

Synthesis Succinic Galactomannan from Galactomannan *Arenga pinnata* Merr. and Succinic Anhydride using Microwave Method

Juliati Br. Tarigan*, Mutiara H. Siregar

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jl. Bioteknologi No. 1 Kampus USU, Medan, Indonesia

Keywords: *Arenga pinnata* Merr., endosperm, Galactomannan, Succinic Galactomannan, Microwave.

Abstract: The synthesis succinic galactomannan has been conducted through esterification reaction of galactomannan *Arenga pinnata* and succinic anhydride using sodium bicarbonate as catalyst under the radiation of microwave. The experiment divided by two steps which first step was the extraction of galactomannan from *Arenga pinnata* rendering yield of 4.20% and have confirmed by spectroscopy Fourier Transform Infrared (FT-IR). The second step was esterification with succinic anhydride using NaHCO₃ as catalyst under the radiation of microwave for 3, 5, 7, 9 and 11 min. Spectroscopy FT-IR showed the stretching vibration of the carbonyl group (C=O) of the ester at a wavelength of 1735 cm⁻¹ which established the formation of succinic galactomannan. The substitution degree of succinic galactomannan determined by titration method obtained the maximum value at 1.527 for 9 min radiation time. The scanning electron microscopy (SEM) images showed that succinic galactomannan has rough surface morphology than galactomannan *Arenga pinnata*.

1 INTRODUCTION

Galactomannan is a polysaccharide which found abundant and are specifically produced from beans. One source of galactomannan in Indonesia is “kolang – kaling” or *Arenga pinnata* endosperm (APE). APE is a semi-mature, soft, chewy and slightly clear white sugar palm endosperm which is obtained after going through the processing process (Kooiman, 1971). Galactomannan consists of two types of sugar monomer units, namely mannose and galactose. Mannose is the main component and galactose is a minor component. The number of galactose units in the polysaccharide is always smaller than that of mannose (Mathur, 2011). Comparison of galactose and mannose will affect the properties of the galactomannan. The advantages of galactomannan are the chain of galactose branches which is polar and mannose (straight chains) is nonpolar. The molecular weights of galactomannan from APE are diverse and vary from 6000 to 17000 (Kooiman, 1971). Galactomannan has a structure (1-4) -β-D-mannopyranose as a straight chain and unit (1-6) -α-D-galactopyranose as its branch (Dey, 1978). Galactomannan has been extracted from sugar palm seeds using ethanol and water followed

by centrifugation to separate the precipitate. Galactomannan content was obtained at 4.58% and is feasible to eat (Tarigan, 2014). To improve galactomannan properties can be done by modifying the compound using chemical reagents. One way is to convert galactomannan to its ester form.

Esterification reactions of polysaccharides are very common and have been used to modify and increase the functional properties of derivate polysaccharide. Succinic esters of Arabic gum have been used as stabilizers of emulsions and used in microencapsulation processes (Sarkar and Singhal, 2011). Dong and Tian (1999) have been successfully synthesized palmitic ester of guar galactomannan and used as emulsion stabilizers. Prashanth et al. (2006) have synthesized galactomannan esters using succinic anhydride, acetic anhydride and n-octenyl succinate anhydride using catalyst sodium bicarbonate at a temperature of 28°C, 40°C, 60°C for 2 hours. Sarkar and Singhal (2011) demonstrated the synthesis of guar gum esters with n-octenyl succinate anhydrous using sodium bicarbonate as a catalyst at a temperature of 60°C, 75°C, 90°C for 3 hours. Previous researchers have modified galactomannan compounds through acetylation using acetic anhydride using sulfuric acid catalysts under reflux conditions at 50°C for 6 hours. In

general, the reaction of polysaccharide ester production is carried out prolonged reaction time. Therefore it is necessary to find out a novel method to produce polysaccharide ester in short reaction time. Microwave has been known could enhance organic reaction and shorten reaction time producing a high yield of product (Mohd Fuad et al., 2019).

Based on that, the aim of this study was to synthesis succinic galactomannan from the reaction of galactomannan with succinic anhydride using sodium bicarbonate as a catalyst under microwave irradiation. The succinic galactomannan esters obtained were analyzed for functional group changes by FT-IR spectrophotometer, SEM and the degree of substitution by titration.

2 MATERIALS AND METHODS

2.1 Materials

“Kolang-kaling” was bought from a local traditional market in Medan – Indonesia. All chemicals used in this study were purchased from local chemical dealers and have been used without any purification.

