

Characteristic of Cellulose Isolated From Papyrus Fibers (*Borrassus flabellifer L*) And Its Citrate Ester

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ABSTRACT

The chemical modification using esterification method to modify the papyrus fiber cellulose using citric acid was studied. Parameters investigated include the citrate acid concentration (between 0.3 to 0.6 M), and reaction temperature (from 110 to 140°C). The ester cellulose, which was a new product reaction between citric acid and cellulose, had Substitution Degree (SD) from 0.088 to 1.147 and yield from 73.75% to 97.73%. The esterification product was analyzed with FT-IR (Fourier Transform Infrared spectroscopy) and SEM (Scanning Electron Microscopy) to identify the functional groups and the morphology of ester cellulose, respectively. The result shows that modified cellulose have characteristic peak namely ester carbonyl (C=O) at 1740.43 cm⁻¹ and hydroxyl alcohol (O-H) at 3406.82cm⁻¹. Based on SEM image, cellulose has the same shape but ester cellulose citrate has the variety of forms including round and oval with a concave surface. Ester cellulose citrate from papyrus fibers successfully produces by using 0.6 M citric acid at 120° C with 1.147 DS value of the 97.73 brown powder ester cellulose citrate yeild.

Key word: chemical modified; citric acid; agricultural waste; ester cellulose.

INTRODUCTION

Papyrus Tree (*Borrassus flabellifer L*) is a typical flora of Indonesia, especially in East Nusa Tenggara. Papyrus tree is a very useful plant which has higher economic values based on the utilization of its root, bark, leaves, juice, and fruit. Papyrus fruit has a shell that can be used as fuel and activated charcoal. While the papyrus fibers can be used as the substitute both for rope and fuel [1]. The papyrus fiber is a waste processing of papyrus fruit utilization that has low economic value. Even though, papyrus fibers contain 68.94% cellulose, 5.37% lignin, 14.03% hemicellulose and 0.6% wax [2].

Cellulose is a polysaccharide that composed of a polymer of glucose units that connected to each other with β -1,4-glycosidic bond forming a straight and long chain [3]. Three hydroxyl groups in each glucose unit on cellulose can interact with other compounds. This is why cellulose has the potential to be modified [4]. Cellulose modification can be performed to improve cellulose utilization as a starting material for its derivatives. Esterification reaction produces cellulose derivative of cellulose ester. Ester cellulose is widely used in food, Pharmaceutical and cosmetic industry as regulators, emulsifiers, stabilizer and antioxidants [5].

Synthesis of ester cellulose using citric acid has been done in recent years. Low et al, [6] synthesize ester cellulose citrate using cellulose from wood pulp which is reacted with 1.2M citric acid by heating at 140° C. Firmansyah et al, [7] using citric acid on esterification

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process to produces ester cellulose citrate from pineapple leaves at 80° C. The amount of citric acid that can be substituted on cellulose was implied by Degree of substitution (DS) value. Cellulose has the maximum degree substitution of 3 [8]. Furthermore, esterification of cellulose nanocrystal was successfully studied by Ramirez et al, [9] using citric acid and yield DS 0.18 and 0.34. In addition, esterification of pineapple leaf cellulose using 0.3 M citric acid has been successfully performed by 1.925 DS value [8]. The DS value depends on the concentration of substituent and the temperature on esterification process to produce the cellulose citrate ester.

In this research, the citric acid concentrations are varied from 0.3 to 0.6 M as well as the temperature from 110 to 140° C, were investigated. The degree of substituent value was measured. The products from esterification process were characterized by using FTIR and SEM.

EXPERIMENT

Chemicals and instrumentation

Papyrus fibers powder was prepared from papyrus fibers collected from Oesapa district, Kupang city, East Nusa Tenggara, Indonesia. All Chemicals used for this research such as citric acid (Merck), sodium hydroxide (Merck), lead (II) nitrate (Merck) and chloride acid (Merck).

Samples were characterization by FTIR spectrophotometer (Shimadzu FTIR 8400S, the sample was analyzed using KBr plate) in the 4000-400 cm⁻¹ range and SEM (Scanning electron microscopy). This research uses a set of lab-wares, 100 mesh and 120 mesh sieved, oven and analytical balance (Ohaus Pioneer PA214).

