

Separation of Geraniol from Citronellol by Selective Oxidation of Geraniol to Geranial

(Pengasingan Geraniol daripada Sitronelol melalui Pengoksidaan Memilih Geraniol kepada Geranial)

DANIEL CHONG JUN WENG, JALIFAH BINTI LATIP*, SITI AISHAH BINTI HASBULLAH & HARJONO SASTROHAMIDJOJO

ABSTRACT

Rhodinol is a mixture of geraniol and citronellol. It is the second fraction in fractional distillation of commercially grown Cymbopogon nardus. The physical and chemical similarities of these two compounds made them inseparable. The individual use of each compound is of great importance. A selective oxidation (hydrogen peroxide activated by platinum black) of geraniol (in rhodinol) to geranial was done while remaining citronellol intact in order to separate the two compounds into different chemical functionality. A yield of 81% geranial achieved while minimizing citronellal formation from citronellol to 17%. Chemical separation using sodium hydrogen sulfite (NaHSO₃) was done to separate the aldehydes from the unreacted citronellol. Purification using fractional distillation was done to obtain pure geraniol and remove minor fraction of citronellal.

Keywords: Geranial; geraniol; oxidation; rhodinol; selective

ABSTRAK

Rodinol adalah sebatian yang terdiri daripada geraniol dan sitronelol. Dengan menggunakan kaedah penyulingan berperingkat, rodinol adalah pecahan kedua Cymbopogon nardus. Kedua-dua sebatian ini tidak boleh diasingkan disebabkan ciri fizikal dan kimia yang seiras. Kegunaan geraniol dan sitronelol sebagai sebatian yang berasingan adalah penting daripada segi industri. Dalam kajian ini, pengoksidaan memilih (hidrogen peroksida yang diaktifkan oleh platinum hitam) geraniol (dalam rodinol) kepada geranial dilakukan sementara sitronelol kekal utuh supaya kedua-dua sebatian ini boleh diasingkan dengan keadaan fungsi kimia yang berlainan. Tindak balas ini memberikan hasil sebanyak 81% geranial dan berjaya meminimumkan penghasilan sitronelal daripada sitronelol kepada 17%. Dengan menggunakan cara pengasingan kimia, hidrogen sulfit (NaHSO₃) digunakan untuk mengasingkan aldehyd daripada sitronelol. Akhirnya, pecahan kecil sitronelal diasingkan daripada geraniol tulen dengan menggunakan penyulingan berperingkat.

Kata kunci: Geranial; geraniol; memilih; pengoksidaan; rodinol

INTRODUCTION

Rhodinol is a mixture of geraniol (3,7-Dimethyl-2,6-octadien-1-ol) and citronellol (3,7-Dimethyl-6-octen-1-ol) (Figure 1) (Dowthwaite 2009; Laksmono et al. 2007; Sastrohamidjojo 1994). It exists naturally in plants such as *Cymbopogon nardus* (*C. nardus*) which grows invasively in the wild (Byenkya et al. 2013; Ssegawa 2007).

The high value and demand of its essential oil made countries like India, Sri Lanka, Burma, Indonesia and Java to grow *C. nardus* commercially. Geraniol and citronellol, being the two components in the fractional distillation, are known to be inseparable due to their close resemblance in physical and chemical quality (Haake et al. 2004). These two individual compounds are valuable chemicals that are often used in soap, fragrances, cosmetics and pharmaceutical intermediates (Ganjewala 2009; Gilpin et al. 2010; Singh et al. 2012; Wany et al. 2013). Geraniol is especially notable to form geranial which can be used as a starting material for

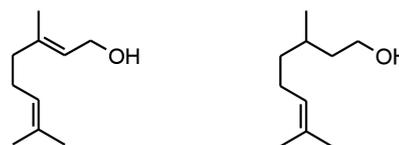


FIGURE 1. Structure of geraniol (left) and citronellol (right)

useful chemicals such as ionones, vitamin A, vitamin E and carotenoids (Roelofs 2001; Roelofs et al. 2000; Xing et al. 2009). Therefore, geraniol and citronellol as a separated individual is greatly sought for. The difference in allylicity between geraniol and citronellol can be manipulated in order to separate these two compounds. There are many articles reporting the oxidation of allylic alcohol with the use of Iron (Fe), Strontium Manganate (SrMnO₄) and supported gold nanoparticles (Abad et al. 2007; Gholizadeh et al. 2004; Join et al. 2011). Recently,

Kon et al. (2008) published a method on chemoselective oxidation of allylic alcohol to aldehyde. This method utilizes hydrogen peroxide (H_2O_2) as an oxidant, producing only water molecules as by-products under a solventless condition. By adapting the method mentioned above, geraniol (allylic alcohol) is aimed to be converted to geranial while leaving citronellol intact. Through this, both oxidised and unreacted citronellol can be separated chemically for individual purposes.

