Potency of different banana bunches cultivar (*Musa sp*) as vegetable tanning agents

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Abstract. Leather tanning with natural tannin sources is expected to reduce environmental issues. Banana plants (*Musa sp*) as one of tropical plants are known to have a high tannin contents. This paper aimed to identify the potency of several banana bunches cultivar as vegetable tanning agents. The study was conducted by analyzing the tannin levels of banana bunches extract from three banana plant cultivars. The banana bunches used were Kepok (*Musa parasidiaca* L.), Raja (*Musa textilia*) and Ambon (*Musa acuminata* Cavendish). Tannin extraction were assessed using shoxhlet extractor with 70% ethanol. Determination of tannin content using 10 grams sample with processing conditions temperature were 70°C and 60 minutes extraction time using spectrophotometer at wavelenght 700 nm. Tannin level data were analyzed by descriptive analysis. Based on the concentration of the standard solution and the absorbance produced, the standard gallic acid curve regression were y = 0.0063x + 0.1082 with R^2 = 0.8543. Results showed that kepok produced highest tannin levels between 0.87% – 2.04%, while Raja between 0.04% – 0.67% and Ambon were between 0.05% – 0.33% at the standard solution concentrations of 20 – 100 ppm. It is concluded that Kepok banana bunches has the best potential as vegetable tanning agent. Further laboratory studies are needed to determine the quality of tanned leather resulting from banana bunches tanning.

1. Introduction

Leather tanning with natural tannin sources is expected to reduce environmental issues. The vegetable tanning agents can be used alone or in combination with others to improve efficiency. The plant parts used for tanning in order of importance were barks, roots and tubers [1]. Vegetable tanned leather has excellent fullness, moldering properties, wear resistance, air permeability and solidness. Hence, it is of great significance to reduce chrome pollution in leather making process [2,3]. Vegetable tanned leather is used in making heavy leather such as furniture leather, garment leather and shoe upper leather. Researchers worldwide are paying particular attention to the use of vegetable tanning agents to replace chrome tanning agent and progress has already been achieved. Some plants are preferred for tanning over others due to the level of their tannin content. Tannin is found in various parts of plant such as tree bark, wood, fruit, pod, leaf, root, tuber and many other parts, indicating that different plant parts are used in tanning [4].

Mimosa (a leguminose growing in a short time) derived from acacia wood is a material that is often used for vegetable tanning. Mimosa has been largely used to obtain tanning extracts employed in the tanning of hide, due to their reduced environmental impact [5]. Mimosa has a weakness that still an imported material at high prices in Indonesia. Acacia and mangrove plants, if widely used as a

source of tannin, will reduce plants in the forest as a source of oxygen [6]. Other plants are needed as an alternative source of tannin which does not threaten the environment.

The banana plant (*Musa sp*) is a popular type of fruit crop that is widely spread throughout the tropics, including Indonesia. In addition to producing fresh and processed fruit, the banana plant has the potential to be used as feed for animals. Banana plant produce high byproducts, such as leaves, tillers and stems. Banana stem and bunches tannin content, based on to the results of chemical analysis, vary depending on the type of banana plants [7]. The content of tannins in leaves, trees and banana peels varies between 3.7 to 5.5%, making it possible to be used as vegetable tanners [8]. The use of banana bunches can reduce the use of chemicals in the process of tanning and the manufacture of leather products [9]. Based on this potency of tannin content, it is may possible as vegetable tanning agents. This paper aimed to identify the potency of several banana bunches cultivar as vegetable tanning agents.

2. Materials and Methods

2.1. Materials

The materials used were bunches from three varieties of banana, namely Kepok (*Musa parasidiaca* L.), Raja (*Musa textilia*) and Ambon (*Musa acuminata* Cavendish). Fresh banana bunches were taken from ripe bananas. Other materials used are 70% ethanol, folin denis reagent, aquadest, $FeCl_3$, Na_2CO_3 and tannic acid. The tools used include scales, ovens, watch glass, spatulas, a series of extraction apparatus and UV-Vis spectrophotometer.

