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Physicochemical Characteristics of Breadfruit (*Artocarpus altilis*) Starch Based on Starch Preparation and Modification Methods

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ABSTRACT

Breadfruit (*Artocarpus altilis*) is a starchy and nutritious food, particularly in carbohydrates. Breadfruit can be turned into starch to increase its usefulness and shelf life. The study aimed to evaluate how different starch preparation and modification procedures affected the physical and chemical properties of the final starch. This study applied a factorial Randomized Block Design (RBD) approach, namely starch preparation (porridge and chips) and modification methods (heat moisture treatment/HMT, acetic acid immersion, and autoclaving-cooling). The overall yield, starch content, air content, ash content, amylose content, swelling power, solubility, and clarity were all examined. Data is processed using Analysis of Variance (ANOVA) in the SPSS application version 21, and if there are any differences between treatments, a Duncan Multiple Range Test (DMRT) will be performed. Breadfruit starch produced using the autoclaving-cooling modified porridge method had the highest characteristics, with a total yield of 10.81%, starch content of 86.73%, water content of 9.59%, ash content of 0.42%, amylose content of 24.18%, swelling power of 9.02 g/g, solubility 8.93%, and paste clarity 71.86%T.

Keywords: Acetic acid, autoclaving-cooling, chips, HMT, porridge

INTRODUCTION

Breadfruit or traditionally called sukun (*Artocarpus altilis*) is a local fruit that is spread in various regions, especially Indonesia (Prasesti *et al.*, 2016) and is often used as a staple food by some people because it contains high carbohydrates and has a texture and taste that tends to resemble bread (Harmanto, 2012). This tropical fruit with the *Moraceae* family has a complex nutritional content, starch 68%, protein 4%, fat on a dry basis 1%, fiber 25%, phosphorus, magnesium, potassium, thiamine (B1), niacin (B3) and carotenoids that are not found in white rice or white potatoes (Ragone, 2014). Besides being consumed by frying or steaming, breadfruit can also be processed into an economical product such as starch. Breadfruit's high starch content makes it ideal for extraction and use as a thickener, binding agent, texture shaper, and fat substitute in yogurt and marshmallows. Processing breadfruit into starch can also be a good alternative to extend the shelf life of breadfruit (Putri and Nisa, 2015).

Starch can be produced in various ways, such as by reducing its size by using a blender to convert it into pulp and cutting it into chips. Research by Ariyanti et al. (2017) stated that differences in starch processing methods (taro starch obtained directly from taro tubers or taro flour) can affect the chemical and functional properties of the starch produced.

Native starch, including breadfruit starch, has various disadvantages in its features, such as requiring a long time to cook, not being resistant to acids, being insoluble in water, and forming a paste that is not clear, hard, and very sticky (Alay and Meireles, 2015). Native starch is also not resistant to high temperatures and mechanical processing, and difficult to form homogenous gels (Nagy *et al*., 2021). In general, the desired starch in the food industry is low viscosity, resistant to acidic conditions and high temperatures, clear and soft gel, low stretch strength, high gelatinization temperature and time, low retrogradation, and starch granules that are more easily broken with low temperature and time (Alay and Meireles, 2015).

Modification is expected to change the physical and chemical characteristics of native starch, while still maintaining the the starch's granule structure (Millati and Nurhayati, 2020). Starch modification is carried out with the aim that starch can dissolve in water and has functional characteristics such as emulsion stability, viscous power, and high water absorption (Erika, 2010). There are several methods of starch modification, physical (autoclaving-cooling, preheating, annealing, and heat moisture treatment/HMT), chemical (hydrogen peroxide oxidation, acetic acid soaking, and HCl soaking), and fermentation using bacteria, and enzymatically (Agustiani et al., 2020).