EXPERIMENTAL DETAILS

GAS CHROMATOGRAPHY/ GAS CHROMATOGRAPHY-MASS SPECTROMETRY

The quantification of each compound was done with calibration curves below using GC Chemstation Rev. A. 10.01 [1635] software. GC and GC-MS analysis are performed on an Agilent 7890A gas chromatograph coupled with a mass spectrometer system of an Agilent 5975C inert mass selective detector (MSD) with a triple-axis detector. The gas chromatograph was equipped with a fused silica capillary column DB-5 (5% phenylmethylpolysiloxane, 30 m \times 0.32 mm, film thickness 1.50 μ m). The injector and interface were operated at 250 and 300°C, respectively. The oven temperature was raised from 50 to 300°C at a heating rate of 8°C/min and then isothermally held for 5 min. The constant head pressure was 0.6 bars. Helium was used as carrier gas at 1.0 mL/min. The samples were injected in a pulsed split mode. Mass selective detector was operated at ionization energy of 70 eV, in the 35-500 amu range with a scanning speed of 0.34 s.

STEAM DISTILLATION OF *C. NARDUS*

C. nardus leaves were harvested at Section 16 Bandar Baru Bangi, Selangor, Malaysia. Leaves were then dried and steam distilled for 3.5 h. The citronella oil extracted was dried from moisture using anhydrous sodium sulfate (Na_2SO_4). Gas chromatography-mass spectrometry (GC-MS) was used to identify the composition of the oil.

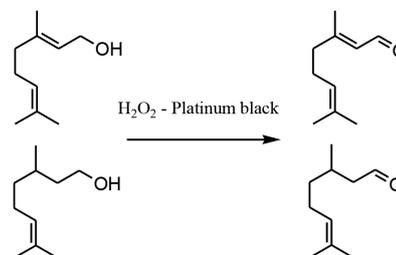
FRACTIONAL DISTILLATION UNDER REDUCED PRESSURE

Fractional distillation under reduced pressure was done on the citronella oil to obtain rhodinol in the second fraction. Purity of geraniol and citronellol was identified using the individual calibration curves.

OXIDATION OF RHODINOL TO GERANIAL USING 5% HYDROGEN PEROXIDE IN THE PRESENCE OF PLATINUM BLACK

The oxidation of rhodinol (Scheme 1) was done according to the molar ratio in Table 1. 0.5 g of rhodinol (1.26 mmol of geraniol) was mixed with 7.4 mg (0.0378 mmol) of platinum black. The mixture was stirred at 90°C in a reflux for 10 min. Drop-wise addition of 5% hydrogen peroxide (2.55 mmol) was added into the mixture over a course of 1 h. The mixture was then heated at 90°C for

2 h and then cooled to room temperature. Then organic phase was washed with sodium thiosulfate ($Na_2S_2O_3$) and then extracted using chloroform. Solvent was removed under vacuum and then product was sent for GC analysis and quantification.



SCHEME 1. Oxidation of rhodinol

TABLE 1. Molar ratio of [geraniol (in rhodinol): hydrogen peroxide (5%): platinum black]

| Geraniol (in rhodinol) | Hydrogen peroxide (5%) | Platinum black |
|------------------------|------------------------|----------------|
| 1 | 2.03 | 0.03 |
| 1 | 4.06 | 0.03 |

The isolation of geranial from the unreacted citronellol was done chemically by using saturated solution of sodium hydrogen bisulfate ($NaHSO_3$). The final product was mixed with saturated solution of $NaHSO_3$ and stirred for 20 min. The white crystals (bisulfite adducts) formed was filtered and washed with chloroform and dried. The filtrate was vacuum evaporated to yield unreacted citronellol. The dried white crystal was dropped with 25% sodium hydroxide ($NaOH$) (w/v) to obtain an organic and aqueous layer. The organic layer was extracted with chloroform. Solvent was then vacuum removed to yield the original geranial.

