



Synthesis Study of Precursor Mixture of verdantiol, aurantiol and lyrame Schiff Base and Its Characterization Using GC-MS

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ABSTRACT

A mixture of verdantiol, aurantiol, and lyrame based schiff base precursors has been prepared by a simple condensation method. The mixture product has been characterized by gas chromatography and mass spectrophotometer (GC-MS). The color of product has been compared with the standard of the mentioned schiff base which was confirmed as yellow colored solution. The lyrame was not detected and the verdantiol showed as the most obtained product.

Keywords: Schiff base, Mixture, GC-MS, Fragrance.

INTRODUCTION

Perfume is one of chemical products which is used in daily life by men and women.¹ In its production process, raw materials such as fragrances are needed.^{2,3} Fragrances are pure aroma oil or extracted oil from aroma compound which has not been added by alcohol or other chemicals.⁴ Therefore, the smell of these compounds is very strong and the form is like an oil.⁴ Raw material of this natural aroma depends on the result of natural products and weather condition. Consequently, many perfume producers have been developing synthetic aroma compound which can be easily produced continuously.⁵

Synthetic raw material are is used in the production of aroma compounds is Schiff base. Schiff base is an aldehyde- or ketone-like compound in which the carbonyl group is replaced by an azomethine or imine group.⁶⁻⁸ The advantage of using schiff base is its specific aroma characteristic and long-lasting, hence it can improve the quality of aroma compound.^{9,10} There are several types of schiff bases such as lilyantine, jasmea, verdantiol, aurantiol, lyrame dan cyclantine.¹¹ Verdantiol, aurantiol and lyrame are a popular schiff bases which are used in the production of flower aroma compounds.¹²

In order to produce verdantiol, aurantiol



and lyrame Schiff base, methyl anthranilate is mixed with lilyall, hydroxycitronellal, and lyral, respectively.¹³ In the previous studies, our group has synthesized lyrame Schiff base using a simple condensation method at the temperature of 110°C for 30 min and has characterized the product using GC-MS.¹⁴ Our group has also observed the effect of synthesis time to obtain aurantiol Schiff base and we found that the best time was around 30 to 60 minute.¹⁵ In the present study, we combined the precursor of mentioned three schiff bases to produce schiff base and observed the product using GC-MS. We tried to find out which schiff base would be highly produced.

METHODS

Synthesis of Schiff Base Mixture

Methyl anthranilate solution, lilyall solution, lyral solution, hydroxycitronellal solution and ethanol 99% are used as the precursors of schiff bases. The mixture solution was heated and stirred at temperature about $110 \pm 5^\circ\text{C}$ for 30 minutes.

Color Test of Schiff Base Mixture

The product solution is poured into a tube that is 1.3 cm in diameter and 10 cm high to a specified limit of ± 1 cm. Color observation is carried out by the panelist from the front of the tube and parallel to the eye. The picture is taken in a place that has enough light, avoids the reflection of light, and the base is white.

Characterization using GC-MS

Schiff base confirmation using gas chromatography mass spectrometer (GC-MS) Agilent 5975C. Schiff base confirmation was carried out by interpreting based on MS data. Then, fragmentation pattern was made to explain the reaction mechanism. The analysis on condition of GC-MS could be seen at Table 1 below.

Table 1: GC-MS Analysis Condition¹⁴

	Information
Column	Capillary Column : HP-5 (5% Phenyl Methyl Siloxane 325°C)
Carrier Gas	Helium
Carrier Gas Pressure	7,0531 psi
Injection Technique	Split
Injector Temperature	100°C
Injection Volume	0,2 L
Split Ratio	80:01:00
Temperature Program (Column)	
Initial Temperature	100°C hold for 5 min
Temperature rate	15°C per min
Final Temperature	250°C hold for 5 min

RESULTS AND DISCUSSION

The obtained product was displayed in Fig. 1 which also exhibited the color of the standard of verdantiol, aurantiol and lyrame schiff base as a comparison. It is noted that the obtained product showed the weakest color among the others.

