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Methanol extract from kesambi (*Schleichera oleosa* (L.) oken) stem bark as a natural antioxidant to increase crude palm oil (CPO) quality

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Abstract: The content of active compounds in methanol extract of kesambi stem bark (*Scheleicera oleosa*) is known to have good antioxidant activity. Methanol extract of kesambi stem bark contain flavonoid and fenolic compounds. The purpose of this study was to evaluate the methanol extract of kesambi in inhibiting the oxidation of crude palm oil (CPO). In this study, the extraction of kesambi stem bark was carried out with methanol solvent. Antioxidant activity test of methanol extract of kesambi using the DPPH method. The parameters observed were free fatty acids (FFA) values, acids value, and DOBI (Deterioration of Bleachability Index). The used concentration of natural antioxidant were 200; 400; 600; 800 and 1000 ppm. Based on the results of this study, the natural antioxidant of methanol extract of Kesambi stem bark (*Schleichera oleosa*) can reduce levels of free fatty acid numbers, acid value, and DOBI value. Actioxidant activity methanol extract of kesambi stem bark shown IC50 42.092 ppm. The lowest FFA levels and acid numbers were obtained from samples with addition of 1000 ppm natural antioxidants with free fatty acid (4.1%), acid value (7.7 mg KOH/g) while the DOBI value increased to 1.331. Furthermore, FFA value meets the CPO quality standard, according to SNI-01-2901-2006.

Keywords: Crude palm oil, antioxidant, free fatty acid (FFA), acid value

1. Introduction

One of the main raw materials of cooking oil is palm oil. The most important part to be processed from palm oil is the fruit. The flesh of the fruit produces crude palm oil which can be processed into raw material cooking oil (Ameida et al. 2019). Palm oil produces two different types of oil, Crude Palm Oil (CPO) and Palm Kernel Oil (PKO). CPO is obtained from

the mesocarp of oil palm fruit, while PKO is obtained from the kernel (kernel) of oil palm fruit. The food industry uses up to 90% of total palm oil production, while another 10% is used for soap-making applications and oleochemichal industries (Adam and Moss, 2008).

Oil palm is one of the important foreign exchange-earners from the non-oil and gas sector. In Indonesia, the development of oil palm agribusiness has had a very positive impact on national development. The benefits of oil palm development include increasing farmers' income, providing raw materials for other downstream industries, increasing employment opportunities, and supporting regional development efforts to be more advanced and developed (Baharin et al. 2001; Hilma et al. 2020).

The problem that often occurs in CPO factories is the decrease in CPO quality caused by an increase in free fatty acid (FFA) levels, acid numbers and a decrease in DOBI numbers. The quality and stability of palm oil are the main factors influencing its acceptability and market value, as well an minimize the degration process during the deep friyng. One of the most important indicators of the keeping quality of oil is its oxidative stability (Sembiring et al. 2019). In its turn, the oxidative stability of vegetable oils depends on temperature, light, oxygen, metals, enzymes, the presence of antioxidants or proxidants, fatty acid composition, and the use of oxygen permeable packages (Pimpa et al. 2009). High levels of free fatty acids (FFA) cause rancidity, changes in taste and color in the oil. One of the factors causing the increase in free fatty acid (FFA) levels in oil is morphological and microorganism damage in oil palm fruit. Damage to oil palm fruit is triggered by the careless process of harvesting, transporting and piling oil palm fruit (Morad et al. 2010).

Antioxidants are substances that can inhibit or prevent the occurrence of free radical reactions. There are two antioxidant substances, natural antioxidants and synthetic antioxidants. Synthetic antioxidants are antioxidants obtained from the synthesis of chemical reactions such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ), and propyl gallate. Synthetic antioxidants often used as oil or fat antioxidants because they are cheap and effective to be used as antioxidants (Ayucitra et al. 2017; Syafitri et al. 2020). But now the use of synthetic antioxidants is starting to get a negative response because it has the potential to cause cancer in the body. Therefore, the use of natural antioxidants as substitutes is increasingly in demand because it is believed to be safer for health (Holil and Griana, 2020). Natural antioxidants are antioxidants obtained directly from nature.