RESULTS AND DISCUSSION

The GC chromatogram of the citronella oil steam distilled from *C. nardus* is shown in Figure 2. The extracted oil was fractionated in three fractions, to obtain rhodinol (Figure 3) in the second fraction (65°C-70°C at 1.40 mmHg). The amount of geraniol and citronellol in the rhodinol extracted was quantified using individual calibration curve, respectively. It was found that the purity of geraniol is 38.8% while citronellol is 57.0%.

In the oxidation of rhodinol, geraniol is aimed to be converted to geranial while leaving citronellol being intact. The chemoselective oxidation of allylic alcohol to aldehyde done by Kon et al. (2008) was adapted for this purpose. The results of the oxidation are shown in Table 2.

The molar ratio [1: 2.03: 0.03] suggested in the paper was utilised to oxidise geraniol to geranial but only 64%

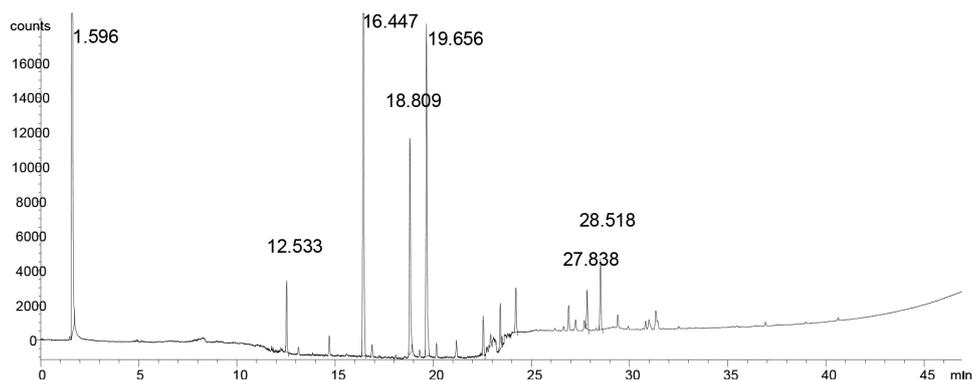


FIGURE 2. Gas chromatogram of citronella oil

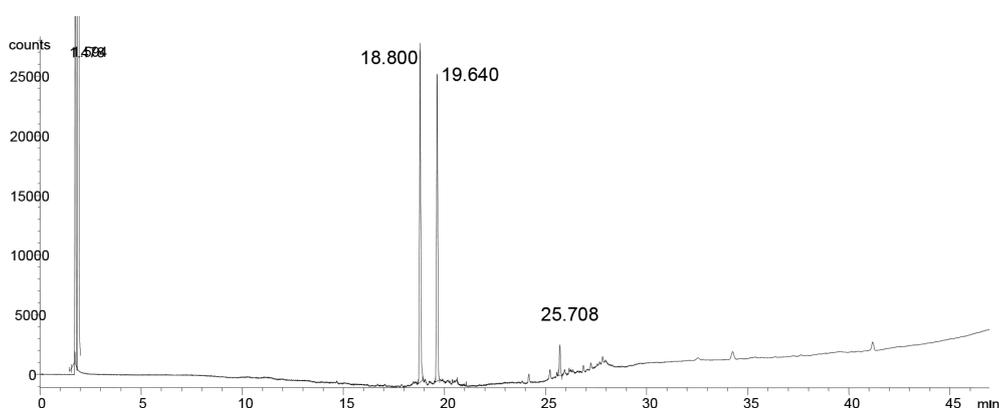


FIGURE 3. Gas chromatogram of rhodinol (citronellol and geraniol at retention times of 18.800 and 19.640, respectively)

TABLE 2. Conversion and yield of reaction

| Molar ratio [geraniol: hydrogen peroxide (5%): platinum black] | Conversion of geraniol (%) ^a | Yield of geraniol (%) ^b |
|---|--|---------------------------------------|
| [1: 2.03: 0.03] | 64 | 57 |
| [1: 4.06: 0.03] | 100 | 81 |

^a Based on total geraniol used^b Based on geraniol formed divided by expected yield

of the geraniol was converted (Figure 4). An incomplete conversion of geraniol will still lead to a mixture of geraniol and citronellol at the end of the chemical separation. Therefore, the amount of 5% hydrogen peroxide was increased two-fold to achieve full conversion of geraniol. As a result, geraniol was fully converted (Figure 5). Minor citronellal was formed from citronellol. This might be due to the oxidation of individual hydrogen peroxide as it oxidizes very weakly without catalytic activation (Kon et al. 2008). The yield of citronellal formed from citronellol was shown in Table 3.

