Characterization of Seedlac Hydrolysis from Kesambi (Schleicera oleosa Merr) as an Intermediate Compound for Fragrance Synthesis

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Abstract: Seedlac is the organic resin obtained from secretion of female insect Laccifer lacca Kerr on a selected plant, one of them is Kesambi (Schleicera oleosa Merr). Seedlac contains almost 80% polyester which can be hydrolysed to ester compounds such as aleuritic acid which is an intermediate compound for the fragrance synthesis of the perfume industry. One of the problems in the seedlac hydrolysis is the presence of natural dyes (laccaic acid) which interfered with the hydrolysis process and affect the purity of the hydrolysis products. In this research, hydrolysis was carried out by first removing the natural dyes of shellac (decolorized process). The hydrolysis results were characterized using Gas Chromatography-Mass Spectrometry to determine the type of ester and its composition. The decolorized process of seedlac before hydrolysis in this experiment could improve the percentage of aleuritic acid up to 56%. Therefore, seedlac hydrolysis by decolorized process before hydrolysis can be considered for the production of esters from seedlac, especially aleuritic acid.

1 INTRODUCTION

Lac is an organic resin secreted by the insect Laccifer lacca Kerr on a selected plant (Sutherland and Río, 2014) (Nagappayya and Gaikar, 2010). In Indonesia, Kesambi (Schleicera oleosa Merr) is a plant prioritized for use as the host plant in the cultivation of the insects (Taskirawati *et al.*, 2017). Lac forms a solid material on the branches of host plants attacked by the insects, and when collected in this form it is referred to as sticklac. The sticklac is crushed and sieved to remove impurities to get seedlac. Further processing in the refining of seedlac produced shellac.

Lac in Indonesia is developed by Perhutani (Probolinggo) and the insect's cultivation has spread evenly in Nusa Tenggara Barat and Nusa Tenggara Timur (Taskirawati *et al.*, 2017). Pehutani produced lac in the form of seedlac to fulfil domestics and foreign market and used mainly as varnish. So far there was no diversification of other lac products were done by Perhutani.

Shellac consists of 68% resin, 6% wax, and 1-2% dyes (such as laccaic acid and erythrolaccin). The resin of seedlac is a mixture of cross-linked polyester or cyclic aliphatic polyhydroxy acid with sesquiterpenic acid (Biswas, 2014) (Sutherland and Río, 2014) (Nagappayya and Gaikar, 2010). The composition varies depending on the insect species and the host plant where seedlac is obtained (Farag and Leopold, 2009). The main compositions of polyester in shellac consists of aleuritic acid, butolic acid, shellolic acid and jalaric acid (Farag, 2010).

Aleuritic acid (9,10,16-trihydroxyhexadecanoic acid) was used as the starting material because of its multi functionalities (Ravi, Padmanabhan and Mamdapur, 2001). Aleuritic acid is mainly used in the perfumery industry, as a starting material for preparation isoambritolite is the main ingredient fragrance compounds "musk" (Biswas, 2014). Derivatization of shellac to aleuritic acid can increase shellac added value up to 15 times (Prasad, 2014).

The most common method in the isolation of aleuritic acid is alkaline hydrolysis of lac resin, separation, and purification. Besides containing polyester, seedlac also contains natural dyes which the presence influences the isolation of aleuritic acid. It is possible that polyester could be transferred into the colorant matrix (Berbers *et al.*, 2019) and so the otherwise that colorant matrix could have been

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transferred when attempting the separation, it can prolong the purification process. In this experiment, seedlac was hydrolysis after decolorized. The dyes were obtained in the decolorized process ca be used as natural dyes. Product hydrolysis was compared with seedlac hydrolysis product without the decolorized process.

2 MATERIALS AND METHOD

2.1 Materials

Seedlac was used in this experiment obtained from Perhutani. The chemical materials used in this experiment were methanol (Merck), potassium hydroxide (Merck), ethyl acetate (Merck), hydrochloric acid (Merck), n-hexane, and activated charcoal.

