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Synthesis of Methyl Citronellate through Fischer Esterification Reaction between Methanol and Citronellic Acid from Oxidation Product of Citronellal

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ABSTRACT
The purpose of this research was to synthesis methyl citronellate through *Fischer* esterification reaction between methanol and citronellic acid from oxidation product of citronellal and characterize the methyl citronellate of esterification product by TLC method, IR spectroscopy, and GC-MS. This research was started by oxidizing citronellal to citronellic acid using silver oxide (Ag_2O) oxidator obtained from reaction between silver nitrate ($AgNO_3$) with sodium hydoxide (NaOH) and oxidation reaction at temperature of 55-60°C for 35 minutes. Then, the oxidation product of citronellal was reacted with methanol through *Fischer* esterification reaction using concentrated sulfuric acid (H_2SO_4) catalyst at 46°C for 2 hours. The products of citronellal oxidation and esterification were identified using TLC, IR spectrophotometer, and GC-MS. The result of this research showed that the Fischer esterification reaction between methanol with citronellic acid from oxidation product of citronellal was produce methyl citronellate in the form of brownish yellow liquid and smelled fragrant. The result of methyl citronellate from esterification product characterization by using TLC method, IR spectroscopy, and GC-MS showed that the methyl citronellate has a purity of 17 % and a yield of 13.76 %.

Keyword: Adsorption, Peanut shell, Continuous system

1. INTRODUCTION

Utilization of citronella oil in Indonesia is limited as raw material products which are then exported abroad to be further processed into finished products (Fatimah et al, 2008). Studies related to citronella oil have been done and there are at least 50 compounds of citronella oil components that have been identified using GC-MS (Gas Chromatography-Mass Spectroscopy), but there are some dominant compounds namely citronellal, linalool, citronellol, geraniol and have been studied that citronella oil also has low antimicrobial activity (Malaluan et al, 2015).

Citronellal is one of the main compounds contained in citronella oil with a yield of 32-45% (Guenther in Sastrohamidjojo, 2004). Citronellal is a fragrance compound commonly used in perfume and flavorings in foods (Syunbayev et al, 2016). Citronellal has a distinctive aroma that is not favored by certain insects, so it is also widely used as an insect repellent agent (Lu et al, 2014).

Citronellal has a functional group -CHO, so that these compounds belong to the class of aldehyde compounds. The presence of an aldehyde group in a citronellal compound allows the compound to undergo an oxidation reaction to a carboxylic acid compound. Citronellal not only has

an aldehyde group but also has an alkene group. Therefore, to oxidize the aldehyde group to the carboxylic group without oxidizing the alkene group, a selective oxidizer is required. Silver oxide is one of the selective oxidizers which can oxidize only aldehyde groups in a compound even though there is an alkene group in the compound (Hart, 2003).

Citronellic acid is a compound of oxidation reaction from citronellal. This compound is a class of carboxylic acid compounds because it has a -COOH functional group. The carboxylic acid group compounds and derivatives may be used to prepare the ester compound by esterification reaction with the alcohol. Ester compound is a compound widely used as raw material in the manufacture of perfume because the characteristic of this compound has a smell of fragrant.

The ester compound can be synthesized from the carboxylic acid group compound by an esterification reaction. The esterification reaction involving carboxylic acids and alcohols with the aid of an acid catalyst which produces esters and water is referred to as *Fischer* esterification (Carey, 2000). This reaction has several advantages, one of which is the yield is relatively large. In addition, the procedure in doing this reaction is also not too difficult.

This research aimed to synthesis and identified methyl citronellate compounds. This research was started by oxidizing citronellal to obtain citronellic acid compounds using silver oxide. Then, the esterification reaction was performed by reacting to the oxidized citronellic acid with methanol to obtain the methyl citronellate compound with the aid of a concentrated sulfuric acid catalyst. The synthesis compounds were analyzed by TLC, IR spectrophotometer, and GC-MS.

