Effect of reaction time on the ratio of palm oil based glucosides anomers

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***Abstract*—PKO based glucosides were synthesized using the glycosylation method. The synthesis method comprised three steps: peracetylation, glycosylation and deacetylation. The reaction produced a mixture of α and β anomers which configurations differ at C1 carbon. Alkyl glucosides consist of glucose with aliphatic chains that vary by the PKO fatty acids compositions. Three types of anomeric mixtures were produced from this synthesis such as α-dominant mixture, β-dominant mixture and equal mixture controlled by reaction time.**

Keywords— Glucosides, Palm kernel oil, Glycosylation

I. INTRODUCTION

Demand for the surfactants is increasing rapidly since to raise the standard living thing as well as growing population in the development countries. Surfactants or surface active agents are broadly defined as the organic compound that can enhance the cleaning efficiency, emulsifying, wetting, dispersing, foaming or defoaming and lubricity of water-based compositions. Surfactants consist of the hydrophilic groups (head) and hydrophobic groups (tail) [6]. The hydrophobic group is typically a linear or branched alkyl chain while the head group of the surfactant molecule can be either a non-ionic, cationic, or anionic group which determined the properties of the surfactants.

Development of technology nowadays introduced promising natural surfactants in term of ecological factor by preventing the adverse environment impacts associated with land and water use. So, natural surfactants can easily to biodegradable without any problem issues arise [1-4].

Glucoside is a subcategory of glycoside derived from the glucose that has been studied extensively in this research. Glucose is a carbohydrate and known as a simple sugar or monosaccharide. In the cyclic form, glucose can exist into two form which is α- and β- based on the position of the substituent at the anomeric center. The Figure 1 shows the structure of α- and β- D-glucose.

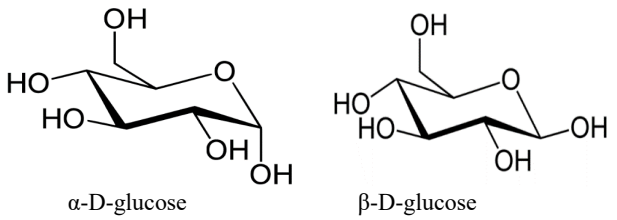


Fig.1: The structure of α-D-glucose and β-D-glucose

In α- form where the exocyclic O group at the anomeric center is on the opposite face to the -CH_2OH group while β-form the exocyclic O group is on the same face as the -CH_2OH group [3].

A new mixture of alkyl glucosides produced from synthesizing of palm kernel oil (PKO) and sugars. Alkyl glucosides (AG) are classified as the non-ionic surfactants which are relatively non-toxic [1]. Non-ionic surfactants are widely use in the pharmaceutical, food and cosmetic industries [1-2]. They have a green chemistry character as their toxicity is low and less harmful as well as it also have high skin compatibility [1]. AG is considered as the natural surfactants because it is synthesis from the natural resources such as vegetable oil [5-6]. This is because most of development is starting a trend toward ‘’green’’ product by concerning the environment condition.

Alkyl glucosides comprise of sugar head group and aliphatic chain connected via ether linkage [7]. Aliphatic chain may vary meanwhile sugar head group remains the same with initial starting sugar without the polymerization of sugar occurred [1]. Besides AG, the commercial glucosides known as alkyl polyglucosides (APG) which comprised of mixture glucosides with a various degree of polymerized sugar head group [1-2]. APG can be categorized as a natural surfactant too since it is synthesis from natural renewable resources. Thus, it is not toxic or harmful according to the acute toxicity tests [1-2].

In this research, glucose is used as sugar head group while long alkyl chain derived from the palm kernel oil (PKO). PKO has different fatty acid compositions. PKO is composed mostly of saturated fatty acids [1-2]. Glucose and PKO have been used since it is economical and availability of the materials.

The aims of this research are to synthesis palm kernel oil (PKO) based glucosides with the reaction of time and to determine through chemical analysis α and β anomers ratio. The glycosylation method used to synthesis the glucosides produced different anomeric mixtures depending on the reaction time. Two types of anomers (α/β) are produced which configurations differ at the C1 [1-2].