Isolation of geraniol from unreacted citronellol was done chemically using sodium hydrogen sulfite (NaHSO_3). All aldehyde will form bisulfite adduct (white crystal) when react with NaHSO_3 (Armarego & Chai 2009).

The white crystals were filtered and washed with chloroform. The filtrate was vacuum evaporated to yield the unreacted citronellol (Figure 6). White crystals collected were reverted back to aldehyde form by adding 25% sodium hydroxide (NaOH) (w/v). The extracted organic phase contains both geraniol and the minor citronellal formed. The little amount of citronellal was removed from the mixture by fractional distillation under reduced pressure (60°C at 1.5 mmHg) to yield geraniol (Figure 7).

Platinum black is a precious material that is used frequently in catalysis reaction. Therefore, it can be economical if it is reusable in industrial scale synthesis. The reusability of platinum black on the oxidation of rhodinol was done and the results are shown in Table 4.

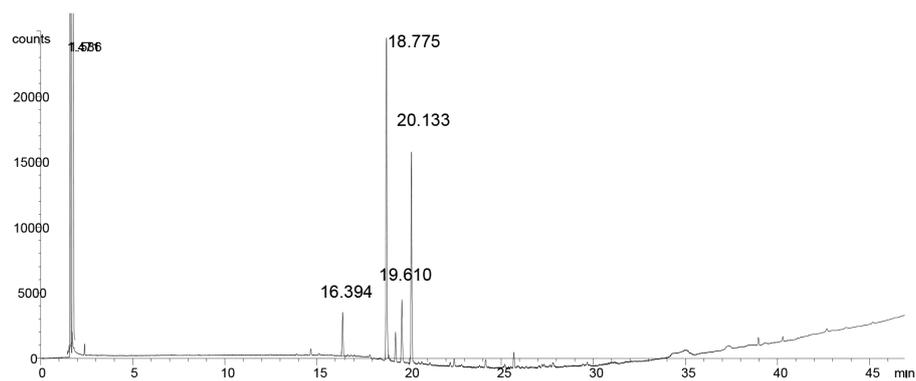


FIGURE 4. Gas chromatogram of incomplete conversion of geraniol (citronellal, unreacted citronellol, unreacted geraniol and geraniol at retention times of 16.394, 18.775, 19.610 and 20.133, respectively)

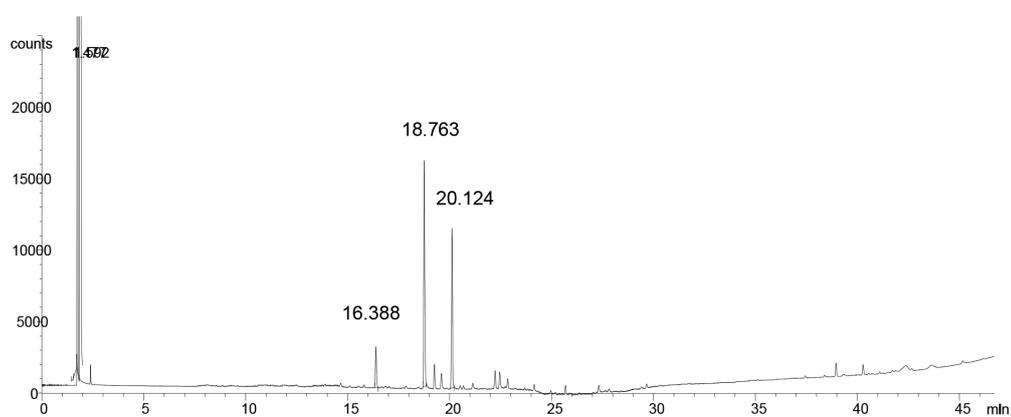


FIGURE 5. Gas chromatogram of complete conversion of geraniol

TABLE 3. Yield of citronellal formed from citronellol

| Molar ratio [geraniol: hydrogen peroxide (5%): platinum black] | Yield of citronellal (%) ^c |
|---|--|
| [1: 2.03: 0.03] | 6.7 |
| [1: 4.06: 0.03] | 17.0 |

