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Synthesis of *l*-Methyl Acetic by Esterification *l*-Menthol and Acetic Anhydride with Variation of Time

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***Abstract** : l-methyl acetic is an ester with specific aroma that synthesized by reaction of l-menthol and acetic anhydride and useful in fragrance industry. This paper reports influenced variation of time reaction toward ester product and characteristics l- methyl acetic based on TLC, FTIR, GC and GC-MS. Reaction using l-menthol, acetic anhydride and catalyst H_2SO_4 98 % in diethyl ether solvent at temperature 60 °C with variation of time reaction (45, 60, 75, 90, 105 minutes). The result of research is variation of time influence product with highest yield 88,43 % for 90 minutes. Monitoring TLC achived $R_{f\ of}$ 0,82; analysis by FTIR achived specific wave number ester 1736,96 cm^{-1}; analysis by GC achived $t_{r\ of}$ 14,82 minutes and analysis by GC-MS achived $t_{r\ was}$ 16,13 minutes with base peak m/z which was 95.*

***Keywords:** esterification, l-methyl acetic, synthesis, variation of time.*

INTRODUCTION

Menthol is a major component in peppermint oil that can be produced from the distillation of leaves *Mentha x pipertits* (Raharjo, 2013), with a distinctive aroma of peppermint and give effect to the taste. *l*-menthol compounds included monocyclic monoterpenes class (Moon, 2004) with the chemical formula $C_{10}H_{20}O$ (Stolle and Hopf, 2009). Conversation *l*-menthol to ester can be form by reaction using acetic anhydride by esterification with sulfate acid as catalyst (Sastrohamidjojo, 2004). This reaction known as esterification Fischer (Carey, 2000).

Chasana research (2014), gained influence ratio mole from *l*- menthol: acetic anhydride (2:1) with the highest yield *l*-methyl acetic 28,28 % at temperature 60 °C for 60 minutes, but have not obtained information influence variation of time between *l*-menthol and acetic anhydride in esterification reaction to yield *l*-methyl acetic. So, in this study will reaction with variation of time for 45, 60, 75, 90, 105 minutes (Hikmah dan Zuliyana, 2010).

Variation of time provide information the influence the variation of time to yield of an ester to be obtained. Theoretically, increasing reaction time at Fischer esterification can increase the amount of product formed, this is caused by the increase in the intensity of collision between the reactants in the form of products (Fatmawati and Shakti, 2013).

RESEARCH METHODS

Materials and Tools

The tools used are refluxed with funnel (250 mL), 3-neck flask, chamber elucidation, thermometer, separating funnel 250 mL, vacuum pump, hot plate, watch glass, vaporizer cup, oven, mortar, funnel glass, stir bar, spatula, drop pipette, measuring pipette 10 mL, flask 100 mL, flask 25 mL, capillary tube, pycnometer 2 mL, measuring pipette 5 mL, beaker glass 250 mL and 500 mL, universal pH paper, TLC plate GF_{254}, tube vial, Atago Hand Refractometer, Chromatography Gas-Mass Spectroscopy (GC-MS) Aglient 6980N Network GC System, Chromatography Gas HP 5890 and FTIR Varian 1000 Scimitar Series.

The materials used are *l*-menthol, acetic anhydride, diethyl ether 99,5 %, sulfate acid 98 %, ethanol 95 %, distilled water, sodium bicarbonate, magnesium sulfate heptahydrate, acetic ethyl, methanol and nitrogen gas (N_2).

Procedure

Synthesis l-methyl Acetic

A set of tools reflux prepared and assembled. *l*-menthol then weighed as much as 31.25 g (0,2 mole). Then put in a 3- neck flask which was equipped with a magnetic stirrer, condenser and heating. Further added diethyl ether solvents as 10.38 mL (0,1 mole) in the 3 -neck flask and added as much as 9.45 mL of acetic anhydride (0,1 mole) drop by drop. Then the catalyst was added H_2- SO_4 98 % of 0.5 mL (0,1 mole) are per drop. Refluxed with variation of time :45; 60; 75; 90 and 105 minutes.