HMT is one of the physical starch modification methods. The principle is to apply a certain amount of heat to the starch, which ranges from 80 to 140 ^{o}C for 1 to 24 hours with a low moisture content (below 35%). Controlling the temperature and moisture content will change the physical characteristics of starch due to changes in the starch granule structure (Agustiani et al., 2020). The method of starch modification using acetic acid can improve the functional properties of starch by replacing acetyl groups and hydroxyl groups. In addition, soaking starch in an acetic acid solution will allow the appearance of white starch to be maintained due to the inhibition of the phenolase enzyme (Syamsir et al., 2012). Autoclaving-cooling is one method of physically modifying starch to increase viscosity, stability, tendency of starch to retrogradation, gelatinization temperature, and limiting starch swelling (Wiadnyani et al., 2017). When the heating process with autoclaving takes place, damage and swelling will occur in the starch granule structure so that the shape is irregular, and during the cooling process the starch begins to retrograde which is resistant to digestive enzymes (Herawati et al., 2020). Therefore, this study was conducted to determine the effect of different starch processing methods (porridge method and chips method) and types of starch modification using HMT, acetic acid soaking, and autoclaving-cooling (heating-cooling) on the characteristics of breadfruit starch produced.

MATERIALS AND METHODS

Tools and Materials

The tools used are water bath (Memmert WNB14RACK), autoclave (EYELA MAC-501), pH meter (AMT20 Benchtop), 21 cm vacuum desiccator, furnace, (Nabertherm LT3 1200 B140), spectrophotometer Uv-Vis (Shimadzu UV-1700), vortex Mixer (DLAB MX-S), and centrifuge (Hettich EBA 20).

The materials used were breadfruit from Lambaro Market (Aceh Besar, Aceh), acetic acid, Luff Schoorl solution ($CuSO_4.5H_2O$, $Na_2CO_3.10H_2O$, and citric acid), HCl 25%, NaOH 1M, KI 20%, H_2SO_4 25%, iodine solution 0,01 N, $Na_2S_2O_3$ 0,1N, starch indicator, 95% ethanol, ice water, and distilled water.

Experimental Design

The research used a factorial Randomized Block Design with 2 factors. The first factor is the preparation method of breadfruit starch (P) which consists of 2 levels, namely P1 = Porridge and P2 = Chips. The second factor is the starch modification method (M) which consists of 3 levels, namely M1 = HMT, M2 = acetic acid immersion, and M3 = autoclaving-cooling. Three replications were performed on each treatment, total of 18 experimental units.

Preparation of breadfruit starch using the porridge method

The process for making breadfruit starch with the porridge method follows Anwar et al., (2020). Peeled and cleaned breadfruit pieces were added with water in a ratio of 1:5 and crushed into a porridge using a blender. The porridge was filtered using a filter cloth and the liquid was soaked for 12 hours and every 6 hours water was changed. Then, the sediment was taken out and dried using an oven for 24 hours at 70ºC. The dried starch was then blended and filtered using a 60-mesh sieve to obtain a fine breadfruit starch.

Chips method of breadfruit starch preparation

The process for making breadfruit starch with the chips method follows the procedure of Aryanti et al., (2019). The breadfruit flesh has been cleaned, sliced, and rinsed with water. After draining, the breadfruit slices were oven-dried at 50ºC for 24 hours. The dried breadfruit slices were crushed to produce breadfruit flour. Breadfruit flour was extracted by adding water (1:5) and filtered using a filter cloth. The filtered water was left in a basin for 12 hours and water was changed every 6 hours. Then, the precipitate was dried using an oven at 70ºC for 24 hours. It was then cooled and sieved (60-mesh) to obtain fine breadfruit starch.

HMT modification

Breadfruit starch was adjusted for moisture content using the mass balance method until it reached 30%. Furthermore, the breadfruit starch was wrapped using aluminum foil and put into a refrigerator at 4ºC for 24 hours so that the moisture content of the sample was uniform. Then, the starch was heated using an oven for 5 hours at 110ºC. Then, aluminum foil containing starch was cooled at room temperature for 1 hour. Then, it was dried using a drying oven at 50ºC for 4 hours. The starch obtained was blended and sieved (80-mesh). This method referred to Herawati et al., (2010).

Acetic acid immersion modification

Acetic acid immersion modification according to Nurhaeni et al., (2018). Breadfruit starch 100 g of was dissolved in 225 ml of distilled water and stirred using a magnetic stirrer on a hot plate for 60 minutes and at 25ºC. NaOH 3% was added until the pH became 10 and continued with the addition of 50 ml of 0.25% (v/v) acetic acid solution while stirring and allowed to stand for 20 minutes. Then, 0.5 N HCl was added to the solution until the pH reached 4.5. Then, filter and wash the precipitate using distilled water. Next, it was dried in an oven for 24 hours at 45ºC. The starch was blended and sieved using an 80-mesh.

