Synthesis of Rhodinol Ester from Citronella Oil Reduction Product

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Abstract: Rhodinol is a mixture of citronellol and geraniol that can be esterified using organic acids into citronellol esters and geraniol esters to generate a specific odour as fragrances. Rhodinol esters in this study were synthesized from citronella oil by first reducing to convert the citronellal in citronella oil into citronellol. Reduction was carried out using $NaBH_4$ in conditions with ethanol as a solvent and without a solvent and the variation of mole ratio. Esterification of reduction product (rhodinol) was done to produce rhodinol ester. Reduction citronellal in citronella oil was efficient without solvent in the mole ratio of citronellal and $NaBH_4$ 1:1, and successfully converted citronellal to citronellol with the rhodinol total (citronellol and geraniol) was 65.85%. Esterification of rhodinol produced 69.69% rhodinol ester which contains 55.16 % citronellyl acetate and 14.53% geranyl acetate.

1 INTRODUCTION

Citronella oil is one type of essential oil which widely exported by Indonesia with a production of 700MT-800MT (Dewan Atsiri Indonesia, 2017).Citronella oil is an essential product to produce the basic ingredients of perfume in perfumery, cosmetics, soaps, and detergent. Citronella oil also has characteristic as insect and mosquito repellent. Citronella oil contains three main components consisting of citronellal, citronellol, and geraniol (Simic *et al.*, 2008) (Wany *et al.*, 2014) (Eden *et al.*, 2018). Citronellal (3,7-dimethyl-6-octenal) is a monoterpene that with an aldehyde group and has an important role in the synthesis of fine chemicals as terpene derivatives (Lenardão *et al.*, 2007). Citronellol and geraniol are alcohol monoterpene and the mixture of both is commonly named rhodinol. Rhodinol was known to have a much finer and flowery rose odour than citronellol.

Rhodinol can be converted into rhodinol ester to generate a specific odour as the raw material in fragrance. Geranyl acetate presents a sweet fruity flavour and rose and lavender aroma (Murcia *et al.*, 2018). The synthesis of rhodinol ester was an effort to derivatize citronella oil thus increase the added value of citronella oil.

Synthesis of rhodinol ester in this experiment was done in two steps. The first step was the reduction of citronellal in citronella oil directly without separation. The reduction reaction was done using $NaBH_4$. This step was converted citronellal into citronellol with the aim of increase the rhodinol (citronellol and geraniol) content. The second step was esterification of rhodinol to produce rhodinol ester (citronellyl acetate and geranyl acetate). This experiment was interesting because of the reduction reaction and the esterification reaction were done in citronella oil directly. Some of the previous study was done these process (Yu *et al.*, 2000) (Yadav and Lande, 2006).

2 MATERIALS AND METHODS

2.1 Materials

Citronella oil was used in this experiment obtained from a small industry in Yogyakarta. The chemical materials used in this experiment were natrium borohydride (NaBH4) (Merck), ethanol technical grade, hydrochloric acid (HCl) technical grade, sodium hydroxide (NaOH) technical grade, anhydrous acetic acid (Merck), and anhydrous sodium sulphate (Na_2SO_4).

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2.2 Methods

2.2.1 Gas Chromatography Mass Spectrometry Identification

The citronella oil and the product from the reaction were identified by gas chromatography with a mass spectrometer detector (GC-MS) 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 a constant pressure of 65 kPa. The sample was injected with a volume of 1 μL in a split ratio of 1:25. The increasing of oven temperature was programmed from 60-240°C with a step of 3°C per minute until reaching 240°C.

2.2.2 Reduction of Citronella Oil

Reduction using Ethanol as the Solvent. The reduction was carried out in round-bottomed flask with reflux. The reaction contained $NaBH_4$ and ethanol. $NaBH_4$ was dissolved with ethanol in flask and the citronella oil was added with variation in the mole ratio of the citronellal and $NaBH_4$ (1:1 and 1:3). The reduction reaction was done at 78 °C for 3 hours. The ethanol solvent was evaporated. The white solid obtained from this reaction was diluted with water and acidified with 20% HCl to pH reached 2, then heated at 50°C for 1 hour. The reaction mixture was extracted with ether, washed with water to neutral, and dried with anhydrous Na2SO4. The product was identified with GCMS.