Preparation and isolation cellulose of papyrus fibers powder

Papyrus fiber was separated from other part of papyrus fruit, and it was cleaned into the water. Papyrus fibers were cut (\pm 1mm) and washed in distilled waters, then dry 24 h at 50° C. Samples were blend and sieved to retain 100 mesh to 120 mesh fraction. The powder sample was called sample B.

3.000 grams powder sample B was added to 60 mL sodium hydroxide 0.1M in a flask. The sample was mixed at 200 rpm for 2 hours. Samples were washed with distilled water to remove unreacted sodium hydroxide. The presence of sodium hydroxide in washing waters was tested until the pH of the filtrate was neutral. Dry the sample 24 h at 50° C. The samples were called sample B_{0.1}.

Esterification reaction of papyrus fibers with various concentration of citric acid

The esterification procedure was conducted based on the research of Marshall et al. [10] and Low et al. [6] Each 0.3 grams sample B_{0.1} were added to 2,1 mL citric acid (in a ratio of 1 gram sample to 7 mL citric acid) with various concentration of citric acid (0.3, 0.6 and 0.9 M). Samples were mixed at 200 rpm for 2 hours. Then samples were dried 24 h at 50° C. The temperature of the dried was increased to 120° C and dried again for 90 minutes. Cooled the samples and added 6 mL distilled water and stirred at 200 rpm for 1 hour to remove of unreacted citric acid. After that, the sample was washed with distilled water until the pH of the filtrate was neutral. The presence of citric acid in washing waters was tested by adding 10 mL lead (II) nitrate solution into 10 mL filtrate. The filtrate of the sample which still containing excess citrate unreacted with B_{0.1} will form white precipitation of Pb (citrate). After that, samples were dried 24 h at 50° C. The product of esterification process with

various concentrations of citric acid such as 0.3, 0.5, 0.6, 0.7 and 0.9 M were called sample C₁, C₂, C₃, C₄, and C₅.

Esterification reaction of papyrus fibers with various temperatures

Each 0.3 grams B_{0.1} were added to 2.1 mL citric acid 0.6 M which has highest DS (in a ratio of 1 gram adsorbent to 7 mL citric acid). Samples were mixed at 200 rpm for 2 hours. Samples were dried 24 h at 50° C. The temperature of the dried was increased to various temperatures such as 110, 130, 120, and 140° C and dried again for 90 minutes. Cooled the samples and added 6 mL distilled water and stirred at 200 rpm for 1 hour to remove unreacted citric acid. After that, the sample was washed with distilled water until the pH of the filtrate was neutral. The presented of citric acid in washing water were tested by adding lead (II) nitrate solution. The samples wasted with distilled waters until no turbidity of lead (II) citric was observed. After that, samples were dried 24 h at 50° C. The product of esterification process at various temperatures such as 110, 120, 130 and 140° C were each called sample T₁, T₂, T₃, and T₄.

Characterization of esterification product

The esterification products were analyzed with FTIR spectrophotometer to identify the functional groups of citric cellulose in 4000 until 400 cm⁻¹ with the adsorbent prepared as KBr pellet. The morphology was analyzed by Scanning Electron Microscopy.

The yield degree of the product was calculated by ratio mass of the product reaction between the mass of samples. The Substitution degree (SD) was analysis using saponification on the heterogeneous system (ASTM D871-96-2014) and Genung et al. [11]. Each 0.1 gram sample was added in 8 mL NaOH 0.5 M and keep on room temperatures for 48 h. Added 3 drops indicator of phenolphthalein and titrated with HCl 0.5 M. The same procedure was used to titrated blank that contains 8 mL NaOH 0.5 M. DS was calculated with equation 1 and 2.

$$A \text{ (}^{meq}/g\text{)} = \frac{(B-C) \times D}{E} \quad (1)$$

$$DS = \frac{0.162 \times A}{1 - (0.19213 \times A)} \quad (2)$$

Where DS is the degree of substitution, A is milliequivalents of consumed acid per gram specimen, B is volume of consumed HCl in blank, C is volume of consumed HCl in sample, D is HCl concentration, E is gram sample, 0.162 is molecular weight of anhydrous glucose unit and 0.19213 is molecular weight of citric acid.

