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Synthesis of Glucopyranosyl Acetic from Sago Flour as Raw Material for the Synthetic Polymers

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Abstract

Synthesis of glucopyranosyl acetic from sago flour as raw material for the synthetic polymers has been successfully carried out. The synthesis product is obtained through two reaction stages, namely the hydrolysis and esterification reactions. Sago flour is hydrolyzed with 25% HCl and neutralized with 45% NaOH. Glucose hydrolysis of sago starch and acetic anhydride was esterified using a zinc chloride catalyst. Synthesis product was obtained as a white solid substance (57.31% recovery), a melting point of 110 - 111ºC, and R_f 0.79 on TLC (SiO_2, *n*-hexane : ethyl acetate = 9:1 v/v). The results of the analysis of synthesis products with FTIR and GC-MS spectrometers showed that the synthesis product was glucopyranosyl acetic or 2,3,4,6-tetra-O-acetyl glucopyranose.

Keywords: Synthesis, glucopyranosyl acetic, sago flour, hydrolysis, esterification

INTRODUCTION

The main product of the sago tree (*Metroxylon sp*.) is sago flour. Sago flour is a starch extract obtained by extracting the pith of the sago tree trunk. Extraction is carried out using water solvent so that the starch and other water-soluble components are released. Sago flour is one of the staple foods of people in Indonesia. Sago flour has good nutrition for the body because the nutritional content in sago is relatively complete. In 100 g of dry sago flour, there are 209 kcal of energy, 0.3 g of protein, 51.6 g of carbohydrates, 0.2 g of fat, 27 mg of calcium, 13 mg of phosphorus, and 0.6 mg of iron. Sago flour also contains vitamin A of 0 IU, vitamin B1 of 0.01 mg, and vitamin C of 0 mg. The amount of sago flour that can be consumed is 100% (Usman, 2020). Sago flour can be used as a raw material for producing glucose because it contains 98.49% of carbohydrates (Djoefrie, 1999; Flach and Rumawas, 1996; Rahmawati et al., 2019).

Sago flour can be used as a raw material for making meatballs, crackers, peanut brittle, pempek, dry and wet cakes (Heryani and Silitonga, 2017; Bantacut, 2011; Haryanto and Pangloli, 1992). Sago flour has many health benefits. The carbohydrate content in this product is safe for diabetics because it can help slow down the increase in blood sugar levels. Sago flour is also able to boost the immune system. Apart from being a gluten-free food ingredient, sago flour can also be used as a raw material for various modern industries, such as the food industry, textiles, cosmetics, pharmaceuticals, pesticides, flavorings, perfumes, synthetic polymers, and other chemical industries.

Sago flour or starch is a polymeric carbohydrate consisting of numerous glucose units joined by glycosidic bonds. The glycoside bonds can be broken by hydrolysis reaction using an acid catalyst (Purwanti and Dampang, 2017; Ardiansyah et al., 2018). Glucose is a carbohydrate compound that has a hydroxyl (-OH) functional group. The -OH group can be converted into an ester through an esterification reaction (Arniah, 2010; Bandjar et al., 2014). Esterification reactions can be carried out using three types of the alkylating agent, namely carboxylic acids, acyl halides, and acid anhydrides. For the same alcohol, the reactivity sequence of the alkylating agent for the corresponding acyl groups is acyl halide > acid anhydride > carboxylic acid (Carey, 1992; Solomons, 1988).

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If the glucose produced by sago flour hydrolysis is esterified, the resulting compound will have a fragrant aroma, so that this compound can be used in the fragrance industry as well as other ester compounds. Ester compounds can also be used as raw materials for the production of synthetic polymers. So, the results of this study are expected to develop synthetic organic chemistry based on natural ingredients and improve the welfare of sago farmers because it can increase the economic value of sago.

METHODOLOGY

Materials and Instrumentals

The materials used are the sago flour, HCl 25% (Merck), NaOH 45% (Merck), iodine solution with dropping pipette (Merck), Benedict's reagent with dropping pipette (Merck), anhydrous zinc chloride (Merck), acetic anhydride (Merck), glucose (Merck), aquabidest (Onelab Waterone), methanol (Merck), filter paper (commercial), and TLC plate.

The instrumentals used are Erlenmeyer, analytical balance (Explorer Ohaus), Electrothermal 9100, dropper pipette (Pyrex), measuring cup (Pyrex), chemical beaker (Pyrex), stirring rod, chamber, thermometers (100 ^{o}C), 1 cm magnetic stirrers, heating mantles, funnels, and a set of reflux devices consisting of 100 mL three-neck round bottom flask and Liebig coolers. Spectrometers used included the FTIR Prestige-21 Shimadzu and GC-MS.

