SYNTHESIS AND CHARACTERIZATION OF CITRAL-METHYLANTHRANILATE SCHIFF BASE, RELATIONSHIP BETWEEN SYNTHESIS TIME AND SOME PHYSICAL PROPERTIES

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ABSTRACT

Citral-Methylantranilate Schiff base was synthesized by the reaction of citral and methylantranilate in simple condensation technique. The synthesis was carried out at temperature $(90 \pm 5)^\circ\text{C}$ and various synthesis times of 15 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, and 4 hours. Product of Citral-Methylantranilate Schiff base spreads color in bright red to black brown as the synthesis times increases. The results of the refractive index of synthesis time variation were 1.541 to 1.561. The values of density at various synthesis times were 1.017 to 1.042 g/mL. The results of the specific gravity of synthesis time variation were 1.026 to 1.050. Analysis with GC-MS was performed to prove that citral-methylantranilate was actually formed and resulted in the peaks at 18.023 and 19.123 minutes.

Keywords: Schiff Base, Citral-MethylAntranilate, Condensation, Citral, MethylAntranilate

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INTRODUCTION

In the past few years, synthesis of Schiff bases was a synthesis model that has attracted plentiful interest to study. Schiff bases known as imines are the class of compounds that consists of azomethine group. They are made in condensation of aldehydes or ketones with carbonyl compounds and were first synthesized by Hugo Schiff in 1864¹. Formerly, synthesis of Schiff bases was reported by Schiff which formed condensation of reaction between the amine group and active carbonyl group contains nitrogen and oxygen donor atoms². The synthesis condition of Schiff base was arranged under azeotropic distillation with the simultaneous removal of water¹.

Schiff bases are another important field of organic compounds. The variety of amine and carbonyl compounds in Schiff base can create the various Schiff bases. Schiff base has drawn considerable attention from the researcher due to its wide range of promising application as antimicrobial activity³, antibacterial⁴, anticancer⁵, antidepressant⁶, antioxidant and analgesic⁷. Several Schiff bases have been clearly inspected for the removal and extraction of metal ions^{8,9,10}. Zhao et al. reported the synthesis of Schiff base used super paramagnetic (Fe_3O_4) to remove Pb(II) and Cd(II) from solution⁸. Schiff base was also used by the fragrance industry because the characteristic was so evocative and can increase chemical stability and resilience of fragrance blends¹¹.

In this paper, the Schiff base was prepared by simple condensation method. According to Arctander (1969)¹², citral-methylantranilate Schiff base was made by the condensation reaction of citral and methylantranilate. It was prepared with the various synthesis times of condensation at 15 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, and 4 hours.

EXPERIMENTAL

Material and Methods

The methylantranilate solution, citral solution, aquadest, 95% ethanol, 99% ethanol, and dipropylene glycol were purchased from Merck.

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The equipment used in this research was GC-MS *Agilent 5975C inert MSD*, refractometer *Atago R-5000α*, hotplate stirrer *IKA C-MAG HS 7*, analytical balance *Denver Instrument TP-214* and analytical balance *ML-204*, cup glass 50 mL, alcohol thermometer, pycnometer 10 mL, vial, magnetic stirrer.

Synthesis of Citral-Methylantranilate Schiff Base

Briefly, 10 g citral-methylantranilate solution and 10 g methylantranilate solution were weighed and entered to beaker glass. The weighing process was carried out three times. The mixtures were heated and stirred on the hotplate stirrer for 15 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, and 4 hours ($90^{\circ}\text{C} \pm 5^{\circ}\text{C}$). The product solutions were saved at room temperature and tested after the Schiff base was left for 7 days.

Analysis by GC-MS

The product was weighed 0.1 g to the vial and diluted to 1 g in 99% ethanol than was measured with GC-MS. Confirmation of the molecular weight of *citral-methylantranilate* in the product was performed by fragmentation pattern making from the top of the mass spectrum of the product. The measurement was done on GC-MS instrument condition can be seen in Table-1.