2.2. Methods

Banana bunches extraction. Three varietes of banana bunches (Kepok, Raja and Ambon) were washed, then cut into small, made thin pieces and stored for 7 days until dry. A total of 10 grams of fine banana bunches were extracted by the soxletation method using 200 mL of 70% ethanol solvent with a temperature of 70°C and a time of 60 minutes. The extract results obtained were used for qualitative analysis and quantitative analysis of tannins [10,11]

Qualitative and quantitative identification. The tannin qualitative test included the $FeCl_3$, Ammonia, Gelatin and HCl tests using the method from Harborne [10]. Quantitative tannin analysis includes total tannin content used methods from Harborne [10], it is carried out by means of the extract of banana bunches taken 5 ml then added distilled water to a volume of 100 ml, homogenized and centrifuged. Taking 1 ml of sample solution were carried out and then 0.5 ml of Follin-Ciocalteu reagent were added and then 1 ml of 20% Na_2CO_3 solution is added. Dilution were carried out by adding aquadest to a volume of 10 ml and mixed until homogen. Absorbance readings of the samples were carried out using a spectrophotometer at a wavelength of 720 nm. The total content of tannin were expressed as the amount of equivalent tannic acid per gram of extract. The percentage (%) of tannin content is equal to the dilution factor divided by the weight of the sample multiplied by 100%.

Data analysis. The data obtained were analyzed descriptively.

3. Results and Discussion

3.1. Qualitative identification

Qualitative analysis aims to estimate the presence of tannin in banana bunch extracts. The results of the qualitative determination of tannins carried out on the extract of Kepok banana bunches, ambon banana bunches and dried Raja Banana bunches using 70% ethanol has a blackish brown color with a very thick texture. The use of ethanol solvents can optimize the extraction process of secondary metabolites [12]. The results of the qualitative tannin test can be seen in **Table 1**.

Table 1. Qualitative identification of tannin from Kepok, Ambon and Raja banana bunches extract

Reactor	Kepok	Ambon	Raja	Conclusion
FeCl3	Green	Turbid Green	Green	+
Gelatin test	Sediment	Sediment	Sediment	+
Ammonia	Turbid Green	Green	Turbid Green	+
HCl	Brown-orange	Brown-soft orange	Brown-dark orange	+

Note: + (positif containing tannin) ; - (does note containing tannin)

Based on the results of Table 1, it can be seen that the identification of tannins carried out with $FeCl_3$ and gelatin solution in banana bunch extracts changes color from brown to dark green turbid green and formed sediment. This after adding $FeCl_3$ to each bunch is formed a rather dark green color, which means that the phenol group in tannins will bind to $FeCl_3$ to form a blue complex. This is consistent with the theory that the formation of blackish green or blue ink in the extract after adding to $FeCl_3$ is due to tannins forming complex compounds with Fe_3^+ ions [13].

Gelatin test in this study produced sediment for all of the banana bunches extract. This is in accordance with the opinion of Harborne [10], that the nature of tannins can precipitate proteins, all tannins cause little or a lot of sediment if gelatin is added, because gelatin is a natural protein.

Table 1 shows that identification of tannin extraction in banana bunches includes condensed tannins or catechols with the addition of concentrated hydrochloric acid and heating. This is based on the theory that catechol tanners are usually reddish brown in color and will enlarge their molecules when heated in acidic solutions. Proanthocyanidin is classified as procyanidin and prodelphinidin and the most abundant in plants is procyanidin [14,15]. Catechol / condensed tannins are known as proanthocyanidins which are products of flavan-3-ols polymerization and flavan-3,4-diol or a mixture of two polymers, which are called flavans [16].

3.2. Quantitative identification

Quantitative tannin tests in banana bunch extracts were performed by spectrophotometer using the Folin-Ciocalteu reagent. The formation reaction that occurs is the reduction of oxidation in which tannin as a reducing agent and Folin-Ciocalteu as an oxidizer. The results of oxidation will form a blue color that can be read at maximum waves. The method is first made a standard curve from a standard solution in the form of tannic acid. Tanic acid is used as a standard solution because tanic acid is a natural polyphenol compound containing phenolic hydroxyl groups and carboxyl groups and tannic acid is found in many plants [13].