Methods

Hydrolysis of Sago Flour

Sago starch (20 g) and aquabidest (100 mL) are put into a 250 mL beaker. The mixture was stirred with a magnetic stirer for 1 hour. The suspension was washed with aquabidest until the filtrate volume was 250 mL. The suspension is filtered and the residue is removed from the filter paper into the Erlenmeyer. Aquabidest (250 mL) and 25% HCl (40 mL) are added to the Erlenmeyer which contains the residue. Erlenmeyer covered with cooling back and heated in a water bath for 6 hours. The solution was tested with iodine solution every 2 hours to control the starch hydrolysis time. Once cool, the solution is neutralized with 45% NaOH then the solution is diluted to a volume of 500 mL (Sudarmadji, 1984).

The solution was filtered and the filtrate was pipette 2 mL into test tubes 1 and 2. Iodine solution (2 drops) were added to test tube 1 and the colour change was recorded. Benedict's reagent (2 mL) was added to the test tube 2. The mixture was heated in a water bath at a temperature of 60 ^{o}C for 3 minutes and the colour change was recorded (Eduqas, 2020; Amrita, 2020).

Esterification of Glucose

Anhydrous zinc chloride (0.5 g) and acetic anhydride [13.5 g (12.5 mL, 0.13 mol)] of were put into a 100 mL three neck round bottom flask. The flask was connected to the Liebig cooler. The mixture was refluxed at 60 ^{o}C for 1 hour. Furthermore, glucose (2.5 g, 0.014 mol) was added slowly to the mixture while stirring with a magnetic stirer. Cold water (125 mL) was added to the mixture while stirring with a magnetic stirer for 30 minutes without heating. After that, the solution was filtered and washed with cold water. The filtrate was recrystallized with methanol (Furmiss et al., 1989). The crystals were identified by TLC test, melting point, FT-IR and GC-MS spectrophotometer (Arniah, 2010).

Determination of the Glucopyranosyl Acetic Structure

The glucopyranosyl acetic was determined using spectroscopic techniques, namely FTIR and GC-MS. The physical data, spectrum of FTIR and GC-MS of the glucopyranosyl acetic are as follows. Results: 57.31% yield; mp 110 - 111 °C; TLC (SiO_2, *n*-hexane : ethyl acetate = 9 : 1 v/v, $R_f = 0.79$); FTIR (KBr) ν_{maks} (cm^{-1}): 3442.7 (-OH stretch of alcohols), 1436.9 (C-OH deformation of alcohols), 1043.4 (C-OH stretch of secondary alcohols), 1755.1 (C=O stretch of esters), 1149.5 (C-O-C stretch in dialkyl ethers), 1232.4 (C-O-C stretch in cyclic ethers), 2933.5 (C-H stretch in $C-CH_3$ compounds), 1371.3 ($-O-CO-CH_3$ sym deformation), 2916.2 ($-CH_2-$ antisym stretch), 2885.2 (C-H stretch in >CH-); GC-MS (m/z): 348 $[C_{14}H_{20}O_{10}]^{+\bullet}$, 333 $[C_{13}H_{17}O_{10}]^+$, 318 $[C_{12}H_{14}O_{10}]^+$, 301 $[C_{12}H_{13}O_9]^+$, 242 $[C_{10}H_{10}O_7]^+$, 198 $[C_9H_{10}O_5]^+$, 154 $[C_8H_{10}O_3]^+$, 95 $[C_6H_7O]^+$, and 81 $[C_5H_5O]^+$.

RESULT AND DISCUSSION

The glucopyranosyl acetic was obtained as a white solid substance (57.31% yield), a melting point of 110 - 111 ^{o}C, and R_f 0.79 on TLC (SiO_2, *n*-hexane :ethyl acetate = 9 : 1 v/v). The glucopyranosyl acetic was obtained through a two steps of the reactions. The first step is the hydrolysis reaction of sago flour. Sago flour hydrolysis is the hydrolysis reaction of starch (amylose) to glucose. Hydrolysis reaction of acid-catalyzed sago flour (starch) forming glucose is shown in Figure 1.

