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The Chemical Contents of the Starch of *Palado* Seed (*Aglaia sp*) with Pregelatinization, Cross-linking, and Acetylation Modifications

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Abstract

Indonesia has a great potential of raw materials for the production of starches. One of which is *palado* seed that has a fairly-high carbohydrate content which is potential to be developed into starches. The utilization of the native starch is still very limited due to lack of physical and chemical properties for widely use. It is related to the low level of retrogradation, stability and resilience of the pasta. This is the reason in conducting starch modification in order to obtain suitable properties for a particular application. The starch modification methods used in this study are pregelatinization, cross-linking, and acetylation. The purpose of this research is to study the effect of modification method on the chemical contents of the modified starch of *palado* seed. The research was conducted in three stages; the first stage is making the starch, the second stage is starch modification and the third stage is the proximate analysis, as well as the chemical properties of the starch of *palado* seed.

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The results showed the proximate analysis of the modified starch of *palado* seeds on the water content ranged from 10,15 – 10,48%, ash content ranged from 0,47 – 1,18%, fat 2,01 – 4,37%, protein 0,40 – 0,81%, and the carbohydrate content ranged from 83,75 – 87,19%, while the chemical properties include the starch content ranged from 40,86 – 75,29%, amylose 1,92 – 3,01%, and amylopectin 37,97 – 69,28%. These results showed that the starch of *palado* seed, in accordance with SNI (Indonesian National Standard) for starch, that maximum water content is 14%, maximum ash content is 15%, and the minimum starch content is at least 75%, obtained from pregelatinization modification treatment.

Keywords: *chemical content; starch palado seeds; with modification.*

1. Introduction

The high-level biodiversity in Indonesia has not been maximally exploited/utilized. The agricultural productivity decreases and results in import of various basic needs. On the other hand, there are many agricultural products which are *under-exploited* and *under-utilized* as well as for the basic information regarding these products which is still minimum [1]. Therefore, it highly needs to conduct a basic research to understand the characteristics of the agricultural products of Indonesia itself as the foundation of the development of agro-industry.

Report one of floral types which has a relatively high carbohydrate content that is the *palado* seed (*Aglaia sp*) (Fig 1) [2]. In 100 g of *palado seed* containing 64,04 g carbohydrates; 8,94 g protein; 14,75 g fat; and 3.36 g ash content. *Palado* seed can be used as a source of carbohydrates, since most of its constituent carbohydrates are starches. The starch content of *palado* flour is (naturally) quite higher (52,78%) than to the natural starch content (47,55%). In West Sulawesi, *palado* seeds are traditionally consumed by the local people, especially for the boiled nuts. The boiled alado nuts contain oil, and are filling and very popular to consume.



Figure 1: Seeds of *palado* (*Aglaia sp*)

One of the important processed *palado* seed products and has not been made by the local community is the *palado* nut starch. Therefore, there is a need of innovation in the utilization of *palado* seed in order to make it storable for a relatively long period, one of which is by the modified processing of *palado* seed starch. According to [3], the development of knowledge about the molecular structure of starch leads the experts modify the natural structure of the starch. Native starch has a weakness on its characteristics that are not soluble in cold water, requiring a long time to cook, solid produced pasta, and have a low stability. Furthermore [4], suggested that the native starch generally has a weak structure, cohesive gel, high gelatinization temperature,

has an ability to form the high gel in starch dispersion, low water resistance at low temperature, low resistance of the starch dispersion low to acid, agitation, and the pasta has a tendency to retrogradation.

Added that the weakness in the properties of native starch makes its utilization, especially in the food industry, limited due to the diversity in modern food industry and high variation of food products which requires tolerant raw starch materials in a broad range in various processing techniques since the preparation, storage, until the distribution [4]. Similarly [5], explained that the native starch has several problems associated with retrogradation, stability, and low durability of pasta. It becomes the reason for the need for modification of starch, so that there will be suitable properties obtained for specific applications, thus, the starch can be improved for wider utilization in the food industry.

Report the world's starch productions are from corn starch (64,6 million tons/year), cassava starch (10,2 million tons/year), wheat starch (6,0 million tons/year), potato starch (3,4 million tons/year) and rice starch ($\leq 0,05$ million tons/year) [6]. Meanwhile, the major starch producing countries are the USA, Japan, China, and South Korea (corn starch), Thailand, Indonesia, Brazil, and China (cassava starch), France, Germany, USA, and China (wheat starch), Netherlands, Germany, French, and Chinese (potato starch), and Belgium, Thailand, and Italy (rice starch). Report that Indonesia imports a variety of modified starches to support the development of various industries, both food and non-food industries. The import volume of modified starches in 2001 reached 87,927 tons with a value of 50,184,576 US dollars and in 2002, reached 80,319 tons with the import value of 41,875,152 US dollars [7].