Sari et al. (2019), reported that antioxidant activity test of the methanol extract of the bark of the kesambi stem (*Schleichera oleosa* (L.) Oken) had an IC50 value of 7.801 ppm. This shows that the methanol extract of the bark of kesambi (*Schleichera oleosa* (L.) OKen) has a very strong ability to ward off free radicals and can be used as a source of antioxidants derived from natural ingredients (Sari et al. 2019).

Based on the data above, it is necessary to conduct a study to test the quality of CPO oil samples with the addition of methanol extract of kesambi stem bark (*Schleichera oleosa* (L.) Oken) with various concentrations and length of homogenization time. Next, an analysis of the DOBI number (Deterioration of Blachability Index) parameter, free fatty acid (FFA) and acid number was carried out. The purpose of this study was to evaluate the methanol extract of kesambi in inhibiting the oxidation of crude palm oil (CPO).

2. Methods

2.1 Materials and sample

In this research, methanol extracts were made from stem bark of kesambi. The equipment used in this study was rotary evaporator, distillation equipment, spectrophotometer UV Vis optima . While the materials used were : kesambi stem bark from Cimerak Cilegon, crude palm oil (CPO) from kalimantan, NaOH, n-hexane, chloroform, indicator pp, methanol, KOH, and distilled water.

2.2 Sample extraction

2000 g of kesambi stem bark were sorted and separated from the dirt, washed, and air-dried. The stem bark of kesambi were blended to give powder form. As much as 500 g of powder was obtained and then stored in a clean container and protected from light. 1750 g kesambi stem bark that have been finely divided into 1000 g each for macerated methanol 96%. Methanol were used as much as ± 2000 mL each, and the sample was completely submerged. The mixture was stirred for 6 hours, then allowed to stand for 2x24 hours in a tightly closed container. Then, the filtrate was filtered and concentrated with a rotary evaporator. Maceration was repeated until a clear (colorless) maceration solution was obtained. Concentration results are then collected, dried, and weighed. The weight of methanol extract was 96 g.

2.3 Free fatty acid procedure

The Crude Palm Oil sample was heated at a temperature of 60 - 70 oC. Heated stoped after sample melted. Then a sample of liquid CPO was taken and weighed as much as 3 g, and then sample put into a 250 mL erlenmeyer and added 50 mL of 96% ethanol netral. After that, it was heated on a water bath and set the temperature at 40 oC until all the oil was dissolved. After dissolving, 3-5 PP indicator added to sample solution. Then titrated with 0.1 N NaOH solution, until it reaches a pink colour (Ulfa et al. 2017).

$$\text{FFA Value} = \frac{Vol\ NaOH\ x\ N\ NaOH\ x\ 25.6}{weigh\ of\ sample\ (g)}$$

2.4 Acid value procedure

The Crude Palm Oil sample was heated at a temperature of 60 - 70 oC. Heated stoped after sample melted. Then a sample of liquid CPO was taken and weighed as much as 3 g, and then sample put into a 250 mL erlenmeyer and added 50 mL of 96% ethanol netral. After that, it was heated on a water bath and set the temperature at 40 oC until all the oil was dissolved. After dissolving, 3-5 PP indicator added to sample solution. Then titrated with 0.1 N KOH solution, until it reaches a pink colour.

$$\text{acid value} = \frac{Vol\ KOH\ (mL)\ x\ N\ KOH\ x\ 56.1}{weigh\ of\ sample\ (g)}$$

2.5 Deterioration of bleachability index (DOBI)

Weighed 0.1 g of the sample into a 25 mL volumetric flask and dissolved with n-hexane to the mark. Then the UV-Vis spectrophotometer was turned on and allowed to stabilize. Then the absorbance of the sample was measured at a wavelength of 319 nm for the UV range and at a wavelength of 446 nm for the Visible range using n-hexane solution as a blank and the resulting absorbance value was recorded.