II. METHODOLOGY

A. Materials

Chemical and material used in this study were purchased at several company. Crude palm kernel oil (PKO) was obtained from Golden Jomalina Food Industries Sdn. Bhd (Malaysia). β-D-glucosepentaacetate and boron trifluoride (BF_3) required for glycosides syntheses were purchased from Sigma Aldrich (USA). The solvents used in this synthesis were dichloromethane (99.99%), acetonitrile (99.99%), hexane (98.11%), methanol (99.85%), acetic anhydride (98.5%) and 1-Butanol (99.5%) were purchased from Merck respectively. Others chemical such as sodium methoxide (100%), sodium acetate anhydrous (98%), sodium hydrogen carbonate (99.7-100%), Ion resin Amberlite IR-120 (particle size: 0.3-1.1 mm > 90%) were purchased from Merck. Magnesium sulphate anhydrous (99.5%) was purchased from Acros Organics. For NMR analysis, Chloroform-d (99.8%) and methanol d-4 (99.8%) were purchased from Aldrich and Merck respectively.

B. Synthesis method

The glucosides were synthesized by using the glycosylation method. The synthesis method consisted of three steps which

was peracetylation, glycosylation and deacetylation. PKO was reduced to alcohol first using a general reduction method [1].

Hydroxyl group of sugars were protected with acetyl group to activate the anomeric carbon as well as to enable selectivity glycosidic bonding with alkyl chain. 20g sodium acetate and 100 ml acetyl anhydride were mixed in two necks round bottom flask (RBF). The solution was heated and stirred in a beaker containing oil with temperature at 120 ºC. The temperature of oil was maintained at 120ºC along the heating process. 20g of D-glucose was added slowly into the solution and then further heated at 120 ºC for 1h. The hot solution was poured into ice water and stirred until sticky white solid was formed [1]. A white powder was obtained after several washed with distilled water. Pure peracetylated sugar was recrystallized from ethanol [1].

6 g of peracetylated sugar and the alcohol were dissolved in the 60 ml dichloromethane and stirred in a closed apparatus at room temperature. 2.3 ml boron trifluoride was slowly injected into the solution and the glycosylation reaction took several hours to complete depending on the desired mixture. The reaction was stopped by neutralizing the solution with saturated sodium bicarbonate solution and the organic layer was washed two times with water. Magnesium sulfate anhydrous was added to absorb moisture contents and filtered using the filter paper. Dichloromethane was evaporated by using the rotary evaporator and 60 ml acetonitrile was added later to the product. Hexane was added a few times to the acetonitrile solution completely remove the excess alcohol. Acetonitrile was evaporated from the peracetylated glucosides.

Deacetylation step was done by adding the 50 ml methanol and a catalytic amount of sodium methoxide to induce a basic medium. The solution was stirred and left for overnight. The amberlite IR was added a few drop to induce the neutral medium and also removed the alcohol. The solution was filtered and methanol was evaporated later to the product. The product was purified from the unreacted sugar with n-butanol and water extractions. n-butanol was evaporated and the product was dried in vacuum oven for 48 h.

C. Nuclear magnetic resonance (NMR)

PKO based glucosides were characterized by ^{1}H NMR. Methanol-d4 was used in the product sample preparation and chloroform-d4 used in the sample preparation of β-D-glucosepentaacetate.

III. RESULTS AND DISCUSSION

A. Synthesis and characterization of PKO based glucosides

The synthesis method required three major steps such as peracetylation, glycosylation and deaceytylation (Fig.2). Peracetylation of sugar was required which the hydroxyl groups of sugar was protected by acetyl groups in order to activate as well as to have a selective glycosylation at the anomeric carbon [1]. Peracetylated sugars were checked with NMR spectra to ensure the quality of product (Fig.3).Chloroform-d4 was used to prepare the sample of peracetyleted sugars.

