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Antioxidant Activity and Physico-Chemical of Dark Chocolate Made with Cocoa Butter Substitute (Cbs) from Virgin Coconut Oils

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ABSTRACT
This study aimed to investigate the effect of different concentration of virgin coconut oil to antioxidant activity, physical characteristics, and organoleptic of dark chocolate, and knows the best addition of virgin coconut oil on dark chocolate making. This study used a Completely Randomized Design (CRD) with 6 treatments and repeated 3 time, so that 18 experimental units were obtained. The data obtained were analyzed using the analysis of variance (ANOVA) at 5% and 1% levels. Parameter with significantly affect was further analyzed using Duncan's new multiple range test (DNMRT) at the 5% level. The results showed that different concentration of virgin coconut oil had significant effect (1%) on antioxidant activity. The best concentration of virgin coconut oil is 10% with antioxidant activity value 70,38% and, good melting quality

Keywords: *Cocoa butter substitution, virgin coconut oil, dark chocolate.*

1. INTRODUCTION

Cocoa (Theobroma cacao) is one of the plantation commodities that plays an important role in the economy in Indonesia. Cocoa production is increasing because cocoa beans can be processed into various products such as cocoa powder, cocoa butter and other derivative products [1].

Processed cocoa will produce cocoa powder and cocoa butter which are used as raw material for making chocolate. Processing processes such as fermentation, drying, and other thermal processes in cocoa processing can cause reduced polyphenol content and antioxidant activity in cocoa beans and processed products [2].

Dark chocolate is a chocolate bar made from cocoa powder with cocoa butter and a small mixture of sugar, vanilla and lecithin. According to Ide [3] dark chocolate can improve one's mood. Chocolate can induce the release of chemicals that can reduce pain, improve mood and feelings of happiness. So far, most of chocolate processing uses cocoa butter, which has a high price. This is because cocoa butter carries a distinctive aroma of cocoa and has a characteristic fat that matches the characteristics of chocolate [4].

Furthermore, In Asmawit's [4] study, the substitution of cocoa butter with palm oil in making chocolate bars obtained the best treatment with a percentage of palm fat to total fat of 25%. In the test, the melting point of chocolate bars with a palm fat concentration of 25%, the melting point is the same as chocolate bars using 100% cocoa butter and a good liking level.

This study aims to determine the effect of substitution of cocoa butter with virgin coconut oil on antioxidant activity, physical properties, and organoleptics in dark chocolate.

2. MATERIAL AND METHODS

2.1. Materials

Details of chemicals and materials were cocoa powder, cocoa butter, virgin coconut oil, refined sugar, lecithin, and vanilla. While the materials used for analysis were C2H5OH and DPPH solution. The instruments used in this research are spectrophotometer UV-Vis and Minolta color reader.

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2. MATERIAL AND METHODS

2.1. Materials

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2.2. Preparation of Dark Chocolate Making

All ingredients were weighed (cocoa butter according to treatment, virgin coconut oil according to treatment, 1g of vanilla, 6.57g of cocoa powder, 15g of sugar and 3 mL of lecithin). Next, put the sugar, vanilla and lecithin (1/3) into a container and mix well. The cocoa butter is preheated at 35°C to produce liquid cocoa butter. Then mix the liquid cocoa butter with pure coconut oil according to various concentrations and add cocoa powder then mix it using a mixer until blended. After that, add additional ingredients and mix using a mixer to make a paste, then add more lecithin to the mixture (2/3) and stir until blended. The addition of lecithin is gradually used to facilitate mixing of cocoa butter with powdered ingredients such as refined sugar. After all the ingredients are evenly mixed, the tempering process is carried out at a temperature of 45°C; 26°C; 32°C. After that, the printing is done and cooled in the refrigerator until the chocolate hardens.

This study used a completely randomized design (CRD) with the percentage of Cocoa Fat: Pure Coconut Oil as denoted by K consisting of 6 treatment levels and 3 replications so that 18 experimental units were obtained.

Treatment factors: K1 = 100%: 0%, K2 = 90%: 10%, K3 = 80%: 20%, K4 = 70%: 30%, K5 = 60%: 40%, K6 = 50%: 50%.

2.3. Antioxidant Activity Test

Dark chocolate samples were weighed ± 1 g using an analytical balance, put into a 100 mL volumetric flask then ultrasonic for ± 15 minutes, left to stand until room temperature was reached. After that the sample is dissolved with 96% ethanol as much as 50 mL until it dissolves, and ethanol is added again until the mark is then homogenized. Then the solution is filtered using filter paper.

