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The tocol content of crude palm oil based on the level ripeness and their relationship to the quality and their stability

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Abstract. Palm oil contain tocol and betacarotene which has an antioxidant function to protect the oil from oxidation processPalm oil comes from different maturity have not been specifically determined their tocol and betacarotene content, and their relation to quality and stability. The purpose of this research was to find the content of tokol and betacarotene in palm oil which comes from different maturity and to determine its stability of quality. The level of maturity was fraction 1 (unripe), fraction 2 and fraction 3 (ripe), fraction 4 (over-ripe).The result showed that palm oil which comes from different level of maturity from fraction 1, 2, 3 and 4 contained different amount of tocol and betacarotene. The quality of crude palm oil which were analysed by the value deteoriation of bleachability index (DOBI) had closed relationship to the number of beta-carotene in the palm oil. The color stability and oxidation were different in every level of maturity. The level of maturity which had the best quality and its stability was fraction 3. The tokol and betacarotene compound were 346 ppm and 727 ppm respectively, while the DOBI value was 2,75.

1. Introduction

Crude palm oil (CPO) which produced from palm oil fruit (*Elaeis guineensis*) is the main vegetable oil in the world market today. Crude palm oil is rich in carotenoids with concentrations between 500-700 ppm, where the content of beta carotene as retinol equivalent was 15 times more than carrots and 50 times more than tomatoes. Beside carotenoids, which consist of alpha- and beta carotene, crude palm oil is also rich in other minor components that provide unique nutritional properties, especially the tocopherol and tocotrienol components, both of which are also called tocol. Crude palm oil contains 600-1000 ppm of tocol. Tocol was nutritional substance and has antioxidant activity that contribute to the oxidative stability of crude palm oil. Tocopherol may prevent oxidation of fat by blocking the formation of hydroperoxides in the propagation chains as well as the process of decomposition and formation of aldehyde compounds [1]. The fruit maturity level is very influential on the productivity and quality of crude palm oil produced. Change in the color of the palm fruit flesh to yellowish green after three months indicates that the oil has formed the formation of carotene. In addition, the change of fruit color from green to yellow because the loss of chlorophyll content in the fruit is replaced by the formation of carotenoids and will increase along with the fruit [2]. Fat-soluble carotenoids are very sensitive towards heat and also susceptible to enzymatic, chemical, and photochemical oxidation. During the storage process these carotenoids is oxidized and form oxidation compounds [3].The effect of fruit maturity level on the quality and stability of crude palm oil is estimated to be related with the

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minor component content which is found in the palm fruit, especially the antioxidant component such as beta carotene and tocol. Due to its easily oxidized characteristics, the beta carotene component issuspected of not contributing greatly to crude palm oil quality's stability.

2. Method

2.1. Materials

The materials used in this research were the DxP crossbreeding palm oil fruit derived from Kebun Sampali owned by Perkebunan Nusantara (PTPN) II Ltd. The chemicals materials used are; 3:2 (v/v) acetic acid solution-chloroform, 0.01 N sodium thiosulfate solution, saturated KI solution, starch indicator solution, N-hexane pa, methanol pa, methanol licrosolv, standard tocopherol with isomer A-T1, δ-T1, α-T3, γ-T3, and δ-T3.

2.2. Palm Oil Extraction

Palm oil fruits were peeled using machetes, then boiled using autoclave with a temperature of 120°C for 90 minutes and extracted the oil using a hydraulic press. The resulting crude palm oil is separated by centrifuges to obtain crude palm oil that is free from impurities. The oil extraction results are stored in the refrigerator (LG brand freezer) at -5°C until the extraction of all samples is completed to proceed with the sample analysis.

2.3. Analysis of Tocopherol and Tocotrienol Content in Palm Oil (In house method PPKS, 2011)

The crude palm oil sample was weighed 2 g in a 10 ml measuring flask (measuring flask 1), then hexane was added to the marker boundary marker. The crude palm oil sample is homogenized, then taken 2 ml with a volume pipette, put into a 10 ml measuring flask (measuring flask 2), then added with pa methanol to the marking margin and homogenized. The sample solution on the second measuring flask is inserted into the centrifuge tube, then centrifuged for 10 minutes at 2500 rpm. The solution at the top layer was separated, then analyzed the content of tocopherol and tocotrienol by using Shimadzu LC-6A High Performance Liquid Chromatography (HPLC) with Fluoresence Detector.

2.4. Beta Carotene Content (MPOB, 2004)

The crude palm oil sample is melted at 60-70°C and shaken until homogeneous. Crude palm oil is filtered with Whatman No.1 paper, and then crude palm oil is weighed as much as 0.04 g and put into a 10 ml measuring flask. In the sample solution the crude oil is added N-hexane solvent up to the mark line. Absorbance of crude palm oil is read by spectrophotometer at $\lambda = 446$ nm.