Table-1: GC-MS Method for Schiff Base *Citral-Methylantranilate*

Condition	Information
Column	Capiler column (Semi Polar) : HP-5 5% <i>Phenyl Methyl Siloxan</i> 325 °C
	Long = 30 m; Internal diameter = 320 μm; Film coating thickness = 0,25 μm
Carrier gas	Helium
Carrier gas pressure	7,05 Psi
Detector	Mass spectrometer detector
Detektor	Spektrofotometer Massa
Injector temperature	100 °C
Injection volume	0,2 μL
Injection technique	Split
Split Ratio	80:1
Temperature program (column) :	
Initial temperature	100 °C, hold for 5 minutes
Temperature rate	15 °C/minute
Final temperature	250 °C, hold for 5 minutes
Interval	20 minutes

Color Test of Citral-MethylAnthranilate

The product solutions were observed by trained panellists. The color test was carried out by a minimum of three panelists. The product solutions were poured into a tube with a diameter of 1.3 cm and a height of 10 cm to a specified limit of ± 5 cm. Then the tube was given an identity with label paper. The color test was carried out from the product documented using the camera. The picture was taken in a place with enough light, avoiding the reflection of light, and a white base.

Odor Test of Citral-MethylAnthranilate

The product solutions were tested for odor descriptions by trained panelists. The odor descriptions test was carried out by a minimum of three panelists. Schiff base product was diluted to 50 % (v/v) in dipropylene glycol. Test paper was marked by name or number of the solution that was clearly tested, then dipped into the solution tested to 5 mm or up to 2 cm at the opposite end of the product code. The results of the odor test were written on the panelist form.

Measurement of Refractive Index on Products Using Refractometer

This product was measured using refractometer *Atago RX-5000α*. The temperature of refractometer was regulated at 20 °C. The product solutions were dripped over the prism surface until evenly distributed and

then closed. The result was analyzed by the relationship of value refractive index the product making on synthesis times variation 15 minutes, 30 minutes, 1 hour, 2hours, 3hours, and 4 hours.

Measurement Density and Spesific Gravity

The solution of the product was measured using pycnometer (10 mL) at room temperature. Pycnometer was cleared with 95 % ethanol and dried. Empty pycnometer was weighed and then aquadest was filled until full and weighed. The determination of the solution pycnometer was the same as that.

RESULTS AND DISCUSSION

Synthesis of Citral-Methylanthranilate

Citral-methylanthranilate was obtained by reacting citral and methylanthranilate with a simple condensation technique. This synthesis was carried out with various times of 15 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, and 4 hours, respectively. The results of citral-methylanthranilate with the various synthesis times appear in Fig.-1.

Fig.-1: Color Citral-Methylanthranilate Product with Various Synthesis Times: (a) 15 minutes, (b) 30 minutes, (c) 1 hour, (d) 2 hours, (e) 3 hours, (f) 4 hours

The colors of the obtained citral-methylanthranilate of Fig.-1 were bright red, red, dark red, dark brown, and black-brown, respectively. When the synthesis time rose from 15 minutes to 4 hours, the color changed from bright red to black brown. The color of citral-methylanthranilate was concentrated as the synthesis time go up. This color result is supported by the statement of Arctander (1969)¹² that the citral-methylanthranilate produced dark color. However, the color that is too dark should be avoided. It is not good to be used as a large number of fragrances in the interest of the industry¹³.

Citral-methylanthranilate was condensate at $(90 \pm 5) ^\circ\text{C}$. In addition to speed up the reaction, heating also serves to eliminate side products like water and to prevent the formation of a turbid citral-methylanthranilate that separated into two phases. Citral has double bond isomers that the Z-isomer is known as neral and E-isomers is known as geranial¹⁴. The citral-methylanthranilate formation reaction is as follows:

Scheme-1: Formation Reaction of Citral-Methylanthranilate

Fig.-2: GC-MS Chromatogram of Citral-Methylanthranilate with 3 hours Synthesis Time