2 mL of the filtered solution are taken, then put into a closed test tube containing 2 mL of DPPH solution. The solution mixture was homogenized using vortex and stored for 30 minutes in a dark room. Absorption was measured using a spectrophotometer UV-Vis at a wavelength of 517 nm [5]. The absorbance data obtained were used to determine% inhibition. The DPPH ability of the extract is calculated using the following equation:

Total antioxidant (%) = ((absorbance of control-absorbance of sample)) / (absorbance of control)

2.4 Color

Color testing was performed using the Konica Minolta CR-10 Color Reader. The sample to be tested, first put in a transparent zip lock plastic, turn on the Color Reader by pressing the power switch, then attach the optical head to the zip lock plastic (sample) and press the measuring button, the results obtained include L * (lightness), a * (redness) and b * (yellowness). Furthermore, the measurement of L *, a *, and b * values is carried out on the sample. The L *, a *, and b * values obtained from the color capture by Color Reader are then searched for the color name (hue) using color-hex on ***www.colorhexa.com*** [6].

2.5 Stability Test

The stability test or melting properties is carried out by observing what happens to the form of dark chocolate produced in the presence of a change in shape from solid to melt. The stability test was carried out in an incubator with a temperature of 37oC for a certain time. Observed a change in shape in the dark chocolate [7].

2.6 Fat Blooming Test

The fat blooming test is marked by the presence of white spots on dark chocolate. This test is carried out by storing dark chocolate for 21 days at room temperature. Then observed every week to see if there is a bloom on the surface of the sample [8]

2.7 Statistical Analysis

The statistical analyses were conducted using one-way analysis of variance (ANOVA). Data were reported as mean values ± standard deviation

3. RESULTS AND DISCUSSION

3.1. Antioxidant activity

The antioxidant activity of dark chocolates are presented in Table 1.

Table 1. Inhibition activity of dark chocolates with difference cocoa butter substitute percentage from virgin coconut oils concentration.

CBS from VCO Composition (%)	Inhibition (%)
100% : 0%	69,58 ± 0,4 [a]
90% : 10%	70,38 ± 0,4 [ab]
80% : 20%	71,27 ± 0,5 [b]
70% : 30%	73,34 ± 0,5 [c]
60% : 40%	74,46 ± 0,4 [d]
50% : 50%	74,67 ± 0,5 [d]

Noted : Means with different superscript letters in the same column indicate significant differences (p 0.05) between the carriers.

Apart from the phenol and flavonoid content in cocoa, virgin coconut oil also affects the antioxidant

activity of dark chocolate. This can be seen from the value of the antioxidant activity obtained, namely the higher the percentage of virgin coconut oil, the higher the antioxidant activity in dark chocolate. Pure coconut oil contains tocopherol and beta-carotene compounds which are very high [9]. The virgin coconut oil used has an antioxidant activity value of 75.16%.

Based on Lany's research [10] stated that the antioxidants contained in chocolate not only come from catechins and other antioxidants in chocolate itself, but other additives such as honey and almonds also have an effect in increasing the value of antioxidant activity.

3.2. Stability test

The stability test of dark chocolates are presented in **Table 2**.

Table 2. Stability test of dark chocolates with difference cocoa butter substitute percentage from virgin coconut oils concentration.

CBS from VCO Composition (%)	0 Min	10 Min	20 Min	30 Min
100% : 0%	H	H	H	SS
90% : 10%	H	H	H	SS
80% : 20%	H	H	SS	M
70% : 30%	H	SS	S	M
60% : 40%	H	SS	S	M
50% : 50%	H	SS	S	M

H = Hard, SS= slightly soft, S = soft, M = Melting

Based on **Table 2**, it is known that the stability test of dark chocolate in treatment K1 (100%: 0%) and K2 (90%: 10%) still has a hard texture at 15 minutes, while other treatments begin to experience changes in texture within 15 minutes. The hard texture referred to in this test is the dark chocolate texture which still looks solid. While the texture is melted, that is, it looks melted. At 30 minutes, all treatments experienced a change in texture. But only the K1 (100%: 0%) and K2 (90%: 10%) treatments the shape remains hard (H) like the initial texture (H), but when touched the texture is very soft. Meanwhile, other treatments experienced a change in shape which was seen to be Melting (M)

Stability test on dark chocolate can be stated that the more virgin coconut oil is added, the faster the melting of dark chocolate will be. This is due to the basic nature of virgin coconut oil which has a melting point of 20-25oC [11]. In the research of Indarti [7] the use of VCO as CBS in the manufacture of chocolate bars has a decreasing melting point as the VCO concentration increases.

