Esterification of Rhodinol Fraction with Acetic Anhydride using Zeolite Catalyst

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Abstract: This research has been conducted on the effect of esterification reaction in the chemical composition of rhodinol fraction from java citronella oil (Cymbopogon winterianus). The reaction process in this research is done at 230 ° C by using rhodinol fraction and acetic anhydride with zeolite as a catalyst. Based on the research, the optimum reaction time is 1 hour and the optimum mole ratio of reactants is 1: 1. The% yield of citronellyl acetate and geranyl acetate are 74.06% and 95.92%.

1 INTRODUCTION

Indonesia is a country rich in the diversity of essential oil-producing plants. As many as 40 types of essential oils produced from these plants have been traded and one type of essential oil that has the potential to be developed commercially is citronella oil (Gunawan, 2009).

Citronella oil consists of 40 components, but the identity of citronella oil scent is only determined by three compounds namely citronellal, citronellol, and geraniol (Kaul *et al.*, 1997).

Citronellal, citronellol, and geraniol are single components that have a higher selling price than fragrant citronella essential oils in the form of crude oil (Aldrich, 2019). Separation of fragrant citronella oil using batch scale vacuum fractionation distillation has been able to separate the citronellal fraction and rhodinol fraction (a mixture of citronellol and geraniol) (Eden *et al.*, 2018).

Citronellol and geraniol can be further enhanced for its selling value by converting them into compounds that are widely used in the food, cosmetics and pharmaceutical industries, namely citronellyl acetate and geranyl acetate (Claon and Akoh, 1993).

Citronellyl acetate and geranyl acetate are ester compounds that can be synthesized through an esterification reaction between an acidic compound and alcohol using an acid catalyst (Fessenden and Fessenden, 1999). The HZSM-5 zeolite catalyst was used in a previous study to synthesize isopentyl acetate and succeeded in obtaining a yield of 95.1% (Ma *et al.*, 1996)

Therefore, to increase the higher selling value of the rhodinol fraction obtained from citronella oil, it is necessary to esterify the rhodinol fraction to obtain citronellyl acetate and geranyl acetate.

2 METHOD

2.1 Esterification of Rhodinol Fraction

Rhodinol of 10 mL (citronellol = 0.02 mole and geraniol = 0.01 mole) were taken into a 20 mL boiling flask flat and then added 2.92 mL of acetic anhydride (0.03 mole) and 0.14 g of zeolite. after that, the flask is heated at 130°C with stirring using a magnetic stirrer and after 1 hour the catalyst can be separated by filtering.

The organic liquid from the previous reaction is washed with distilled water repeatedly until the pH of the water phase is equal to 7. after that, the organic phase is separated and weighed.

The same method is used to find out the optimum reflux times by repeating the previous method with the variation of reflux time (2 hours and 3 hours). The reflux time method that produces optimum citronellyl acetate and geranyl acetate products is used to find out the optimum mole ratio of acetic anhydride (0.06 mole and 0.9 moles) for this esterification reaction.

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2.2 Characterization using Gas Chromatography Mass Spectrometry (GC-MS)

Each sample was dissolved in n-hexane solvent in a ratio of 1: 100, then 0.1 µL was taken and injected using a syringe on GCMS-QP 2010S Shimadzu instruments to obtain chromatogram and compound prediction.

3 RESULT

3.1 Component Analysis of Rhodinol Fraction

Figure 1 is a chromatogram that we obtained from the GC-MS instrument, from that figure we can observe that there are 12 peaks found in the rhodinol fraction.

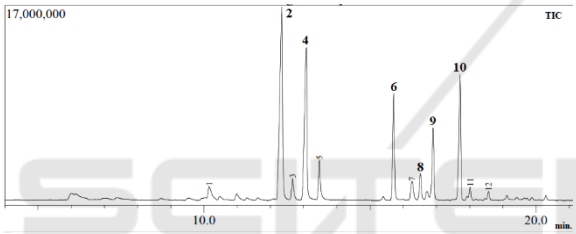

Figure 1: Chromatogram of rhodinol fraction.

Six peaks in figure 1 is a component that we should focus on because we would observe the different before and after esterification reaction, the effect of variation time reaction and mole ratio acetic anhydride, for more details look at table 1.

Table 1: Tabulation from chromatogram of rhodinol fraction.

Peak	Time Retenion (min)	Area (%)	Estmation	
			SI	Compound
2	12,34	31,51%	SI: 97	Citronellol
4	13,08	21,50%	SI: 97	Geraniol
6	15,71	11,10%	SI: 97	Citronellyl Acetate
8	16,51	2,26%	SI: 97	Geranyl Acetate
9	16,89	7,19%	SI: 96	β-Elemen
10	17,71	14,18%	SI: 97	Caryophyllene

3.2 Synthesis of Esters (Citronellyl Acetate and Geranyl Acetate)

The synthesis of ester compounds (Citronellyl acetate and geranyl acetate) is based on the Fischer esterification reaction, which is the reaction between the acetyl group (-$COCH_3$) on the anhydride acetate and the alcohol group (-OH). According to Fracotte the formation of ester compounds using acetic anhydride will produce a high% yield compared to using acetic acid because the carbonyl group of acetic acid is not strong enough as an electrophile to be attacked by alcohol (Fracotte and Lohmann, 1989).