An analysis with GC-MS was performed to prove that citral-methylanthranilate was actually formed (Fig.-2). Based on GC-MS chromatogram in Fig.-2, it illustrated the peaks of neral and geranial obtained from Citral and the peak of methylanthranilate, which shows the retention times at 8.077, 8.480, and 9.465 minutes respectively. Furthermore, in Fig.-2, it was seen that the citral-methylanthranilate obtains six peaks at the peaks 4, 5, 6, 7, 8, 9 with the % similarity above 90%. The appearance of the six peaks is the result of a reaction between citral (neral and geranial) with methylanthranilate which produces six different % areas and forms of compounds. The different % areas are affected by the structure of citral-methylanthranilate formed. Citral-methylanthranilate with % areas 0.76% and 1.46% still contain a hydroxyl group (-OH). The % areas of 6.09% and 2.37% are cis form of citral-methylanthranilate ((2E)-methyl 2-((Z)-3,7-dimethylocta-3,6-dienylideneamino)benzoate and (2E)-methyl 2-((E)-3,7-dimethylocta-2,6-dienylideneamino)benzoate). The % areas of 23.49% and 35.07% are trans form of citral-methylanthranilate (methyl 2-((Z)-3,7-dimethylocta-3,6-dienylideneamino)benzoate and methyl 2-((E)-3,7-dimethylocta-2,6-dienylideneamino)benzoate). Based on the % area results, citral-methylanthranilate

tends to obtain the trans form than the cis form. Liao (2015) found that the trans form has greater conjugation and more stable conformation than the cis form. The results of citral-methylanthranilate analysis with GC-MS at various synthesis times are as follows:

Table-2: Results of Citral-MethylAnthranilate Analysis with GC-MS

Synthesis Times	% Area – GC Yield		
	Citral	MethylAnthranilate	Citral-MethylAnthranilate
15 minutes	42.14	51.87	5.99
30 minutes	38.58	51.29	10.15
1 hour	28.64	45.18	26.17
2 hours	13.55	35.01	51.44
3 hours	4.91	25.84	69.24
4 hours	7.91	34.02	58.06

Table-2 shows the analysis of citral-methylanthranilate using GC-MS that gives % area of citral, methylanthranilate, and citral-methylanthranilate. The longer synthesis times of citral-methylanthranilate Schiff base, the smaller % area of citral and methylanthranilate. It is due to citral and methylanthranilate forming citral-methylanthranilate Schiff base, which supported with % area of citral-methylanthranilate being greater. Figure-3 shows clearly that the charts of citral and methylanthranilate decrease as the synthesis times go up while the Schiff base product increases.

Fig.-3: The Relationship between Citral-Methylanthranilate Yield and Synthesis Times

Odor Test of Citral-MethylAnthranilate

The odor test was carried out by six panelists. The odor test results are shown in Table-3. The results show the odor description have the same aroma between Schiff base citral-methylanthranilate at synthesis times 30 minutes, 1 hour and 2 hours lie in the aromas of attribute Orange Blossom, Floral, and Lemongrass. Schiff base odor characteristics are obtained from the Schiff base constituent structures themselves^{1,15}. The synthesis times for 3 and 4 hours give an additional aroma of attribute Neroli. This is due to the structure of the citral which is a terpenoid group leading an oxidation process which will be isomerized with water to formaldehyde, organic acid, and ketone which causes unwanted sharp odor¹³.

Table-3: Results of Citral-MethylAnthranilate Odor Test

Synthesis times	Odor
15 minutes	Citrus, sweet, orange blossom, lemongrass
30 minutes	Orange blossom, floral, lemongrass
1 hour	Orange blossom, floral, lemongrass

2 hours	Orange blossom, floral, lemongrass
3 hours	Orange blossom, floral, lemongrass, neroli
4 hours	Orange blossom, floral, lemongrass, neroli, sweet

Refractive Index, Density and Specific Gravity Test of Citral-MethylAnthranilate

Based on Table-4, it is known that the longer the heating process of the citral-methylanthranilate synthesis, the greater the density, refractive index, and specific gravity values. This is due to the forming citral-methylanthranilate causing the product quantities being increased so that the density, refractive index, and specific gravity get greater. the density, refractive index, and specific gravity values increase from 1.017 to 1.042 g/mL, 1.541 to 1.561, and 1.026 to 1.050 as the synthesis times increase, respectively. The refractive index values at the synthesis times of 1, 2, and 3 hours are not read by refractometer *Atago RX-5000a*. They are due to the range of refractometer about 1.327 – 1.580 so that the refractive index value that greater than 1.580 is not read.