2.2 Method

2.2.1 Seedlac Characterization

The characterization of seedlac includes moisture contents, ash contents, and acid value. A Fourier Transform Infrared (FTIR) spectra were collected for seedlac to determine the functional group.

2.2.2 Extraction of Natural Dyes (decolorized process)

Seedlac that have been crushed macerated using water with a ratio of seedlac: water is 1:10. Maceration is carried out for 3-4 hours at room temperature while stirring (Yaqub *et al.*, 2014), 2014). After maceration, filter the products, take the filtrate as natural dyes and the pulp for hydrolysis.

2.2.3 Hydrolysis of Seedlac

There are 2 types of hydrolysed seedlac, one is seedlac from the 2.3 process, namely decolorized seedlac, and the second is pure seedlac. To a reflux apparatus add 20 g of seedlac granules, 80 mL of methanol and 11 g of potassium hydroxide dissolved in 100 mL water, reflux for 15 minutes. Then the methanol is distilled off completely and the solution is then neutralized until pH 5 is reached. Then add 4 g of activated charcoal, filter while hot and let stand for 3 days. Then the solution is filtered and the filtrate is added to a beaker with boiling water. Add just enough of ethyl acetate until all of the crude product dissolves. 800 mg of activated charcoal and 2-4 g of sodium sulphate is added and the solution is brought to boil. The solution is filtered and few drops of n-hexane are added, the solution is then allowed to stand for 24 h and it is then filtered and dried.

2.2.4 Characterization of Seedlac Hydrolysis

A Fourier Transform Infrared (FTIR) spectra were collected for seedlac hydrolysis to determine the functional groups. Seedlac hydrolysis compounds were identified by gas chromatography with a mass spectrometer detector (GCMS) Agilent 6890 series with capillary column HP-5MS, 30 m x 0.25 mm id x 0.25 μm film thickness. Helium gas was used as the carrier gas at constant flow mode at 1.5 mL/min. The sampel was injected with a volume of 2 μL in splitless mode. The increasing of oven temperature was programmed from 50-320°C with step of 10°C per minute until reaching 320°C and hold 12 min.

3 RESULTS AND DISCUSSION

3.1 Characterization of Seedlac

Moisture content, ash content and acid value in this experiment are presented in Table 1. The acid value (AV) is a good indicator of the quality of seedlac (Farag and Leopold, 2009). AV indicates the content of acid available in the seedlac. AV was expressed as the weight of KOH in mg needed to neutralize the organic acids. Some studies reported seedlac has various AV, ranging from 55 to 85 (Prasad, 2014). During storage, polymerization induced by esterification takes place, resulting in a decrease in the AV (Farag and Leopold, 2009). AV in this study is very low compared to AV in the literature already mentioned.

The seedlac used in this experiment may have been stored for a long time. Aldehydes are susceptible to oxidation and the aldehyde groups in seedlac are converted to carboxylic acid groups over time (Shearer, 1989). The polymerization of carboxylic acid can occur over time during storage. There are also a large number of free hydroxyl groups which are susceptible to further esterification during storage. Therefore, AV has decreased.

Tabel 1: Water content, ash content and acid value of seedlac

Specification	Unit	Result
Water content	% (wt)	3.60
Ash content	% (wt)	6.60
Acid value	mg KOH / g	13.14