2.2 Methods

2.2.1 Extraction Galactomannan from APE

The APE which has been cleaned and chopped as much as 100 grams is mashed with a blender by adding 1000 mL of distilled water and stored in the refrigerator for 24 hours. Then, it was centrifuged at an average speed of 8500 rpm for 50 minutes. Ethanol is added to the supernatant with a volume ratio of 1: 2 and stored in a refrigerator for 24 hours. The precipitate formed is then soaked using ethanol and dried in a desiccator.

2.2.2 Synthesis Succinic Galactomannan

One gram of galactomannan was added with 0.5 gram of sodium bicarbonate and 2 mL of ethanol. Next, 2 g of succinic anhydride was added followed by stirring for 20 minutes. Then the mixture is heated in the microwave for 3 minutes. After that, the mixture was added with 10 mL ethanol 50% and then followed by neutralization using NaOH 2N. The precipitate was washed with 75% ethanol and then washed with ethanol. The precipitate was dried in a desiccator (Prashanth et al., 2006).

2.2.3 Determination of Substitution Degree

One gram of succinic galactomannan was put in Erlenmeyer and then added with 10 mL of water containing 5 mL NaOH 0.5M followed by stirring for 30 minutes at room temperature. The solution then titrated with HCl 1N using phenolphthalein indicators (Sarkar and Singhal, 2011). The value of the degree of substitution can be calculated based on the equation below.

$$W = \frac{(V_{blank} - V_{sample}) \times M \times N \times 100}{Weight\ of\ sample \times 1000} \quad (1)$$

$$DS = \frac{162 \times W}{100 \times M - \{(M-1) \times W\}} \quad (2)$$

Where W is substitution of succinic acid, V_{blank} is the HCl volume for the blank solution and V_{sample} is the HCl volume required for neutralizing the sample. N is normality of HCl, M is molecular weight of succinic acid.

3 RESULTS AND DISCUSSIONS

3.1 Extraction of Galactomannan from APE

About 300 grams of APE was extracted using distilled water and then centrifuged at a speed of 8500 rpm for 50 minutes and then the supernatant was added ethanol 96% to formed precipitate which was washed using ethanol. The galactomannan extracted was 12.6205 grams (4.20%) which were then characterized by FT-IR.

3.2 FT-IR analysis

The galactomannan obtained was analyzed using FT-IR to determine the presence of functional groups. The FT-IR results obtained are shown in Figure 1.

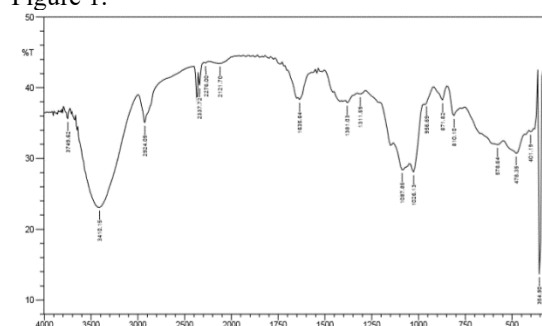


Figure 1: F-IR spectra of galactomannan

The FT-IR spectrum of galactomannan showed vibration peaks in the wavenumber area of 3410 cm^{-1} represent a stretching vibration of the -OH group from polysaccharides. This is supported by absorption bands at wave number 1635 cm^{-1} which showed vibrations -OH bending from water absorption (Gong et al., 2012). The absorption band at wave number 2924 cm^{-1} shows the stretching of -CH vibration, which is supported by the presence of absorption bands at wave number 1381 cm^{-1} represent the bending -CH vibrations (Singh et al., 2009). The 871 cm^{-1} band shows the characteristics of β -D-mannopyranose bond in the polysaccharide and in the 810 cm^{-1} band shows the characteristics of α -D-galactopyranose bonds (Buriti et al., 2014).

3.3 Synthesis and Characterization Succinic Galactomannan

The result obtained from the esterification galactomannan with succinic acid anhydride is white solids. The yields of succinic galactomannan are shown in Table 1.