Starch modification can be performed physically and chemically. One of the physically modification starch methods is the pregelatinization modification. Stated that pregelatinized starch is the starch experiences the process of gelatinization and is then dried. This starch will be changed in its physical and the native properties [8]. Furthermore [8], the pregelatinized flour or starch modification through *parboiling* can improve the flour or starch paste. Meanwhile, chemical starch modification can be done by several methods such as cross-linking, and acetylation. Subsequently [4], stated that the cross-linking reaction can improve the hydrophobic properties of starch, viscosity stability, and resistance of starch at high temperature and high friction.

Meanwhile [9], explained that the acetylation is a very important method to modify the characteristics of starch since it can also provide the coagulating effect (as the *thickening agent*) on various food products. Regarding this matter, the purpose of this research is to study the characteristics of chemical properties of the modified *palado* seed starch as the raw material for further utilization in both food and non-food industries.

2. Materials and Method

2.1. Materials and method

The raw material used is the *palado* starch extracted from *palado* seed obtained from the forests around the Karama watershed (DAS) in Sampaga Sub-District, Mamuju District, West Sulawesi Province, Indonesia. The chemicals used for the analysis are the chemicals available in the Laboratory of Food Science and Technology, Faculty of Agriculture, Hasanuddin University (UNHAS), and in the Laboratory of Food Science and

Technology Department, Faculty of Agricultural Technology, Bogor Agricultural Institute (IPB).

The equipment used for proximate and chemical content analysis on *palado* seed starch are blender (Philips), *disc mill* FFA 23 A model, *automatic siever*, *cabinet dryer* (H.ORTH.GmbH D-6700, ITHU type, West Germany), *color reader*, kiln (*tanur*), oven (Memmer U-30), analytical balance (Explorer), *Stable Micro System* (TAXT-2 *Texture Analyzer*), desiccator, *Soxhlet* device, Kjeldahl device, *waterbath* (Memmert P Selecta Precisterm), *sentrifuge* (Hettich Zentrifugen-EBA 20), viscometer, digital balance (Adventurer Pro), and *texture analyzer*, *colorimeter*, oven, filter cloth, beaker, petri dish, erlenmeyer, measuring cup, mohr pipette, thermometer, dan *spectrophotometer* (UV-Vis Shimadzu UV Mini 1240), 80 mesh strainer (*ayakan*), cylinder, Griffin flask shaker (*labukocok*), and other equipment available in those laboratories.

This research was conducted in three stages; the first stage is the starch extraction from *palado* seeds, the second stage is starch modification with three treatment methods: pregelatinization, cross-linking, and acetylation conducted by the Laboratory of Food Science and Technology, Faculty of Agriculture, Hasanuddin University (UNHAS) and the third stage is the proximate and characteristic analysis of the chemical properties of the modified *palado* nut starch conducted at the Laboratory of Food Science and Technology Department, Faculty of Agricultural Technology, Bogor Agricultural Institute (IPB).

2.2. *Palado seed starch extraction process*

The method used for the extraction of *palado* starch is the method usually used for making starch refers to the method developed by [10], to obtain the optimization of making of arrowroot starch. So that, in order to obtain the *palado* seed starch, there were some steps conducted as follows: a) peeling, cleaning, washing and 12-hour soaking into natrium bisulfite (sodium bisulfite) solution, b) milling for 3 times with the ratio of starch : water for 1 : 3.5 (b/v), c) filtering with a hole size of 80 mesh, d) precipitation for 24 hours, e) drying, f) milling, and g) sieving.

2.3. *Palado nut starch modification*

The modification of *palado* seed flour was conducted in three stages of treatment, they were; pregelatinization, cross-linking, and acetylation modifications. The procedures of pregelatinization referred to the method conducted by [11]. The cross-linking modified starch was conducted based on the procedures conducted by [12], and the acetylation modified starch was conducted using the approach conducted by [9].