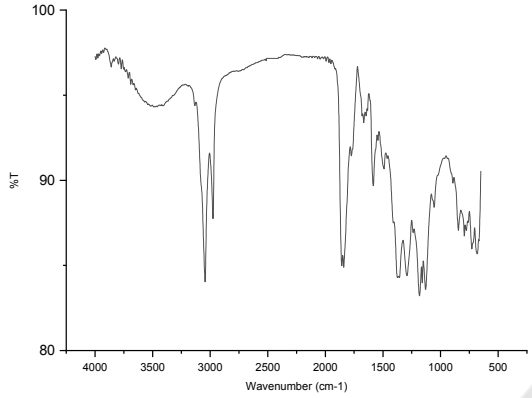

Figure 1: FTIR spectra of seedlac

FTIR spectroscopy was performed to determine the functional groups in seedlac, the result was shown in Figure 1. The carbonyl groups absorption of seedlac has three shoulder in the region of 1640 cm^{-1}, 1610 cm^{-1} and 1550 cm^{-1}. A broad peak in the range between 3400 cm^{-1}-3300 cm^{-1} indicated the stretching vibration of hydroxyl group (O-H), and bands at 2934 cm^{-1}-2920 cm^{-1} and 2857 cm^{-1} was the C-H stretching. The carbonyl band from ester formation was visible at 1730 cm^{-1}, and the band at 1715 cm^{-1} corresponds to acid groups. An olefinic band from C=C stretching was present at 1630 cm^{-1}, while C-O bands from ester, acid and alcohol groups are present at 1240 cm^{-1}, 1163 cm^{-1}, and 1040 cm^{-1}, respectively (Derry, 2012). The region between 1500 cm^{-1} and 900 cm^{-1} was very characteristic for shellac.

3.2 Seedlac Hydrolysis

Aleuritic acid (9,10,16-Trihydroxyhexa-decanoic acid) was a major constituent acid of lac resin and founded in the lac resin about 35% (Prasad, 2014). The terminal hydroxyl and carboxyl functional groups on aleuritic acid made it an excellent starting material for the synthesis of perfumery chemicals like macrocyclic lactones such as civetone, ambrettolide, isoambrettolide (Nagappayya and Gaikar, 2010). Aleuritic acid in the seedlac was in the form of polyester.

Aleuritic acid was obtained from seedlac through four steps. The first step was the hydrolysis of seedlac by sodium or potassium hydroxide. The second step involves the filtration of hydrolysate and washing of the precipitates with saturated saltwater to yield sodium aleuritate. The third step was acidified sodium aleuritate using hydrochloric acid or sulphuric acid to yield aleuritic acid. The last step was the purification of aleuritic acid.

Lac contains natural dyes, namely erythrolaccin and laccaic acid which are still present in seedlac. Erythrolaccin forms a violet coloured salt when reacted with alkali. This could interfere with the purification process. In this experiment, seedlac was decolorized to reduce interference. Decolorized of seedlac was carried out by maceration at room temperature and get natural dyes. The residue of maceration was used in hydrolysis to yield aleuritic acid. From this process, the natural colour was obtained beside the aleuritic acid.

3.3 FTIR Spectrum of Product Hydrolysis

Several analytical techniques have been applied to study the resin of lac, and spectroscopic methods are most widely used (Sutherland and Río, 2014). The FTIR spectroscopy was used to investigate the hydrolysis product of seedlac and decolorized seedlac in this experiment. When they were compared, FTIR spectrum of hydrolysis product from seedlac and decolorized seedlac showed the same pattern, there was no significant difference (Figure 2.). The main band at 1702 cm^{-1} corresponded to the C=O of carboxylic acid groups (Heredia-Guerrero *et al.*, 2010). If the spectra were compared with seedlac spectra, there were some differences.

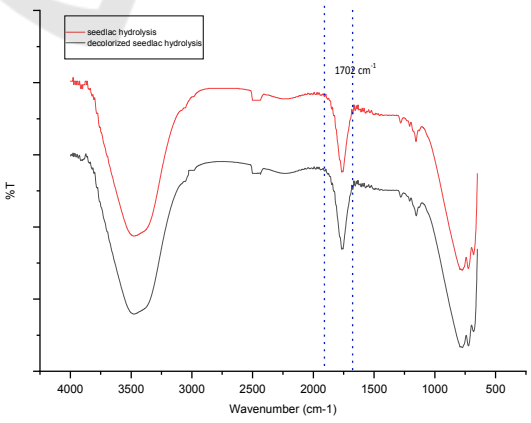

Figure 2: FTIR spectra of hydrolysis product from seedlac and decolorized seedlac

Characterization of the hydrolysis product of seedlac and decolorized seedlac using GCMS was

shown in Figure 3. The chromatogram of decolorized seedlac has three dominant peaks in retention time 13,87 minutes; 35,73 minutes and 42,80 minutes. The chromatogram of seedlac has more peaks but not all of the peaks were dominant peaks. Several peaks in the chromatogram of seedlac indicated the impurities of hydrolysis products. Decolorized process of seedlac could eliminate the natural dyes which interfere with the purification process, therefore the chromatogram of decolorized seedlac has fewer peaks. The aleuritic acid was suspected in retention time 42,80 minute by comparing mass spectrum with reference (NIST Chemistry WebBook).

