

Chemical Structure of Mangrove Species *Rhizophora stylosa* as Natural Dyes

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Abstract

Textile dyes are divided into two types, natural dyes and synthetic dyes. Natural dyes commonly made from extraction. Extraction is a process in which one or more components are separated selectively from a liquid or solid mixture, the feed, by means of a liquid immiscible solvent. Extraction can be classified into two groups, liquid extraction and solid-liquid extraction. Solvents that are usually used in the extraction of natural dyes are aquades and ethanol. The purpose of this research was to determine the chemical structure, especially tannin in natural dyes from mangrove species *Rhizophora stylosa* through several samples testing natural dyes. *Rhizophora stylosa* that have been extracted and evaporated will be conducted several tests to obtain chemical structures in natural dyes and yield of tannin in natural dyes. Tests carried out include testing FT-IR, and HPLC. Based on FT-IR analysis, the extraction of *Rhizophora stylosa* containing tannin indicated by the presence of hydroxyl (O-H) in the area of 3385.36 cm^{-1} , aromatic (C-H) in the area of 1365.53 cm^{-1} , carbonyl (C=O) in the area 1646.36 cm^{-1} , esters (C-O) in the area 1217.30 cm^{-1} . While tannin content obtained from the analysis of HPLC were 6.087 ppm.

Keywords : chemical structure.mangrove, tannin

INTRODUCTION

Batik in Indonesia has a comparative advantage in the economic field (Setiawati *et al.*, 2015). The high demand for batik both domestically and abroad, the more dyes are used. Textile dyes are divided into two types, natural dyes and synthetic dyes. Synthetic dyes can be derived from coal or crude oil which are the product of aromatic hydrocarbon such as benzene, naphthalene, and anthracene. The use of synthetic dyes has been proven to be cheaper but have a negative impact because they are carcinogenic, due to the heavy metal content of synthetic dyes (Paryanto, *et al.*, 2012). Compared to natural dyes, synthetic dyes have the advantage in the resulting color, color variations, price, availability, to stability (Lee, *et al.*, 2005). However, judging from its constituent components, the use of dyes that contain chemicals to the use of wax that is insoluble in water causes problems in the surrounding

environment (Manurung, 2012). Natural dyes are biodegradable and less toxic and allergenic than synthetic dyes, they are considered to be environmentally friendly (Punrattanasin *et al.*, 2013). Natural dyes can be obtained from various plants, one of which is mangrove tannin content in mangroves can be used as a natural coloring agent (Purnaningtyas, 2014).

Natural dyes are known for their use in coloring of food, leather, wood, as well as natural fibers like wool, silk, cotton and flax since ancient times (Punrattanasin *et al.*, 2013). Subsequent developments in the use of natural dyes were displaced by synthetic dyes found, because of their superior color resistance properties, they are not easy to fade, are easily produced, the color direction is more varied, and the price is cheaper than natural dyes (Kasmudjiastuti, 2017).

Natural dyes comprise of colorants that are obtained from animal or vegetable matter without any chemical processing (Umbreen *et al.*, 2008).

Natural dyes have been used for many purposes especially in textile sector such as the colouring of natural fibres, cosmetic, to produce ink, watercolour and artist's paints (Baha *et al.*, 2011). Most dyes are obtained from plants because plants have a variety of color pigments unlike in animals. Pigments contained in plants depend on the chemical structure contained in these plants. Tannin is a natural coloring pigment in the form of a brown coloring agent (Rahim *et al.*, 2007). The purpose of this research was to determine the chemical structure, especially tannin in natural dyes from mangrove species *Rhizophora stylosa* through several samples testing natural dyes.

METHODOLOGY

Extraction of natural dyes was carried out at the Chemical Engineering Laboratory, Faculty of Engineering, Sebelas Maret University. Extraction is carried out for ± 1 hour and evaporation is carried out ± 45 minutes 4 times. The following materials and tools will be used for the extraction of natural dyes *Rhizophora stylosa* mangroves and water. The tools used in this study were extractor-evaporator, HPLC (High pressure liquid chromatography), and FT-IR spectrophotometer.

The preparation stage is by chopping and drying the mangrove *Rhizophora stylosa* in an oven at 100°C for 3 hours. The extraction stage is carried out by inserting dried mangrove *stylosa* into the extractor-evaporator tube and adding water with a ratio between mangrove: water, that is 1:10 (Paryanto *et al.*, 2016). Arranging the extractor-evaporator then igniting the stove and the stirring

motor. The extraction process lasts for 1 hour at a temperature of 96°C . The evaporation stage is carried out by opening the evaporator faucet for 45-60 minutes. Equation by Crisholithus (2008).