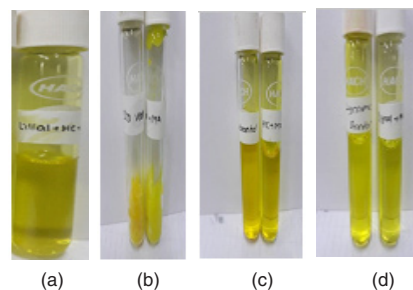


Fig. 1. Color comparison of (a) mixture, (b) verdantiol standard, (c) aurantiol standard, and (d) lyrame standard

The three Schiff bases pass through the reaction of crossed aldol condensation. The reaction of crossed aldol condensation will occur when an aldehyde or ketone without α -hydrogen is mixed with aldehyde which has α -hydrogen. The reaction between aldehyde with a primary amine will produce an imine as its product that is a compound having a $\text{C}=\text{N}$ group.¹⁶

Confirmation of the schiff base formation was carried out by GC-MS. The GC result of the mixture is shown in Table 2.

Table 2: The GC result of mixture

Retention Time (Min)	Compounds	Competition (%)	Molecular Formula
8.679	Hydroxycitronellal	14.99	$\text{C}_{10}\text{H}_{20}\text{O}_2$
9.458	Methyl Anthranilate	4.45	$\text{C}_8\text{H}_9\text{NO}_2$
11.4	Lilyall	32.64	$\text{C}_{14}\text{H}_{20}\text{O}$
12.512	Lyral	5.06	$\text{C}_{13}\text{H}_{22}\text{O}_2$
12.571	Lyral	17.98	$\text{C}_{13}\text{H}_{22}\text{O}_2$
16.628	Verdantiol	5.8	$\text{C}_{22}\text{H}_{27}\text{NO}_2$
20.103	Verdantiol	2.42	$\text{C}_{22}\text{H}_{27}\text{NO}_2$
23.696	Verdantiol	6.18	$\text{C}_{22}\text{H}_{27}\text{NO}_2$
16.916	Aurantiol	3	$\text{C}_{18}\text{H}_{27}\text{NO}_3$
16.981	Aurantiol	5.41	$\text{C}_{18}\text{H}_{27}\text{NO}_3$
18.137	Aurantiol	2.06	$\text{C}_{18}\text{H}_{27}\text{NO}_3$

The result indicated that there were only three verdantiol isomers and three aurantiol isomers formed as product. Based on the structure, there should be six verdantiol isomers and four aurantiol isomers obtained from the condensation reaction. This result might be caused by the competition

reaction where reactive isomers would be easily formed.

From Table 2, verdantiol was the most obtained schiff base because it has aromatic group in lilyall compound which attracts electrons.¹⁶ The aromatic group will affect the closest carbon atom to carbonyl becoming electron-poor so that α -hydrogen becomes more acid. Then, lilyall will be faster to react with amine group in methyl anthranilate which is a base. The competition reaction between mixed raw material with amine in methyl anthranilate caused the most acid aldehyde becoming more reactive to amine. Lyrame could not be detected due to lyral as its precursor was the weakest base among other evaluated compounds. The schiff base precursor mixture was analyzed using MS to confirm the compounds in the product as shown in Figure 2.

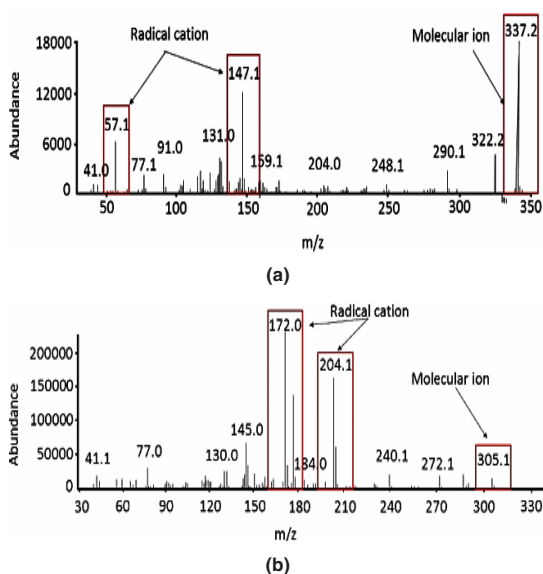


Fig. 2. Mass spectra of (a) verdantiol and (b) aurantiol in the schiff base mixture