The results of qualitative identification of sago flour hydrolysis by iodine test showed a blue black discoloration of the starch solution before hydrolysis became colorless after hydrolysis (Table 1). This

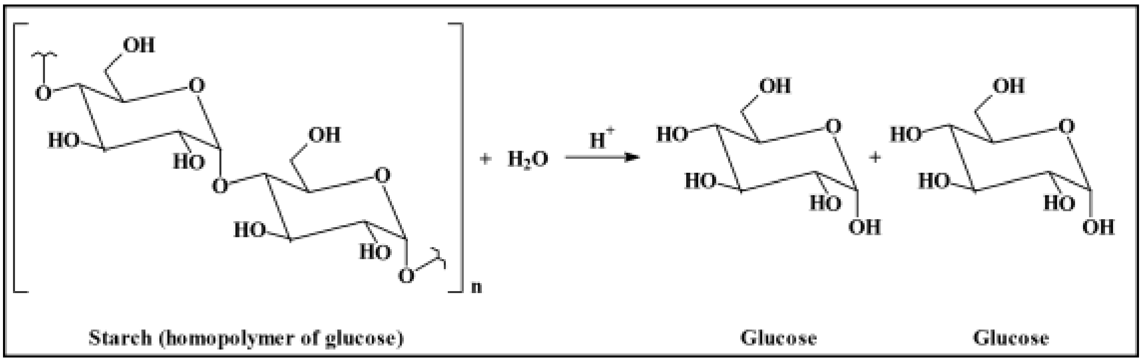

Figure 1. Hydrolysis reaction of acid catalyzed sago flour (starch) to form glucose (Carey, 1992)

Table 1. Results of qualitative identification of sago flour hydrolysis by iodine and Benedict's test

Time of hydrolysis (hr)	0	2	4	6
Observation (colour changes of sample + iodine solution)	 Blue black colour	 Violet colour	 Red colour	 Colourless
Interpretation	Polysaccharides (starch/amylose) is present	Dextrins		Monosaccharide (glucose) is present
		Oligosaccharides is present	Disaccharides is present	
Observation (colour changes of sample + Benedict's reagent)	 Deep blue colour	 Deep blue colour	 Deep blue colour	 Brick red colour
Interpretation	Non-reducing sugar present in the sample	Non-reducing sugar present in the sample	Non-reducing sugar present in the sample	Reducing sugar present in the sample

shows that starch (amylose) has been fully hydrolyzed into glucose after the starch has been hydrolyzed for 6 hours. The blue black colour of starch solution before hydrolysis arises because iodine in an aqueous solution of potassium iodide reacts with starch to form a starch-iodide complex. The starch-iodide complex is formed as the charge is transferred between the starch and iodide ions - triiodide or pentaiodide. The transfer of charge between the starch and the iodide ion changes the spacing between the energy levels orbitals. This change results in the starch-iodide complex absorbing light at a different wavelength which gives the characteristics of blue black colour to the reaction mixture. showed a deep blue colour change from the starch solution before and during hydrolysis to brick red after hydrolysis (Table 1). The qualitative identification results of the hydrolysis of sago flour with the Benedict's test.

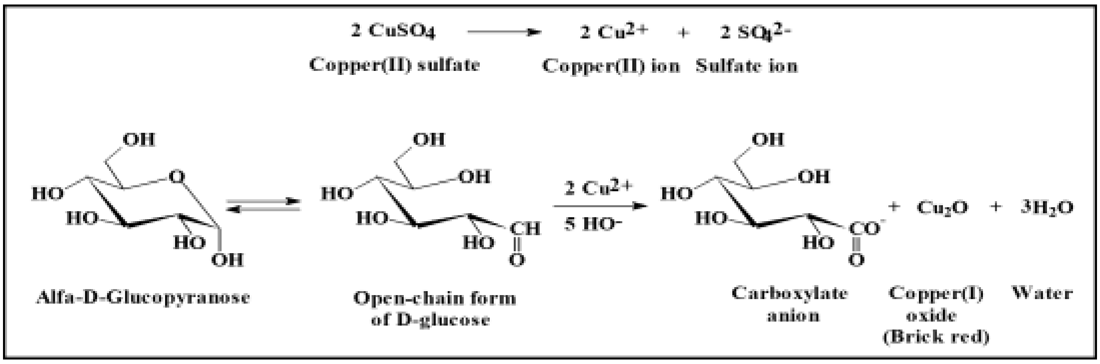

Figure 2. The formation of a brick red precipitate of copper(I) oxide by reduction of Cu(II)

