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Effect of the Adding of Natural Antioxidant in the Stored Traditional Coconut Oil on the Free Fatty Acid Value

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Abstract: Coconut oil is one of edible oil that still produce in large quantity and sell traditionally. Coconut oil that is made and sells traditionally generally easy to become rancid and cannot be stored in a longer time. One of the main factors that caused rancidity in oil is the microbial activity that may hydrolyse oil to become glycerol and free fatty acid. The antioxidant is usually added in edible oil to prevent rancidity happened. This study aims determine free fatty acid value changing in the stored traditional coconut oil that had added with some nature antioxidants. Four natural antioxidant here are cinnamon, mangosteen peel, turmeric and cassumunar ginger. The free fatty acid value was determined using acid base titration for three weeks of stored traditional coconut oil. Results show that mangosteen peel as a natural antioxidant in traditional coconut oil gives the lowest change percentage in free fatty acid value (4.2%), while other natural antioxidant shows the same and higher change percentage of free fatty acid value. Several factors that caused the antioxidant didn't work properly are the presence of moisture and impurities of material antioxidants. However, natural antioxidants become promise alternative antioxidants in edible oil because of healthy, not harmful, easy to obtained, cheap, less volatile, and more stable at high temperatures.
Keywords: coconut oil, free fatty acid, natural antioxidant.

Running Title : Effect of the Adding of Natural Antioxidant in the Stored Coconut Oil

INTRODUCTION

Coconut oil is an edible oil derived from the kernel of Cocos nucifera L., a tropical plant, and is largely consumed for edible and non-edible purposes which include cooking, bakery, confectionary, pharmaceutical and cosmetics (Krishna et al, 2010). Coconut oil is produced by crushing copra, the dried kernel, which contains about 60-65% of the oil. The oil has the natural sweet taste and contains 92% of saturated fatty acids (in the form of triglycerides), most of them (about 70%) are lower chain saturated fatty acids (45-56% of lauric acid) (Mc Donald et al, 2018).

In Indonesia, coconut oil can be preparing by fermentation method, warming methods and filtering method. Generally, production of traditional coconut oil is using fermentation method or warming method. While filtering method usually used in virgin coconut oil production. Commercial traditional coconut oils in Kupang are using warming method for production in large quantity. Coconut milk that had obtained from extracting of mature coconut meat, then cooking until the containing water in oil evaporated and left oil and residue. Coconut oils are obtained by separating oil from its residue. Cooking time in coconut oil processing is influenced to the colour of the oil (Mahmud et al, 2019).

To prevent rancidity in coconut oil, factories usually add synthetic antioxidant in their commercial coconut oil product so it can be stored for longer time. However, using synthetic antioxidants such as benzoic acid, BHA (Butylated Hydroxy Anisol), BHT (Butylated Hydroxy Toluene) or TBHQ (Tertier Butylated Hydroxy Quinone) can cause negative side effects in human body. BHA and BHT was studied and caused tumour in testing animal if using in longer time and cause liver damaging if consumed in excessive amounts (Tomagola et al, 2016).

Coconut oil that made and sell traditionally, generally did not use antioxidant. Therefore, it easy to become rancid and cannot be stored in longer time. Traditional coconut oil that become rancid reduce consumer interest in buying because its bad odour and flavour.

The presence of the negative side effect of synthetic antioxidant become a reason for researcher to find natural antioxidant that safer and have ability to decrease free radical in the body. Generally, natural antioxidant comes from spices, herbal plants, fruits, vegetables and seeds (Tomagola et al, 2016). These natural antioxidants have phenolic compounds that have antioxidant activity. Total phenolic concentration showed close correlation with the antioxidant activity. Plant phenolics present in fruit and vegetables have received considerably attention because of their potential antioxidant activity. Natural polyphenols have chain-breaking antioxidant activities and are believed to prevent many degenerative diseases, including cancer and atherosclerosis (Dasgupta & De, 2004).