RESULT AND DISCUSSION

Esterification reaction of papyrus fibers with various concentration of citric acid

The addition of citric acid caused the activation of cellulose hydroxyl group which leads to the nucleophilic attack on the citric anhydride moieties. The identical situation has also been reported by Xu et al. [12], except they used starch instead of cellulose. Hypothetically the reaction of cellulose with citric acid to form ester cellulose citrate can be seen in Figure 1.

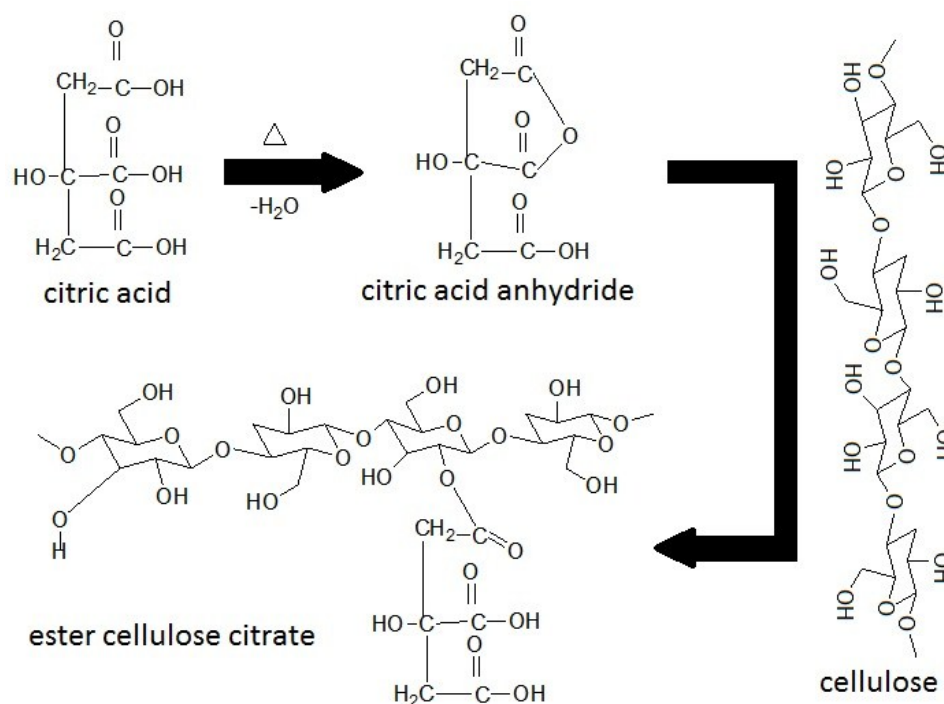


Figure 1. The prediction of esterification reaction of ester citric cellulose [13].

Based on Figure 2, the DS value of cellulose ester citric was increased from various concentrations of citric acid 0.3 to 0.6 M and turn to decrease for 0.9 M concentration of citric acid. The increasing of DS value 0.088 to 1.140 from using 0.3 to 0.6 M citric acid is due to increase of amount citric acid molecule which has the ability to interact with the active site (O-H) of cellulose for bond formation. But on the using citric acid above 0.6M, there was the slight decrease of DS value 0.945 and 0.526, respectively. It is because of the equilibrium reaction.

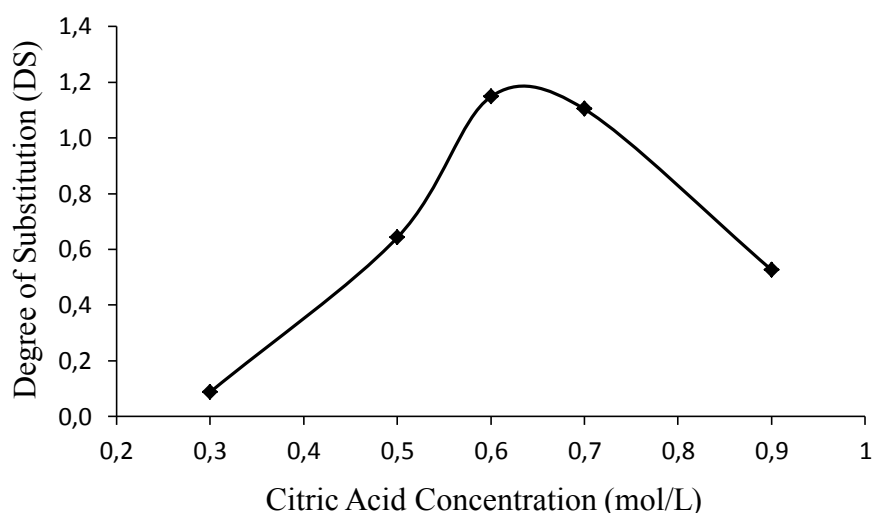


Figure 2. The degree of substitution from cellulose ester citric with various concentration of citric acid.

