Copigmentation Of Anthocyanin Extract of Purple Sweet Potatoes (Ipomea Batatas L.) Using Ferulic Acid And Tannic Acid

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Abstract. Copigmentation is one of the methods to improve the color stability and intensity of anthocyanin extract. This study aimed to do the copigmentation of the anthocyanin extract of purple sweet potato using ferulic acid and tannic acid. The anthocyanin extraction was conducted with distilled water at pH 7 and pH 2 while the copigmentation was conducted by varying the concentration of ferulic acid and tannic acid. The results showed that best anthocyanin extraction method of the purple sweet potato was using distilled water at pH 2. The yield of freeze dried anthocyanin on the extraction with distilled water at pH 2 was 1710 ppm, while the yield when using distilled water at pH 7 was 888 ppm. Ferulic acid and tannic acid can be used for the copigmentation of anthocyanin extract of purple sweet potato by observing the maximum wavelength shift (bathochromic effect, Δλmax) and increase of color intensity (hyperchromic effect, ΔAmax). The bathochromic effect of ferulic acid began to occur at a concentration of 0.01M, while the hypochromic effect on tannic acid occurred at a concentration of 0.005M and remained up to a concentration of 0.02M. The best copigmentation concentration of ferulic acid was 0.015M, while tannic acid was 0.02M. The use of tannic acid 0.02M is recommended compared to ferulic acid 0.015M because with the same bathocromic effect (Δλmaks = 3.9) results hyperchromic effect (ΔA = 0.258) higher by tannic acid.

Keywords : copigmentation, anthocyanin, purple sweet potato, ferulic acid, tannic acid

1. Introduction

Food colorant is a natural ingredient as well as a chemical that is added to the food in order to give a particular appearance or an attractive color. The use of colorant has been significantly commercialized since more than 25 years ago. The role of food coloring is quite important for the food industry because of its role to improve the appearance of food. Colorant that are widely used in the food industry so far are synthetic dyes. The use of synthetic colorant in food products is growing rapidly both in large industries and in the home industry, this is because the color produced by synthetic colorant more intense and stable. However, the use of excessive synthetic colorant is feared will cause health problems.

Colorants are widely used in food products to make the desired product color variations, to replace the color lost during processing and during storage, to provide color and appearance to products that are naturally colorless (jelly, cake, cake, beverage, etc.) provide identification of products consumed through color appearance, and improve the natural appearance of the product.

Natural colorant are widely used derived from plants such as suji leaves, cocoa fruit, turmeric, red peppers, carrots, caramel, brown sugar, grape wine, tomatoes, purple sweet potatoes and others. In Indonesia, purple sweet potatoes are common used as traditional food and snacks. the pigment in purple sweet potatoes known are anthocyanins which give red, purple and blue pigments common to plant species. Anthocyanins are amphoteric compounds, which have the ability to react with both acid and alkaline. In acid medium anthocyanins are red, and on alkali media turns into purple and blue.[1]
Anthocyanins may replace the use of synthetic colorant of rhodamine B, carmoisin, and amaranth as a red colorant in food products. Natural colorant preparations are needed so it can be an alternative for the food industry to improve the appearance and increase the color intensity of food products by minimizing the risk of health problems.

The natural anthocyanin color substance is susceptible to color degradation which results in the color becoming faded. In food matrix, Anthocyanins are highly unstable molecules. several factors that affect the stability of the color are pH, temperature, anthocyanin concentration, oxygen, light, enzymes, and other accompanying substances. Antocyanin degradation can be reduced by the presence of copigmentation. Copigment are defined as a colorless or colorless but very thin, generally yellowish, or colored molecule naturally present in plant cells around anthocyanins. Given the interaction with the copolymer compound, the intensity of the pigment color will increase (hyperchromic) or a maximum wavelength shift (batochromic) occurs [2][3][4][5]. The result obtained from copigmentation is colorantb expected that it can be use on a wider pH range. This study aimed to do the copigmentation of the anthocyanin extract of purple sweet potato using ferulic acid and tannic acid.

2. Materials and Methods

2.1. Materials
The research materials used were local purple sweet potatoes obtained from Bogor area, aquades, pH paper, tannic acid, fumeric acid, DMSO, ammonium acetat, and citric acid.