2.5. DeteriorationofBleachabilityIndex/DOBI (MPOB, 2004)

The crude palm oil sample is melted at 60-70°C. Samples were filtered with Whatman no. 1 paper then weighed 0.04 g. Put into a 10 ml measuring flask and add n-hexane solvent up to the mark line. Absorbance of crude palm oil sample is read by spectrophotometer at $\lambda = 446$ nm and 269 nm

2.6. Color (AOCS Official Method Cc 13e-92)

Measurement of oil sample color is done with Lovibond Tintometer in soft light atmosphere and not exposed to direct sunlight. The crude palm oil sample is inserted into a 1" size glass cell and the readings are corresponding on the glass cell limit containing the crude palm oil sample placed in the light cabinet close to the observation tube. The color of crude palm oil is measured using a color rack with ratio of 10 for yellow and 1 for red. Correction till the accurate color matching were obtained using the minimum number of blue or neutral, where the color obtained is no more than blue 9.0 and neutral 3.0. The results of the red and yellow readings of the oil samples are then recorded.

3. Result and discussion

3.1. The Content of Tocol Components in Crude Palm Oil

Crude palm oil contains 600-1000 ppm tocopherol and tocotrienol, where these two compounds can be called tokol compounds. Tocopherol and tocotrienols are composed of 4 different isomers i.e. as α-, β-, γ- or δ-, which corresponds to the number and position of the methyl group attached to the chroman ring [1]. Vitamin E has alpha, gamma and beta forms, and delta-tocotrienols serves as a natural antioxidant in protecting cell membranes from oxidative damage [4]. The analysis results of tocol components which is contained in crude palm oil was derived from the palm fruit with different levels of maturity showed different of tocol total content, as shown in Figure 1. Analysis of variance indicated that fruit maturity level had significantly different effect ($P < 0.05$) on tocol content. Further test results using Duncan test showed a difference of tocol component content of crude palm oil from each level of palm fruit maturity.

Figure 1 shows trend of tocol total content that has increased along with the increasing maturity level of the palm fruit. This indicates that palm fruit maturity level have an important role in the formation of tocopherols and tocotrienols in palm oil. The amounts of Vitamin E in fruits and vegetables are affected by species, varieties, maturity, growth conditions (weather, growing season, solar intensity,and soil), distribution of unbalanced tocopherol, and harvesting time/process [6].

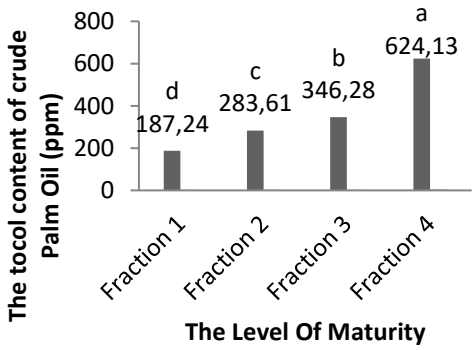


Figure 1. The Content of Tocol Component in Crude Palm Oil

In the early stages of fruit maturation (fraction 1 and fraction 2) the composition of tocol compounds in crude palm oil consists of γ-tocotrienol (90.04 and 146.94 ppm), δ-tokotrienol (66.45 and 49.57 ppm), and α-tocotrienol (25.35 and 68.54 ppm), also α-tocopherol (5.40 and 18.56 ppm). In the final stages of fruit maturation (fractions 3 and 4) the composition of tocol compounds contained in crude palm oil consists of γ-tocotrienol (104.56 and 313.75 ppm), α-tocotrienol (154.36 and 196.06 ppm), δ-tocotrienol (20.48 dan 44.19 ppm) and α-tocopherol (66,88 dan 70,13 ppm), the number of tocol compounds in the form of their respective isomers increases with the age of the palm fruit. Tocotrienols contained in fruits and vegetables, usually consist of α-tocotrienol and γ-tocotrienol which is quite low in concentration compared to tocopherol. Palm oil contains higher α-tocotrienol and δ-tocotrienol than fruit and vegetable [7].

3.2. The Content of Betacaroten in Crude Palm Oil

The content of betacarotene has increased in fraction 1 and fraction 2. The content of beta-carotene reaches the optimum limit at fraction 3 or at the level if the fruit ripening process has been completed and then at fraction 4, i.e the expected phase of the fruit has entered the level of passing through, then the content of beta-carotene in palm oil is decreased. The decrease of beta carotene content after reaching this optimum point is related to the research result of carrot, where it is stated that the carotene will accumulate and reach the maximum point after the carrot tuber is about 90-120 days old and will gradually decrease [8].

Figure 2 shows the graphic trend of beta-carotene content that increases with the increasing maturity level of palm fruit, but the content of beta carotene decreases at the last fruit maturity level (fraction 4). The increase in beta carotene content in palm oil which derived from different fruit maturity levels is also not the same, where at the beginning of fruit maturity, the increase in the amount of beta carotene is greater, and the amount of beta carotene decreases thereafter.