RESULTS AND DISCUSSION

In the process of taking pigments of natural dyes required a comparison between ingredients and solvents is 1:10. Dried mangroves used as much as 250 grams and as much as 2.5 liters of water solvent. The extraction process lasts for 1 hour at a temperature of 96°C followed by an evaporation process for ± 45 minutes. From the extraction and evaporation process a volume of concentrate of 1.8 L. was obtained.

The test results with FT-IR obtained FT-IR spectrum data of mangrove fruit species *Rhizophora stylosa* shown in Figure 3. In the FT-IR spectrum of mangrove fruit *Rhizophora stylosa* species showed the presence of hydroxyl (O-H) in the area of 3385.36 cm^{-1} , aromatic (C-H) in the area of 1365.53 cm^{-1} , carbonyl (C=O) in the area of 1646.36 cm^{-1} , esters (C-O) in the area of 1217.30 cm^{-1} .

Table 1. Results of FT-IR Mangrove *Rhizophora stylosa*

Functional Groups	Peak (cm^{-1})
O-H (hydroxyl)	3385.36
C-H (aromatic)	1365.53
C=O (carbonyl)	1646.36
C-O (esters)	1217.30



Figure 1. Extraction-Evaporator

According to Danarto *et al* (2011), the main tannin element is the hydroxyl group and there are other groups such as carboxyl. According Kasmudjiastuti (2014) in his research on the characterization of high bark as a vegetable tanner. High wood bark containing tannins was tested by FT-IR spectrophotometry obtained that the results of the high FTIR spectrum showed the presence of hydroxyl groups (ν O-H; ν N-H) in the area (3467,418-3057,025) cm^{-1} , aromatic group (ν C-H) in the area of 2875,733 cm^{-1} , ν C = O (ester group in tanned material) in the area (1747,442-1612,422) cm^{-1} , ν -OH; R-COO- in the area of 1444,626 cm^{-1} and ν (SO₄)²⁻; R-SO₃; R-SO₃H in the area (1112,823-1062,729) cm^{-1} .

In a study conducted by Fatma *et al.* (2018) analyzed mangroves of rhizophora mucronate with FTIR spectrophotometer. Generate FTIR spectrum data of mangrove fruit species of Rhizophora mucronate on the absorption of 3370.58 cm^{-1} . The next absorption occurs at 1650.50 cm^{-1} . The last absorption is also the weakest at 1271.11 cm^{-1} . When compared to studies conducted by Fatma *et*

al. (2018) mangroves have hydroxyl (OH) groups, carbonyl groups (C = O), and ester groups (CO). This was confirmed by Marais *et al.* (2006) revealed that flavonone is a building unit of proanthocyanidin compounds which are condensed tannins. Parubak (2013) who found that the flavonoid compounds from the flavonone group had a OH OH functional group, CH aliphatic, C = O, C = C Aromatic, C-O and C - H aromatic. So it can be said that the research we have done is right.

Test results with High-Performance Liquid Chromatography (HPLC) with the following operating conditions: 1. Flowrate: 1 mL / min; 2. The mobile phase: MeOH: H₂O (50:50); 3. λ (long gel): 271 nm; 4. Column: C18, 250 mm. From the results of three replicas of the tannin standard (Figure 4) using a chromatogram, the following data are obtained (Table 2). From the results of two replicas of the mangrove *Rhizophora stylosa* natural dyes (Figure 5), the following data were obtained Table 2.

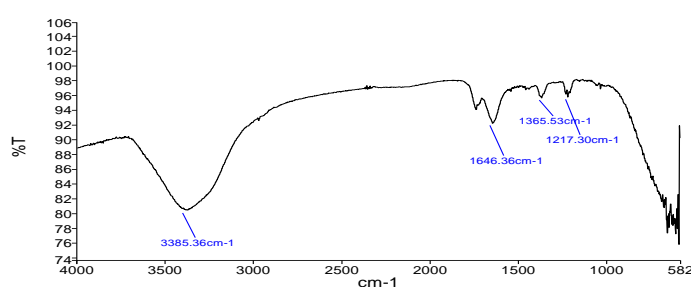


Figure 2. *Rhizophora stylosa* FT-IR Spectrum

Table 2. Standard Tanin Chromatogram Analysis

Sample	Retention time (min)	Area (mAu)	High
Standard tanin 4 ppm	2,886	215585571	35292817
Standard tanin 4 ppm (2)	2.949	233383331	35409043
Standard tanin 4 ppm (3)	2.959	218262186	33942994
Average		222410363	