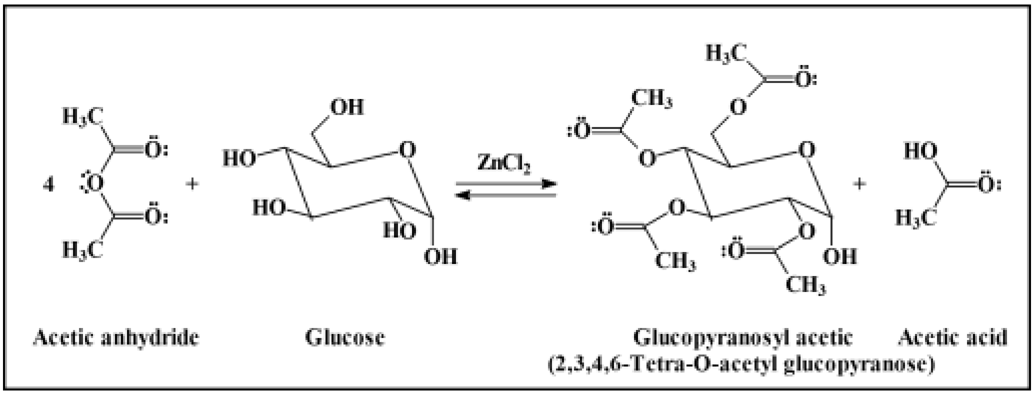

Figure 3. The reaction of glucose esterification with acetic anhydride by zinc chloride catalyzed to form glucopyranosyl acetic and acetic acid

The result shows that starch (amylose) has been completely hydrolyzed into glucose after the starch was hydrolyzed for 6 hours. The qualitative identification results of the hydrolysis of sago flour with the Benedict's test The The deep blue colour formed before and during the hydrolysis process of the starch solution it indicating the polysaccharides (starch/amylose), oligosaccharides, and disaccharides cannot reduce Benedict's reagent. The ability of a sugar to reduce alkaline test reagents depends on the availability of an aldehyde or ketone group for reduction reactions. A number of sugars especially disaccharides or polysaccharides have glycosidic linkages which involve bonding a carbohydrate (sugar) molecule to another one, and hence there is no reducing group on the sugar; like in the case of sucrose, glycogen, dextrin and starch (Carey, 1992).

The brick red color formed after hydrolysis of the starch solution indicates that monosaccharide (glucose) can reduce a solution of copper(II) sulfate as its citrate complex (Benedict's reagent). Carbohydrate that contains a free hemiacetal function is a reducing sugar. In order to oxidation occur, the cyclic hemiacetal form must first ring-open to give the reactive aldehyde. Therefore, these sugars become potential agents capable of reducing deep blue solution of copper(II) ions (Cu^{2+}, cupric ions) to copper(I) ions (Cu^+, cuprous ions). These ions form precipitate as brick red coloured cuprous [copper(I) oxide] (Amrita, 2020) (Fig. 2).

The second stage is the esterification of glucose with acetic anhydride by zinc chloride catalyst. The reaction of esterification of glucose with acetic anhydride by zinc chloride catalyzed to form glucopyranosyl acetic and acetic acid is shown in Figure 3. In this reaction, acetic anhydride, a derivative of carboxylic acid anhydride, acts as an oxidizer and glucose, a monosaccharide containing the -OH group, acting as nucleophile. The most important reaction of acetic anhydride involves breaking the bond between oxygen from one of the carbonyl groups. The single bonds found in oxygen are converted into acyl groups. The acyl group (CH_3CO-) attacking nucleophiles (glucose) to form glucopyranosyl acetic.

Table 2. The comparison of FTIR spectrum of starch (raw material) and glucopyranosyl acetic (product)

No	Frequency (cm^{-1}) and Intensities		Frequency Ranges (cm^{-1}) and Intensities*	Group or Class	Remarks
	Raw Material)	Synthesis Product			
1	3450.5 (s)	3442.7 (s, br)	3500-3200 (s, br)	Alcohols	-OH stretch
2	1439.7 (s)	1436.9 (s)	1440-1260 (s)	ROH	C-OH deformation
3	1057.5 (s)	1043.4 (s)	1120-1080 (s)	Secondary -CHROH	C-OH stretch; lower when R is a cyclic
4	-	1755.1 (s)	1765-1720 (vs)	Esters RCOOR’	C=O stretch
5	1145.3 (vs)	1149.5 (vs)	1150-1110 (vs)	Ethers ROR’	C-O-C stretch in dialkyl ethers
6	1245.9 (s)	1232.4 (s)	1250-1170 (s)		C-O-C stretch in cyclic ethers
7	-	2933.5 (s)	2970-2850 (s)	Aliphatic RH	C-H stretch in $C-CH_3$ compounds
8	-	1371.3 (s)	1385-1365 (s)	Methyl $-CH_3$	$-O-CO-CH_3$ sym deformation
9	2850.79 (s)	2916.2 (s)	2940-2920 (s)	Methylene $-CH_2-$	$-CH_2-$ antisym stretch
10	1465.9 (m)	2885.2 (m)	2890-2880 (w)	Methine >CH-	C-H stretch in >CH-