Esterification reaction of papyrus fibers with various temperature

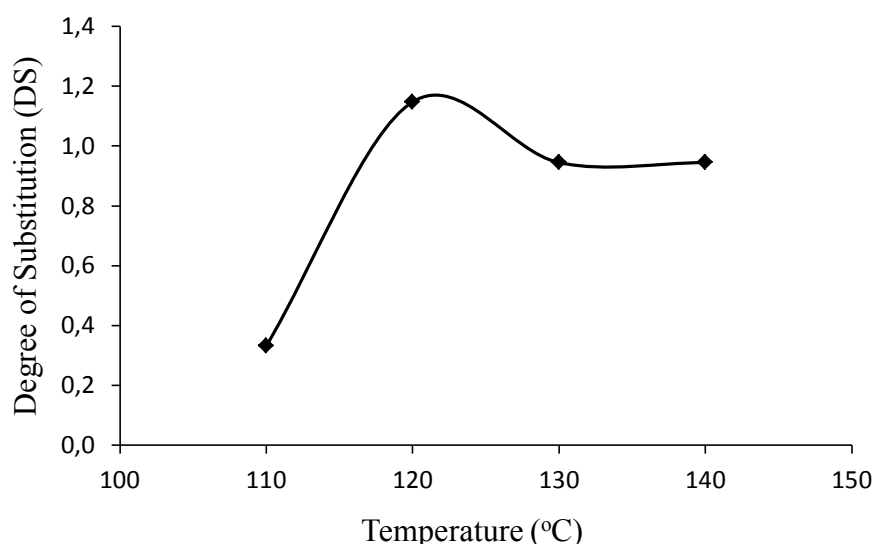


Figure 3. The Degree of Substitution from cellulose ester citric with various temperature of esterification process

The DS value of cellulose ester citric from esterification process with 0.6 M citric acid at various temperatures shows in figure 3. The effect of the temperatures is the important aspect of esterification process because the esterification reaction should be carried out in a free water state [14]. Based on the figure, the DS value was increased from 110° C to 120° C and slightly decrease and become stable at the temperature above 120° C. The DS value was sharply increased from 0.341 to 1.147. The increased of DS value might be caused by reducing water molecules to form the citric anhydride during esterification process. The increasing of temperature can cause citrate acid become dehydrated to produce anhydride, which can react with cellulose to form cellulose citrate ester [15]. Further heating generates additional dehydration with cross-linking thus increase DS value.

In the temperature above 120° C, the value slightly decreases of DS value 0.945. Decreasing of DS value was an effect of overheating condition. Overheating causes degradation of cellulose citrate ester resulting in decreased of DS value. From this research, it can be concluded that esterification process using cellulose from papyrus fiber modified with 0.6 M citrate acid was happened at 120° C to form the ester cellulose citrate with DS value 1.147.

Characterization of Cellulose and Ester Cellulose Citrate from Papyrus Fiber

Modification of papyrus fibers that contain cellulose used esterification method produces the cellulose ester. Cellulose ester was a product reaction from carboxyl acid and alcohol. In this research, the ester cellulose citrate was successfully produced using 0.6M citrate acid at 120° C. The 97.73% yield as brown powder of ester cellulose citrate can be seen in Figure 4C.



Figure 4. The powder of papyrus fiber (A), cellulose (B) and cellulose ester citrate by using 0.6M citric acid at 120 °C (C).

The FT-IR was used to identify the characteristic functional group of the product. In this research, the cellulose ester can make from this procedure that showed the changes of absorption area and absorption intensity between cellulose and cellulose esterification yields.