In Fig. 2 (a), molecular ion at m/z 337.2 is equal to the molecular weight of verdantiol schiff base of 337.47 g/mol. Furthermore, the fragmentation result fragmentation obtained ion at m/z 147 and 57 as seen in Fig. 3 (a). Fig. 3 (b) showed molecular ion (M^+) of aurantiol schiff base (Methyl-N-3,7-dimethyl-7-hydroxyoctylidene anthranilate) at m/z 305.1 which is equal to the molecular weight of aurantiol schiff base of 305.42 g/mol. The highest peak at m/z 172.0 and the peak at m/z 204.1, m/z 287, m/z 272 are cation radicals as displayed in Figure 3 (b).

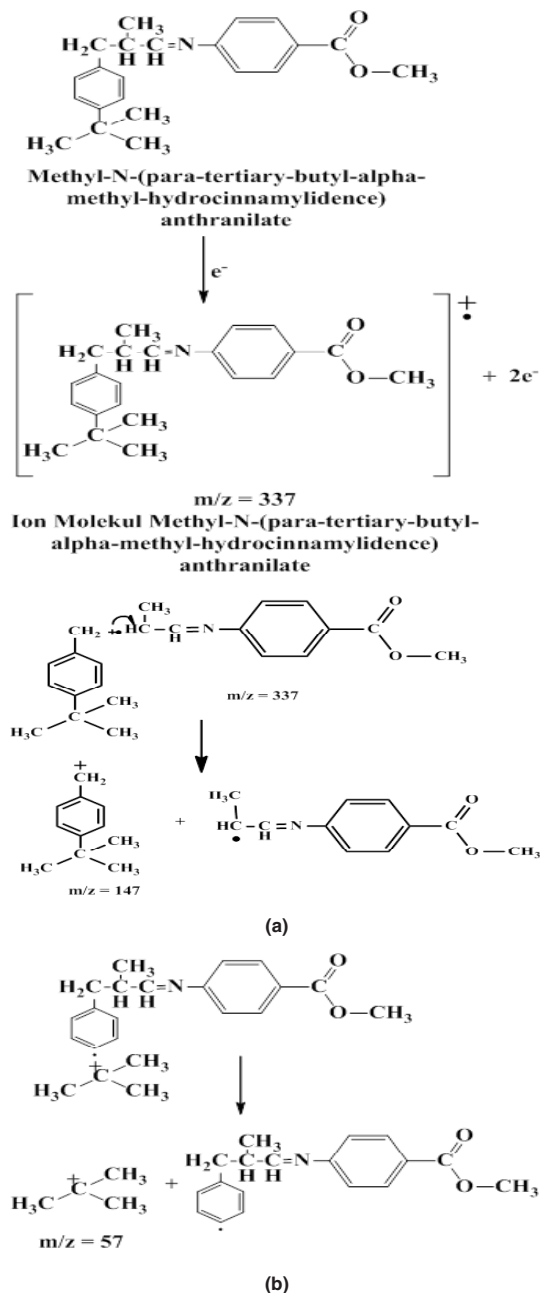


Fig. 3. Fragmentation of (a) verdantiol and (b) aurantiol

CONCLUSION

Based on the experiment results, schiff base precursor mixture had lighter yellow color than the standard of verdantiol, aurantiol and lyrame. The MS results showed that verdantiol as cyclic compound and aurantiol peaks at m/z 337.2 and 305.1, respectively. Verdantiol was the most obtained

product while lyrame was not detected due to the competition reaction.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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