2. RESEARCH METHOD

2.1. Materials

Citronellal p.a. Merck 95 %, $AgNO_3$ p.a. Merck, Pellet NaOH p.a. Merck, aquadest, concentrated H_2SO_4 solution, methanol p.a. Merck, Na_2SO_4 anhydrous p.a. Merck, n-hexane, p.a. Merck and chloroform p.a. Merck.

2.2. Procedures

2.2.1. Oxidation Reaction

The procedure used in this oxidation reaction is a modification of the citronellal oxidation research procedure with Ag_2O which has been done by Darnasmara (2017) in her thesis entitled "Synthesis of Citronellic Acid Through Citronellal Oxidation Reaction With Silver Oxide." $AgNO_3$ crystals of 5.95 grams (0.035 mol) were dissolved in 15 mL aquadest and 1.48 grams (0.037 mol) NaOH in 10 mL of aquadest and mixed in a beaker glass while stirring using a magnetic stirrer with a 4-6 switch scale for ± 5 minutes. Ag_2O brown precipitate formed then filtered with Whatman 42 paper and washed with aquadest. Then, the Ag_2O precipitate, 75 mL of aquadest, and 2.96 grams (0.074 mol) NaOH into a three-neck flask equipped with ball cooler, magnetic stirrer, thermometer, rubber stopper, water bath and raised temperature. When the temperature reaches at range of 55-60^oC, it was added 4.62 grams (0.030 mol) citronellal into the mixture and then stirred for about 35 minutes. Then the mixture was filtered with Whatman 42 paper and the filtrate was acidified with concentrated H_2SO_4 until saturated. The solution was silenced to form two phases, namely liquid phase and organic phase which was further separated by using separating funnel. After that, anhydrous Na_2SO_4 was added into the organic phase and separated to obtain an organic phase free of water. The resulting compounds were then identified using TLC, IR spectroscopy, and GC- MS.

2.2.2. Esterification Reaction

This esterification reaction procedure is a modification of a research that has been done by Damayanti (2016) in her thesis entitled "Synthesis of Citronellyl Formate Through Fischer Esterification Reaction Between Formic Acid And Citronellol From Reduction Product of Citronellal." A total of 1.02 grams of citronellal oxidation result (citronelic acid purity 74.98%, so that in the citronellal oxidation result there was citronellic acid as much as 0.765 grams = 0.0045 mol) inserted into a three-neck flask equipped with a cooling back, thermometer, rubber plug , a constantly rotated magnetic stirrer, and a water bath. Then, the concentrated sulfuric acid was added

into the three-neck flask by 1 drop and the mixture is stirred for 15 minutes. During stirring, 0.208 g (0.0065 mol) of methanol was added to the three-neck flask and then stirred for 2 hours with the temperature kept constant 46°C. Then the result of the obtained reaction was inserted into the separating funnel then silenced to form two phases, namely organic phase and liquid phase. After that, it was separated between the organic phase and the water phase then the organic phase was weighed. The resulting compounds were then identified using TLC, IR spectroscopy, and GC-MS. The result of citronellal oxidation compound was identified using TLC to determine the ongoing oxidation process by obtaining stain differences and the Rf (Retardation factor) value of the base material (citronellal) and the oxidation compound. TLC was performed with a silica plate and a chloroform: n-hexane (2: 1) eluent ratio.

3. RESULTS AND DISCUSSION

3.1. Oxidation of Citronellal

In this research, the oxidation reaction was repeated twice in the same temperature conditions, but the mol ratio was different in each experiment. In oxidation 1 using the ratio of Ag_2O: citronellal (1:1), while in oxidation 2 using the ratio Ag_2O: citronellal (3.7:3.5). Compounds of citronellal oxidation reaction results from each experiment are presented in Table 1.