Modification of breadfruit starch using autoclaving-cooling method

Modification using autoclaving-cooling method referred to Wiadnyani et al., (2017). The 100 g breadfruit starch was adjusted to reach 20% moisture content. Furthermore, breadfruit starch was packaged using HDPE plastic and put into a refrigerator for 12 hours at 4°C, so that the spread of water in the starch occurred evenly. Then, the starch was heated using an autoclave for 15 minutes at 121ºC. Then, the starch was cooled for 1 hour at room temperature to prevent further gelatinization. The starch was placed in a refrigerator for 24 hours at 4°C and dried again using an oven for 4 hours at 50°C. The dried starch was blended and sieved using an 80-mesh.

Analysis of chemical characteristics of modified breadfruit starch

Analyses performed on native (control) and modified breadfruit starch included moisture content (AOAC, 2005), ash content (Polnaya et al., 2018), starch content (Ifmaily, 2018), and amylose content (Polnaya et al., 2018).

Analysis of physical characteristics of modified breadfruit starch

Analyses conducted on native (control) and modified breadfruit starch included total yield (Wiadnyani, 2017), swelling power and solubility (Wiadnyani, 2017), and paste clarity (Polnaya *et al.*, 2018).

Statistical Analysis

The data were analyzed using the Analysis of Variance (ANOVA) and Duncan Multiple Range Test (DMRT) if there were significantly different treatments. In this study, native starch was used as a control.

RESULTS AND DISCUSSION

Chemical Characteristics of Modified Breadfruit Starch

Based on the research that has been conducted that the interaction of starch preparation and modification method had a significant effect ($P<0.01$) on the moisture content, ash content, and starch content of breadfruit starch. The starch preparation and modification method did not significantly affect the amylose content of breadfruit starch.

Moisture Content

Table 1 shows that the moisture content of breadfruit starch ranged from 4.27%-15.70%. The moisture content of native breadfruit starch by the porridge method was 10.72% and the chips method was 15.45%. This moisture content is higher than Palijama *et al.* (2017), the moisture content of native breadfruit starch ranged from 3.74%-6.64%. The moisture content of breadfruit starch in the chips method was higher than the porridge method. The difference in the preparation of breadfruit starch in the pulp method is due to the direct crushing of the breadfruit, which will facilitate the release of trapped water molecules from the fibers and tissues of the breadfruit. The process of releasing water from the breadfruit will take place more easily and quickly compared to the chips method of breadfruit starch where the crushing process is not done directly on the breadfruit (Pratiwi *et al.*, 2020).

Based on the research of Sardiman et al. (2020), the moisture content possessed by HMT-modified sweet potato starch is 8.02%. This result is not much different from the moisture content of HMT-modified breadfruit starch produced by this study which is 8.12%. Based on Table 1, the modification of acetic acid immersion in breadfruit starch has a lower moisture content than other modification methods. This result follows the research of Aryanti et al. (2017), where acid treatment can cause the starch structure to be more tenuous and water evaporation will be easier.

Ash Content

Table 1 shows that the ash content of modified breadfruit starch ranged from 0.26%-1.48%. The highest ash content was found in the autoclaving-cooling modified chips method which was 1.48%. The ash content was higher than the native breadfruit starch in the porridge method which was 0.19% and in the chips method which was 1.25%.

The ash content of breadfruit starch in the porridge method was lower in the chip method. This result can be caused by the repeated heating experienced by the chips method which will affect the increase in ash content (Sabatini et al., 2021). The same applies to the modification process of breadfruit starch that requires longer oven heating causing an increase in ash content. In this study, the ash content of breadfruit starch modified by autoclaving-cooling was higher than the HMT modification and acetic acid soaking (Table 1). Based on Anugrahati and Widjanarko's (2018) research, the ash content of autoclaving-cooling red bean flour was 3.97%, and cassava starch by Nazhrah et al. (2014), which was 0.32%. The difference in ash content can be influenced by differences in starch processing that require washing and soaking, allowing minerals to dissolve in water. In addition, the difference in ash content in starch is also influenced by heating. The longer the heating, the higher the ash content (Sabatini et al., 2021). Therefore, breadfruit starch from the chips method which requires more oven drying contains higher ash content compared to breadfruit starch from the porridge method which only requires oven drying once.