Reduction without Solvent. The reduction was carried out in round-bottomed flask with reflux. The citronella oil and $NaBH_4$ were added to the flask with variation in a mole ratio of the citronellal and $NaBH_4$ (1:3; 1;1; 1: 0.5 and 1:0.025). The reduction reaction was done for 3 hours at 150 °C. After completion, the mixture was cooled, added H_2O and stirred for half an hour and added with the HCl 20% until pH reached 2. The mixture was extracted with ether, washed with water until neutral, and dried with anhydrous $Na2SO_4$. The product was identified with GCMS.

2.2.3 Esterification of Rhodinol

The optimum product reduction (rhodinol), anhydrous acetic acid, and 5% of NaOH were arranged in a round-bottomed flask with a mole ratio of rhodinol and acetic acid was 1:3. The mixture was stirred and heated at 180 °C for 3 hours. This was followed by the neutralization with 1% of HCl solution to separate it from the NaOH catalyst. The rhodinol ester from this reaction was identified using GCMS.

3 RESULTS AND DISCUSSION

3.1 Chemical Compounds Composition of Citronella Oil

Characterization using GC-MS showed the chromatogram profile detected several peaks in citronella oil (Figure 1). The compounds identified based on a comparison of the mass spectrum with reference data from the database (Wiley 7) and the results were presented in Table 1.

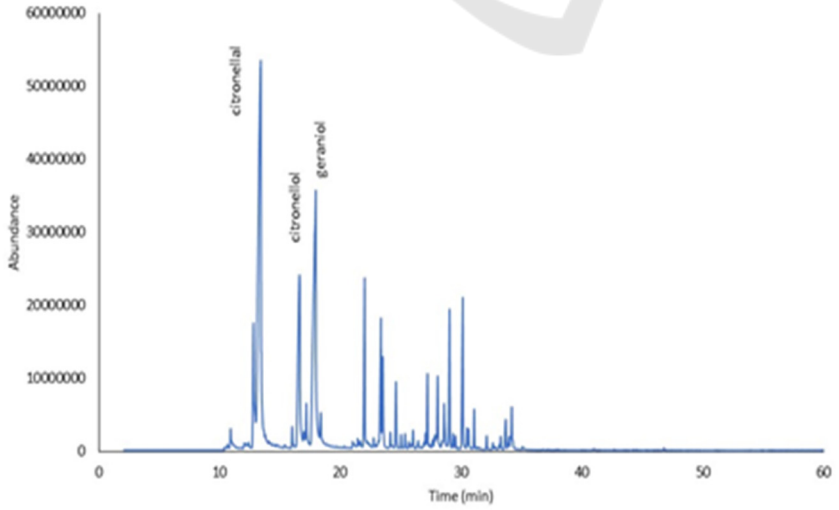

Figure 1: GCMS chromatogram of citronella oil.

Table 1: Chemical compounds of citronella oil

No	Retention time	Identified compound	Relative percentage area (%)
1	13.11	Citronellal	55.93
2	16.62	Citronellol	7.40
3	17.97	Geraniol	10.84
4	22.01	Citronellyl acetate	3.30
5	23.36	d-carene	2.27
6	23.51	β-elemene	2.59
7	24.61	Geranyl acetate	3.30
8	27.21	Germacrene	2.35
9	28.05	Methyl isoeugenol	2.28
10	29.04	d-cadinene	3.30
11	30.16	Elemol	4.29

The compounds were citronellal, citronellol, geraniol, citronellyl acetate, d-carene, β-elemene, geranyl acetate, d-cadinene, and elemol. The main compounds in citronella were citronellal (55.93%), geraniol (10.74%), and citronellol (7.40%. These results appropriate with the previous finding in the literature, citronellal, geraniol, and citronellol has been described as the main compounds of citronella oil (Simic et al., 2008) (Wany et al., 2014) (Eden et al., 2018).

3.2 Reduction of Citronella Oil using Ethanol as the Solvent

The reduction of citronellal to citronellol was carried out using $NaBH_4$ with the reaction in Figure 2. Borohydrides are very routinely used for selective reduction in preparatory synthesis and also on a commercial scale (Yadav and Lande, 2006). The results of reducing citronellal to citronellol in citronella oil was shown in Table 2.