2.2. Methods
2.2.1 anthocyanin extract. The sorted and washed sweet potatoes are cut into sizes about 3 cm x 0.5 cm x 1 cm. The sweet potato pieces are then blanched at 90 ° C for 10 minutes. After that it is then heated by adding 1:2 (w/v) water at 70 °C for 1 hour. The anthocyanin extraction was conducted with distilled water at pH 7 and pH 2, for pH 2 condition the water used has been added citric acid so that the pH of water becomes 2. The sweet potatoes is then mashed and filtered to obtain the extract. The extracts obtained are then dried with freeze drier and ready for copigmentation processed.

2.2.2 Copigmentation. Tannic acid and fumeric acid variations as copigment has concentration of 0.005 M; 0.010 M; 0.015 M; 0.02 M; 0.03 M; and 0.04 M. Tannic acid (MW 1701.2) or ferulic acid (MW 194.18) dissolve in 10% DMSO of 0.02 M ammonium acetate solution. This means if the tannic acid copigment will be made 0.02 M as much 250 mL then it should be weighed as much 8,5059 g while ferulic acid 0.9709 g in 0.3854 g ammonium acetate (dissolved in 250 mL aquades) and 25 mL DMSO.

3. Results and Discussion
Purple sweet potatoes is one type of sweet potato that is found in Indonesia in addition to the white, yellow, and red [6]. The plant is rich in anthocyanin content. Some research has been carried out about the anthocyanin from purple sweet potato used as the functional compound due to its obvious anticancerogenic, antioxidant, antimitution, and antineoplastic activities [7][8][9][10][11].The content of anthocyanin in sweet potatoes is also potential as a natural colorant, for food and beverages. Figure 1 showed the raw material that used in this reserearch.
In fruits or vegetables, anthocyanin pigment is generally located on cells near the surface, it is expected that hot water can denature the cell membrane of the plant then dissolve the anthocyanin pigment out of the cell. Solvent extraction is based on the solubility of the component against other components in the mixture to extracted the pigment from a complex matrix [12]. The anthocyanin pigments are soluble in water because they are equally polar. Water has a high degree of polarity. This is indicated by the polarisability value of water molecules in an electric field or dielectric constant ($E'$) of 78.50 at 20 °C. The value is greater than other solvents such as ethanol, methanol, hexane, and acetone. Of The two pH treatments performed there were differences in the results obtained from the sweet potato extract produced. The results showed in Table 1.

| Sample                              | Color appearance   | Anthocyanin (ppm) |
|-------------------------------------|--------------------|-------------------|
| Raw purple sweet potatoes           | Dark purple        | 235.40            |
| extraction with distilled water at pH 7 | Browning           | 888               |
| extraction with distilled water at pH 2 | Bright red purple | 1710.6            |

The results showed that best anthocyanin extraction method of the purple sweet potato was using distilled water at pH 2. It is seen from the appearance of the color and the resulting anthocyanin levels Chemically the anthocyanin is a derivative of a single aromatic structure, cyanidine, and all formed from cyanidine pigments by addition or subtraction of hydroxyl groups, methylation and glycosylation [13]. Anthocyanins are amphoteric compounds, which have the ability to react with both acid and alkaline. In red antosianin acid medium, and on basic media turns into purple and blue (1).

The color of the purple sweet potato antosianin is highly dependent on the pH of the solution. Figure 2. shows the color pattern of purple sweet potato extract from pH 2-12. The anthocyanin color of purple sweet potato is influenced by the pH of the solution, ie, respectively red, purple, and blue under acidic, neutral and basic conditions [14].
The color of the anthocyanin extract tends to change as the pH 2-12 increases from red, purple, blue, green to yellow. Purple sweet potato extract at strong acid pH 2-3 is red, in weak acid pH 4-6 pink, pH 7 is blue, at pH of weak base 8-10 is green and pH 12 is yellow. Results of research conducted by Cevallos-Casals and Cisneros Zevallos [15], showed the color of red sweet potato anthocyanin extract at pH 0.9 to pH 4 red, at pH 5 to 7 green.

A study conducted by Nikijuluw 2013 on anthocyanin flowers of pearls at pH 1 and ph 2 is red, at pH 3 purple, at pH 4 samapai pH 9 is blue, at pH 10 to pH 12 is green and at pH 13 and pH 14 is colored yellow [16]. Differences in anthocyanin color in purple sweet potato, red sweet potato, flower of teleng caused by difference antosian compilation compound. The main anthocyanin composer in purple sweet potato is a cyanidine compound. The color change of anthocyanin extract in purple sweet potato along with pH change is caused by a change of anthocyanin structure. The changes of anthocyanin structure are from flavilum cation (red) to pseudobasa carbinol (colorless), quinonoidal (blue), quinonide anion (blue) or kalkon (yellow).