Table-4: Density, Refractive Index, and Specific Gravity of Citral-Methylanthranilate at Various Synthesis Time

Synthesis time	Density (g/mL)	Refractive Index	Specific Gravity
15 minutes	1.017	1.541	1.019
30 minutes	1.021	1.550	1.023
1 hour	1.027	1.561	1.029
2 hours	1.040	-	1.042
3 hours	1.048	-	1.050
4 hours	1.042	-	1.044

CONCLUSION

Based on the results of this study, it can be concluded that the synthesis of citral-methylanthranilate with simple condensation technique has been successfully obtained with an optimum synthesis time of 1 hour to 2 hours. The longer synthesis time, it will produce citral-methylanthranilate products with darker colors and greater refractive index, density, and specific gravity. Therefore, this optimum synthesis time of 30 minutes to 1 hour can be used as a reference for the synthesis of citral-methylanthranilate on an industrial scale.

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REFERENCES

1. C. Irawan, S. Juhana, Hanafi, H. Rochaeni, M.Y. Fajri and R.P. Putri, *International Journal of Chemical Studies*, **5(5)**, 475 (2017), DOI:10.22271/chemi
2. B. Pooja, M. Lalit, G. Richa and P. Tanay, *Res. J. Chem. Environ*, **22(8)**, 19 (2018)
3. S.M. Anush, B. Vishalakashi, B. Kalluraya and N. Manju, *Int. J. Biol. Macromol.*, **119**, 446 (2018), DOI: 10.1016/j.ijbiomac.2018.07.129
4. G. Singh, J. Singh, A. Singh, J. Singh, M. Kumar, K. Gupta and S. Chhibber, *Journal of Organometallic Chemistry*, **871**, 21 (2018), DOI:10.1016/j.jorganchem.2018.06.024
5. Z. Saedi, E. Hoveizi, M. Roushani, S. Massahi, M. Haidan and K. Salehi, *J. Mol. Struct.*, **1176**, 207 (2018), DOI:10.1016/j.molstruc.2018.08.072
6. A.B. Thomas, R.K. Nanda, L.P. Kothapalli and S.C. Hamane, *Arab. J. Chem.*, **9**, S79 (2016), DOI:10.1016/j.arabjc.2011.02.015
7. K. Karrouchi, L. Chemlal, J. Taoufik, Y. Cherrah, S. Radi, M. E. A. Faouzi and M. Ansar, *Ann. Pharm. Fr.*, **74(6)**, 431(2016), DOI: 10.1016/j.pharma.2016.03.005
8. J. Zhao, Y. Niu, B. Ren, H. Chen, S. Zhang, J. Jin, Y. Zhang, *Chem. Eng. J.*, **347**, 574(2018), DOI: 10.1016/j.cej.2018.04.151
9. P. Kaur, R. Singh, V. Kaur and D. Talwar, *Sensors and Actuators B*, **254**, 533 (2018), DOI:10.1016/j.snb.2017.07.077

10. P.P. Soufeena and K.K. Aravindakshan, *J. Lumin.*, (2018), DOI: [10.1016/j.jlumin.2018.09.025](https://doi.org/10.1016/j.jlumin.2018.09.025)
11. C. Sell, *The Chemistry of Fragrances: From Perfumer to Consumer*, The Royal Society of Chemistry, Cambridge (2006)
12. Arctander, *Perfume and Flavor Chemicals*, Montclair, N.J.USA (1969)
13. W.P. Silvestre, F. Agostini, L.A.R. Muniz, and G.F. Pauletti, *J. Food Eng.*, **178**, 90 (2018), DOI: [10.1016/j.jfoodeng.2016.01.011](https://doi.org/10.1016/j.jfoodeng.2016.01.011)
14. P.C. Liao, T.S. Yang, J.C. Chou, J. Chen, S.C. Lee, Y.H. Kuo, C.L. Ho and L.K.P. Chao, *J. Funct. Foods*, **19**, 248 (2015), DOI: [10.1016/j.jff.2015.09.034](https://doi.org/10.1016/j.jff.2015.09.034)
15. C. Irawan, S. Indryati, E.S. Lestari, A. Hidaningrum, and Supriyono, *Orient. J. Chem.*, **34(1)**, 394 (2018), DOI: [10.13005/ojc/340142](https://doi.org/10.13005/ojc/340142)

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