Table 3. Table of Analysis of Natural Dyes Chromatograms from Mangrove *Rhizophora stylosa*

Sample	Retention time (min)	Area (mAu)	High
Stylosa natural dyes	2,964	37630883	5177837
Stylosa natural dyes (2)	2.969	30061043	4568279
Average		33845963	

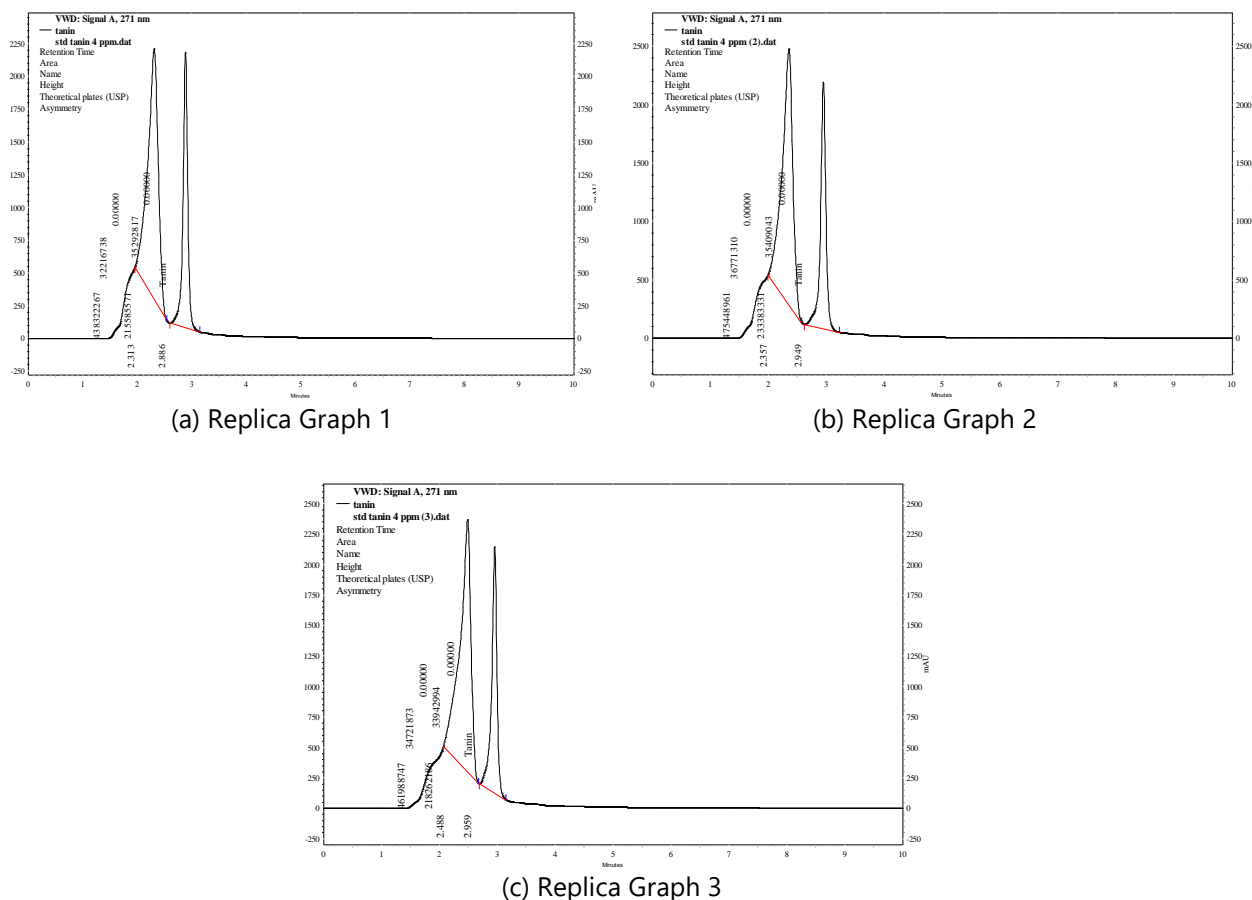


Figure 3. Tanin Standard Replica Chart

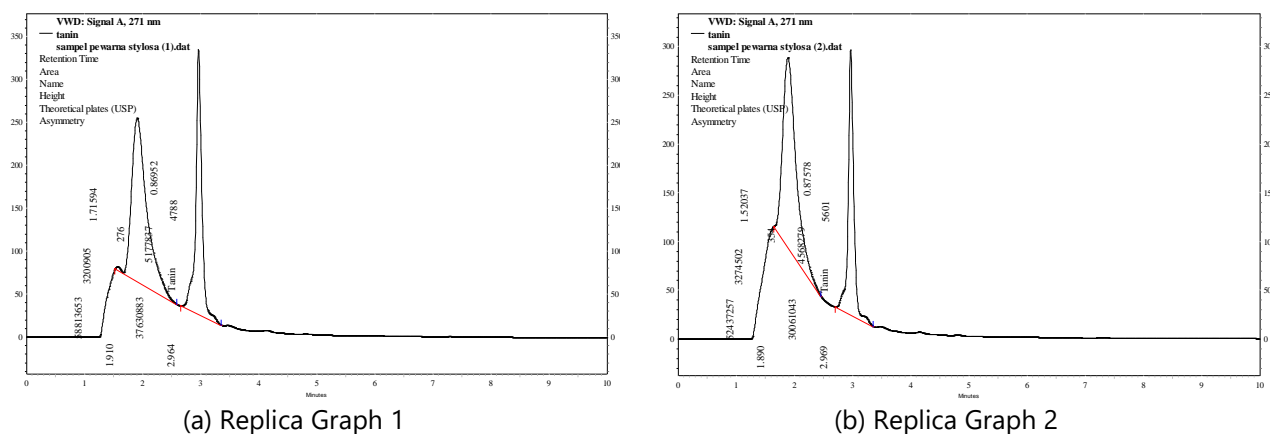


Figure 4. Graphic Replication of Natural Dyes from Mangrove *Rhizophora stylosa*

From the results of two replicas of the mangrove *Rhizophora stylosa* natural dyes (Figure 4), the following data were obtained Table 3. With the data that has been obtained from the replica

results, it can be calculated the concentration of tannins in natural dyes from mangrove species *Rhizophora stylosa*. The initial sample is diluted 10 times then taken 1 mL and diluted again 10 times.

So the dilution factor is 100 times. Average wide standard area of 4 ppm = 222410363 mAU Average wide stylose sample area = 33845963 mAU Standard concentration = 4 ppm => 0.004 mg / mL

$$\begin{aligned} \text{Tannin content} &= \frac{33845963 \text{ mAU}}{222410363 \text{ mAU}} \times 0,004 \frac{\text{mg}}{\text{mL}} \times 10 \\ &= 0,00608712 \text{ mg/mL} \\ &= 6,08712 \text{ ppm Tanin} \end{aligned}$$

So, tannin content in the *Rhizophora stylosa* sample were 609 ppm.