Table 1. Citronellal Oxidation Products

Parameter	Observation Results	
	Oxidation 1	**Oxidation 2**
Mass	Two phases are formed (but cannot be separated because the result is very little)	1,877 g
Form	Liquid	Liquid
Color	Brownish Black	Colorless
Smell	Sting	*Green grassy odor*

Based on observations under UV lamps, citronellal compounds have Rf value of 0.82 and citronellal oxidation products are suspected to have an Rf value of 0.26 because there are still other stains on TLC chromatogram is also possible there are other compounds. The result of citronellal oxidation compounds has higher polarity properties than citronellal so that the citronellal oxidation product compounds have a lower Rf value. This is consistent with the theory that carboxylic acid compounds are more polar than aldehyde compounds, so that the distance of the citronellal oxidation compounds on the polar silica plate is shorter than the citronellal compound. Thus, it can be estimated that there has been a reaction because the Rf value of the citronellal oxidation compound has been different from the citronellal Rf. However, in the chromatogram obtained there are some widespread stains, tailing, and there are other stains, this can be caused by a non-pointed capillary tube so the patches too large or the possibility of compounds that are too thick that causes the resulting stain to be wide and tailing. In addition, the possibility is also caused because the citronellal as initial raw material synthesis has been oxidized into other compounds because citronellal is a group of aldehyde compounds that easily oxidized, causing the appearance of other stains.

Further identification using IR spectroscopy to determine the presence of functional groups on an analyzed compound whose results are shown in Figs. 1 and 2.

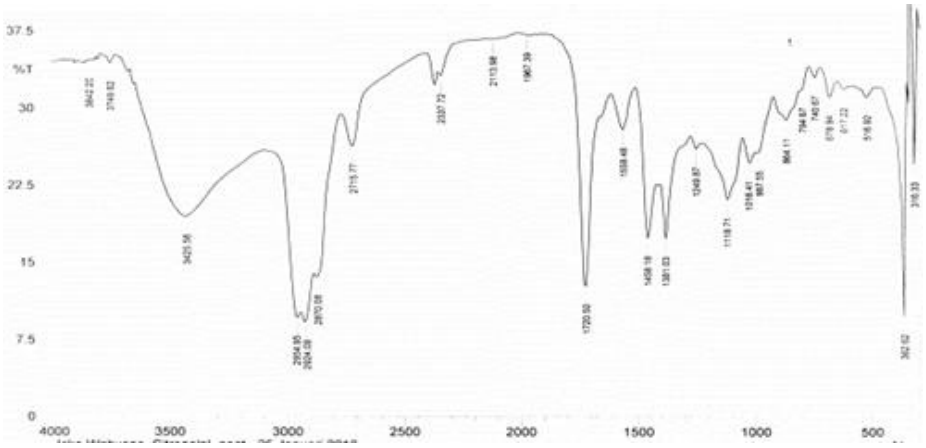

Figure 1. IR Spectrum of Citronellal Compound

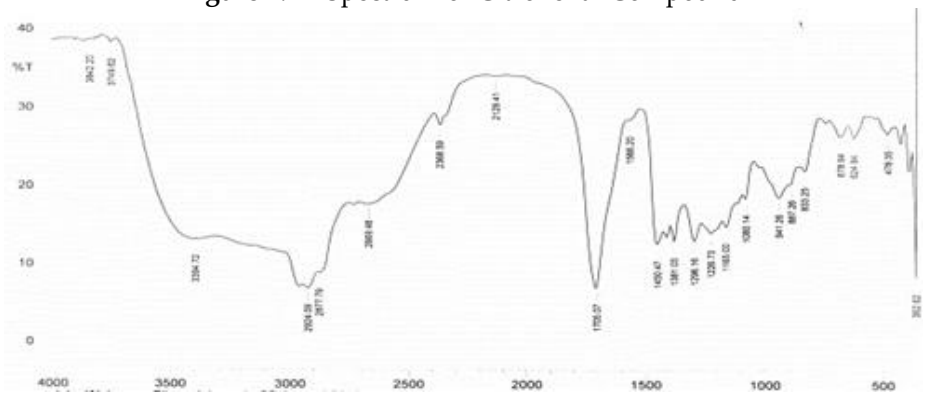

Figure 2. IR Spectrum of Citronellal Oxidation Product

Based on the result of IR spectrum analysis of citronellal oxidation product, it showed that the oxidation process has succeeded. It was reinforced by the absorption loss in area 2715,77 and 2870,08 cm^{-1} which are characteristic of the functional group C-H aldehyde. The presence of widespread uptake in area of 3300-2400 cm^{-1} overlapping with an aliphatic C-H functional group in an absorption area of 2877.79 cm^{-1} and 2924.09 cm^{-1} indicates the presence of an O-H group of carboxylic acids. In addition, the shift in the uptake of the C=O carbonyl functional group in area 1720,50 cm^{-1} is the functional group C=O aldehyde to the absorption area 1705.07 cm-1 showing the functional group of C = O carboxylic acid.