Table 1: The yield of succinic galactomannan

Reaction Time (min)	Weight of Galactomannan (g)	Weight of Succinic Galactomannan (g)
3	1.0608	1.2884
5	1.0065	1.1765
7	1.0870	1.0289
9	1.0089	1.0023
11	1.0054	0.9473

The galactomannan reacted with succinic anhydride produces succinic galactomannan which has different weights. The decrease in weight of succinic galactomannan produced was due to the increasing reaction temperature during heating which caused degradation of the polysaccharide chain in the galactomannan. The degradation of the polysaccharide chain causes a decrease in molecular weight produced rendering increasing solubility which during washing it dissolves. Prashanth et al. (2006) stated that the molecular weight of gum acetate ($\sim 1500\text{ kDa}$ with HPSEC) decreases when the reaction takes place at a temperature of 60°C compared to gum and other esters which are reacted at low temperatures ($\sim 2000\text{ kDa}$). Succinic galactomannan from various reaction time obtained was analyzed using FT-IR to determine the changes in functional groups. The FT-IR results obtained are shown in the following Figure 2.

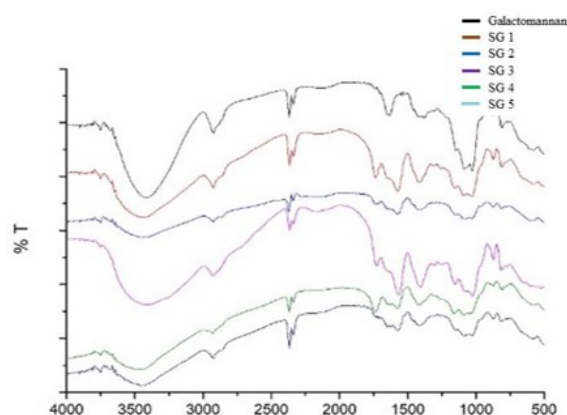


Figure 2: FT-IR spectra of galactomannan and succinic galactomannan in various time reaction

FT-IR was used to confirm the formation of succinic galactomannan. The FT-IR spectrum showed the absorption band appears at wavenumbers of $1730 - 1750\text{ cm}^{-1}$ which is represent the stretching vibration of C=O which and it is supported by absorption bands at wave number of 1379 cm^{-1} which shows the CH bending vibration and the vibration stretching of CO in the group of -O-(C=O)-CH₃ at wavelength of $1245 - 1250\text{ cm}^{-1}$. The changes of wavelength from 1024 to 1031 cm^{-1} shows the vibration stretching of C-O-C on galactomannan to galactomannan ester (Prashanth et al., 2006).

3.4 The Substitution Degree

The substitution degrees of succinic galactomannan determined by titration method are presented in Table 2.

Table 2: The substitution degree of succinic galactomannan in various reaction time

Reaction time (min)	Substitution degree value
3	0.404
5	0.460
7	0.503
9	1.527
11	1.090

As can be seen from Table 2, the substitution degree was increased in the increasing of reaction time in the microwave with the highest of substitution degree values occurred at 9 minutes is 1.527. However, the substitution degree value was decreased at 11 minutes showed of 1.09. This is probably due to the temperature that was too high in the microwave at reaction time of 11 minutes which caused the degradation of the galactomannan

indicated by the product was blackish brown. Based on that observations, the longer the reaction time in the microwave, the temperature increases and thus if the temperature increases, the value of the substitution degree is higher. Prashanth et al. (2006) also showed that increasing in temperature could increase in the substitution degree value.

3.5 SEM Analysis

The SEM images of succinic galactomannan produced from 9 minutes reaction time is presented in Figure 3. As can be seen in Figure 3, galactomannan and succinic galactomannan showed changes in surface morphology. The galactomannan showed a smooth surface shape that is irregular and fused to one another, whereas succinic galactomannan showed that the surface is a bit rough and bumpy indicates an esterification reaction on galactomannan has been occurred.