Previous study was reported some natural plant that have antioxidant activities such as leaf Piper betle L leaf (Dasgupta & De, 2004), Cinnamomun cassia bark (Brodowska et al, 2016; Tomagola et al, 2016), bamboo leaf, tea polyphenols, and rosemary extract (Bai et al, 2018), guava leaves, corn cobs, and mangosteen peel (Putra et al, 2019), cassumunar ginger rhizome (Bua-in and Paisooksantivatana, 2009), and turmeric (Abriana and Johannes, 2014). In this study, we use four natural antioxidants, i.e. cinnamon, mangosteen peel, turmeric and cassumunar ginger.

Cinnamon is known spices that use in food for a long time and have great potential for natural antioxidant. Cinnamon contains chemicals i.e. phenol, terpenoid and saponin that can be use as antioxidant. Cinnamon bark extract has been identified its antioxidant activity to prevent rancidity in cooking oil (Tomagola et al, 2016).

Mangosteen peel is known to contain xanthone compounds such as antioxidants, antiproliferative, and antimicrobials which are not found in other fruits. Xanthone compounds include mangostin, mangostenol

A, mangostinone A, mangostinone B, trapezifolixanthone, tovophyllin B, alpha-mangostin, beta-mangostin, garcinone B, mangostanol, flavonoid epicatechin, and garthanin. The contents make mangosteen peels extract have very strong antioxidants. Mangosteen peel has been used as preservative and antioxidant for brown sugar (Putra et al, 2019).

Turmeric (Curcuma longa L.) is a plant native to Southeast Asia that belongs to the family Zingiberaceae. The therapeutic properties of turmeric include insecticidal, antimicrobial, antifungal, and antioxidant actions. Turmeric plants contain curcumin that potential as natural antioxidant. Curcumin is an important component isolated from turmeric that is used as traditional medicines and food additive substance (Abriana and Johannes, 2014).

Cassumunar ginger (Zingiber montanum) belongs to the Zingiberaceae family. The rizhomes are used for food flavouring and are used medicinally in tropical Asia (Bua-in and Paisooksantivatana, 2009). Phytochemical screening revealed the presence of alkaloids, saponins, tannins, flavonoids, terpenoid and phenolic compounds in its rhizome (Joram et al, 2018). Previously study was also reported that the antioxidant activities of the rizhome extract that screened by DPPH assay are around 57.63%-80.88% (Bua-in and Paisooksantivatana, 2009).

In this study we add each natural antioxidant powder in coconut oil then stored them for 3 weeks. The effect of natural antioxidant adding in coconut oil was studied by determined their acid value in day 1, 1st week, 2nd week and 3rd week. Acid value shows the amount of free fatty acid in oil that occur because of oxidation and hydrolysis reaction of oil. These fatty acids were in free molecules form and did not bend to triglycerides. The higher acid value of oil indicates the lower quality in oil (Ketaren, 2005). Adding some amount of antioxidant in oil is useful to prevent oxidation process occur, so can reduce the forming of free fatty acid (Yudha and Ayucitra, 2011).

MATERIALS AND METHODS

Materials

Samples here are commercial traditional coconut oil, cinnamon powder, mangosteen peel powder, turmeric powder and cassumunar ginger powder. The chemicals here are ethyl alcohol 96%, phenolphthalein, KOH 0.1 N and aquadest. The chemicals here was analytical grade.

Methods

Preparation of natural antioxidant sample

Cinnamon and turmeric were obtained in powder form. Cinnamon powder has red-brown colour with a highly fragrant odour and has spicy and sweet flavour. Turmeric powder has bold yellow colour, mildly aromatic, and has pungent and bitter flavour. Mangosteen peel powder was prepared from mangosteen peel. The peel was dried and milled to obtain its powder form. Mangosteen peel powder has dark-orange colour and odourless. Cassumunar ginger rhizomes was cut in small pieces then dried. The powder of cassumunar ginger was obtained after milled the dried rhizome. It has pale-yellow colour with the sharp odour.