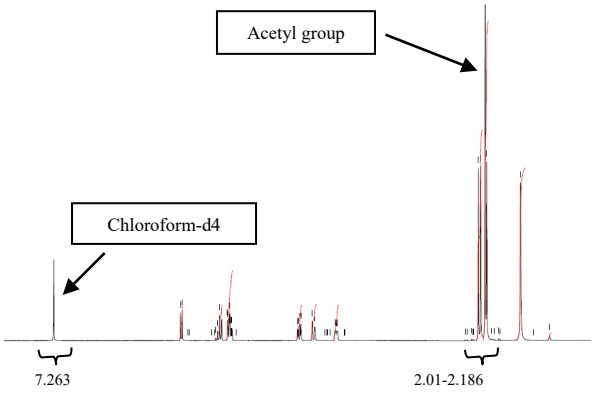


Fig.3: β-D-glucosepentaacetate

PKO based glucosides were synthesized using the glycosylation step. Glycosylation of PKO based glucosides were done at certain reaction time such as 12, 24 and 48 h (Fig.4). Glycosylation reaction was catalyzed by boron trifluoride (BF_3) to produce a mixture α and β anomers which configuration differs at C1 carbon.

The synthesis method produced three types of mixtures such as α-dominant, β-dominant and mixture containing an equal amount of anomers. The ratio of α and β anomers were controlled by reaction time and obtained in different pathways. The ratio α/β was determined by comparing the integration of nuclear magnetic resonance (NMR) spectra peaks of both anomers [1]. An α anomer showed a double peak at 4.77 ppm and β anomer at 4.26 ppm [1].

Figure 5 shows the integration of α and β anomers peaks for β-dominant mixture.

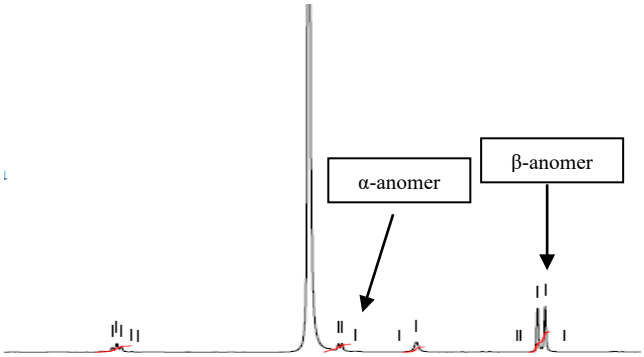
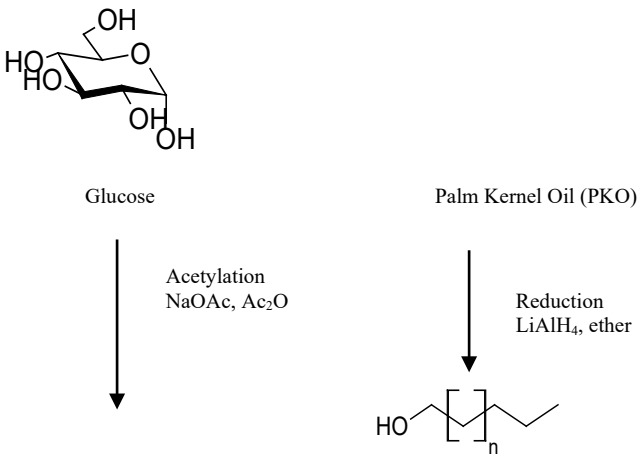
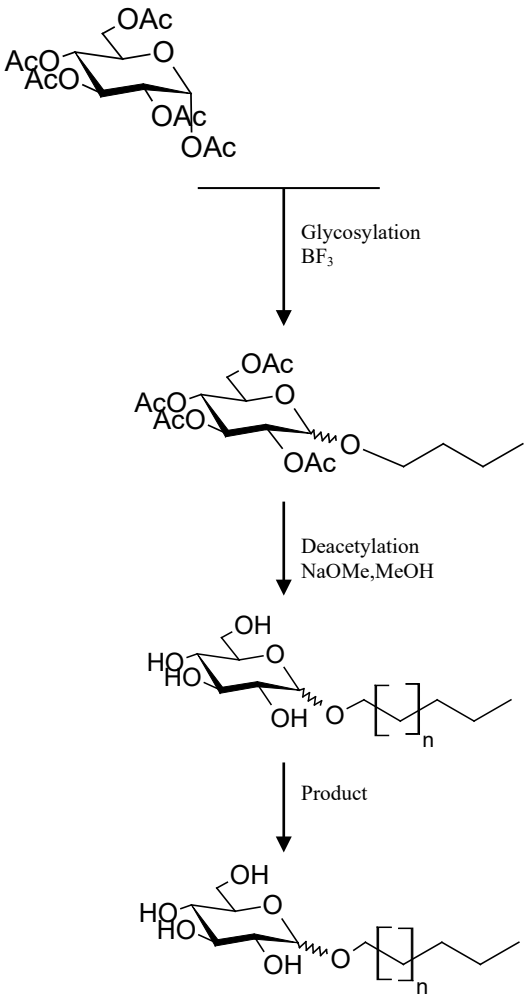