◦Notes: vs = *very strong*; v = *variable*; s = *strong*; m = *medium*; w = *weak*; br = *broad*.
*Sources: (Kemp, 1991; Lambert et al., 2011; Silverstein et al., 1981; Sastrohamidjojo, 1992)

Table 3. The GC-MS spectrum of synthesis product

m/z	Groups Associated with the Mass Lost	Ion	Missing Fragment	Remarks
348	$[C_{14}H_{20}O_{10}]^{+\bullet}$	$M^{+\bullet}$	-	Molecular ion
333	$[C_{13}H_{17}O_{10}]^{+}$	M-15	$[^{\bullet}CH_3]$	Methyl radical
318	$[C_{12}H_{14}O_{10}]^{+}$	M-15	$[^{\bullet}CH_3]$	Methyl radical
301	$[C_{12}H_{13}O_{9}]^{+}$	M-17	$[^{\bullet}OH]$	Hydroxyl radical
242	$[C_{10}H_{10}O_{7}]^{+}$	M-59	$[^{\bullet}O_2C_2H_3]$	Acetate radical
198	$[C_{9}H_{10}O_{5}]^{+}$	M-44	$[CO_2]$	Carbondioxide
154	$[C_{8}H_{10}O_{3}]^{+}$	M-44	$[CO_2]$	Carbondioxide
95	$[C_{6}H_{7}O]^{+}$	M-59	$[^{\bullet}O_2C_2H_3]$	Acetate radical
81	$[C_{5}H_{5}O]^{+}$	M-14	$[^{\bullet}CH_2]$	Methylene radical

While the acetate ion ($CH_3CO_2^-$) attacking protons from nucleophiles (glucose) to form acetic acid. The success of the glucopyranosyl acetic synthesis reaction from sago flour (starch) can be seen from the FTIR spectrum. The comparison of the FTIR spectrum of starch (raw material) and glucopyranosyl acetic (product) is shown in Table 2.

The FTIR spectrum of the synthesis product showed a strong absorption band at 1755.1 cm^{-1} originating from the vibrations of the C=O ester range. The absorption band of the C=O ester stretch vibration is not found in the starch spectrum (raw material). The FTIR spectrum of the synthesized product also showed a strong absorption band at 2933.5 and 1371.3 cm^{-1} derived from the vibrations of the C-H range in $C-CH_3$ and the deformation of symmetry $-O-CO-CH_3$. These two strong absorption bands are also not found in the starch spectrum (raw material). The emergence of vibrations of the C=O ester, C-H in $C-CH_3$, and deformation of symmetry $-O-CO-CH_3$ in the FTIR spectrum of the synthesis product showed that the