2.4. *The analysis of proximate and chemical contents of the starch*

The proximate analysis of *palado* seed starch was conducted by adopting the standard method of [13], as conducted by [14], including the determination of contents of water, protein, fat, and ash. The water content was determined using the hot air oven method (AOAC Method 934.01), crude protein by the Micro-Kjeldahl method (AOAC Method 960.52), crude fat by Soxhlet extraction (AOAC Method 963.15), ash content by the dry ashing method (AOAC Method 923.03) and carbohydrate content by the *by-difference* method [15]. Meanwhile, the analysis of chemical content of *palado* starch was conducted by using the analysis of starch content determined

by the *Luff Schoorl* titrimetry method [16], and the amylose content of *palado* starch was determined by using the method described by [17], to determine the amylose content of ripe banana flour and wheat flour.

3. Results and Discussion

3.1. The analysis of proximate and chemical contents of the starch

The results of analysis of proximate and chemical contents of the modified *palado* seed starch, including water, ash, fat, protein, carbohydrate, starch, amylose and amylopectin contents are shown in Table 1.

Table 1: Data proximate analysis and chemical content of starch seed palado modification (in 100 g)

Characteristics	Starch modification			
	Non-modification	Pregelatinization	Cross-linking	Asetylation
Water content (%)	19,64	10,15	10,48	10,30
Ash content (%)	0,49	0,47	1,18	1,18
Fat content (%)	2,56	2,01	3,58	4,37
Protein content (%)	0,27	0,81	0,45	0,40
Carbohydrate content (%)	77,04	87,19	84,31	83,75
Starch content (%)	47,55	72,29	64,54	40,86
Amylose content (%)	4,74	3,01	1,92	2,89
Amylopectin content (%)	42,81	69,28	62,61	37,97

Source : Data after processing (2017)

3.2. Water content

The analysis of the water content of the native *palado* seed starch is 19,64%, while the water content of the modified *palado* seed starch ranging from 10,15 – 10,48% (Table 1). The result of the analysis of water content of the modified *palado* seed starch shows that the highest water content was obtained from the cross linking modification of 10,48%. It shows that the water content of *palado* seed starch with cross-linking modification is smaller than water content of *canna discolor* (ganyong) and yam (*gadung*) starches with cross-linking modification as reported by [4], ranging from 11,68 – 13,07% and from 13,22 – 14,46%, respectively, and the water content of corn starch with pregelatinization modification ranging from 11,42 – 12,72% [18]. According [19], the high water content in the cross-linked starch is due to the phosphate group which is penetrated into the starch granules is ionic, so that it binds water. It is thought due to the differences in the length of drying and

storage conditions prior to the analysis [4]. Similarly [4], explained that the influencing factors in the drying process of a food material is the initial water content, environmental humidity, and heat transfer media of the material.

While the least water content of the *palado* seed starch was obtained with pregelatinization modification, that is 10,15%. It shows that the water content of the *palado* seed starch is higher than the water content of corn starch with pregelatinization modification of 8,86% [18]. However, the water content of *palado* seed starch with pregelatinization modification is lower than of cassava starch with physical modification process (*autoclaving*) which is ranging from 11,99 – 13,77% [20].

3.3. Ash content

Ash content indicates the mineral content of a material. The higher the ash content, the higher the mineral contained in the material, which affects its nutritional value. The ash content of the modified *palado* seed starch produced is ranging from 0,47 – 1,18%, while the ash content of the non-modified *palado* seed starch is 0,49%. The result of the analysis of the ash content of *palado* seed starch, both with cross-linking and acetylation modifications, does not show any difference, that is 1,18%. It is higher than the ash content of rice starch with acetylation which is ranging from 0,06 – 0,10% [21] and the ash content of corn starch with fermentation process which is ranging from 0,25 – 0,47% [22]. However, the ash content of the *palado* nut starch is lower than the ash content of the corn starch with enzymatic modification, ranging from 1,53 – 1,99% [22].

Quantitatively, the value of the ash content in starch is obtained from the mineral contained in seeds, and can also from the soil and air contamination during processing. The effect of processing on food material can also affect the availability of mineral within the body [23]. Explained that the ash content is strongly affected by the process of extraction and water-washing of the flour/starch, so that the water-soluble mineral will be easily wasted along with the dregs [20].