^c Based on citronellal formed divided by expected yield

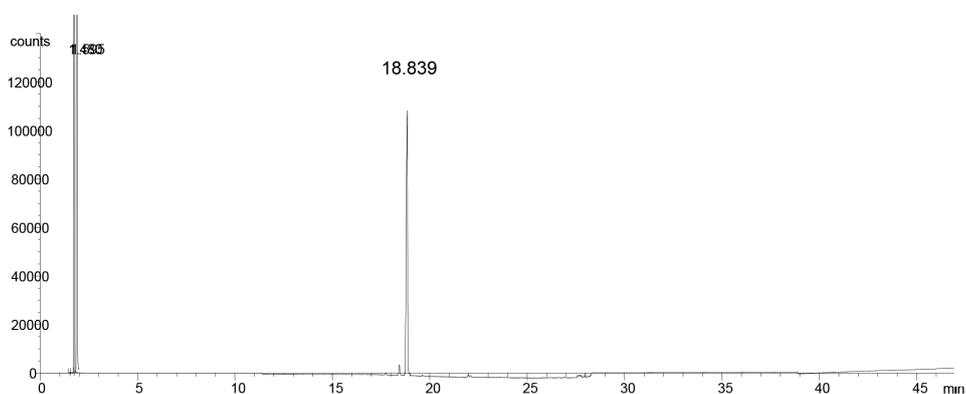


FIGURE 6. Gas chromatogram of isolated citronellol

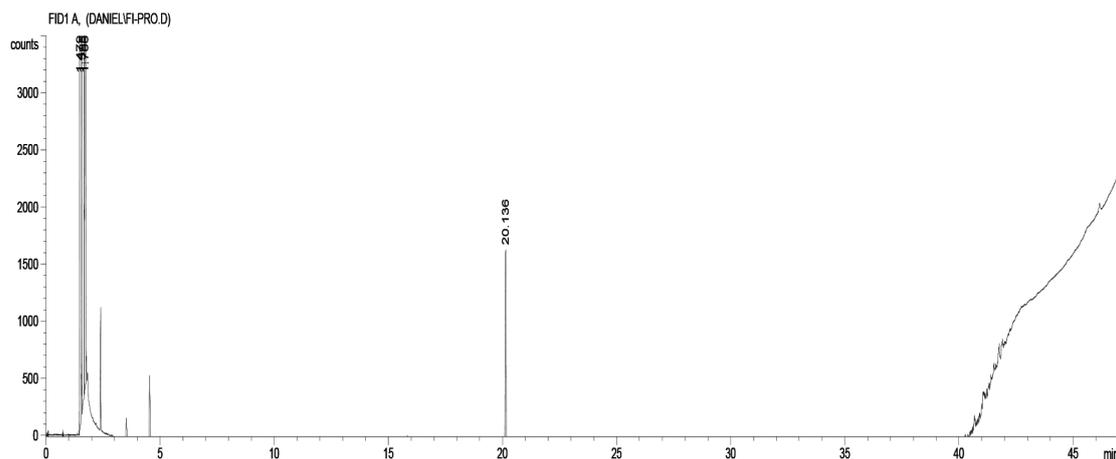


FIGURE 7. Gas chromatogram of isolated geranial

TABLE 4. Reusability of platinum black

| Number of reuse | 1 | 2 | 3 |
|-----------------------|----|----|----|
| Yield of geranial (%) | 81 | 80 | 83 |

The catalytic ability of platinum black shows that it can be used three times without significant drop in reactivity.

CONCLUSION

The separation of geranial and citronellol as a separate individual was successfully carried out. The selective oxidation using activated hydrogen peroxide (H_2O_2) by platinum black managed to fully convert geraniol to geranial with a yield of 81% while minimizing the formation of citronellal from citronellol to 17%. This method is environmental benign because it is solvent-free and produces only water as by-product. The geranial formed was isolated from the unreacted citronellol using sodium hydrogen sulfite ($NaHSO_3$).

ACKNOWLEDGEMENTS

The financial support was obtained from the Ministry of Education, Malaysia under the grant No. FRGS/1/2012/ST01/UKM/02/6.