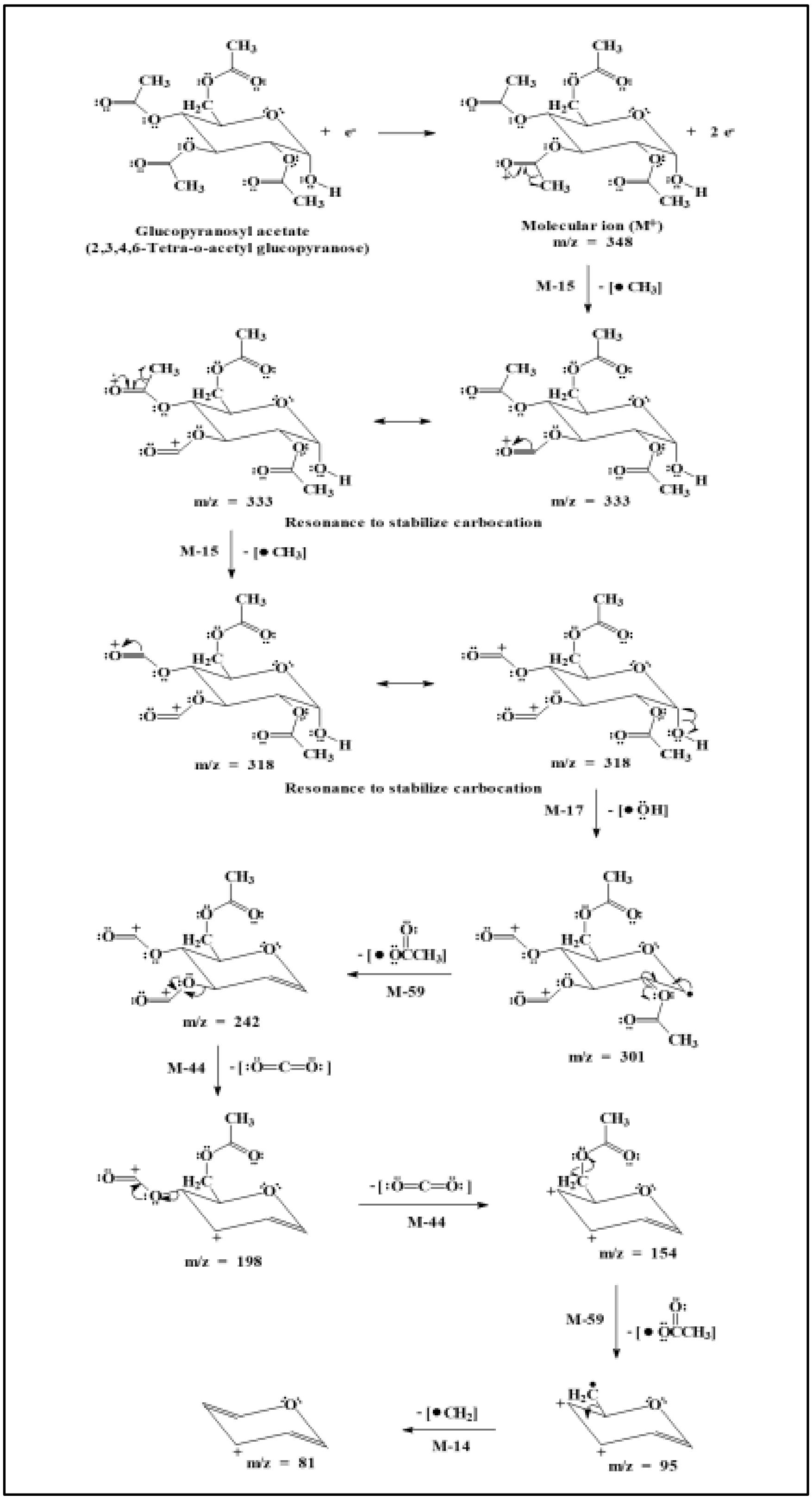

Figure 4. Rationalization of glucopyranosyl acetic fragmentation

reaction of glucose esterification of starch hydrolysis to form glucopyranosyl acetic has been successful. The success of the glucopyranosyl acetic synthesis reaction from sago flour (starch) was also supported by GC-MS spectrum data of the synthesis product (Table 3). The m/z peak 348 indicates molecular ions

($M^{+\bullet}$) or the molecular weight of the compound. The m/z peaks of 333 and 318 show the breakdown of a methyl group, respectively. The m/z 301 peak indicates the breakdown of the hydroxyl group. Peak m/z 242 shows loss of acetate fragments. The m/z 198 and 154 peaks indicate the loss of one carbon dioxide fragment, respectively. The m/z 95 peak indicates loss of acetate fragments. The m/z 81 peak indicates loss of the methylene fragment. The results of the GC-MS spectrum interpretation of the synthesis product above show that the compound produced was glucopyranosyl acetic or 2,3,4,6-tetra-O-acetyl glucopyranose. This can also be seen in the rationalization of glucopyranosyl acetic fragmentation in Figure 4.

CONCLUSION

The synthesis product was obtained through two reaction stages, namely the hydrolysis and esterification reactions. Synthesis product was obtained as a white solid substance (57.31% recovery), a melting point of 110-111 ºC, and Rf 0.79 on TLC (SiO_2, *n*-hexane : ethyl acetate = 9: 1 v/v). The results of the analysis of synthesis products with FTIR and GC-MS spectrometers showed that the synthesis product was glucopyranosyl acetic or 2,3,4,6-tetra-O-acetyl glucopyranose.

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