Starch Content

The starch preparation and modification method had a very significant effect ($P<0.01$) on the starch content of breadfruit. The determination of starch content of breadfruit starch using the *Luff Schoorl* method ranged from 79.56%-93.87% (Table 1). The highest starch content was found in the HMT-modified breadfruit starch chips method at 93.87%, while the lowest one was found in acetic acid-immersion porridge starch at 79.56%. This result can occur because, during the acetic acid soaking process, the acetyl group causes the bond between starch molecules to be reduced and there is a decrease in starch content (Alay and Meireles, 2015).

The starch content in this study of native breadfruit starches the porridge method was 83.72% and the chips method was 88.44%. Research by Ifmaily (2018) stated that the starch content of native breadfruit starch was lower at 71.67%, while in Wiadnyani et al. (2017), the starch content of autoclaving-cooling taro was slightly higher, ranging from 92.32%-94.60%. Starch content will be influenced by its constituents, namely amylose and amylopectin. In addition, heat treatment during the starch processing and modification process will also make starch granules tend to break away, the higher the temperature, the starch will be more easily gelatinized which results in a decrease in starch content (Wiadnyani et al., 2017).

Amylose Content

The amylose content of modified breadfruit starch ranged from 12.49%-26.70% (Table 1). The amylose content of native breadfruit starch from the porridge method was 19.23%, and the chips method was 11.89%. According to Widyastuti et al. (2021), amylose content can increase due to the HMT modification process which causes the interaction of amylose and amylopectin in the amorphous region of the granule. This result makes the starch structure compact and tends to make gelatinization limited and more resistant to heat treatment. Based on the research of Putri and Zubaedah (2015), amylose content is not affected by the modification method. The modification will make breadfruit starch more resistant to hydrolysis so that the breakdown of starch molecules into simpler forms will be more difficult.

The amylose content of breadfruit starch in the porridge method tends to be higher than that of breadfruit starch in the chips method. Amylose will decrease along with the length of drying. Drying will cause the starch granules to break down and make the water in the starch granules easily come out along with the water-soluble amylose. When drying progresses, there is a break in the polymer chain of some starch constituent molecules thus the resulting amylose fraction has a low molecular weight that is easily soluble (Pratiwi et al., 2020). Therefore, the chips method of breadfruit starch, which requires 2 times of oven drying, contains lower amylose content than the porridge method of breadfruit starch, which only requires one time of oven drying. Aryanti et al. (2017) also stated that starch produced directly from taro tubers has a higher amylose content of 5.55%, compared to starch produced from taro chips which is only 3.75%.

Physical Characteristics of Modified Breadfruit Starch

Based on the research that has been conducted, the starch processing and modification method had a significant effect ($P<0.01$) on the total yield of breadfruit starch. While the modification method had a significant effect ($P<0.01$) and starch processing method had no significant effect ($P>0.05$) on the swelling power of breadfruit starch. The method of making starch has a significant effect ($P<0.05$) on the solubility of breadfruit starch, while the modification method does not have a significant effect ($P>0.05$) on the solubility of breadfruit starch. The starch processing and modification method did not significantly affect ($P>0.05$) the clarity of breadfruit starch paste.

Total yield

The yield is produced through the comparison between the weight of breadfruit starch produced and the initial weight of breadfruit, which is usually expressed as a percentage. In Figure 1, the total yield obtained from breadfruit starch ranged from 2.28%-10.81%.

The highest yield was found in the autoclaving-cooling modified pureed breadfruit starch at 10.81%. The yield was slightly lower than the native breadfruit starch porridge method which was 10.96% and higher than the native breadfruit starch chips method which was 9.07%. This value is not much different from the yield of breadfruit starch in the research of Prasesti et al., (2016), which was 10.62%. The results are also in compliance with Sankhon et al., (2012), that is, parkia starch modified by autoclaving-cooling has a higher yield of 48.56% compared to HMT-modified parkia starch which is only 36.33%. Moreover, autoclaving-cooling modification is classified as a physical modification that is quite easy and efficient, where the process only requires heating for a short time without repetition so that the resulting yield can be optimized (Mushollaeni et al., 2021). This difference in yield can be also influenced by differences in varieties, differences in harvest periods, and differences in starch processing and processing when breadfruit starch is modified.