Fig.5: The integration of α and β anomers peaks for β-dominant mixture





Alkyl glucosides

Fig.2: Synthesis steps of PKO based glucosides

(a) 12 hours

(b) 24 hours

(c) 48 hours

Fig.4: The glycosylation of β-D-glucosepentaacetate

Other than that, NMR spectra showed sugars and fatty alcohol peaks only (Fig.6). Alcohol peaks were not detected since the excess alcohol during synthesis removed completely by acetonitrile-hexane extraction [1] .The results obtained from the spectral data were systematically combined to elucidate the structure of the sugar and fatty alcohol. The analysis of structure sugars is quite difficult to interpret, because the information about the sugar is not available. So, peaks of sugar were showed roughly. Analyses from the spectra showed that no degradation of double bond occurred during the synthesis [1]. The unsaturation of PKO was the same according to the initial amount found in the oil [1]. NMR spectra estimated the average alkyl chain length for PKO consisted of 12 carbons.

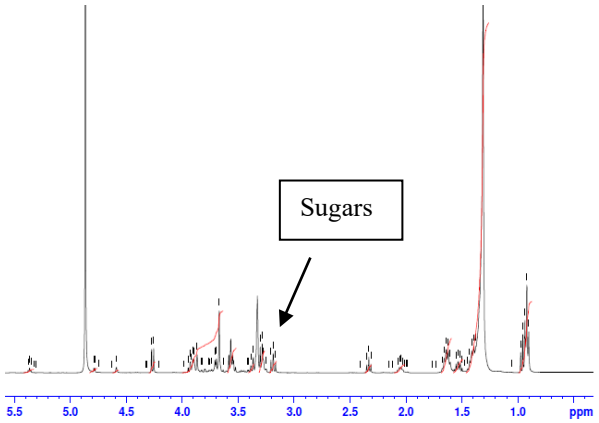


Fig.6: NMR spectra for β-dominant mixture

Furthermore, fatty alcohols analyzed by comparing the other compound which is cis-9-octadecen-1-ol by referring their orientation structure only (Fig 7) [8]. This is because the spectra database for C12 is not available. Table 1 shows the analysis integration peaks for alkyl glucosides.

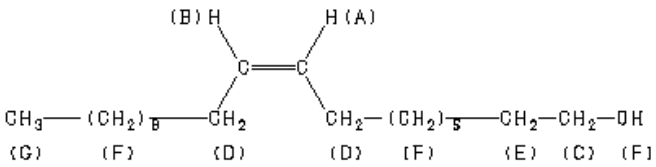


Fig 7: cis-9-octadecen-1-ol

Table 1: Analysis integration peaks for alkyl glucosides

Assign	Shift (ppm)
A	5.35
B	5.34
C	3.629
D	2.00
E	1.57
F	1.45 to 1.23

G	0.881

Compliance to main objectives, the results showed the percentage of α anomer was significantly increased with increasing the time reaction while β anomer was significantly decreased with increasing time reaction (Fig.8). For 12 h yielded β-dominant mixture which synthesized by kinetically controlled glycosylation while 48 h was α-dominant mixture from the thermodynamic controlled pathway. Kinetic pathway required a short reaction of time compared thermodynamic pathway because has the lowest energy transition state. An α anomers required a long reaction of time to generate the most thermodynamic stable product due to the anomeric effect. For 24 h, an equal amount of anomers are obtained. According to previous studied Aripin et al., [1] results obtained were theoretically compatible.