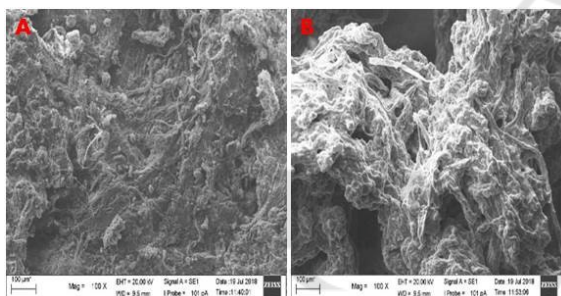


Figure 3: The SEM images of (A) galactomannan and (B) succinic galactomannan

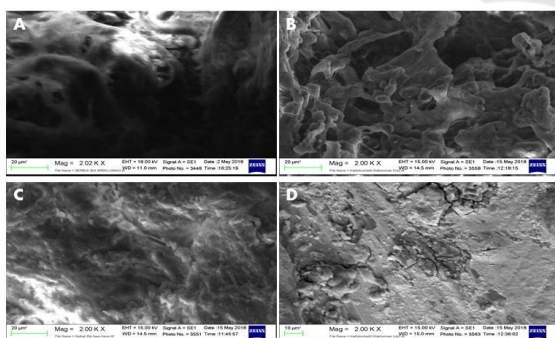


Figure 4: The SEM images polysaccharide of (A) hard APE, (B) soft APE and carboxymethyl polysaccharide from (C) hard APE, (D) soft APE

4 CONCLUSIONS

The yield of galactomannan extracted from APE using ethanol solvent was 12.6205 grams. Succinic galactomannan has been synthesized through a reaction between galactomannan and succinic acid anhydride with NaHCO_3 as a catalyst under microwave irradiation for several reaction times. The FT-IR spectra confirm the formation of galactomannan ester by appearance a spectrum at a wavelength of 1735 cm^{-1} indicating the vibration of $\text{C}=\text{O}$ of the ester compound. The highest degree of substitution obtained was 1.527 which occurred from reaction time of 9 minutes. The SEM images showed the changes in the morphology of galactomannan which were smooth and fused to one another and rough and bumpy on succinic galactomannan.

REFERENCES

Buriti, F. C. A., Dos Santos, K. M. O., Sombra, V. G., Maciel, J. S., Teixeira Sá, D. M. A., Salles, H. O., Oliveira, G., De Paula, R. C. M., Feitosa, J. P. A., Monteiro Moreira, A. C. O., Moreira, R. A. & Egito, A. S. 2014. Characterisation of partially hydrolysed galactomannan from *Caesalpinia pulcherrima* seeds as a potential dietary fibre. *Food Hydrocolloids*, 35, 512-521.

Dey, P. M. 1978. *Biochemistry of Plant Galactomannans. Advances in Carbohydrate Chemistry and Biochemistry*.

Dong, C. & Tian, B. 1999. Studies on preparation and emulsifying properties of guar galactomannan ester of palmitic acid. *Journal of Applied Polymer Science*, 72, 639-645.

Gong, H., Liu, M., Chen, J., Han, F., Gao, C. & Zhang, B. 2012. Synthesis and characterization of carboxymethyl guar gum and rheological properties of its solutions. *Carbohydrate Polymers*, 88, 1015-1022.

Kooiman, P. 1971. Structures of the galactomannans from seeds of *Annona muricata*, *Arenga saccharifera*, *Cocos nucifera*, *Convolvulus tricolor*, and *Sophora japonica*. *Carbohydrate Research*, 20, 329-337.

Mathur, N. 2011. *Industrial galactomannan polysaccharides*, CRC Press.

Mohd Fuad, M. a. H., Hasan, M. F. & Ani, F. N. 2019. Microwave torrefaction for viable fuel production: A review on theory, affecting factors, potential and challenges. *Fuel*, 253, 512-526.

Prashanth, M. R. S., Parvathy, K. S., Susheelamma, N. S., Harish Prashanth, K. V., Tharanathan, R. N., Cha, A. & Anilkumar, G. 2006. Galactomannan esters—A

- simple, cost-effective method of preparation and characterization. *Food Hydrocolloids*, 20, 1198-1205.
- Sarkar, S. & Singhal, R. S. 2011. Esterification of guar gum hydrolysate and gum Arabic with n-octenyl succinic anhydride and oleic acid and its evaluation as wall material in microencapsulation. *Carbohydrate Polymers*, 86, 1723-1731.
- Singh, V., Srivastava, A. & Tiwari, A. 2009. Structural elucidation, modification and characterization of seed gum from *Cassia javahikai* seeds: A non-traditional source of industrial gums. *International Journal of Biological Macromolecules*, 45, 293-297.
- Tarigan, J. B. 2014. Karakterisasi Edible Film Yang Bersifat Antioksidan Dan Antimikroba Dari Galaktomanan Biji Aren (*Arenga pinnata*) Yang Diinkorporasi Dengan Minyak Atsiri Daun Kemangi (*Ocimum basilicum* L.). Doktor Disertasi, Universitas Sumatera Utara.