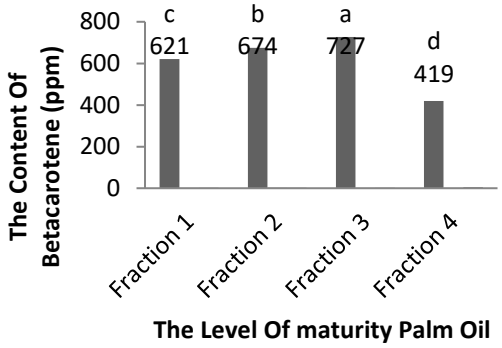


Figure 2. The Content of Betacarotene in Crude palm Oil

Carotene content in crude palm oil from raw fruit is significantly smaller than ripe fruit and ripe fruit [9]. Carotene also has relatively less stable properties, which can be degraded by environmental factors [10].

3.3. The Deterioration of Bleachability Index (DOBI Index) in Crude Palm Oil

Crude palm oil from palm fruits derived from different degrees of maturity in Figure 3 can explain that the value of DOBI obtained is still within the standard number of ≥ 1.5. A good DOBI value is ≥ 1.5. A good DOBI value for the purification process is ≥ 1.5 so that the resulting oil color does not darken [11]. Figure 3 shows the graphical trend of decreasing DOBI value in the final stages of the fruit maturity level. The analysis of variance shows that the maturity level of the palm fruit gives a significant effect (P <0,05) to the value of DOBI. The maturity level in immature palm fruit i.e. fraction 1 and fraction 2 is having enough high of DOBI value compared to maturity level of ripe and over ripe palm fruit i.e fraction 3 and fraction 4.

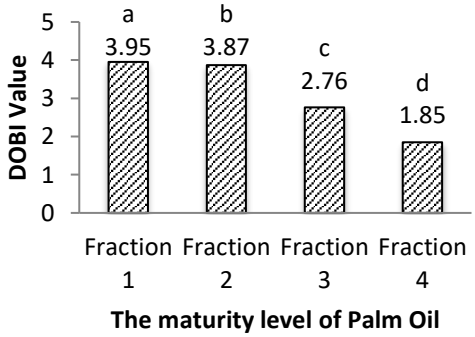


Figure 3. The DOBI Value in Crude Palm Oil

3.4. The oxidative stability of crude palm oil as measured by color

Red color changes in crude palm oil is due to heating process at 100 ° C for 24 hours as can be seen in Figure 4. Red color stability is reduced after 12 hours of heating on crude palm oil which derived from

fruit with maturity levels of 1, 2 and 4. In crude palm oil which derived from fraction 3, a decrease in the stability of the red color occurs in 18 hours of heating. This is because the content of beta carotene in the fruit with maturity level 3 higher than the level of maturity 1, 2 and 4 (Figure 2). Although fraction 4 has higher total tocol content than fraction 3 but its beta carotene content is much lower than fraction 3 so that its oxidative stability is lower.

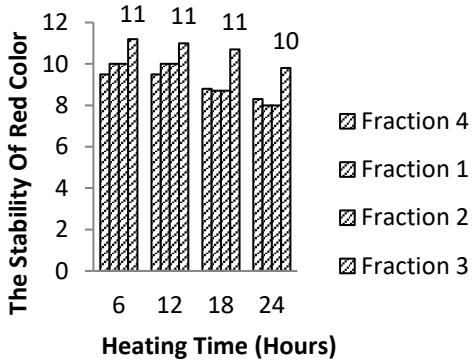


Figure 4. The Oxidative Stability Of Red Color in Crude Palm Oil

3.5. The Oxidative Stability of crude palm oil as measured by peroxide index

The oxidative stability of crude palm oil for each different maturity level at the end of heating (24 hours) of fractions 3 and 4 has better stability than fraction 1 and fraction 2. This is because the content of beta carotene and tocol contained in those fractions is high enough to maintain the stability of crude palm oil. Beta carotene becomes an antioxidant that first works to prevent oxidation damage, then followed by the performance of tocopherol and tocotrienols as antioxidants. When linked to previous studies on antioxidant properties derived from beta carotene, red palm oil has the potential to slow down oil damage or slow the formation of free fatty acids and peroxides during heating [12].

4. Conclusion

Tocol content in crude palm oil is influenced by the fruit maturity level, where the higher the fruit maturity level then the content of tocol will increase. The content of beta carotene in crude palm oil is influenced by the fruit maturity level. The higher the fruit maturity level, the beta carotene content will increase, but in fraction 4 beta carotene content decreased again. DOBI value content in crude palm oil is influenced by the maturity level of the palm fruit. This is related to the content of beta carotene and the condition of the fruits to be processed. The highest of beta carotene amount is oxidized, the lower the DOBI value and the resulting oil will become darker. The content of tocol and beta carotene in crude palm oil acts as an antioxidant that protects crude palm oil from oxidation damage. Beta carotene becomes an antioxidant that first works to prevent oxidative damage to palm oil then followed by the performance of tocopherol and tocotrienol as antioxidants.

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