Methylation of Brazilein on Secang (*Caesalpinia sappan* Linn) Wood Extract for Maintain Color Stability to the Changes of pH

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Abstract. The stability of natural dyes to the changes of pH is really necessary when the natural dyes are applied either on fabric or food. This research aimed to increase the stability of brazilein, a compound contained within the secang wood extract, to the changes of pH. The methylation process was done by reacting Dimethyl Carbonate (DMC) with the brazilein on the secang wood extract. DMC acts as a substance that substitute hydroxyl group on brazilein. The methylation reaction of brazilein on secang wood extract was operated on a three-necked round-bottomed flask fitted with mercury-sealed stirrer and reflux condenser under 80°C temperature and 250 rpm stirring speed. There were two variables observed in this research; the DMC amount ratio to the amount of secang wood extract and the time of the methylation process. The research showed that at the 1:10 the DMC amount ratio to the amount of wood extract and 8 hours of the methylation process give the better stability of color of the secang wood extract than the variation of the other variables.

Keyword : Secang wood, *Caesapinia sappan* L., brazilein, pH, methylation.

1. Introduction

Indonesia has thousands of types of natural dye-producing plants that have been used since a long time ago. All this time, the natural red dye can be obtained from root bark of *Morinda citrifolia*. Therefore, the natural red dye for textiles is still difficult to produce in large capacity, due to the limited amount of raw materials that can be obtained [5]. Mean while secang wood is very potential to be used as a source of natural red dye because the amount of the secang wood which is very abundant in Indonesia and has not been utilized optimally. The negative side of secang wood is its instability of the brazilein, a compound contained within the secang wood extract itself. Hence engineering enhancement of the quality of the brazilein as a source of red dye is required. From all of the plant species which can be used as natural dye producers, not all of them have been tested for their stability and discoloration yet. Some plants that already evaluate for its stability according to re Merbau wood (*Instia bijuga*), Tegeran wood (*Cudraina javanensis*), Tingi bark (*Terminalia bellirica*), and Coconut coir (*Cocus nucifera*) [9].

Secang (*Caesalpina sappan* L.) wood is a member of the *Caesalpiniaceae* which mostly exist in Indonesia. Aside from its use as healthy drink ingredients, secang (*Caesalpina sappan* L.) wood can also be used as raw material of natural dyes for food or textile. The part of the tree that taken as a
natural dyes is the stem. Secang wood extract produces a red traffic color at neutral pH (pH 6-7) and tend to be red purple by the increase of pH [8].

Brazilin is a dahlia yellow colored compound while brazilein is a reddish colored compound. The change-over of brazilin into brazilein is due to the delocalization of the electrons because of the presence of carbonyl groups as a result from the oxidation process of brazilin. Therefore the pigments from secang wood extract contain more brazilein [3]. The pigments or the dye molecules is a composite of three constituent components i.e unsaturated organic compounds, chromophore groups, and auxochrome groups. The color carrier chromophores group were unsaturated covalent bond compounds, which lead to the electron uptake. The substance attached to a chromophore group may be impaired or reinforced. It called as the auxochrome group, which is saturated, and it is a part of the dye molecular structure that binding with the fabric [11]. The brazilein pigment is a chemical structure with a hydroxyl group (OH), which is an auxochrome group.