REFERENCES

- Abad, A., Corma, A. & García, H. 2007. Supported gold nanoparticles for aerobic, solventless oxidation of allylic alcohols. *Pure and Applied Chemistry* 79(11): 1847-1854.
- Armarego, W.L.F. & Chai, C. 2009. *Purification of Laboratory Chemicals*. 6th ed. Burlington, MA: Butterworth-Heinemann.
- Byenkya, G.S., Gumisiriza, G. & Kasigwa, H. 2013. Evaluation of control strategies for *Cymbopogon nardus* in grazing areas of Uganda. *Journal of Agricultural Science and Technology B* 3: 656-660.
- Dowthwaite, S.V. 2009. Empowering the independent perfumer. *The Professional Perfumer's Bulletin* © 3.01-3.28. pp. 1-39.
- Ganjewala, D. 2009. Cymbopogon essential oils: Chemical compositions and bioactivities. *International Journal of Essential Oil Therapeutics* 3: 56-65.
- Gholizadeh, M., Mohammadpoor-Baltork, I. & Kharamesh, B. 2004. Selective oxidation of benzylic and allylic alcohols using strontium manganate in the presence of lewis acids in solution and under solvent-free conditions. *Bulletin of the Korean Chemical Society* 25(4): 566-568.
- Gilpin, S., Hui, X. & Maibach, H. 2010. *In vitro* human penetration of geraniol and citronellol. *Dermatitis* 21: 41-48.
- Haake, M., Gerlach, T. & Funke, F. 2004. U.S. Patent 6743956 B1.
- Join, B., Möller, K., Ziebart, C., Schröder, K., Gördes, D., Thurow, K., Spannenberg, A., Junge, K. & Beller, M. 2011. Selective iron-catalyzed oxidation of benzylic and allylic alcohols. *Advanced Synthesis & Catalysis* 353(16): 3023-3030.
- Kon, Y., Yazawa, H., Usui, Y. & Sato, K. 2008. Chemoselective oxidation of alcohols by a H_2O_2 -Pt black system under organic solvent- and halide-free conditions. *Chemistry, An Asian Journal* 3(8-9): 1642-1648.
- Laksmono, J.A., Agustian, E. & Adilina, I.B. 2007. Predicting the azeotropic of citronellal enrichment using process simulator. *International Conference On Chemical Sciences*. pp. 1-5.
- Roelofs, J.C.A.A. 2001. Activated hydrotalcites as solid base catalysts in Aldol condensations. PhD Thesis. Utrecht University, Netherlands (unpublished).
- Roelofs, J.C.A.A., Dillen, A.J. & Jong, K.P. 2000. Base-catalyzed condensation of citral and acetone at low temperature using modified hydrotalcite catalysts. *Catalysis Today* 60: 297-303.
- Sastrohamidjojo, H. 1994. Kimia minyak sereh= The chemistry of citronella oil. *Berkala MIPA* (1).
- Singh, D., Kumar, T.R., Gupta, V.K. & Chaturvedi, P. 2012. Antimicrobial activity of some promising plant oils, molecules and formulations. *Indian Journal of Experimental Biology* 50: 714-717.
- Ssegawa, P. 2007. Removing barriers to invasive plant management in Africa. Final report on activity 3,4 of component 3 of the UNEP/GEF-IAS funded project (NARO). Makerere University (Kampala).
- Wany, A., Jha, S., Nigam, V.K. & Pandey, D.M. 2013. Chemical analysis and therapeutic uses of citronella oil from *Cymbopogon winterianus*: A short review. *International Journal of Advanced Research* 1: 504-521.

Xing, K., You, K., Yin, D., Yuan, Z. & Mao, L. 2009. A simple and efficient approach for synthesis of pseudoionone from citral and acetone catalyzed by powder LiOH.H₂O. *Catalysis Communications* 11: 236-239.

Daniel Chong Jun Weng, Jalifah binti Latip*
& Siti Aishah binti Hasbullah
School of Chemical Sciences & Food Technology
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor Darul Ehsan
Malaysia

Harjono Sastrohamidjojo
Department of Chemistry
Gadjah Mada University, Yogyakarta
Indonesia

*Corresponding author; email: jalifah@ukm.edu.my

Received: 4 December 2014

Accepted: 9 April 2015