Table 2. Reaction products of citronella oil reduction using $NaBH_4$ with ethanol solvent.

Compounds	Initial	Reduction product in mole ratio citronellal and $NaBH_4$	
		1:1	1:3
Citronellal	55.93	26.48	-
Citronellol	7.40	38.66	50,42

Based on Table 2, there was a change in the amount of citronellal and citronellol at the end of the reaction when compared to the initial amount, both at a mole ratio of 1: 1 and 1: 3. This means that the reaction under these conditions successfully reduced citronellal to citronellol. In the 1: 3-mole ratio there was no citronellal at the end of the reaction which means that the citronellal has been converted completely. However, in this condition, citronellal was not completely converted into citronellol as indicated by the amount of citronellol formed. The imperfect citronellal reduction in this experiment was predicted because of the ethanol solvent used.

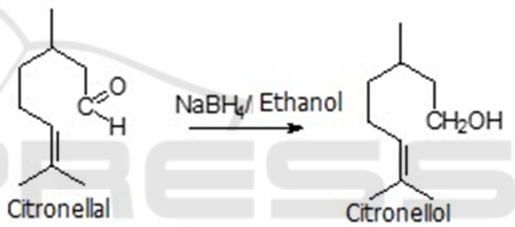

Figure 2: Reduction of citronellal to citronellol

This experiment used technical ethanol which still contains a lot of water thus there was $NaBH_4$ which reacted with water before reacting with citronellal. The possibility of $NaBH_4$ reacting with water was observed with the appearance of foam when dissolving $NaBH_4$ in ethanol. So, the use of solvents will require expensive costs because the solvent must be free of water. For this reason, it is necessary to try hydrogenation without ethanol as a solvent.

3.3 Reduction without Solvent

Aldehyde reduction using $NaBH_4$ can be carried out in the absence of a solvent (Zeynizadeh and Behyar, 2005). To improve the efficiency and effectiveness of the reduction process, the citronella oil reduction reaction was carried out with $NaBH_4$ without the use of a solvent. The results of reducing citronellal to citronellol without solvent were shown in Table 3 and the GCMS chromatogram of reduction product were described in Figure 3.