In the process of copigmentation, it is necessary to optimize the use of copigments which will be used for the process of copigmentation. The copigment used for copigmentation is an organic acid. Copigment concentrations must be greater than those that will be digitized. In this study, the copolymers used are synthetic chemicals, which have higher purity than the crude extracts obtained from nature (eg tea leaves). Maximum wavelength shift (batokhromik effect) and increased color intensity (hyperchromic effect) are a cooling effect in the anthocyanin co-opment process. These two effects indicate the success of the copigmentation process and the increased intensity of color after added copigments. The copigmentation process in this study is to use tannic acid and ferulic acid which is a commercial organic acid that can function as copigment. The results of optimization of copigmentation with tannic acid and ferulic acid shown in Table 2.

### Table 2. The results of optimization of copigmentation with tannic acid and ferulic acid

| No | Copygment | Concentration (M) | λ max (nm) | Δλ max | A | ΔA max |
|----|-----------|-------------------|-----------|--------|---|--------|
| 1  | Blanko    | 0                 | 527.9     | 0      | 0.382 | 0      |
| 2  | Ferulic acid | 0.005            | 527.9     | 0      | 0.398 | 0.016  |
| 3  | Ferulic acid | 0.01             | 531.0     | 3.9    | 0.430 | 0.048  |
| 4  | Ferulic acid | 0.015            | 531.0     | 3.9    | 0.489 | 0.107  |
| 5  | Ferulic acid | 0.02             | 532.0     | 4.9    | 0.441 | 0.059  |
| 6  | Ferulic acid | 0.03             | 531.0     | 3.9    | 0.437 | 0.055  |
| 7  | Tannic acid | 0.005            | 531.0     | 3.9    | 0.522 | 0.140  |
| 8  | Tannic acid | 0.01             | 531.0     | 3.9    | 0.578 | 0.196  |
| 9  | Tannic acid | 0.015            | 531.0     | 3.9    | 0.610 | 0.228  |
| 10 | Tannic acid | 0.02             | 531.0     | 3.9    | 0.640 | 0.258  |
Table 2 shows the result of anthocyanin purple sweet potato antopian coupling with ferulic acid and tannic acid. The concentration of ferulic acid used was 0.005M-0.03M and the tannic acid concentration used was 0.005M-0.04M. The reaction of copigmentation is influenced by pH, temperature, and concentration [17]. At low pH the antocyanine molecule is a red flavinium cation, while a higher pH will be a pale-colored carbinol pseudobase. Increased temperatures will lead to increasingly unstable co-umption. This happens because of partial damage to the hydrogen bond. The added copolymer concentration will affect the copigmentation process. The amount of copolymers added should be more than the anthocyanin. The concentration of pigment and copolymer ratio is expressed in molar.

The use of both copolymers observed the effect of maximum wavelength shift (batochromic effect, Δλmax) and increased color intensity (hyperchromik effect, ΔAmax). The cytobromatic effect on ferulic acid starts to occur at a concentration of 0.01M and the hypochromic effect on tannic acid occurs at a concentration of 0.005 and remains at a concentration of 0.02M. In the tannic acid copolymer, increased concentration results in an increase in hyperchromic effect while in ferulic acid there is a maximum hyperchromic effect at a concentration of 0.015 M. Based on these results, the best concentration of ferulic acid copolymer is 0.015M and the tannic acid copolymer is at a concentration of 0.02M. The use of tannic acid 0.02M is recommended compared to ferulic acid 0.015M because with the bathocromic effect (Δλmaks = 3,9) results hyperchromic effect (ΔA = 0,258) higher by tannic acid. Figure 3 show the result of copigmentation.

![Figure 3. The result of colors obtained after copigmentation](image)

The phenomenon shown when the process of copigmentation occurs is the effect of the batochromic (Δλmax) that is the absorption of the maximum wavelength (λmax) and in the visible distance there is an increase in bluing effect, such as anthocyanin color changing from red to bluish red or hyperchromatic effect ΔA) is the intensity of the anthocyanin color seen from the increased of absorbance value.

4. Conclusion
The use of tannic acid and ferulic acid which is added to the anthocyanin extract indicating the occurrence of the copigmentation process. The use of 0.02M tannic acid and 0.015M ferulic acid produce hyperchromic effect and bahtochromic effect.  The use of tannic acid 0.02M is recommended compared to ferulic acid 0.015M because with the same bathocromic effect (Δλmaks = 3,9) results hyperchromic effect (ΔA = 0,258) higher by tannic acid.
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