THE EFFORT TO IMPROVE THE ECONOMIC VALUE OF PATCHOULI OIL: THE CONTROLLED ESTERIFICATION AT PRODUCTION OF THE AROMA COMPOUNDS BASE ON PATCHOULI OIL

RURINI RETNOWATI, WARSITO DAN BAMBANG POERWADI
MIPA Faculty, Brawijaya University, Malang
Jl. Veteran No. 1 Malang 65145
E-mail: rurini_retnowati@yahoo.com

ABSTRACT

Patchouli oil is an excellent of the Indonesian essential oil, because 45% of essential oil government-reserve is gained from it. Patchouli oil is commonly used in soap industrial, hair tonic, mouthwash, and high quality perfume. In the utilizing, patchouli oil is mixed with other essential oil, such as: clove oil, rose oil, and vetiver oil; since the fixative nature with flavor substance could chain the other essential oil. The fixative nature and the odor resistance come from the tertier alcohol substance, e.i.: patchoulic alcohol as its main component. Although it has long odor resistance, as an aroma substance, the odor of patchouli oil has less strong. As the base character of aroma substances determined by ester component compiler, so it is interesting to study the esterification reaction controlling the amount of ester product. In this research, patchouli oil was converted into the ester substance by esterification reaction using anhydride acid and $ZnCl_2$ catalyst. The esterification was optimized to various concentration of $ZnCl_2$ catalyst from 1–5% and to obtained the most preferred ester dan patchoulic alcohol ratio. Characterization of trade patchouli oil and the product of esterification were conducted based on determining the physical nature, such as: density and refraction index, and also the patchouli oil component's profile from chromatogram and mass spectrum resulted from GC and GC-MS analysis. To know most preferred ester and pachoulic alcohol ratio, using hedonic test with 25 panelists was conducted. The research resulted that the esterification reaction of patchouli oil using anhydride acid could be done by using $ZnCl_2$ catalyst. Characterization result using GC indicated that the component's profile change under esterification condition; while characterization result using GC-MS showed the existence of patchoulic acetate substance. Variation of anhydride acid composition affected the ratio profile of patchoulic acetate and patchoulic alcohol. Hedonic test results showed that panelists'most preferred ratio of patchoulic acetate and patchoulic alcohol is 0.7934.

Key words: *patchouli oil, patchoulic alcohol, $ZnCl_2$, flavor*

INTRODUCTION

Patchouli oil is an excellent essential oil of among this oils yielded in Indonesia. In this time its oil is exported by Indonesia reach 700–1,500 ton weight and yield government-reserve equal to 14–30 million of American dollars. Every year more than 45% of government-reserve yielded from its essential oil. Indonesia represent producer of the highest patchouli oil in the world and it able to export 90% world requirement of patchouli oil.

Though the patchouli oil has an auspicious prospect for the domestic and international market, but the various problem often founded by producer for example: the low of productivity, the various of quality, the continuity of raw material supplying and the fluctuative of price. One of the nature of patchouli oil, it is typically has high fixation ability, so that in its use, the patchouli oil is of tentimes mixed with other essential oil (Kardinan, 2005). Patchouli oil represent perfume compiler (aroma compound) very strong and it is generally mixed with a sandalwood, neroli, and lavender oil (Anonymous, 2005). The patchouli oil aroma has long odor resistance, it still be odorous until its oil evaporates. This aroma is categorized as base note aroma (Kardinan, 2005). Although it has long odor resistance, as an aroma substance, the odor of patchouli oil has less strong.

The fixative nature and the odor resistance of patchouli oil come from the tertiary alcohol compound, named: patchouli alcohol. This compound is the main component (45,84%) of the patchouli oil (Sastrohamidjoyo, 2004). According to Trifillief (1980), the component compiler of patchouli oil giving aroma is norpathoulenol compound which its amount a few.

The base character of the aroma compound (perfume) determined by the ester compound compiler. The strongness of aroma of alcohol compound can be increased by converting its compound to ester through esterification. One of the methods and the procedures to convert patchouli oil becoming strong aroma compound through estetrification reaction is done by using anhydride acid. This reaction represent most suited for converting alcohol with high steric hindrance. This esterification conducted by adding anhydride acid and $ZnCl_2$ as an catalyst. The solid of $ZnCl_2$ catalyst, operationally, is easier separated from the mixture reaction.