3.3 Color Analysis

The differences in treatment had a very significant effect on the L *, a * and b * values in dark chocolate colour based on ANOVA test. The color name (hue) in this study is obtained by using color-hex, which is a website for reading the color name (hue). The values of L *, a *, b * and a description of the color dark chocolate can be seen in **Table 3.**

Table 3. Color test of dark chocolates with difference cocoa butter substitute percentage from virgin coconut oils concentration.

CBS from VCO CBS from VCO Composition (%) (%)	L*	a*	b*	Color	Description
100% : 0%	32,96^{b}	8,59^{b}	20,01^{b}		*Very Dark Desaturated Orange*
90% : 10%	32,88^{b}	8,49^{b}	19,97^{b}		*Very Dark Desaturated Orange*
80% : 20%	32,76^{b}	8,53^{b}	19,96^{b}		*Very Dark Desaturated Orange*
70% : 30%	32,54^{b}	8,38^{b}	19,81^{ab}		*Very Dark Desaturated Orange*
60% : 40%	32,66^{b}	8,33^{b}	19,94^{b}		*Very Dark Desaturated Orange*
50% : 50%	31,62^{a}	7,60^{a}	19,61^{a}		*Very Dark Desaturated Orange*

Noted: Means with different superscript letters in the same column indicate significant differences (p 0.05) between the carriers.

It can be seen in the table, the highest L *, a * and b * values produced from dark chocolate are found in treatment K1 (100%: 0%). With the value of L * 32.96, the value of a * 8.59 and the value of b * 20.01. The difference in the treatment of dark chocolate has the same color description result, namely Very Dark Desaturated Orange.

According to Prawoto [12] cocoa butter in the food industry can produce a more attractive product color with a distinctive brown color. Dark chocolate generally has a shiny dark chocolate color and appearance. This is due to the addition of cocoa powder and lecithin, where the cocoa powder gives a dark brown color while the lecithin gives a shiny impression. Research results show that the addition of virgin coconut oil can reduce the degree of brightness in dark chocolate. Sujatnika [13] stated that the addition of VCO (Virgin Coconut Oil) to chocolate bars further reduces the color of the chocolate bar to be lighter than the color of the chocolate bar without the addition of VCO, this is due to the clear color that VCO has.

3.4 Fat Blooming Test

The stability test of dark chocolates are presented in **Table 4**

Table 4. Fat Blooming test of dark chocolates with difference cocoa butter substitute percentage from virgin coconut oils concentration.

CBS from VCO Composition (%)	0 weeks	1 week	2 weeks	3 weeks
100% : 0%	–	–	+	+
90% : 10%	–	–	–	–
80% : 20%	–	–	–	–
70% : 30%	–	–	–	–
60% : 40%	–	–	–	–
50% : 50%	–	–	–	–

+= There was whites on the surface of chocolate

- = There was no whites on the surface of chocolate

Table 4 shows that dark chocolate without the addition of virgin coconut oil begins to form fat clots (blooming) at week 2, while dark chocolate with the addition of virgin coconut oil has not yet bloomed or no fat clots have formed. This is due to the addition of virgin coconut oil and addition of lecithin which functions as an emulsifier. The function of this emulsifier is to create a good bond between virgin coconut oil and cocoa butter and other components so that it does not cause fat (blooming) in chocolate [14]

According Halim [15] the addition of cocoa butter substitute (CBS) can reduce the formation of fat blooms. This is because CBS has different crystallization behavior compared to CB (cocoa butter). CBS can crystallize in β form directly, whereas CB cannot form β crystals directly. If the CBS is rapidly cooled, small crystals will form of uniform size. This is what causes the bloom stability to be better.

In the research of [7] chocolate bars without the addition of VCO formed fat clumps (blooming) on the surface of the chocolate bars, while chocolate bars with the addition of VCO concentrations of 4-5% did not form blooming and the brown color remained shiny. .Halim [15] also stated that chocolate with the addition of coconut oil shows good stability against blooming during storage.

4. CONCLUSIONS

The difference in the concentration of virgin coconut oil has a significant effect on antioxidant activity, color degrees of L * and a *, b * color in dark chocolate produced. The best concentration of virgin coconut oil in the manufacture of dark chocolate was 10% which contains antioxidant activity of 70.38%, has a color degree of L * 32.88, a * 8.49, b * 19.97, melting properties (stability) well, there was no fat blooming for 21 days, had a brown color.

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