Monitoring Synthesis Mixture by TLC

Activation of the TLC plate silica GF_{254} use the oven for 20 minutes at 100 ° C. The next *l*-menthol and *l*-methyl acetic spotted at a distance of 1,0 cm from the bottom edge of the TLC plate and eluted using a capillary tube to a distance of 8.5 cm. Eluent used is n-hexane and ethyl acetate in a ratio of 9:1 Then the plate is dried and sprayed with a solution of 5 % H_2SO_4 in methanol. After the plates dry and then heated on a hotplate to show two pieces of brownish yellow stains on the plate. R_f its calculated value and compared with R_f *l*-menthol 0,40 (Pelter, et al., 2008) and *l*-methyl acetic suspected to have R_f 0,80 to 0,83 (Chasana, et al., 2014).

Separation Synthesis Mixed Result

The results of the synthesis mixture is put into separating funnel 250 mL. pH synthesized checked using universal pH paper. $NaHCO_3$ 5 % added in solution until pH up to pH distilled water (pH = 5). Then the mixture was shaken and allowed for 5 minutes until the organic phase and aqueous phase separate apparent. Organic phase containing a mixture of compounds comprising ester compound *l*-methyl acetic, *l*-menthol and solvent diethyl ether while the water phase is composed of neutral salts. The organic phase is collected in glass beaker 250 mL and added Mg_2SO_4 anhydrous. Furthermore, the organic phase is separated from $MgSO_4$ anhydrous by decanted carefully and slowly then accommodated in the tube vial. Nitrogen gas flowed on the surface and the bottom of the tube vial, weighed to constant weight. Having obtained a constant weight, closed tube vial using aluminum foil wrapped up tightly and stored in freezer.

Characterization of Physical Properties Mixed Result Synthesis

Characteristic of physical properties of the mixture of compounds synthesized (aroma and color). Determination of density performed by weighing as much as 2 mL of compounds synthesized using 2 mL pycnometer. Measured temperature of mixture synthesis result using a thermometer. The density value is calculated using the formula:

$$\rho = \rho' + k\,(T-T') \qquad (1)$$

The formula consists of p as density at T (°C), ρ' as density at T'(°C), k is correction factor and T is temperature mixture synthesis

Determination refractive index of compound synthesized were determined by Atago Hand Refractometer. Before the measurement are made, cleaned first the tool refractometer with 95% ethanol and then calibrated using distilled water. Subsequently, the sample was dropped on the prism 2 drops. The reading of the refractive index of samples was made during light-dark boundary of the line right at the intersection of the prism. Refractive index values calculated by the formula:

$$n = n' + k\,(T-T') \qquad (2)$$

The formula consists of n as refractive index at T (°C), n' as refractive index at T'(°C), k as correction factor and T as temperature mixture synthesis

Characterization by FTIR

l-menthol, acetic anhydride, and *l*-methyl acetic dropped into the scouring KBr pellet. Furthermore KBr pellet is placed in the cell holder through which the light beam and made its IR spectrum at wave number range 4000 - 400 cm^{-1}.

Characterization by GC

A total of 0.01 mL of *l*-menthol and *l*-methyl acetic injected into the inlet using syiringe GC HP 5890 instrument with temperature column and detector 250°C, gas flow rate of 2 mL/min, FID detector. The data obtained in the form of a chromatogram. % Peak area is used to determine the ratio of constituent compounds synthesized by the following equation 3.

$$\%\ \text{Rasio} = \frac{\%\ area\ menthyl\ acetic}{\%\ area\ compounds}\,100\ \% \qquad (3)$$

While the mass of *l*-methyl acetic research result obtained using the equation 4.

$$Massa\ l - \text{methyl acetic} = \frac{\%\ area\ menthyl\ acetic}{\%\ area\ compounds}\,m \qquad (4)$$

Furthermore, the yield of the compound *l*-methyl acetic research results obtained using the following equation 5.

$$Yield\ of\ \ l - \text{methyl acetic} = \frac{mass\ menthyl\ acetic}{mass\ compounds} X100\% \qquad (5)$$

Characterization by GC-MS

A total of 0,01 mL of *l*-menthol and *l*-methyl acetic using syringe injected into the GC-MS instrument inlet Aglient 6980N Network GC System with detector temperature at 300 °C , gas flow rate of 1,3 mL/min, detector Aglient 5973 inert MSD, Data from instrument such as mass spectra GC-MS, further interpretation of spectral data and comparing the mass spectra of *l*-menthol and *l*- methyl acetic with the standards of library Willey version 7.0.