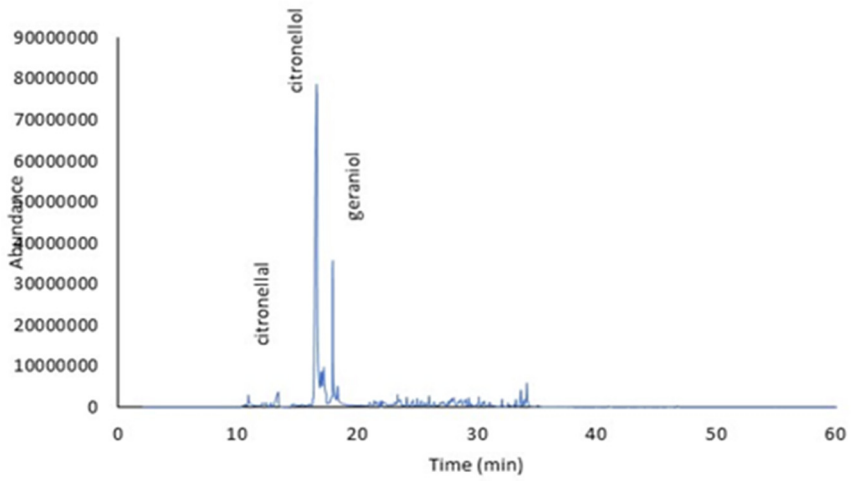

Figure 3: GCMS chromatogram of citronella oil reduction product

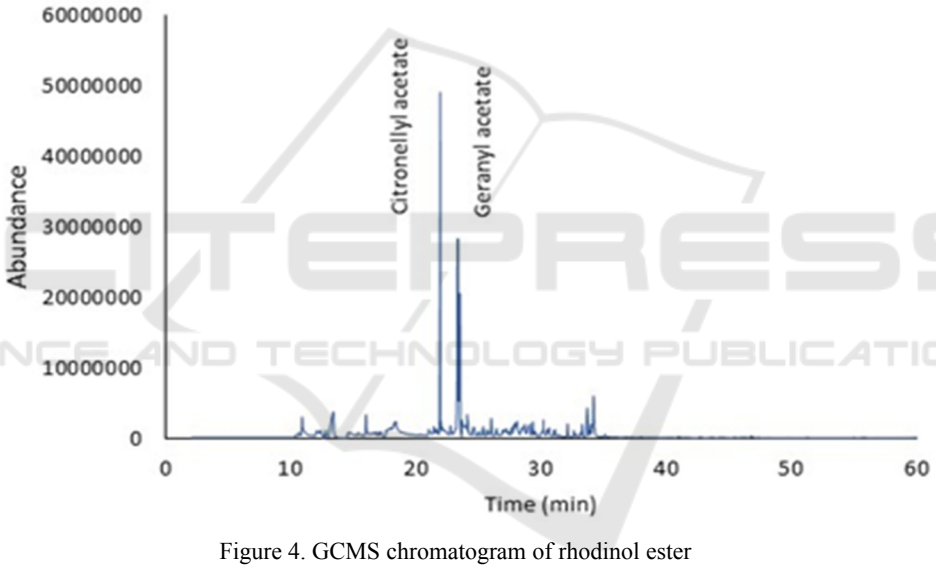

Figure 4. GCMS chromatogram of rhodinol ester

Table 3. Reaction products of citronella oil reduction using $NaBH_4$ without solvent

Mole ratio of citronellal and $NaBH_4$	Citronellal	Citronellol	Geraniol
Initial	55.934	7.40	10.84
1 : 3	-	59.73	16.67
1 : 1	2,14	51.56	14.29
1 : 0,5	1,98	46.51	13.43
1 : 0,25	1,76	40.21	13.60

Table 3 showed that citronellal can be converted into citronellol with $NaBH_4$ without the use of solvents as indicated by decreasing levels of citronellal and increasing levels of citronellol in reaction products. In the variation of the mole ratio, the higher the mole of $NaBH_4$, the reduced citronellal was higher. Citronellal was reduced completely at 1:3-mole ratios. The product contained 59.73% citronellol and 16.67% geraniol so the amount of rhodinol was 76.4%. Although optimal, this process was inefficient because it required a large number of moles of $NaBH_4$. Therefore, for the next process used rhodinol from the reduced mole ratio of 1: 1 because need less NaBH4 and this was considered more efficient. The rhodinol from this process contains 51.56% citronellol dan 14.29% geraniol with rhodinol total was 65.85%.

3.4 Esterification of Rhodinol

Esterification of rhodinol was conducted to obtained rhodinol ester that has a specific smell. Geranyl acetate presents a sweet fruity flavour and rose and lavender aroma (Murcia *et al.*, 2018). Rhodinol ester (citronellyl acetate, geranyl acetate) can be isolated by vacuum fractionation, but the availability of these natural raw materials was limited. However, this method was not suitable for large-scale industrial production. For the alternative, these esters may be produced by chemical synthesis and enzymatic extraction or catalysis (bio catalysis) (Paroul *et al.*, 2012) (Wu *et al.*, 2018) (Murcia *et al.*, 2018). Chemical synthesis was often performed using acetic acid anhydride or direct acetic acid esterification (Jian *et al.*, 2014). This method was the traditional chemical synthesis and commonly used in large-scale industries. Rhodinol ester in this experiment was synthesized using acetic acid.

Table 4. Rhodinol ester product from esterification

Compounds	Rhodinol (%)	Rhodinol ester (%)
Citronellol	51.56	-
Geraniol	14.29	-
Citronellyl acetate	3.00	55.16
Geranyl acetate	-	14.53

The GCMS analysis showed that all rhodinol (citronellol and geraniol) have changed to rhodinol acetate esters. This result was observed with the loss of the rhodinol peak and the appearance of the rhodinol acetate peak, as shown in Figure 4. The complete data on the results of the experiment are shown in Table 4.

4 CONCLUSIONS

Reduction citronellal in citronella oil was successfully converted citronellal to citronellol with the rhodinol total (citronellol and geraniol) was 65.85%. Esterification of rhodinol produced 69.69% rhodinol ester which contains 55.16 % citronellyl acetate and 14.53% geranyl acetate.

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