Based on the research, it is also known that the yield of breadfruit starch from the modified chips method of acetic acid

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soaking produces the lowest value. This can occur due to starch that was wasted during the washing process with distilled water after soaking with acetic acid. The yield of breadfruit starch in the chips method also tends to be lower due to the process of crushing and screening in the form of flour so that it is more easily separated and wasted. This is inversely proportional to the breadfruit starch porridge method which has a higher yield because the screening process is carried out in the form of crushed fruit. The direct crushing process also affects the yield, and as a result, the breadfruit starch produced by the porridge method has a higher yield than the starch from the chips method (Aryanti et al., 2017).

Swelling Power

Swelling power is one of the functional properties of starch that proves that amorphous and crystalline starch has movement. Swelling power will show the ability of starch to expand in water based on its maximum weight and volume increase (Haryanti et al., 2014).

In Figure 2, it can be seen that the swelling power obtained by HMT, acetic acid soaking, and autoclaving-cooling breadfruit starch were 9.48 g/g, 15.06 g/g, and 9.02 g/g, respectively. Acetic acid-soaking modified breadfruit starch produced the highest swelling power. This result occurred due to the alternation between hydroxyl groups and acetyl groups which caused a change in the functional properties of starch where there was a reduction in hydrogen strength between starches so that starch granules were easier to expand and had high solubility in water (Nurhayati, 2019). This value is still lower than the control breadfruit starch of the porridge method which is 17.09 g/g. Based on the research of Kaur and Singh (2019), Indian oat starch HMT decreased from 13.1-19.1 g/g to 11.4-14.3 g/g. The breakdown of starch chains during HMT modification may influence the decrease in swelling power value, leading to changes in clarity and starch strength.

Mutmainah et al., (2013) stated that the swelling power value of acetic acid-modified breadfruit flour was lower at 5.2 g/g and HMT-modified breadfruit flour in the research of Agustiani *et al.* (2020) which was 2.33 g/g. In this study, there was also a decrease in swelling power compared to the control. This can be caused during modification, especially HMT and autoclaving-cooling, which requires a heating process that causes interactions and changes in the arrangement between starch components in the amorphous granule and crystallite areas of starch. Starch granule molecules can also be arranged more tightly so that the granules will find it difficult to swell and experience a decrease in the swelling power value. The lower the value of starch swelling power, the more difficult it will be for starch to expand in water (Kusumayanti, 2014).

Solubility

Solubility is one of the functional properties of starch that shows the percentage of starch that can dissolve in water (Widyastuti et al., 2021). Food processing often requires the addition of water, so the desired starch is starch that can dissolve in water. Solubility is closely related to swelling power, where the lower the solubility, the more difficult it will be for a product to puff up.

In Figure 3, it can be seen that the solubility of breadfruit starch obtained by the modified porridge method was 8.09%, a decrease compared to the control breadfruit starch by the porridge method of 17.15%. Meanwhile, the solubility of breadfruit starch with modified chips method was 13.47%, an increase from the control breadfruit starch with chips method of 9.20%.

The breadfruit starch chips modified by autoclaving-cooling gave the best solubility value of 19.95%. Putri and Zubaedah (2015) stated that modified breadfruit flour has a higher solubility of 16.97%-27.08%. Kaur and Singh (2019) also mention that Indian oat starch also experienced a decrease in solubility compared to control starch, namely 12.4-22.0% which dropped to 4.7-8.5% after being modified by HMT, where the value is not much different from the solubility of this study. The strengthening of bonds in the starch structure can occur along with an increase in the interaction between amylose and amylopectin molecules which results in the penetration of water in starch granules being inhibited and causing a decrease in the percentage of solubility. As stated by Kusumayanti et al. (2014), several things can affect the solubility of starch in water such as amylose and amylopectin content, starch source, and starch swellability.

Paste Clarity

The paste clarity of breadfruit starch ranged from 41.46%T-75.77%T. There was an increase in paste clarity in modified breadfruit starch compared to the control porridge method starch 39.99%T and control chips starch 19.41%T. In native starch, amylose linear molecules will more easily rearrange their linear molecules through hydrogen bonds so that light absorption during clarity measurements increases and is opposite to the %Transmittance which becomes lower (Polnaya et al., 2018). Furthermore, Kaur and Singh (2019) also mention that HMT-modified Indian oat starch has a paste clarity ranging from 58.3%-77.73%T. These values are almost like the results of this study.