Considering that the character of aroma determined by the existence of ester compound in patchouli oil, it is interesting to study the esterification reaction controlling the amount of ester product, in order to the base aroma of patchouli oil do not disappear and also the ratio of the fixative nature and the aroma compound is fullfiled.

METHODS

The main material of the research was commercial patchouli oil from entreprize industry. Chemicals used in this research are categorized as pro analyse degree, except mentioned peculiarly, were: diethyl ether, magnesium sulphate hepta hydrate ($MgSO_4.7\ H_2O$), sodium bicarbonate ($NaHCO_3$), acetic acid anhydride, aquadest, nitrogen, hydrogen and oxygen gas.

Determination of the component compiler profile of patchouli oil based on the chromatograms and mass spectra resulted from Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS) analysis. Esterification of characterized patchouli oil used acetic acid anhydride according to Olver method (Olver, 1980). The reaction was carried out by using the composition of amount of mole of patchouli alcohol and acetic acid anhydride = 1 : 1 and the variations of the concentration of $ZnCl_2$ catalyst were 1–5%. Esterification of characterized patchouli oil was conducted by varying the composition of mole of acetic acid anhydride and patchouli alcohol = 1 : 0.25; 1 : 0.5; 1 : 0.75; 1 : 1 and 1 : 2 at% optimum $ZnCl_2$ catalyst.

Determination of the component compiler profile of aroma compound from the esterification reaction of patchouli oil based on the chromatograms and mass spectra resulted from Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS) analysis. Hedonic test was done base on the favorite level of the panelist to the most aroma of patchouli oil and the patchouli oil resulted esterification.

RESULTS

The profile of components compiler of patchouli oil were determined from chromatograms analysis by GC (HP 8960) using column of Carbowax 20 M. The chromatogram was serverd at Figure1, and the Total Ionic Chromatogram (TIC) of patchouli oil by GC-MS (Shimadzu GC-174, MS QP-5000) analysis using column of Rtx – 5 MS (methyl and diphenyl polyxiloxan) was presented at Figure 2.

The chromatogram analysis by GC used column of Carbowax 20 M showed four main components compiler of patchouli oil. The retention times of

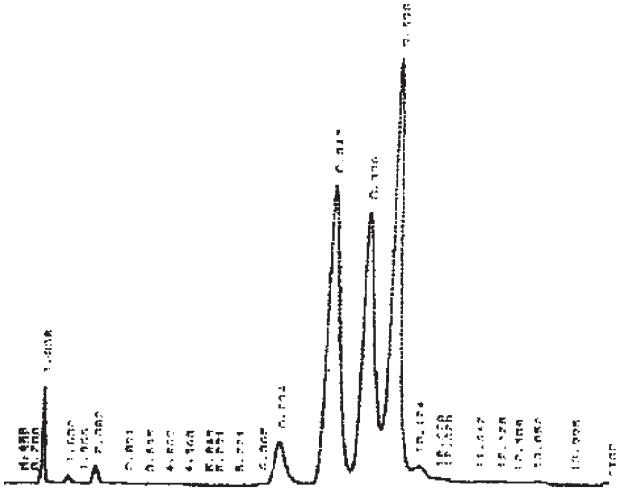

Figure 1. The Chromatogram of patchouli oil by GC analysis used Carbowax 20 M Column

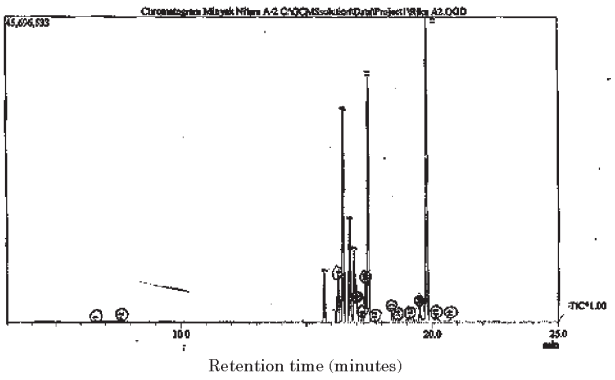

Figure 2. Total Ionic Chromatogram (TIC) of patchouli oil analysis by GC-MS used Rtx – MS5 column