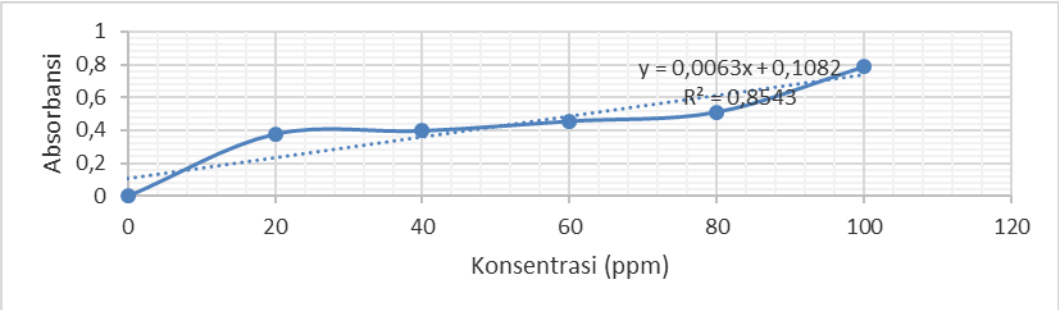

Figure 1. Absorbance graph of banana bunch extraction

In Table 2, it can be seen that the levels of the Kepok bunch (Musa paradisiaca L.) tannins are 2.03%, which shows the highest and best value among the Ambon banana bunches and Raja banana bunches. This is because the banana bunches used are different species. In the Kepok banana bunches, it is suspected that it has a high diversity among tannin structures compared to the Raja Banana bunches and the Ambon Banana bunches. This is in accordance with a study conducted by [17] that different types of raw material kepolaritasan will affect the structure of tannins in pine bark and Acacia Mollissima bark. Research conducted by [18] that tannin levels of various acacia plant species produce different tannin content. Different literature showed that the tannin content of a material is good if the value is ≥ 0.6% [19].

Table 2. The results of the spectrophotometer test were the concentration

Banana varieties	Absorbance (700nm)	Concentration (ppm)	Tannin (mg/L)	Total tannin (g/L)	Extracted tannin (%)
Kepok	0.62	81.43	407158.19	0.407158	2.035
Ambon	0.19	13.20	66006.23	0.066	0.33
Raja	0.27	26.75	133758.44	0.133	0.67

Chromatography results of GC-MS analysis of the Kepok banana bunch extract can be seen in Figure 2. Identification of the compounds was done by comparing the fragmentation patterns of compounds in the Kepok banana extract extract with the fragmentation patterns in the Willey library data bank. GC-MS analysis results that there are 8 other compounds in the sample detected besides tannin. The dominant compound is hexadecanoic acid, 1- (hydroxymethyl) -1,2-ethanediyl ester (CAS) 1,2-dipalmitin $$ Glycerol-1,2-Dihexadecanoate $$ Dipalmitin $$ P. Research conducted Widiyatni (2010), that in the Musa Paradisiaca bunches there are two compounds namely 2-Hydroxy-4- (4-methoxyphenil) -1H-phenalen1-on in the form of a reddish crystal with the molecular formula C10H14O3. and in the form of a white needle crystal with the molecular formula $C_{29}H_{48}O$. Previous study [20] showed that the main tannin element is the hydroxyl group and there are other groups such as carboxyl.

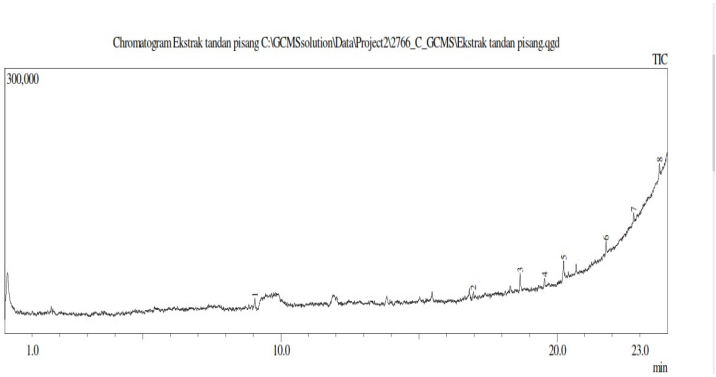

Figure 2. Chromatography GC-MS ethanol extract of Kepok banana bunches

4. Conclusion

It is concluded that Kepok banana bunches has the best potential as vegetable tanning agent. Further laboratory studies are needed to determine the quality of tanned leather resulting from banana bunches tanning.