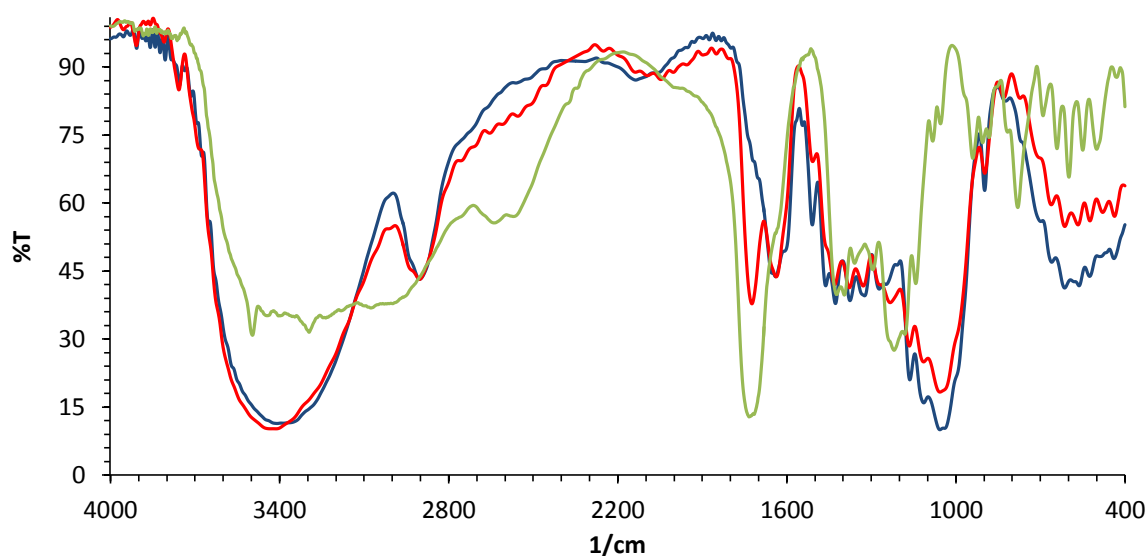


Figure 5. FTIR spectrum of citric acid (green line), cellulose (blue line) and ester cellulose citrate (red line). The ester cellulose citrate produces by using 0.6M citric acid at 120°C.

Based on FT-IR spectrum in Figure 5 Table 1, before reaction, cellulose (Figure 5 blue line) has board absorption band 3387.53 cm^{-1} shows the presence of O-H functional group. The absorption band at 1271.76 and 1163.76 cm^{-1} shows the C-O-H banding vibration. The absorption band at 1040.32 cm^{-1} shows the C-O stretching band.

After modification with citric acid 0.6 M at 120°C , the ester cellulose citrate product successfully formed that can be shown in Figure 5 red line. The board absorption band at 3406.82 cm^{-1} shows the presence of O-H functional group. The peak at 1740.43 cm^{-1} probably corresponds to bending of the ester carbonyl functional group (C=O). Based on this peak, the reaction between citric acid and cellulose was complete and all carboxyl groups were converted into ester bond. The absorption band at 1057.68 cm^{-1} shows the C-O stretching band [16].

In addition, it is observed there is the reduction of O-H group peak at 3387.53 cm^{-1} regions of esterification yields spectra relative to that of its original cellulose. It showed that the esterification of cellulose by citric acid was successful.

Table 1. The functional group of cellulose and ester cellulose citrate

Compound	Functional Group	Waves Number (cm^{-1})
Cellulose	O-H	3387.53
	C-O-C	1040.32
	β -1,4-glycosidic bond	
Citric acid	O-H	3358.60 – 3011.44
	C=O carboxylate	1721.15
Ester Cellulose	O-H	3406.82
Citrate	C=O ester	1740.43