In the synthesis of citronellyl acetate and geranyl acetate, the nucleophilic acyl substitution reaction occurs. The use of the zeolite catalyst aims to reduce the activation energy by changing the reaction mechanism, which is to add the reaction steps. Although the catalyst participates in the reaction stage, at the end of the reaction process will be formed again. With the lower value of the activation energy, effective collisions that produce the product will occur more frequently so the reaction goes faster. In the reaction process, zeolite produces acylium ions which act as electrophiles in the substitution reaction, so that the acylium ion is easily attacked by O atoms which are attached to hydroxyl groups from both citronellol and geraniol. The hydroxyl groups in citronellol and geraniol act as nucleophiles in the presence of free electron pairs on the O atom, then the hydroxyl group attacks the C atom of the carbonyl group in the acylium ion to form oxonium ions. The existence of this attack by nucleophiles causes the substitution of H atoms in the hydroxyl groups from citronellol and geraniol with acyl groups from acetic anhydrides to form citronellyl acetate and geranyl acetate.

At the end of the synthesis process, the liquid and solid phases are produced. The solid phase is a zeolite catalyst and can be separated by filtering. Meanwhile, the liquid phase is containing esters (citronellyl acetate and geranyl acetate) and acetic acid compounds as byproducts.

3.3 Effect of Time on Rhodinol Esterification Reaction with Acetic Anhydride

Table 2 and table 3 are a tabulation of the data produced by the esterification reaction with a fixed number of mole of acetic anhydride but the varying reflux time which is: 1 hour, 2 hours and 3 hours.

Table 2: Effect of Reflux time on Citronellyl Acetate (CA) and Geranyl Acetate (GA) percentage.

Reflux time (hour)	Before Synthesis (%)		After Synthesis (%)		synthesis results (%)	
	CA	GA	CA	CA	CA	GA
1	11,1	2,26	48,33	26,04	37,23	23,78
2	11,1	2,26	45,49	27,23	34,39	24,97
3	11,1	2,26	47,11	10,49	36,01	8,23

Table 3: Effect of Reflux time on Citronellyl Acetate (CA) and Geranyl Acetate (GA) %yield.

Quantity Of Rhodinol	Quantity Of Acetic Anhydride	Reflux Time (Hour)	%Yield	
			CA	GA
10 mL (0,03 mol)	2,92 mL (0,03 mol)	1	74,06 %	95,92 %
10 mL (0,03 mol)	2,92 mL (0,03 mol)	2	66,25 %	97,45 %
10 mL (0,03 mol)	2,92 mL (0,03 mol)	3	65,49 %	30,61 %

From Table 2 and Table 3 we could see that The optimum reflux time to produce the highest %yield citronellyl acetate and geranyl acetate yield is 1 hour.

Hydrolysis of esters by acetic acid is possible so that the formed ester product can converts back into an alcohol compound as the reaction time increases (Figure 2).

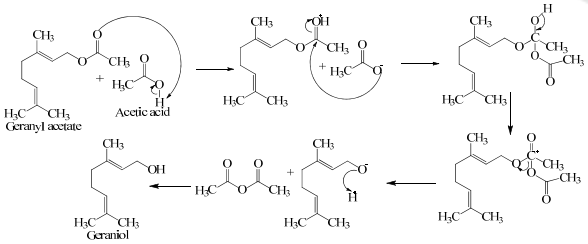

Figure 2: Reaction mechanism of hydrolysis ester (geranyl acetate)

3.4 Effect of Mole Ratio on Rhodinol Esterification Reaction with Acetic Anhydride

Table 4 and table 5 are a tabulation of the data produced by the esterification reaction with a fixed reflux time but the varying number of mole of acetic anhydride which is: 0.03 mole, 0.06 mole, and 0.09 mole.

From Table 4 and Table 5 we could see that The optimum mole ratio between rhodinol and acetic anhydride to produce the highest %yield citronellyl acetate and geranyl acetate yield is 1:1.

There are water molecules in rhodinol so that the reaction of acetic anhydride to acetic acid is possible (Figure 3), after that hydrolysis of ester by acetic acid is possible (Figure 2).

Table 4: Effect of Reflux time on Citronellyl Acetate (CA) and Geranyl Acetate (GA) percentage.

Acetic Anhy-dride (mole)	Before Synthesis (%)		After Synthesis (%)		synthesis results (%)	
	CA	GA	CA	CA	CA	GA
0,03	11,1	2,26	48,33	26,04	37,23	23,78
0,06	11,1	2,26	49,99	20,18	38,89	17,92
0,09	11,1	2,26	45,09	21,25	33,99	18,99

Table 5: Effect of Reflux time on Citronellyl Acetate (CA) and Geranyl Acetate (GA) %yield.

Quantity Of Rhodinol	Quantity Of Acetic Anhydride	Reflux Time (Hour)	%Yield	
			CA	GA
10 mL (0,03 mol)	2,92 mL (0,03 mol)	1	74,06 %	95,92 %
10 mL (0,03 mol)	5,84 mL (0,06 mol)	1	79,60 %	74,49 %
10 mL (0,03 mol)	8,76 mL (0,09 mol)	1	71,29 %	80,61 %

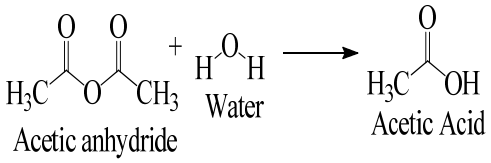

Figure 3: reaction mechanism of hydrolysis ester (geranyl acetate)

4 CONCLUSIONS

Based on research by the author, it can be concluded that:

1. The optimum ratio of rhodinol to acetic anhydride is 1: 1, with the yield of citronellyl acetate obtained is 74.06% while the % of geranyl acetate yield is 95.92%. Based on the results of the GC-MS analysis obtained 37.23% citronellyl acetate and 23.78% geranyl acetate.
2. The optimal reflux reaction time for esterification of rhodinol with acetic anhydride is 1 hour.

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