5. References

[1] Koloka O dan Moreki J C 2011 Tanning hides and skins using vegetable tanning agents in

Hukuntsi sub-district , Botswana *J. Agric. Technol.* **7** 915–22
[2] Faxing L, Yang L dan Youjie H 2005 Preparation and the Properties of Vegetable Extract Used in Low Temperature Tanning *Leather Sci. Eng.* **15** 22–5
[3] Bi S 2006 Tannin-Aldehyde Compound (I):Combination Tanning by Vegetable Tanninmodified Glutaraldehyde *China Leather* **37** 1–12
[4] Kanagaraj J, Sastry T P dan Rose C 2005 Effective preservation of raw goat skins for the reduction of total dissolved solids *J. Clean. Prod.* **13** 959–64
[5] Tambi L, Frediani P, Frediani M, Rosi L, Camaiti M, Madonna I V dan Fiorentino S 2008 Hide Tanning with Modified Natural Tannins *J. Appl. Polym. Sci.* **108** 1797–809
[6] Sutyasmi S 2017 Efektivitas penggunaan gambir sebagai bahan penyamak nabati sistem C-RFP untuk pembuatan kulit jaket dari kulit domba *Maj. Kulit, Karet, dan Plast.* **33** 11–8
[7] Rochana A, Dhalika T, Budiman A dan Kamil K A 2017 Research Article Nutritional Value of a Banana Stem (Musa paradisiaca Val) of Anaerobic Fermentation Product Supplemented With Nitrogen , Sulphur and Phosphorus Sources *Pakistan J. Nutr.* **16** 738–42
[8] Ally K dan Kunjikutty N 2000 Studies on tannin contents of locally available tree leaves commonly fed to goats in kerala *J. Vet. Anim. Sci.* **31** 1–4
[9] Lertchunhakiat K, Keela M dan Yodmingkhwan P 2016 Comparisons of Physical Characteristics of Crossbred Boer Goat Fur Skin tanned by Coffee Pomace and Gros Michel Banana Bunch *Agric. Agric. Sci. Procedia* **11** 143–7
[10] Harborne J B 1987 *Metode Fitokimia Penuntun Cara Modern Menganalisis Tumbuhan* (Bandung: Institut Teknologi Bandung)
[11] Fajrina A, Jubahar J dan Sabirin S 2017 Penetapan Kadar Tanin pada Teh Celup yang Beredar di Pasaran secara Spektrofotometri Ultraviolet Sinar Tampak *J. Sains dan Teknol. Farm.* **19** 17–21
[12] Rahman F A, Haniastuti T, Utami T W, Mulut D B, Gigi F K dan Mada U G 2017 Skrining □ tokimia dan aktivitas antibakteri ekstrak etanol daun sirsak (Annona muricata L .) pada Streptococcus mutans ATCC 35668 *Maj. Kedokt. Gigi Indones.* **3** 1–7
[13] Mangunwardoyo W, Cahyaningsih E dan Usia T 2009 Ekstraksi dan Identifikasi Senyawa Antimikroba Herba Meniran (Phyllanthus niruri L.) *J. Ilmu Kefarmasian Indones.* **757–63**
[14] Ping L, Pizzi A, Ding Z dan Brosse N 2011 Condensed tannins extraction from grape pomace : Characterization and utilization as wood adhesives for wood particleboard *Ind. Crop. Prod.* **34** 907–14
[15] Hoong Y, Pizzi A, Tahir P dan Pasch H 2010 Characterization of Acacia mangium polyflavonoid tannins by MALDI-TOF mass spectrometry and CP-MAS 13 C NMR *Eur. Polym. J.* **46** 1268–77
[16] Zhang L, Wang Y, Wu D, Xu M dan Chen J 2012 Study on the Structure of Mangrove Polyflavonoid Tannins with MALDI-TOF Mass Spectrometry and NMR *Adv. Mater. Res. Vols* **556** 1988–93
[17] Naima R, Oumam M, Hannache H, Sesbou A, Charrier B, Pizzi A dan El F C 2015 Comparison of the impact of different extraction methods on polyphenols yields and tannins extracted from Moroccan Acacia mollissima barks *Ind. Crop. Prod.* **70** 245–52
[18] Haroun M, Khirstova P dan Covington T 2013 Analysis of Commercial Vegetable Tannin materials and Related Polyphenols of Selected Acacia Species in Sudan *J. For. Prod. Ind.* **2** 21–8
[19] Kasmudjiastuti E 2014 Karakterisasi kulit kayu tingi (ceriops tagal) sebagai bahan penyamak nabati *Maj. Kulit, Karet, dan Plast.* **30** 71–8
[20] Danarto Y C, Prihananto S A dan Pamungkas Z A 2011 Pemanfaatan Tanin dari Kulit Kayu Bakau sebagai Pengganti Gugus Fenol pada Resin Fenol Formaldehid *Prosiding Seminar Nasional Teknik Kimia "kejuangan"* (Yogyakarta) hal 1–5