Coconut Oil Sample Preparation

Coconut oil sample was purchased from traditional market and was stored in jerrican. Four natural antioxidants that used are cinnamon (Ci), mangosteen peel (Mp), turmeric (Tc) and cassumunar ginger (Cg) in powder form. The oil was divided and stored in five clear glass bottles i.e. S1 (CO), S2 (CO + Ci), S3 (CO + Mp), S4 (CO + Tc), S5 (CO + Cg).

Sample Storing

Sample was stored in room temperature for 3 weeks. The samples were determined their FFA values for day 1, 1st week, 2nd week and after 3rd week.

Determination of Free Fatty Acid Value

Free fatty acid value was determined using same method as described by Mahmud, et al (2019). Ten gram of sample coconut oil was added with 25 ml of ethanol 96%. Heat the mixture until boiling then wait to cool. Mixture was titrated with KOH 0.1N after previously added with some drops of phenolphthalein. The titration was stopped after the mixture become pink-purple colours. The formula to calculate the acid value (AV) is as shown below.

$$\mathrm{AV} = \frac{\text{titre value} \times \mathrm{N} \times 56.1}{\text{weight sample}}$$

RESULTS AND DISCUSSION

Result

Free fatty acid (FFA) value of coconut oil with antioxidant that stored for 3 weeks was determined and the results are shown in the table 1. The table also shown the change percentage of free fatty acid after 3 weeks of storing compare to its first day.

Table 1. Free fatty acid value of coconut oil with antioxidant and the change of percentage

Sample	Conc	Code	Day 1	1 wk	2 wk	3 wk	%Δ*
Coconut Oil	-	S1A	1,1405	1,2205	1,3886	1,4025	22,9710
Coconut Oil + Cinnamon	1 g/L	S2A	0,9724	1,1405	1,1886	1,2136	24,8096
	2 g/L	S2B	1,0285	1,0805	1,0896	1,1613	12,9091
Coconut Oil + Mangosteen peel	1 g/L	S3A	1,0836	1,1005	1,1292	1,1688	7,8602
	2 g/L	S3B	1,0836	1,1094	1,1205	1,1292	4,2039
Coconut Oil + Turmeric	1 g/L	S4A	0,8527	0,9604	0,9905	1,0805	26,7105
	2 g/L	S4B	0,7816	0,9204	0,9311	0,9804	25,4306
Coconut	1 g/L	S5A	0,9771	1,1005	1,1886	1,2005	22,8708

Oil + Cassumunar ginger	2 g/L	S5B	0,9771	1,0605	1,1292	1,2005	22,8708

*change percentage of free fatty acid value in 3rd weeks compare to 1st day.

Discussion

In this study four natural antioxidant shows varying change percentage of FFA value. Using mangosteen peel and cinnamon (2 g/L) as antioxidants in coconut oil can supress the change of FFA value with smaller change percentage of FFA after 3 weeks than other natural antioxidants. Cassumunar ginger as antioxidant in coconut oil shows similar change percentage of FFA value with stored coconut oil without antioxidant. Coconut oil with turmeric shows the highest change percentage of FFA value.

Adding low concentration of antioxidant in oil can inhibit and prevent autooxidation process occur in oil. Autooxidation mechanism was illustrated below (Gunstone, 2000).

Initiation $RH \rightarrow R\cdot$

Propagation $R\cdot + O_2 \rightarrow RO_2\cdot$

$RO_2\cdot + RH \rightarrow RO_2H + R\cdot$

Termination $RO_2 + RO_2\cdot$

$RO_2\cdot + R\cdot$

$R\cdot + R\cdot$

Figure 1. Autooxidation mechanism in oil

Ayucitra et al (2011) explained that the initiator in initiation step is free radical that formed before from various ways such us heating process, decomposition, photosensitization, and photooxidation. These free radicals will attach oil and causes unsaturated fatty acid will lose H atom and become lipid (alkyl) radical (R·). This radical lipid is very reactive and can react with triplet oxygen and produce peroxi radical (ROO·). During propagation step, this peroxi radical will react with unsaturated fatty acid and will produce hydroperoxide (ROOH) and new radical lipid (R·). this new radical lipid will react with oxygen again and produce new peroxi radical (ROO·). This self-catalysed oxidation reaction will keep repeating and forming oxidation cycle in oil. This autooxidation reaction will stop after both radicals combine and bind to form non-radical product that stable in termination step.