One of the strategies for binding oxygen atoms due to the loss of hydrogen atoms on the brazilein hydroxyl groups is methylation method. The methylation reaction is a replacement reaction of an atom or molecule with a methyl group [13]. The methyl group (CH₃) binds to the unstable oxygen atoms in the brazilein auxochrome group, and then it forms a new auxochrome group; methyl brazilein which is more stable. Commonly used methyl electrophile source is dimethyl sulfate (DMS) reagent with 0,44 g/kg LD₅₀, dimethyl halide (CH₃-X ) with 0.079 g/kg LD₅₀, and dimethyl carbonate (DMC) with 13,8 g/kg LD₅₀. Based on the LD₅₀ value of the three methyl electrophile source, DMC is a green methylation agent that is environmentally friendly[12]. In this research used DMC as a methylation material for secang wood extract structure is applied. The methylation reaction between brazilein and dimethyl carbonate will produce a methyl group attached to an oxygen atom which was previously a hydroxyl group. The mechanism of this reaction is that the methyl group derived from dimethyl carbonate reagent will attack the hydroxyl group that binding with a benzene compound which has no electron resonance in its structure. The hydrogen atom will be easily substituted by the methyl group because of the hydroxyl group attached to the benzene compound that has no electron resonance in its structure tends to remove the hydrogen atom [1], so with the changes of the brazilein auxochrome group which has three hydroxyl groups before, as the effect of the methylation reaction, it will turn into two hydroxyl groups with one oxygen atom attached to a methyl group. The reduction of hydroxyl groups in the brazilein functional group will result on the increased of the color stability of brazilein to the changes of pH. The mechanism of the methylation reaction of brazilein as presented in Fig. 1.

![Figure 1. The reaction of DMC with brazilein](10;14)


2. Material And Method

2.1 Materials

The secang wood used in this research was obtained from the Beringharjo market Kodya Yogyakarta. High purity chemicals were used in this research, which included dimethyl carbonate 99% (Merck, Germany), HCl with purity of 37% was taken from C.V. Chemix Pratama, Yogyakarta, Indonesia, NaOH in the form of crystalline was taken from C.V. Chemix, Yogyakarta, Indonesia.

2.2 Method

The experiment was operated in laboratory scale batch system using a stirred reactor with mantle heater and condenser (Fig. 2).

![Figure 2. The experimental set-up used for brazilein extraction](image)

To obtain the brazilein extract from secang wood, the extraction process was done under optimum condition based on the previous research by Wahyuningrum[8] that conducted using water as solvent, 100°C temperature, and 70 minutes of the extraction time. However, the ratio used in this extraction was 30 g : 500 mL of the weight of the secang wood to the volume of water as solvent. It is intended to obtain the brazilein concentration in the extracts suitable for the methylation reaction. The methylation reaction of brazilein on secang wood extract was operated on a three-necked round-bottomed flask fitted with mercury-sealed stirrer and reflux condenser as shown in Fig. 2. The methylation reaction was done under 80°C temperature, 250 rpm stirring speed with two operation variables; the DMC volume ratio to the secang wood extract volume and the time of the reaction. The variations of the DMC volume ratio to the secang wood extract volume were 1:100; 1:20; 1:10 while the variations of the methylation reaction time were 1, 5, and 8 hours. Each one of the methylation reaction results was tested for its stability to pH; 10 mL of the methylation result was taken to tested in pH 2, 3, 5, 7, and 10. Furthermore 5 mL of the solution was taken, diluted to 100 mL, and then its absorbance was measured using a UV-Vis spectrophotometer at 541 nm wavelength.

3. Result And Discussion

3.1 The brazilein extract stability from secang wood

The brazilein extract gives a certain color for every pH condition. The color of the brazilein at various pH conditions stated in the classic Reichs-Aussch für Lieferbedingungen (RAL) system for color standardization qualitatively, as shown in Fig. 3.
Figure 3. Classic RAL System for color standardization[4]

The brazilein extract around pH 6 to 7 or neutral pH gives pearl ruby red and ruby red color, and changed into purple red until wine red by the increase of pH. The secang extract produce ruby red color. For the low pH condition (pH 2-5) secang extract produce of color dahlia yellow until traffic red [4]. The changes of color of the secang wood extract for various pH condition presented in Table 1 as well as the absorbance value which was measured using a UV-Vis spectrophotometer at 541 nm wavelength presented in Fig. 4. Based on the result, it can be declared that the secang wood extract was unstable by the changes of pH. This was in line with the statement of Mohan et al. [7] that the color stability of the secang wood extract was quite low because of its –OH functional group or conjugated cyclic bond so the attempt to obtain more stable extract color need to be done.