Several factors can affect pasta clarity. Paste clarity will be inversely proportional to amylose content and retrogradation. Retrogradation will cause a decrease in the ability of light to pass through and decrease the clarity of the paste. In addition, heating and the amount of water absorbed into the starch can also affect the clarity value of the paste based on the percentage transmittance. The higher the amount of water, the higher the clarity of the paste (Syafriyanti et al., 2018).

CONCLUSION

The difference in starch processing and modification methods significantly influenced the characteristics of the breadfruit starch produced. The best treatment of this research is the breadfruit starch autoclaving-cooling modified porridge method which has a total yield of 10.81%, starch content of 86.73%, moisture content of 9.59%, ash content of 0.42%, amylose content of 24.18%, swelling power of 9.02 g/g, solubility of 8.93% and clarity of 71.86%T paste.

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Table 1. Chemical characteristics of modified breadfruit starch (%)

Formulas	Moisture content	Ash content	Starch content	Amylose content*
P1M1	8.12 ± 0.42[b]	0.30 ± 0.02[a]	85.98 ± 3.97[b]	21.70 ± 3.62
P1M2	4.27 ± 0.64[a]	0.26 ± 0.01[a]	79.56 ± 1.18[a]	22.10 ± 2.67
P1M3	9.59 ± 0.41[b]	0.42 ± 0.13[ab]	86.73 ± 1.21[b]	24.18 ± 3.62
P2M1	15.70 ± 1.77[d]	0.90 ± 0.12[c]	93.87 ± 1.97[c]	17.30 ± 2.92
P2M2	5.27 ± 1.58[a]	0.61 ± 0.05[b]	88.76 ± 1.09[b]	26.70 ± 7.26
P2M3	12.13 ± 1.13[c]	1.48 ± 0.03[d]	84.95 ± 1.51[b]	12.49 ± 0.45

*: No significant effect
The same letter notation in each column indicates no significant difference at DMRT the 1% level.
P1M1: Breadfruit starch HMT modified with porridge method
P1M2: Breadfruit starch acetic acid immersion modified with porridge method
P1M3: Breadfruit starch autoclaving-cooling modified with porridge method
P2M1: Breadfruit starch HMT modified with chips method
P2M2: Breadfruit starch acetic acid immersion modified with chips method
P2M3: Breadfruit starch autoclaving-cooling modified with chips method

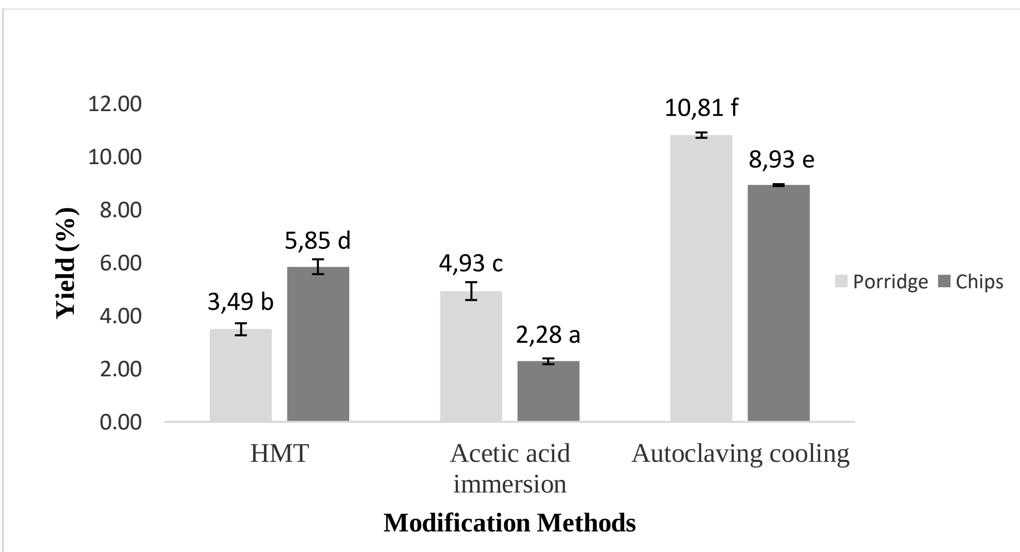

Figure 1. Effect of starch processing and modification methods on the total yield of breadfruit starch (numbers followed by the same letter indicate that the results are not significantly different at $DMRT_{0,01}$)

