measurements

The measurement of dark chocolate texture using puncture method, probe is pressed by a constant style magnitude to penetrate the sample penetrating at a certain depth and time as well as in a predefined condition so that it can be known hardness value from dark chocolate. Sample D3 has the highest hardness value of 7820.533 g force/sec later in order on the sample D4 and D1, which is 7481.671 g force/sec and 5280.287 g force/sec. Lowest hardness value measurements in the D2 sample of 4613.903 g force/sec (Figure 8). The texture quality of chocolate products depends on the melting point and crystallization of cocoa butter used [40–41]. The chocolate texture is strongly influenced by the intrinsic hardness of cocoa fats [42]. In the sample, D3 produces the highest hardness value compared to other samples because of the melting point value of 31.80 °C. the crystal structure between the temperature of 30.7 °C–33.8 °C with a more tightly arrangement led to a harsh texture difference. The texture is a common trait that encompasses the biological, mechanical, and sensory properties of foodstuffs to taste when consumed in the mouth. Good dark chocolate product must have a smooth texture that can melt softly and gently in the mouth. Mixing and stirring process in a long time can reduce the size of the chocolate particles and this affects the texture of chocolate. The large size of sugar particles is one of the causes of sandy and not a smooth texture. Therefore, we need refining or conching treatment process in a long time to reduce the size of the particles to the produced smooth texture of chocolate.

3.6. Sensory Evaluation of Dark Chocolate

Sensory testing systems are developed based on assessment objectives. Test the difference of control applied in the testing of dark chocolate products produced. Products comparator (control) used is a commercial dark chocolate product that already has a market. Product of dark chocolate research results compared with the control product to determine the intensity of difference in various aspects of the assessment. Dark chocolate has a variety of distinctive flavor and aroma that can be scanned through sensory assessment. Organoleptic

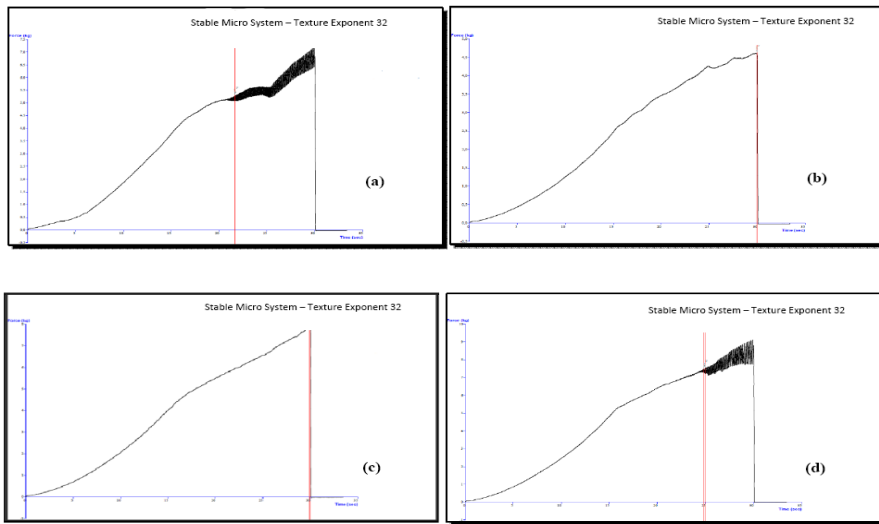


FIGURE 8. Graphic hardness of dark chocolate products (a) 100% cocoa beans without fermentation, (b) 25% of fermented cocoa beans: 75% without fermentation, (c) 50% of fermented cocoa beans: 50% of without fermentation, and (d) 75% of fermented cocoa beans: 25% of without fermentation.

test of dark chocolate products includes flavor and aroma parameters using a difference of control test methods to find out a difference between one or more samples with control and estimate how much difference between control.

Organoleptic testing of dark chocolate products (Table 6), sample 123 obtained the highest mean value of the assessment panelist against the dark chocolate flavor in 249. From the value of the mean, then analyzed using analysis of variance (ANOVA). Results obtained from ANOVA, F count, is higher than the F-value of the table so that it continues with the analysis of the redundant's multiple tests to determine which samples are different.

The method of Duncan's multiple range test can be concluded that samples 132, 213, 312, 123, and 231 which is a product of dark chocolate with a variation of the concentration of cocoa beans without fermentation and fermented cocoa beans have different flavor with control products in which the comparison product (control) used is the commercial dark chocolate products sold in the market. 5% of all samples are different from control products

TABLE 6. Mean value dark chocolate

Formulation dark chocolate	Mean
132	8.032
213	7.225
312	4.838
123	7.193
231	6.161

Legend: Sample 132 (100% cocoa beans without fermentation), sample 213 (25% of fermented cocoa beans: 75% without fermentation), sample 312 (50% of fermented cocoa beans: 50% of without fermentation), 123 (75% of fermented cocoa beans: 25% of without fermentation), sample 231 (dark chocolate commercial products).

or dark chocolate with varying concentrations of cocoa beans without fermentation and fermented cocoa beans (100%, 75%:25%, 50%:50%, 25%:75%) Produce noticeable flavor differences with control products. Panelist chose sample 123 with the highest LSR value of cocoa beans without fermentation 25%: fermented cocoa beans 75% as flavor better than other samples. Organoleptic test results showed that the essential ingredients of chocolate are alkalized cocoa mass, cocoa powder or cocoa butter, sugars, lecithin, and, in the case of milk chocolate, milk powder or crumbs. Chemical compounds dark chocolate is characterized by a praline, chocolate flavor with malty, nutty, and caramel notes, while the typical flavor of milk chocolate is sweet, milky, and honey-like with coconut notes [43] as shown in Tables 7–9.

TABLE 7. Variance analysis of flavor dark chocolate

Sources of diversity	df	JK	JKT	F _{count}	F _{table}	
					5%	1%
Sample	4	491,865	122,966	102,557	3.48	2.45
Panelist	30	301,678	10,056	8,387	1.38	1.25
Error	120	143,935	1,199			
Total	154	937,478				

Legend: df (degree of freedom), JK (sum squares), JKT (mean squares), F_{count} (F calculate), F_{table} (F table).

TABLE 8. F count value and F table of Duncan multiple range test of 5% level

P	2	3	4	5
Ranges	2.77	2.92	3.02	3.09
Least significant ranges (LSR)	0.545	0.574	0.594	0.608

TABLE 9. Comparison between treatments

Sample	Average	LSR	Notes
231	4.83	–	a
123	8.03	0.608	a
132	7.22	0.545	b
312	7.19	0.594	c
213	6.16	0.574	d

4. Conclusion

Dark chocolate products produced meet the criteria of healthy food because it has a high content of polyphenols and flavanoids. Dark chocolate formulation with a comparison of cocoa beans without fermentation and fermented cocoa beans (25%: 75%) has a better aroma and flavor and is more liked by consumers compared to other products; it can be seen from the viscosity value, melting point, lightness, hardness, and flavors of dark chocolate products that resemble commercial chocolate. This research can be useful in developing dark chocolate products that have an equivalent nutritional value with the value of taste, so that can be a reference for chocolate products that are worth the functional food.

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