3.4. Fat content

The results of analysis showed that the fat content on the modified *palado* seed starch is ranging from 2,01 – 4,37%, while for the fat content on the non-modified *palado* seed starch is 2,56%. The highest fat content was obtained in the acetylation modification (4,37%) and the lowest was obtained from the pregelatinization modification (2,01%). In general, the *palado* seed starch contains higher fat than the wheat flour for 1,57% [14], rice flour for 1,00% and tapioca flour for 1,00% [24]. Likewise [6], reported that the fat content on corn starch ranges from 0,6 – 0,8%, wheat starch 0,8 – 1,2%, and rice starch 0,6 – 1,4%.

Nazhrah and his colleagues (2014) Stated that the difference on the processing temperature of physically modified starch also has a significantly different effect on the fat content of the modified starch. For example, the increase in *autoclaving* temperature will result in a decrease in fat content [20]. Furthermore [20]. stated that the modification process does not directly have an effect on the fat component, but rather on the starch components. Furthermore [25], assumed that in the starch extraction, the fat content is still bound with starch so it is not wasted along with the dregs, thereby increases per weight of starch. However, the excessive fat content,

in addition to the consideration in the nutritional factors, is also considered less beneficial in the storage because it can cause rancidity [26]. In addition, most of the fat will be absorbed by the surface of the granules in the form of hydrophobic fat layer around the granules. The fat layer will inhibit the binding of water by the starch granules. It causes the thickness and viscosity of starch is reduced by the reducing amount of water for the development of the starch granules.

3.5. Protein content

Unlike the fat, protein content in starch is actually expected to be high. It is related to the utilization of starch, when the starch has high protein content, it will no longer require any substitute material in the application. The results of analysis showed that the protein content on the modified *palado* seed starch is ranging from 0,40 – 0,81%, while the protein content for the non-modified is 0,27%. The results showed that the *palado* seed starch with pregelatinization, cross-linking and acetylation modifications has a protein content of 0,81; 0,45; and 0,40%, respectively. These results are quite lower than the protein content of cassava starch with physical modification (*autoclaving*) which is ranging from 1,17 – 1,52% [20], lower than protein content of the corn starch with fermentation ranging from 5,07 – 6,84% [22], and lower than the protein content of rice with acetylation modification ranging from 2,23 – 4,76% [21]. According to [25], starch with lower protein content can reduce its viscosity, so that the quality will be decreased and is not expected in its utilization.

The difference in protein content of *palado* seed starch resulted from pregelatinization modification compared to the cross-linking and acetylation modifications is in line with the statement of [22], that the increasing *autoclaving* temperature will increase the protein content of the modified starch. The increasing temperature decrease the water content of the starch, so that there is an increase in protein content of the starch relatively.

3.6. Carbohydrate content

Carbohydrate plays an important role in human life. Carbohydrate, especially for starch, is one of the cheap food sources for human, which provides about 40 – 75% of energy intake, which serves as an energy reserve in the human body in the form of glycogen, and as a source and requirement of the human body. The results of analysis showed that carbohydrate content in the the modified *palado* seed starch is ranging from 83,75 – 87,19%, while the carbohydrate content of the non-modified *palado* seed starch is 77,04%. These results indicate the carbohydrate content in *palado* seed starch is higher than in the wheat flour for 77,3%, rice flour for 80.0%, corn starch for 73,7% [27], which is equivalent to the carbohydrate content in sweet potato flour ranging from 86,35 – 88,40% [28], and in the acetylation-modified rice starch ranging from 84,67 – 86,65% [21].

3.7. Starch content of palado seed starch

The starch content of the modified *palado* seed starch is ranging from 40,86 – 72.29%, while the starch content of the non-modified *palado* seed starch is 47,55%. The highest starch content of *palado* seed starch was obtained from pregelatinization modification (72.29%), while the cross-linking modification (64.54%), and acetylation modification (40.86%). According to [19], in physical modification treatment (*autoclaving*), there is starch retrogradation occurred due to the heating process followed by the cooling process. Furthermore,

retrogradation can change the structure of starch that leads to the formation of a new crystalline structure, so that the starch cannot be easily dissolved.

Meanwhile [3], stated that in the process of cross-linking modification, the increasing trend of starch content is due to the more cross-linking occurred between phosphate compounds with molecules of starch, so that the starch granules are more stable and less easily dispersed in the water during the soaking process. Similarly [19], described the starch content of the cross-linked is higher than the native starch. It is because the phosphate group penetrated into the granules which forms a covalent bond with the starch molecules produce larger molecules, so that it increases the overall weight of the starch molecules. In addition, cross-linking can also strengthen the structure of the starch granules, so that the loss of starch can be inhibited during the washing.