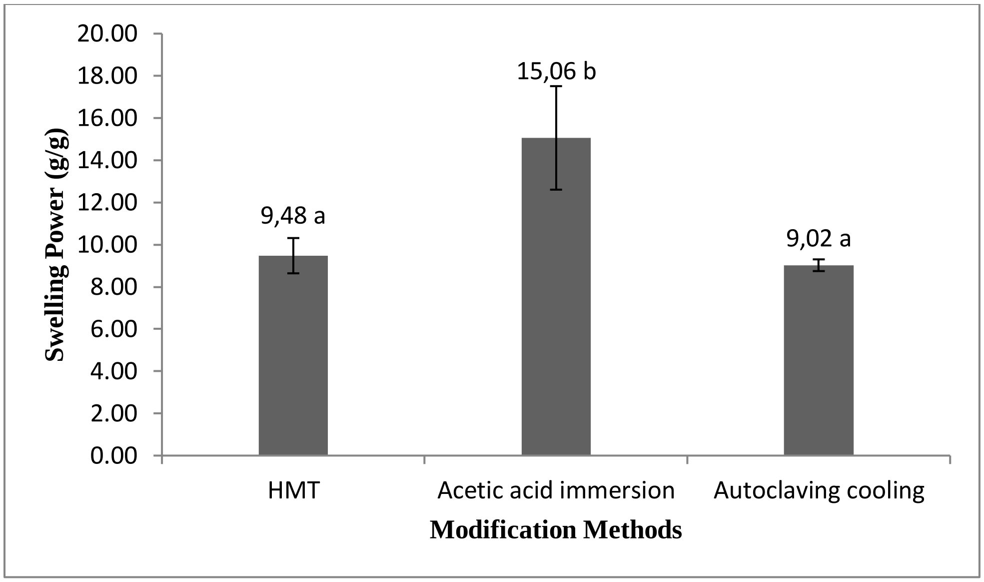

Figure 2. Effect of modification methods on the swelling power of breadfruit starch (numbers followed by the same letter indicate the results are not significantly different at $DMRT_{0,01}$)

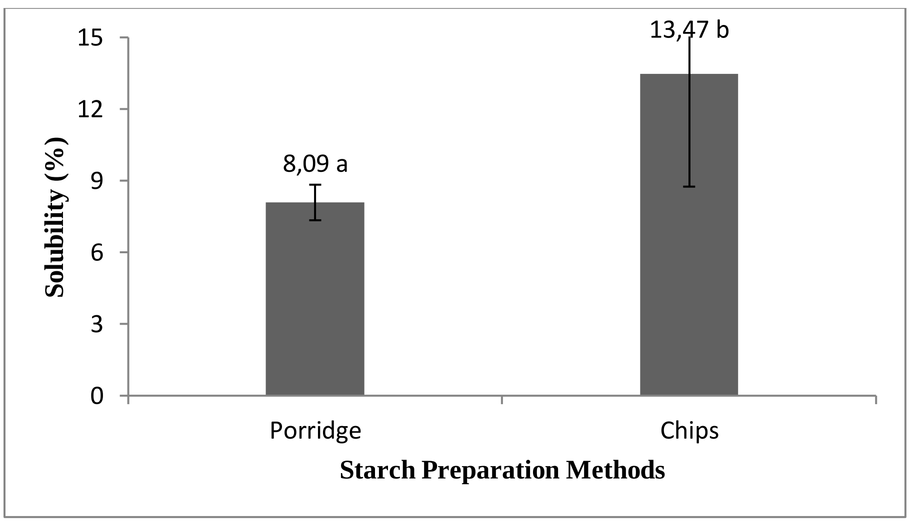

Figure 3. Effect of starch preparation method on breadfruit starch solubility (numbers followed by the same letter indicate the results are not significantly different at $DMRT_{0,01}$)