The oxidation product was identified using GC-MS to determine purity, molecular mass, and fragmentation of citronellal oxidation compounds. GC chromatogram of citronellal oxidation compounds can be seen in Figure 3.

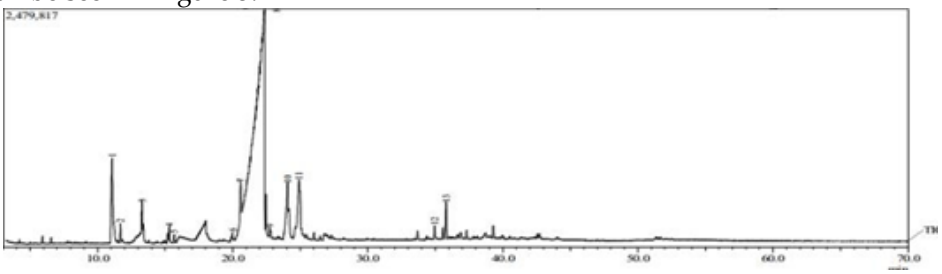

Figure 3. GC Chromatogram of Citronellal Oxidation Product Compounds

Based on Figure 3, the peak of 8 with a retention time of 22.355 minutes and 74.98% of the area was estimated as the peak of the citronellic acid compound. It was reinforced by the relative molecule mass of the citronellal oxidation product of 170 g/mol. The mass spectrum and its fragmentation can be seen in Figures 4 and 5. Theoretically, the resulting citronelic acid is 5.1 grams

(0.030 mol). However, in this research, only a mixture of citronellal oxidation of 1,877 grams was obtained. So, based on calculation of yield obtained from this research was 27.6 %.