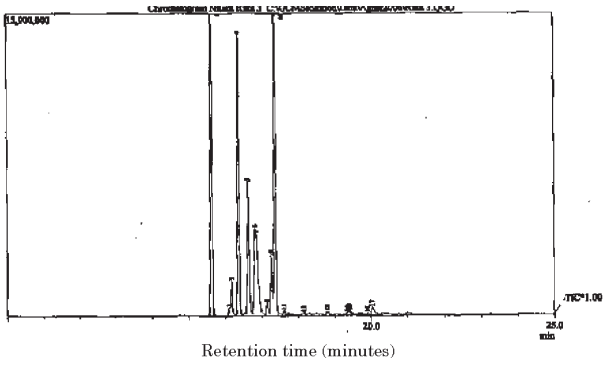

Figure 3. Total Ionic Chromatogram (TIC) of esterification result of patchouli oil analysis by GC-MS used Rtx – MS5 column

these components were: 6.794; 8.347; 8.896; and 9.508 minutes. Further analysis of the TIC by GC-MS used column of Rtx MS5, performed six components compiler of patchouli oil and gave the retention times of 15.708; 16.463; 16.728; 16.913; 17.470; 19.788 minutes. The structure character of each component was determined by the MS QP-5000 mass spectrum. The pattern of fragmentation in the spectrum showed that it similar with the spectrum of six compounds as in the mass spectrum of WILEY7 library, named: α-gurjunene, α-guayene, seychelene, α-patchoulene, δ-guayene and patchouli alcohol.

Esterification reaction of patchouli oil used acetic acid anhydride according to Olver method, was conducted by using the composition of amount of mole of patchouli alcohol and acetic acid anhydride = 1 : 1 and the variations of the concentration of $ZnCl_2$ catalyst were 1–5%. Futhermore, the physical nature of the results, likely: odor, color, refraction index and density were determined. The esterification results showed that the difference existence of odor, colour and physical nature. The odor of patchouli oil resulted from esterification was stronger than patchouli oil. The colour of patchouli oil showed yellow in the beginning then turned into brown color, and so do the refracton index and the density also change.

The chromatogram analysis by GC used column of Carbowax 20 M showed four main components compiler of patchouli oil resulted from esterification reaction of patchouli oil by using acetic acid anhydride and the composition of mole of patchouli alcohol: acetic acid anhydride = 1 : 1, and % $ZnCl_2$ = 3.5%. The retention times of the four components were: 6.504; 7.995; 8656 and 9.547 minutes. Further analysis of the TIC by GC-MS used column of Rtx MS5 was presented at Figure 3, performed six components compiler of patchouli oil resulted from esterification reaction of patchouli oil by using acetic acid anhydride. The composition of mole of patchouli alcohol: acetic acid anhydride = 1:1, and % $ZnCl_2$ = 3.5%. and gave the retention times of 15.632; 16.369; 16.634; 16.820 and 17.374 minutes.

GC analysis results showed the differences profile of components and composition compiler of patchouli oil and patchouli oil resulted from esterification reaction. The retention time of component of patchouli oil at 6.794 minute has% area = 4.86%. After it was esterification reaction treated, the % area of the compound had the retention time at 6,504 minute = 28.48%.

Further analysis of the TIC by GC-MS used column of Rtx MS5 was presented at Figure 3, performed five components compiler of patchouli oil resulted from esterification reaction of patchouli oil by using acetic acid anhydride with comparison of mole of patchouli alcohol: acetic acid anhydride= 1 : 1, and % $ZnCl_2$ = 3.5%, and gave the retention times of 15.632; 16.369; 16.634; 16.820 and 17.374 minutes. The structure character of each component was determined by the MS QP-5000 mass spectrum. The pattern of fragmentation in the spectrum showed that it similar with the spectrum of five compounds in the WILEY7 library,

named: β-patchoulene, α-guayene, seychelene, α-patchoulene and δ-guayene.