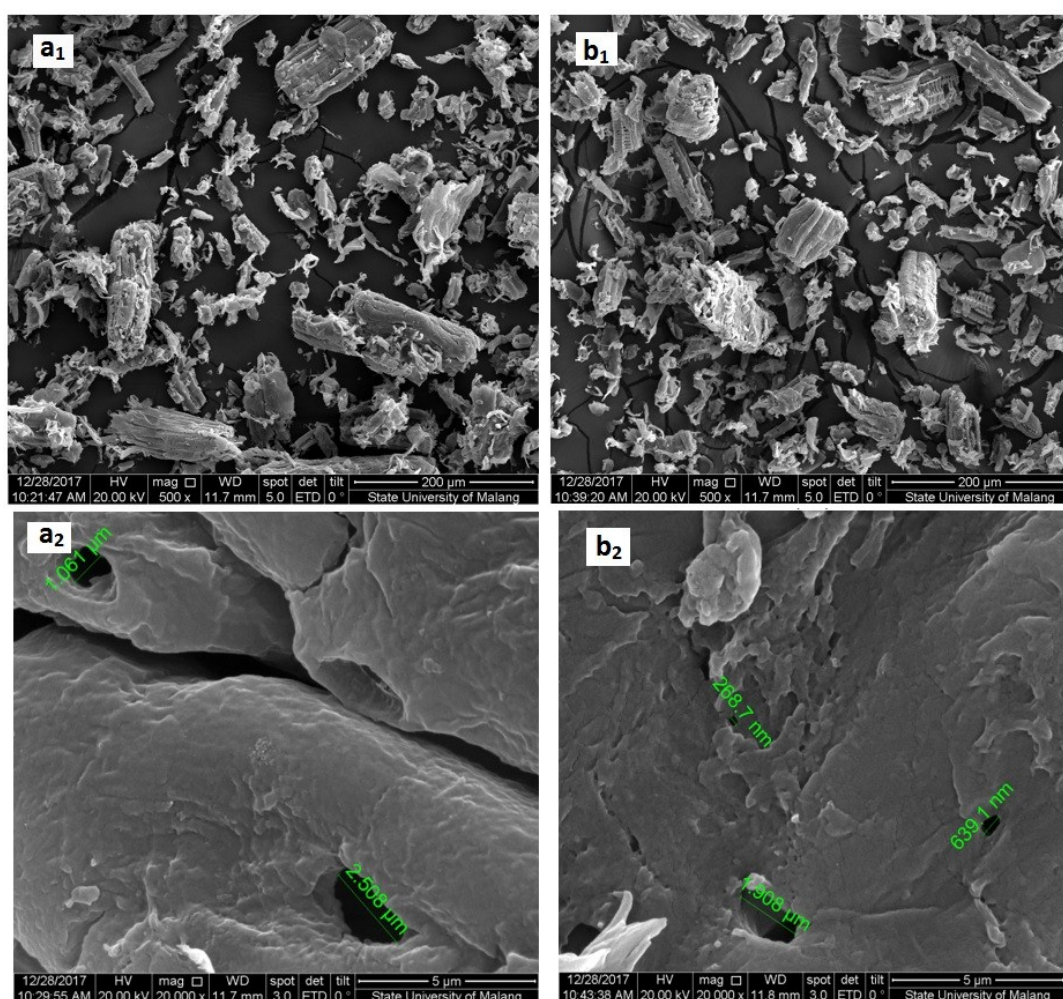


Figure 6. SEM image of (a₁) cellulose and (b₁) ester cellulose citrate (using 0.6 M citric acid at 120°C) in 500x resolution and (a₂) cellulose and (b₂) ester cellulose citrate (using 0.6 M citric acid at 120°C) in 2500x resolution.

SEM (Scanning Electron Microscope) was used to show the surface morphology of ester cellulose citrate. The SEM image is shown in Figure 6. From Figure a₁ and b₁, it is seen that

the surface morphology both cellulose and ester cellulose is significantly different. Magnification 500 times shows that cellulose has same shape and homogeneous surface whereas ester cellulose has a rough surface and variety of the forms including round and oval with a concave surface. The cellulose particles formed diffuse and not agglomerate on an area on the surface of the sample. However, Figure a₂ and b₂ appear that cellulose has a larger particle diameter of 1.061 and 2.508 μm than ester cellulose citrate of 1.908 μm , 268.7 nm, and 639.1 nm. Modification with 0.6M citric acid causes the addition of carboxyl group of citric acid to the cellulose surface thus reducing the pore size of cellulose.

CONCLUSION

Based on this research, it can be concluded that the DS value depends on both the amount of citric acid concentration and temperatures. In this Research, ester cellulose citrate from papyrus fibers (*Borassus flabellifer* L) was successfully produced using 0.6M citric acid at 120° C based on the FT-IR data that have a C=O functional group peak at 1740.43 cm^{-1} . The ester cellulose citrate has brown yield with 1.147 DS value.

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