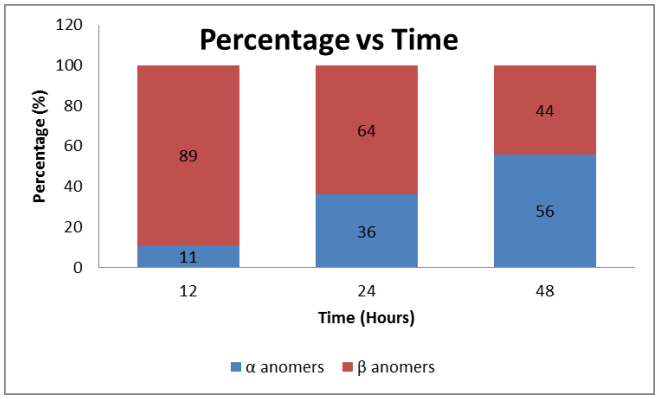


Fig.8: Percentage of α and β anomers at certain reaction time

CONCLUSION

PKO based glucosides are synthesized using the glycosylation method. Glycosylation reaction at certain time is done. For 12 h β-dominant mixture is obtained while 24 h the mixture containing equal amount of anomers. Then, time reaction is increased to 48 h which α-dominant mixture obtained. An α anomers took a long reaction of time to generate the most thermodynamic stable product. The synthesis method consumed a lot of time and the product obtained in small amount of quantity.

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REFERENCES

[1] Nurul Fadhilah Kamalul Aripin, J. W. P., Hyun Jin Park. (2012). *Preparation of vesicle drug carrier from palm oil-palm kernel oil-based glycosides*. Colloids and Surface B: Biointerfaces 144-153.

[2] Nurul Fadhilah Kamalul Aripin, R. H., Thorsten Heidelberg, Dong-Koen Kweon and Hyun Jin Park. (2013). *Effect of vesicle's membrane packing behaviour on skin penetration of model lipophilic drug. Microencapsulation*, 265-273.

[3] Hunt, D. I. (Producer). (2016). Department of Chemistry, University of Calgary. Department of Chemistry, University of Calgary Web Site. Retrieved from http://www.chem.ucalgary.ca/

[4] Rauzah Hashim, H. H. (2006). Branhed chain glycosides: Enhanced diversity for phase bahaviour of easily accesible synthetic glycolipids. Thin Solid Films 509, 27-35.

[5] Larry D. Ryan, E. W. (2001). Alkyl polyglucoside microemulsion phase behaviour. *Colloid and Surfaces A: Physicochemical and Engineering Aspect 176*, 69-83.

[6] Patrick Foley, A. K. p., Evan S. Beach and Julie B. Zimmerman. (2012). Derivation and synthesis of renewable surfactants. Chem Soc Rev, 1499-1518.

[7] Stubenrauch, C. (2001). Sugar surfactants-aggregation, interfacial, and adsorption phenomena. Current Opinion in Colloid & Interface Science 6, 160-170.

[8] National Institute of Advanced Industrial Science and Technology (AIST), J. (3 February, 2017). Spectral Database for Organic Compounds SDBS. Retrieved 31 Mei, 2017, from Spectral Database for Organic Compounds SDBS Web site: http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

[9] Karlheinz Hill, O. R. (1999). *Sugar-based surfactants for consumer products and technical applications*. Fett/Lipid, 25-33.

[10] Guo, J., & Ye, X. S. (2010). Protecting groups in carbohydrate chemistry: influence on stereoselectivity of glycosylations. Molecules, 15(10), 7235-7265. doi: 10.3390/molecules15107235.

[11] Manisha mishra, P. M., K.Surya prabha, P.Sobhita rani, I. A.Satish babu, I. Sarath Chandiran,G.Arunachalam and S.Shalini. (2009). Basics and Potential Applications of Surfactants - A Review. International Journal of PharmTech Research, 1(4), 1354-1365.

[12] Guo, J., & Ye, X. S. (2010). Protecting groups in carbohydrate chemistry: influence on stereoselectivity of glycosylations. Molecules, 15(10), 7235-7265. doi: 10.3390/molecules15107235.

[13] Khamsi, J., Ashmus, R. A., Schocker, N. S., & Michael, K. (2012). A high-yielding synthesis of allyl glycosides from peracetylated glycosyl donors. Carbohydr Res, 357, 147-150. doi: 10.1016/j.carres.2012.05.008