Based on analysis of the mass spectrum patschouli oil resulted from esterification known that the mass spectrum of patchouli alcohol compound (retention time at 19.788 minute) not emerge at the chromatogram, but the new compound, named ß- patchoulena emerged at the retention time of 15,632 minute with high intensity enough (% area = 26,32%). Therefore, it is reasonable to assume that the mass spectrum of ß-patchoulena was possibility of representing fragment from result of fragmentation of patchoulic acetate as the result of esterification of patchouli alcohol.

Considering of the graph of the relationship of the ratio of % area of patchouli alcohol and patchoulic acetate, using various of concentration (%) catalyst, the % optimum catalyst was obtained at 3.5% $ZnCl_2$. Therefore, the mole patchouli and patchoulic acetate alcohol composition = 1 : 1 was used in this reaction. The graph was presented at Figure 4.

Based on the result of the esterification reaction used reactant ratio = 1 : 1, and the mole patchouli alcohol: acetic acid anhydride composition = 1 : 1 showed that the alcohol and ester ratio was optimum ratio in this reaction.

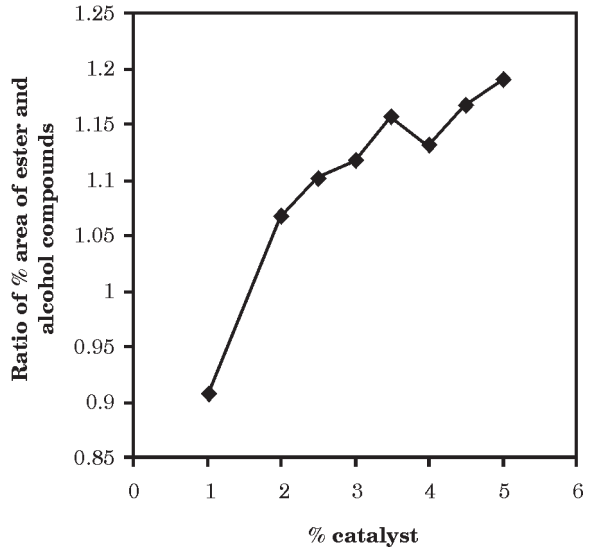

Figure 4. The relationship of ratio% area of patchouli acetate: patchouli alcohol with% catalyst

The test based on the most preferred level of the panelist to aroma of patchouli oil and it of esterification result**,** using 25 panelist was conducted. The panelist used is the user of aroma and aroma formulator compound. The data obtained was tested its diversity by using analysis of Random Device Group. The hedonic test results showed that the aroma sample resulted from esteterification with using mole of patchouli alcohol: acetic acid anhydride composition = 1 : 0.25 and the ratio of patchouli of acetate and patchouli alohol = 0.7934 is the most preferred aroma by the panelist, but statistically, the level was not showed significance difference with the other sample.

CONCLUSION

The research resulted that the esterification reaction of patchouli oil using cetic acid anhydride could be done by using $ZnCl_2$ catalyst. The characterization result using GC indicated that the component's profile change under esterification condition, while the characterization results using GC-MS showed the existence of pathoulic acetate substance. The existence of patchoulic acetate as the result component represents a new compound compoler.

REFERENCES

Anonymous, 2004. *Patchouli Essential Oil*, http://www.craftybubbles.com/ patchouli.htm. accessed on the date of 17 April 2006.

Anonymous, 2005. *Esterification*, http://en.wikipedia.org/wiki/Esterification. accessed on the date of 15 April 2006.

Anonymous, 2005. Zinc Chloride, http://www.jtbaker.com/msds/ englishhtml/ z2280.htm accessed on the date of 31 October 2006.

Kardinan, A., 2005. *Crop of Producer of Esstential Oil,* First Edition. Yogyakarta: *Agro of Book Media*.

Dichoso W.C., 2000. *Plant of Species of With Essential Oil For Perfume Production*. Research Information Series on Ecosystems, 12(1): 1–16.

Sastrohamidjoyo, H., 2004. *Chemistry of Essential Oil*, First Edition. Yogyakarta: Gadjah Mada University Press.

Trifillief, E., 1980. *Isolation of the Postulted Precursor of Norpachoulenol in patchouli Leaves. Phytochemistry*: 19, 2464.