$$\text{DOBI} = \frac{absorbance\ of\ \lambda\ 449\ nm}{absorbance\ of\ \lambda\ 319\ nm}$$

2.6 Addition natural antioxidant procedure

The 1000 ppm natural antioxidant was diluted to 200; 400; 600; 800 and 1000 ppm. 5 pieces of 250 mL erlenmeyer were prepared, and 50 mL of CPO samples were filled each. Then added each antioxidant with a concentration of 200; 400; 600; 800 and 1000 ppm as much as 50 mL (comparison between CPO samples and antioxidants 1:1). The mixture of CPO samples and 200 ppm antioxidant compounds was homogenized for 5 minutes and allowed for 24 hours. The mixture of compounds formed 2 phases between antioxidants and Crude Palm Oil. After being allowed for ± 24 hours, the mixture of compounds with different concentrations is put into a separating funnel to be separated. Then the compounds that are under are taken, CPO and test the quality of crude palm oil. The experiment was repeated on samples with concentrations of 200; 400; 600; 800 and 1000 ppm.

2.7 Antioxidant activity test

The antioxidant activity test was carried out using DPPH method (1,1-diphenyl-2-picrylhydrazyl). Antioxidant measurements were carried out in a dark atmosphere measured at a wavelength of 517 nm. A total of 50 mg of methanol extract kesambi was dissolved in 50 mL methanol (1000 ppm). The sample concentrations of 0; 12; 25; 37.5; 50 and 62,5 ppm was obtained. The sample was added as much as 2.4 and 0.6 mL DPPH with a concentration of 160 ppm, then incubated for 30 minutes. The free radical activity was measured by decreasing the absorbance of DPPH with a test tube and then processing the data. The % inhibition value is calculated using the following formula:

$$\%\ \text{inhibition} = \frac{absorbance\ control - absorbance\ sample}{absorbance\ control}\ x\ 100\%$$

3. Results and Discussion

3.1 Antioxidant values obtained by the DPPH Method

The inhibition percentage of kesambi antioxidant activity using the 2,2-Diphenyl-1-picrylhydrazyl (DPPH) method is presented in Table 1. Table 1 explains that methanol extract of kesambi stem bark have antioxidant activity IC50 42.092 ppm. The antioxidant activity of methanol extract is probably caused by the presence of phenolic compounds and flavonoids. The ability of antioxidant activity of a sample is due to the presence of

compounds that have active groups, i.e., hydroxy groups, which can be free antiradical. Antioxidant activity is performed by donating unpaired electrons to free radical compounds so that free radicals become stable. Compounds that have the potential as natural antioxidants are phenolic and flavonoid compounds. In previous studies, phenolic and flavonoid compounds were known to have various biological effects as antioxidants. The more flavonoid and phenolic compounds in a sample, the higher the antioxidant activity.

Table 1
The result of antioxidant activity test using DPPH

concentration	Absorbance[1]	Absorbance[2]	% inhibition[1]	% inhibition[2]	IC_{50} (ppm)
0	0.301	0.3	0	0	40.987 43.196 X = 42.092
12.5	0.163	0.163	45.847	46.666	
25	0.159	0.157	47.176	47.666	
37.5	0.154	0.152	48.837	49.333	
50	0.146	0.149	51.495	50.333	
62.5	0.139	0.142	53.820	52.666	

3.2 Effectiveness of kesambi steam bark extract addition to CPO quality

Crude Palm Oil (CPO) quality testing is carried out before adding natural antioxidants. Testing was carried out on the parameters of free fatty acids, acid numbers, and dobi. The result of the test shown in Table 2.