RESULT AND DISCUSSION

Results obtained by esterification of the compound in the form of a yellow liquid and a distinctive smell of mint with the results of the monitoring TLC chromatogram obtained in the form of two brownish yellow stains with a stain I Rf = 0,41; while Rf stain II = 0,82 allegedly was Rf product. Characterization of physical properties obtained density of 1,1055 g/ml and the refractive index of 1,4426. Characterization of the results of the synthesis mixture is done by FTI, GC, and GC-MS. IR spectral data indicate that the ester group C = O stretching vibration at wavenumber 1736,96 cm^{-1}, C-O stretching vibration at wavenumber 1245,82 cm^{-1}. Besides the OH stretching vibration at wave number 3454,03 cm^{-1} and C-O stretching vibration of secondary alcohols at wave number 1023,32 cm^{-1} shows that the results of the synthesis mixture still contains *l*-menthol.

Analysis by GC shows have been formed compound *l*-methyl acetic. Analysis of the result of the synthesis mixture with chromatogram obtained GC 2 peaks, peak I with t_r = 11,71 minutes allegedly is *l*-menthol while peak II with t_r= 14,82 minutes is suspected *l*-methyl acetic, the compound had t_r longer than *l*- menthol is because it is nonpolar making it retained on the column . The following analysis of the data presented by GC against the constituent compounds synthesized as in Table 1.

Tabel 1. Yield (%) of *l*-methyl acetic

Time reaction (minute)	Peak I	Peak II	Peak III	Yield *l*-methyl
	% Area			
45	8,41	63,34	23,17	33,28
60	9,06	56,70	32,02	47,37
75	4,99	60,30	32,78	49,04
90	**6,32**	**30,45**	**60,31**	**88,43**
105	4,94	66,42	28,65	33,49

Based the yield results in Table 1, show that the highest yield was obtained at reaction time 90 minutes which is 88.43%. This shows that with increasing reaction time given will increase the yield of the synthesis product, but with a decrease in the yield explain that if a reactant which have reacted has reached the optimum time to collide then the extension reaction time will not yield more (Ozgul and Turkey, 2002 in : Widyawati, 2007 in Kasim, 2012). Then, the highest yield results is analyzed using GC-MS. GC-MS analysis of the obtained two peaks, peak I with t_r = 13.30 minutes suspected *l*-menthol produce fragment ion peak at m/z = 29, 41, 55, 71, 81, 95, 109, 123, 138, 147, 155, 191, 207, 281.

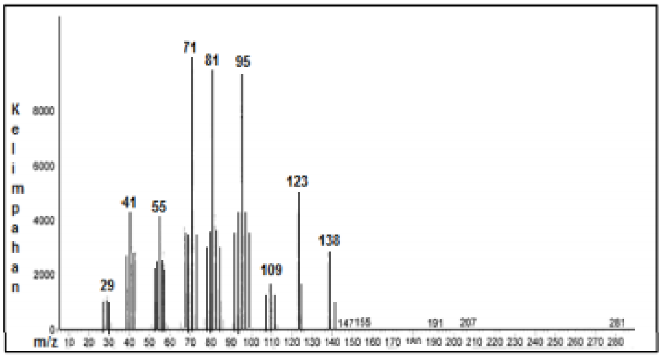

Figure 1. Spectra mass l-menthol

The secondary alcohol, the peak was observed due to release of H atom shown in Figure 2.