In the research of Hardoko *et al.* (2015) mangrove fruit species *Rhizophora Mucronata* has a tannin content of 819 ppm. The tannin content in the mangrove fruit species *Rhizophora stylosa* is smaller than the mangrove type *Rhizophora Mucronata* species, this is because the size of the mangrove fruit species *Rhizophora stylosa* is smaller than the size of the mangrove fruit species *Rhizophora Mucronata*. This was confirmed by the study of Sudarmadji (2004) mangrove *Rhizophora Mucronata* type which has a fruit shaped like a guava, size 2-2.3 cm, yellowish green color, hypocotyl cylindrical diameter of 2-2.5 cm, length can reach 90 cm, while mangrove *Rhizophora stylosa* species have fruit similar to the shape of water guava, brown color, size 1.5-2 cm, hypocotyl 2-2.5 cm in diameter, smooth surface, length can reach 30 cm.

The strength of our research is that it is the first research on the chemical structure of tannins in mangrove fruit species of *Rhizophora stylosa*, so that they can be used as a reference and this research can also optimize the use of natural dyes from *Rhizophora stylosa* mangrove fruits for batik cloth dyes in Indonesia so as to reduce the use of synthetic dyes that are harmful to humans and the environment.

CONCLUSION

Based on FT-IR analysis, the extraction of *Rhizophora stylosa* mangroves containing tannin was indicated by the presence of hydroxyl (O-H) in the area of 3385.36 cm⁻¹, aromatic (C-H) in the area of 1365.53 cm⁻¹, carbonyl (C=O) in the area of 1646.36 cm⁻¹, esters (C-O) in the area of 1217.30 cm⁻¹. While tannin content obtained from the analysis of HPLC were 608.712 ppm.

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