Table 2
Quality of CPO before addition natural antioxidant

Parameters	quality	SNI standart
free fatty acid (%)	7.3	5 max
Acid value (mg KOH/g)	16	6.9 max
Deterioration of Bleachability Index	1.235	1.68 min

The FFA value of CPO is 7.3%. This allowed that CPO oil has out of spec of SNI 01–2901–2006 standart where the standard value is 0.5 %. The high level of FFA is due to the increased activity of the lipase enzyme in CPO. The increase in lipase enzyme activity is caused by several factors, such as delays in processing oil palm fruit, palm oil processing carried out manually, fruit contamination by microorganisms and unstable oil storage temperatures due to temperature instability in the laboratory room. The results of the acid number test is 16 mg KOH/g.

The results also out of spec of SNI 01 – 2901 – 2006 standart where the standard value is Max 6.9 mg KOH/g. The high acid number is due to the poor processing of palm oil, contamination of the fruit by microorganisms and the unstable oil storage temperature due to temperature instability in the laboratory room used in the study. The results of DOBI analysis of CPO samples is 1.253 ppm. This shows that the quality of the DOBI analysis of the CPO sample is poor and does not meet the standard of CPO oil based on PORAM (Palm Oil Refiners Association Of Malaysia). The decline in DOBI numbers was caused by several

factors, such as delays in processing oil palm fruit, poor quality processed palm fruit, and heating of CPO more than 50 oC. The high value of the DOBI give effect for the price of CPO.

3.3 Effectiveness of natural antioxidant addition to CPO quality

The results show that the addition of methanol extract of kesambi stem bark wasable to inhibit the oxidation process in CPO. From the three test parameters, including free fatty acids, acid value, and DOBI it was observed that with the addition of extract, the quality of CPO samples was included in the SNI-01-2901-2006 Quality Standard range, as presented in Table 3.

Table 3
Quality of CPO after addition natural antioxidant

Concentration of Antioxidant (ppm)	CPO sample (50 mL)		
	Free fatty acid (%)	Acid value (mg KOH/g)	DOBI
200	5.4 %	11.4 mg KOH/g	1.263
400	5.2 %	10.5 mg KOH/g	1.277
600	5.0 %	9.9 mg KOH/g	1.283
800	4.6 %	9.3 mg KOH/g	1.296
1000	4.1 %	7.7 mg KOH/g	1.331

3.4 Free fatty acids in CPO

The provision of methanol extract from kesambi significantly affects free fatty acids on CPO at concentration 200, 400, 600, 800, and 1000 ppm. Results of the Least Significant Difference test presented in Fig 1.

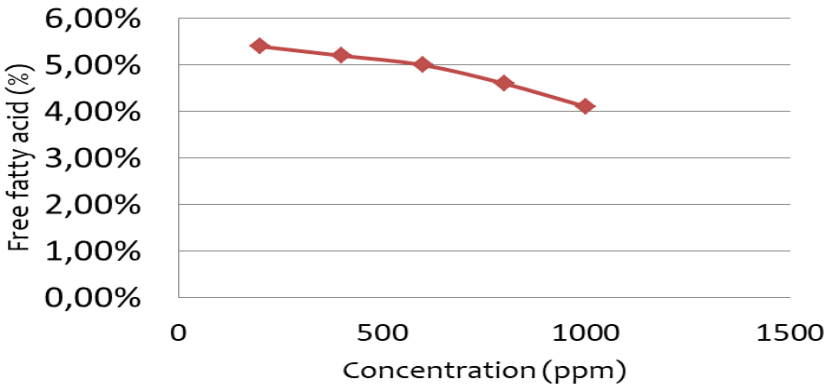

Fig 1. Effectiveness of methanol extract from kesambi on CPO free fatty acid values measured

Fig 1 showed that there was a decrease in the value of free fatty acids (FFA) after added antioxidants. The concentration of 1000 ppm range has a more significant reduction in free fatty acid (FFA) which is 4.1 % compared to the addition of 200 ppm antioxidants which is 5.4 %. This proves that the more concentrated of natual antioxidant added in CPO, greater reduction in free fatty acids (FFA) in CPO.