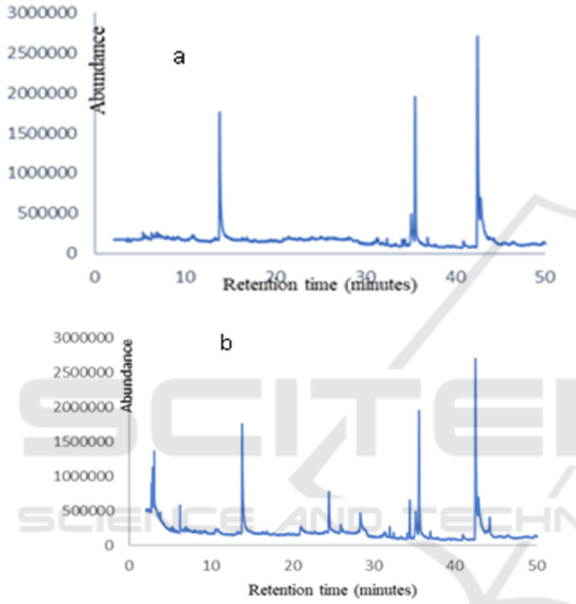

Figure 3: GCMS Chromatogram of product hydrolysis a: decolorized seedlac; b: seedlac

Tabel 2: Relative percentage area of peaks on GCMS chromatogram

Retention time (minutes)	Relative percentage area (%)	
	seedlac hydrolysis	Decolorized seedlac hydrolysis
3.48	2.29	-
6.23	1.76	-
13.86	13.87	20.07
24.52	5.56	-
28.38	6.31	-
34.45	3.20	-
35.16	4.44	6.83
35.58	11.31	19.43
42.51 (aleruritic acid)	28.43	44.30

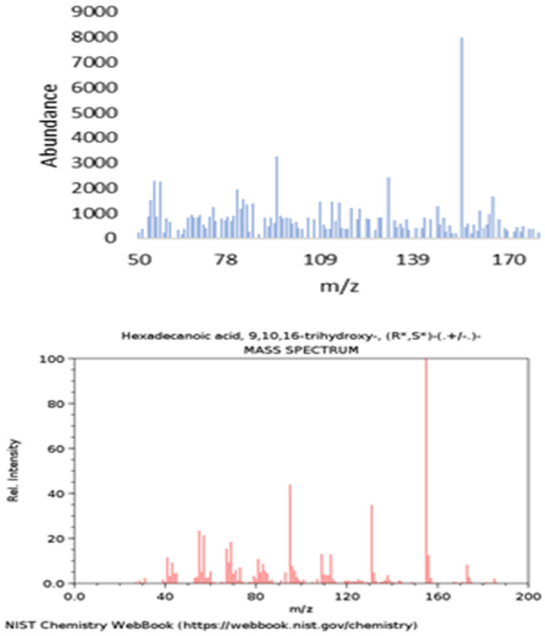

Figure 4: Mass spectrum of peak in retention time 42,80 minutes and reference

The relative percentage area of each chromatogram peak was summarized in Table 2. The percentage area of aleuritic acid from decolorized seed hydrolysis (44.30%) was greater than aleuritic acid from seedlac hydrolysis (28.43). The decolorized process of seedlac before hydrolysis in this experiment could improve the percentage of aleuritic acid up to 56% (from 28.43% to 44.30%).

4 CONCLUSIONS

Characterization of seedlac hydrolysis with the decolorized process before hydrolysis showed that the percentage of aleuritic acid as a hydrolysis product could be improved from 28.43 % to 44.30%. This method could be considered in the production of aleuritic acid from seedlac.

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