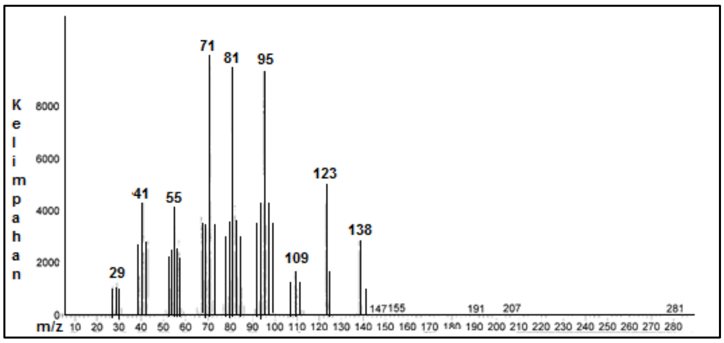

Figure 2. Release of H atom on secondary alcohol (Silverstein, dkk., 2005).

While t_r = 16,13 minutes assumed *l*-methyl acetic resulted in fragment ion peak at m/z = 29, 37, 43, 55, 61, 67, 73, 81, 87, 95, 103, 109, 115, 123, 138, 147, 155, 165, 183, 207.

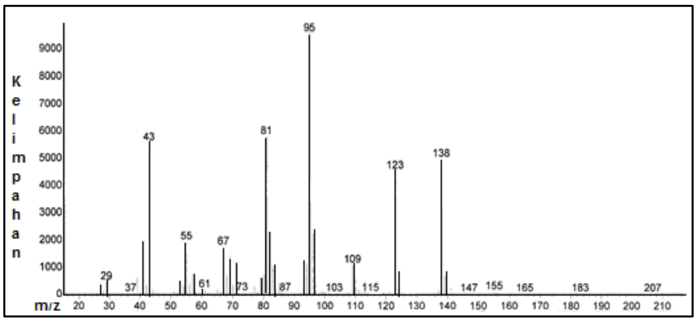

Figure 3. Spectra mass *l*-methyl acetic (90 minutes)

Fragment with m/z = 198 is ion molecule of *l*-methyl acetic with chemical formula $C_{12}H_{22}O_2$ does not appear. Because ester with spesific alcohol dominant easily remove acetic acid so molecular ion peak not detectable (Silverstein, et. al 2005).

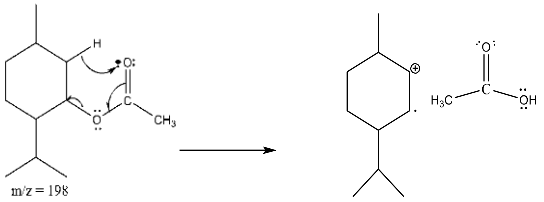

Figure 4. Rearrangement Mc Lafferty (Silverstein, et al., 2005).

While the base peak obtained m/z = 95 shown in Figure 5.

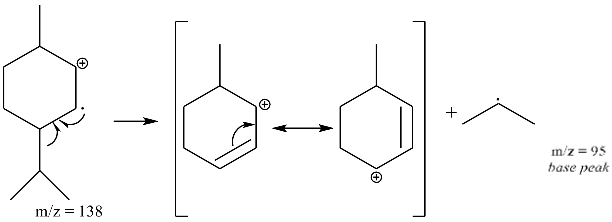

Figure 5. Base peak m/z = 95

Besides the release of atom O at position α is shown in Figure 6 with m/z = 43 obtained result that are spesific termination ester.

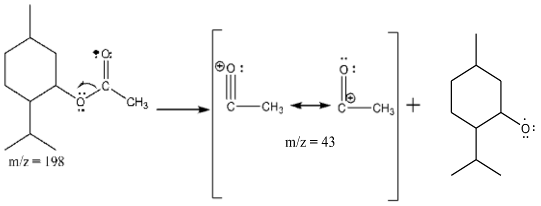

Figure 6. Leaving on α position

CONCLUSION

Variation of time influence yield of *l*-methyl acetic 88,43% with optimum time is 90 minutes and characterization of the product *l*- methyl acetic by monitoring TLC result obtained Rf which was0,41 is *l*- menthol and Rf which was 0,82 is *l*-methyl acetic. FTIR results with typical absorption of functional groups C = O and C-O ester at wave number 1736,96 cm^{-1} and 1245,82 cm-^{1}. Results chromatogram GC with a value t_r which was 14,82 minutes is *l*-methyl acetic. GC-MS results with t_r which was 16,13 minutes is *l*-methyl acetic.

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