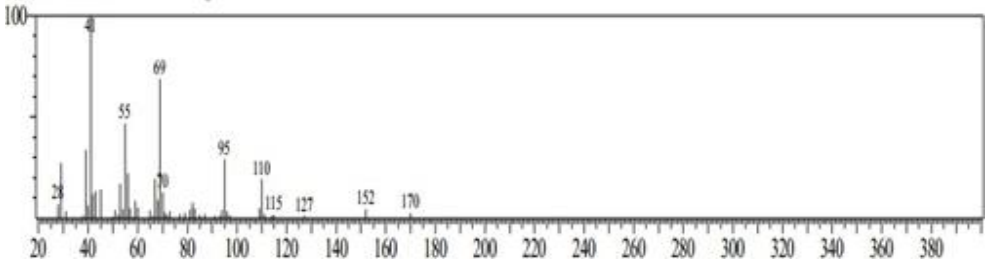

Figure 4. Mass Spectrum of Peak 8th from Citronellal Oxidation Product

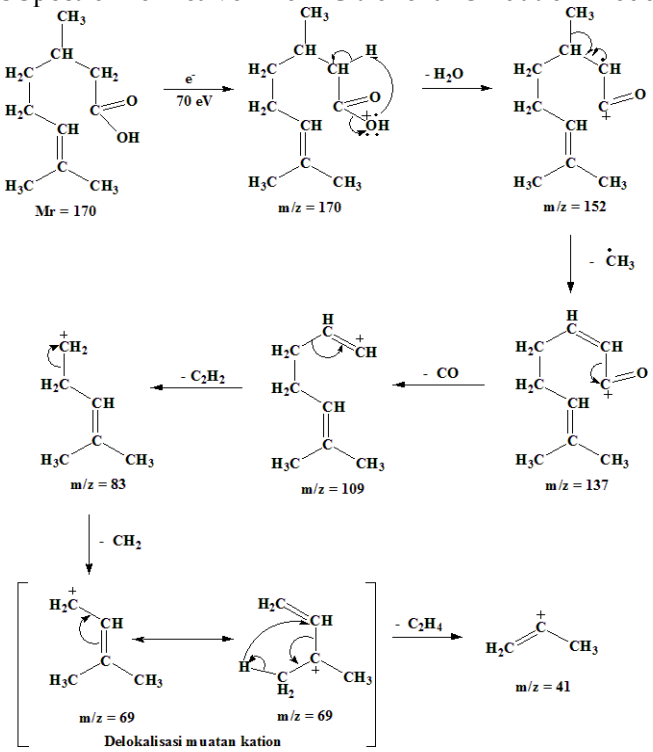

Figure 5. Fragmentation of Citronellic Acid

3.2. Synthesis of Methyl Citronellate

Synthesis of methyl citronellate compounds from methanol and citronellic acid from oxidation product of citronellal by *Fischer* esterification reaction using concentrated sulfuric acid catalyst. The product of esterification reaction are presented in Table 2. The esterified compounds were identified using TLC to determine the ongoing esterification process by obtaining stain differences and the Rf value of the base material (citronellic acid) and the esterified compound. TLC was performed with a silica plate and a chloroform: n-hexane (1: 1) eluent ratio.

Table 2. Product of *Fischer* Esterification Reaction Between Methanol and Citronellic Acid

Parameter	Observation Results
Mass	0,67 gram
Form	Liquid
Color	Brownish yellow
Smell	Fragrant

Based on observations under UV lamps, it can be observed that the citronellic acid compound has Rf value of 0.26 and the esterified compound is suspected to have an Rf value of 0.7 because there are still other stains on the TLC chromatogram which may also have other compounds.

Thus, it can be assumed that the esterification reaction has taken place and the ester compound has already formed due to a stain with different Rf values. However, in the chromatogram obtained there are some widespread stains, tailing, and there are other stains, this can be caused by a non-pointed capillary tube so the patches too large or the possibility of compounds that are too thick that causes the resulting stain to be wide and tailing. In addition, the possibility is also caused because the citronellal as initial raw material synthesis has been oxidized into other compounds because citronellal is a group of aldehyde compounds that easily oxidized, causing the appearance of other stains.

Further identification using IR spectroscopy to determine the presence of functional groups on an analyzed compound whose results are shown in Figure 6. Based on the result of IR spectrum analysis of esterification product, it can be seen that the ester compound has been formed which was indicated the emergence of functional group C=O ester in absorption area 1712.79 cm^{-1} and there is functional group of C-O-C ester in absorption area 1195,87 cm^{-1} is a functional group characteristic of the ester compound.

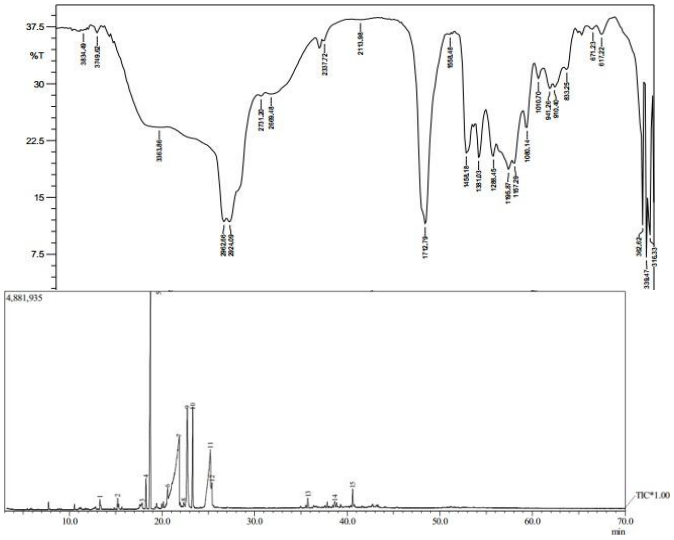

Figure 7. GC Chromatogram of Esterification Product

The esterification product was identified using GC-MS to determine the purity, molecular mass, and fragmentation of the esterification reaction compound. GC chromatogram of the esterified compounds can be seen in Figure 7. Based on Figure 7, the peak of 5 with a retention time of 18.740 minutes and 17 % of the area was estimated as the peak of the methyl citronellate compound. It was reinforced by the relative molecule mass of the esterification product of 184 g/mol. The mass spectrum and its fragmentation can be seen in Figs. 8 and 9.