Antioxidant plays a role as hydrogen donor, namely, by donating hydrogen atom to peroxide radical that formed in initiation step. The inhibition mechanism of radical lipid by antioxidant was shown below (Shahidi, 2005).

$ROO\cdot + AH \rightarrow ROOH + A\cdot$

$R\cdot + AH \rightarrow RH + A\cdot$

$ROO\cdot + A\cdot \rightarrow ROOA$

$RO\cdot + AH \rightarrow ROH + A\cdot$

$RO\cdot + A\cdot \rightarrow ROA$

$A\cdot + A\cdot \rightarrow AA$

Figure 2. Antioxidant inhibition reaction to radical lipid

Adding low concentration of antioxidant (AH) in oil or lipid will inhibit and prevent oxidation reaction both in initiation and in propagation steps. Radical antioxidants (A·) which formed in that reaction more stable and did not have enough energy to react to other lipid molecules to form new radical lipid. Antioxidant radicals are able to bind each other and become non radical product (Trilaksani, 2003).

Natural antioxidants mostly come from spices and herbs, such as green tea, apple peel, olive leaves, rosemary and bamboo leaves, which are known to contain many bioactive phytochemicals that can slow down lipid oxidation (Bai et al, 2018). Generally, the compound in natural antioxidant is phenolic compound or polyphenol which can be flavonoid group, cinamic acid derivatives, cumarin, tocopherol and organic polyfunctional acids (Yudha and Ayucitra, 2011).) Phenolic have been reported to have a capacity to scavenge free radicals. The antioxidant activity of phenolic is mainly due to their redox properties, which allow them to act as reducing agents, hydrogen donators, and singlet oxygen quenchers. (Aku et al, 2018). Polyphenol compound is multifunctional and can act as reductor, free radical scavenger, metal chelating agent, and silencer for the formation of singlet oxygen (O) (Yudha and Ayucitra, 2011).

In the present study mangosteen peel powder and certain concentration of cinnamon show promise potential of natural antioxidant traditional coconut oil compare to the other two natural antioxidant. Natural antioxidants have several advantages than synthetic antioxidant, i.e. safe to consumed, and not only able to inhibit oxidation reaction that can destroy macromolecules and cause problems for health, but also can increase nutrition compound in edible oil (Yudha and Ayucitra, 2011). One factor that caused the natural antioxidant did not work properly is the presence of moisturizer (impurities in natural antioxidant sources). Our two natural antioxidants here was takes from their rizhomes (turmeric and casuumunar ginger). Rhizome is considered a storage house of reserve food material and water enters into it through roots and therefore contains high level of moisture content. (Aku et al, 2018). Therefore, some preparation steps are needed to extract their natural antioxidant compound and decrease their moist before apply as natural antioxidant in oil.

CONCLUSIONS

Cinnamon bark, mangosteen peel, turmeric, and cassumunar ginger can be used as natural antioxidant because of their bioactive phytochemical compounds. Mangosteen peel and certain concentration of cinnamon become promise potential natural antioxidant for

traditional coconut oil. By adding these two natural antioxidants in coconut oil shows the changing percentage of acid value that smaller than coconut oil without antioxidant after three weeks stored. Turmeric and cassumunar ginger did not work properly as natural antioxidant in coconut oil which is most likely caused by water content in their rhizomes. Natural antioxidant has several adventages, namely safe for consumed, able to inhibit oxidation reaction, and increase nutrition compounds.

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