Meanwhile, the lowest starch content of *palado* seed starch was obtained from acetylation modification, compared to pregelatinization and cross-linking modifications. It is assumed due to the damage to the starch during the extrusion process. According to [19], the degradation of amylose and amylopectin occurs during the starch extrusion process. It is due to breakdown of the amylose and amylopectin chains due to the pressure inside the extruder.

The results of the analysis showed that the starch content in *palado* seed starch is higher than in the yam starch for 38,80% [4], higher than the starch content in canna discolor starch for 40,18% [25]. The starch content in canna discolor and yam starches with cross-linking modification used phosphoryl oxychloride (POCl₃) is ranging from 35,87 – 41,35% and from 34,54 – 38,80%, respectively [4]. The starch content of the modified *palado* nut starch is not much different from of the corn starch for 71,3%, from of the rice starch which is ranging from 78,9 – 85,18%, and of the cassava starch for 72,17% [29]. Furthermore [25], described that the starch content is one of the criteria for the quality of flour, both as food and non-food materials

3.8. Amylose-amylopectin contents

The amylose and amylopectin contents of *palado* seed starch can be seen. The amylose and amylopectin content in *palado* seed starch is ranging from 1,92 – 3,01% and from 37,97 – 69,28%, respectively, while the amylose and amylopectin content in the non-modified *palado* seed starch is 4,74 and 42,81%, respectively. This is in contrast to the statement by [9] that the amylose and amylopectin contents after modification are likely to increase than before the modification. This is due to the same moles. The weight of starch molecules after modification become greater than before the modification. However, the results of this research showed the fact that there is only the amylopectin content increasing, especially in the pregelatinization and cross-linking modifications.

These results indicate the higher amylopectin content in *palado* seed starch than the amylose. Pregelatinization increases amylopectin and decreases amylose of *palado* seed starch in the amylopectin and amylose contents of the non-modified *palado* seed starch. It means that the amylopectin contained in *palado* seed starch is more dominant, ranging from 37,97 – 69,28%, higher than the amylopectin content in the pregeleatinized corn starch which is ranging from 54,11 – 55,96%, higher than the amylopectin content in the cross-linked sago starch

which is ranging from 59,92 – 62,88% [9], and then the amylopectin content in the acetylation-modified sago starch which is ranging from 56,32 – 62,77% [9]. According to [6], the differences of several starch-producing types are in amylose and amylopectin, structures and contents, granular organization, the presence of lipid, protein and mineral and the size of the starch granules.

Describes that the ratio of amylose and amylopectin in the starch granules is very important and is often used as a parameter in the selection of sources of starch and is for the application in food processing in order to provide the desired functional properties [30]. This is due to the ratio of amylose and amylopectin will affect the ability of starch paste in forming gel, thickening or forming the film. Amylose components are related to the increase in water absorption ability and in the perfection of the gelatinization process of the product, while the amylopectin components will determine the ability to develop the product [31]. Meanwhile [32], stated that amylopectin plays a role in the *puffing* process. Food products derived from starch with a high amylopectin content is light, crisp and crunchy. In general, the starch of food materials is made up one-quarter of amylose and three-quarters of amylopectin [32].

4. Conclusion

The water and ash content in the modified *palado* seed starch is ranging from 10,15 – 10,48% and 0,47 – 1,18%, respectively, so that they still meet the quality standards of industrial starch in which the water content should be less than 14% and ash content should be less than 15% [29]. The starch content resulted from pregelatinization modification is 75,29% and from cross-linking modification is 64,54%, while the starch content resulted from the acetylation modification is only 40,86%. Thus, there is only the pregelatinization method that meets the quality requirement of the industrial starch, in which the starch content should be 75,29%. The low starch content in the modified starch is due to the degradation occurs in the starch production and modification. The produced amylose content has an average of 2,60%. The low amylose content is due to the low starch content, thus, it has indirect effect on the amylose content. While the amylose content of the modified *palado* seed starch is ranging from 37,97 – 69,28%. The lowest amylopectin content was obtained from the acetylation modification for 37,97%. This is due to the modification is conducted by using acid hydrolysis (acetylation) which results in the decrease of amylopectin. From these results, it can be concluded that the *palado* seeds can be utilized more optimally, not only as snacks. After examination, it was found that the starch content *palado* nut is not much different from the corn, rice and cassava starches.

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