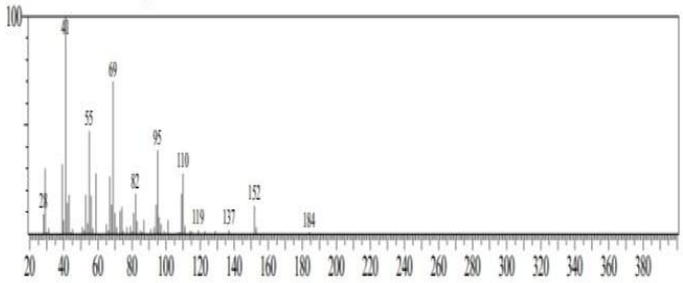

Figure 8. Mass Spectrum of Peak 5th from Esterification Product

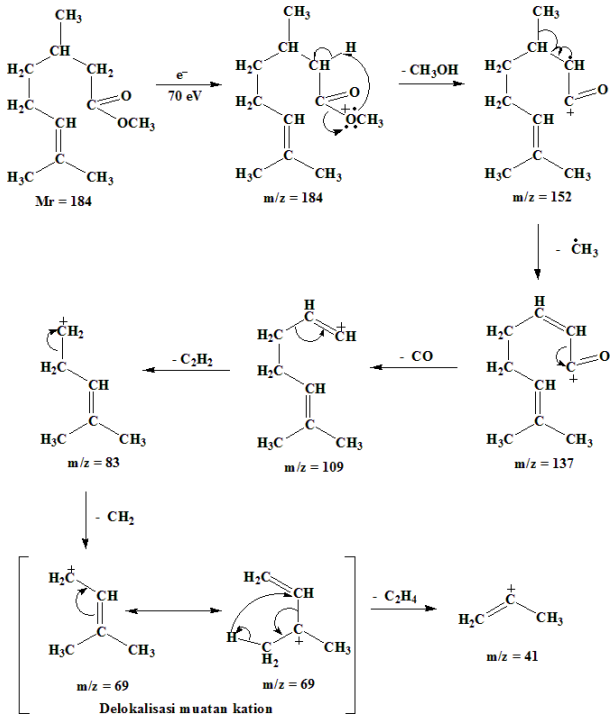

Figure 9. Fragmentation of Methyl Citronellate Compound

Theoretically, the resulting methyl citronellate should be 1,104 grams (0.006 mol). However, in this reserach, there was a mixture of esterification products of 0.67 grams. Thus, the yield produced in this research was 13.76%. In this research the yield produced in the esterification synthesis is small due to several factors. First, esterification reaction is a reversible reaction. So, it is possible that the ester compound that has been formed was hydrolyzed back into reactants. It is known from GC-MS data indicating that there was a peak of citronellic acid compound which is one of the compounds used as reactants. In addition, it is also possible that the methanol mass used is too small at 0.028 g (0.0065 mol) and some have evaporated before being mixed into the mixture causing residual citronellic acid that has not reacted with methanol. Methanol belongs to a class of alcoholic compounds having the shortest bonding chain, so that methanol is highly volatile.

4. CONCLUSION

Fischer esterification reactions between methanol and citronellic acid from oxidation product of citronellal has been successfully performed and obtained a methyl citronellate compound in the form of a brownish yellow liquid and smelling fragrant. The result of methyl citronellate from esterification product characterization by using TLC method, IR spectroscopy, and GC-MS showed that the methyl citronellate has a purity of 17 % and a yield of 13.76%.

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