Table 1. The changes of the secang wood extract color for various pH

| pH  | COLOR (RAL SYSTEM) |
|-----|--------------------|
| 2   | Dahlia yellow      |
| 3   | Dahlia yellow      |
| 5   | Traffic red        |
| 7   | Ruby red           |
| 10  | Purple red         |

Figure 4. The absorbance values of secang wood extract for various pH condition which was measured using a UV-Vis spectrophotometer at 541 nm wavelength.
3.2 The variation of the DMC volume ratio to the extract volume for methylation reaction

The changes of methyl \textit{brazilin} color; the methylation result of secang wood extract for various values of DMC ratio and the secang wood extract to the changes of pH presented in Table 2. As for the absorbance value which was measured using a UV-Vis spectrophotometer at 541 nm wavelength presented in Fig. 5. The successful of methylation reaction can identified by stabilize of absorbance value which was measured for various pH conditions (pH 2, 3, 5, 7, and 10).

![Figure 5](image)

\textbf{Table 2.} The methyl \textit{brazilin} color; the methylation result of secang wood extract for various values of DMC ratio to the secang wood extract for various pH conditions

| pH | The variation of DMC ratio to the secang wood extract |
|----|------------------------------------------------------|
| 2  | Dahlia yellow | Dahlia yellow | Dahlia yellow | Dahlia yellow |
| 3  | Dahlia yellow | Dahlia yellow | Dahlia yellow | Dahlia yellow |
| 5  | Traffic red   | Traffic red   | Traffic red   | Traffic red   |
| 7  | Ruby red      | Ruby red      | Traffic red   | Traffic red   |
| 10 | Purple red    | Purple red    | Ruby red      | Traffic red   |

Figure 5 and Table 2 present the 1:10 DMC volume ratio to the secang wood extract gives the most stable methyl \textit{brazilin} color and the absorbance value to the changes of pH. The research showed that the color stability was increased regardless of the various pH conditions due to the reduction of the hydroxyl group on the \textit{brazilin} because of the methylation reaction. The hydroxyl group attached with chemical structure will reduce the color stability, while the methylation will increase the color stability to the changes of pH [2].

3.3 The variation of the methylation time

The changes of methyl \textit{brazilin} color and absorbance value; the methylation result of secang wood extract for various times presented in Fig. 6 and Table 3
Figure 6. The absorbance values of the methylation result of secang wood extract in the variation of methylation time for various pH condition.

| pH  | The variation of time |
|-----|-----------------------|
|     | 0    | 1 hour | 5 hour | 8 hour |
| 2   | Dahlia yellow | Dahlia yellow | Dahlia yellow | Dahlia yellow |
| 3   | Dahlia yellow | Dahlia yellow | Dahlia yellow | Dahlia yellow |
| 5   | Traffic red   | Traffic red   | Traffic red   | Traffic red   |
| 7   | Ruby red      | Ruby red      | Ruby red      | Traffic red   |
| 10  | Purple red    | Purple red    | Ruby red      | Ruby red      |

Figure 6 and Table 3 present the color stability to the changes of pH which was increased by the longer of the methylation time. The best color stability condition was performed under 8 hours of the methylation time, where the absorbance value did not significantly different on the 2, 3, 5, 7 pH range. As for the 10 pH value, the increase of the absorbance value is quite high, where this condition may be caused of the methyl bond on the brazilein did not strong enough, so the color stability under this pH value has not been reached the optimum condition yet. Therefore, the addition of the methylation time should be done on the next research. According to [6], DMC is a non-toxic methylation agent and it is a green chemical as it takes a long time in the methylation reaction.

4. Conclusion
The best condition achieved from this brazilein methylation on secang wood extract was on 1:10 ratio of the DMC to the secang wood extract, where the stability of color in different pH did not resulted absorbance value that significantly different. Meanwhile the best condition in the variation of the methylation time was the one under 8 hours.

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