3.5 Acid value in CPO

The provision of methanol extract from kesambi significantly affects acids value on CPO at concentration 200, 400, 600, 800, and 1000 ppm. Results of the Least Significant Difference test presented in Fig 2.

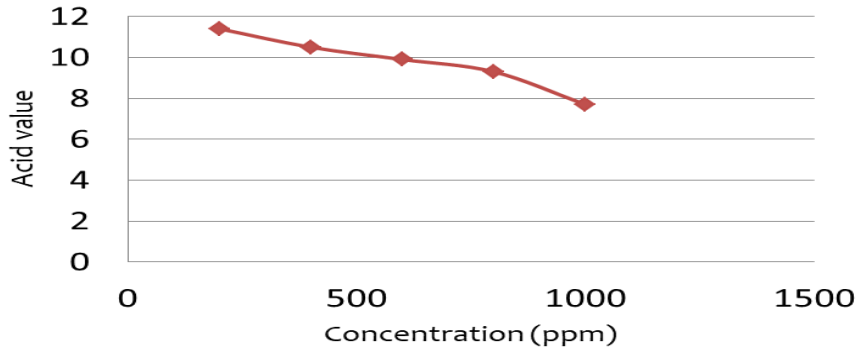

Fig 2. Effectiveness of methanol extract from kesambi on CPO acid values measured

Fig 2 showed that there was a decrease in the value of the acid number after added antioxidants. The 1000 ppm range has a more significant decrease in acid number, which is 7.7 mg KOH/g compared to the addition of 200 ppm antioxidant, which is 11.4 mg KOH/g. This proves that the more concentrated of antioxidants added can decrease acid number in CPO.

3.6 Deterioration of bleachability index (DOBI) in CPO

The provision of methanol extract from kesambi significantly affects Deterioration of Bleachability Index on CPO at concentration 200, 400, 600, 800, and 1000 ppm. Results of the Least Significant Difference test presented in Fig 3.

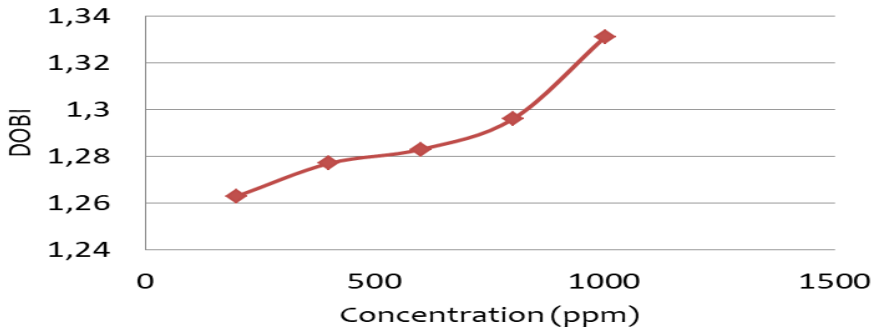

Fig 3. Effectiveness of methanol extract from kesambi on CPO DOBI measured

Fig 3 showed that there was an increase in the DOBI number after added natural antioxidants. The 1000 ppm range has a more significant increase in DOBI number, which is 1.331 ppm compared to the addition of 200 ppm antioxidants, which is 1.263 ppm. This proves that the more concentrated the added antioxidants, the greater the increase in DOBI number in CPO. From measurements of free fatty acid parameters it is observed in concentration of natural antioxidant 1000 ppm, it is still included in the quality standard. Acid value and Deterioration of Bleachability Index still out of spec of SNI 01 – 2901 – 2006.

4. Conclusion

Actioxidant activity methanol extract of kesambi stem bark shown IC50 42.092 ppm. The lowest FFA levels and acid numbers were obtained from samples with addition of 1000 ppm natural antioxidants with free fatty acid (4.1%), acid value (7.7 mg KOH/g) while the DOBI value increased to 1.331. Furthermore, FFA value meets the CPO quality standard, according to SNI-01-2901-2006. Acid value and Deterioration of Bleachability Index still out of spec of SNI 01 – 2901 – 2006.

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