Sugar

by Teguh` Kurniawan

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Effect of heating time on the nutritional value of sap during traditional brown sugar processing from *Arenga pinnata*

Yeyen Maryani[1,2], Agus Rochmat[1], Jayanudin[1] and Teguh Kurniawan[1,2,*]

[1] Chemical Engineering Department, Universitas Sultan Ageng Tirtayasa, Cilegon, Indonesia
[2] PUI-PT Food Security, Universitas Sultan Ageng Tirtayasa, Serang, Indonesia
[*]Corresponding author: teguh@untirta.ac.id

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Abstract

Investigation of the contents of palm sugar is very important to study the quality of the sugar that comes from Lebak in Banten province, Indonesia. In this study, the nutritional value of the sap was analysed every 30 min during the traditional production of Arenga palm sugar. The content of the simple sugars sucrose, glucose and fructose was analysed during the heating of Arenga sap through application of high performance liquid chromatography. Analysis of the mineral content, i.e. of iron (Fe), zinc (Zn), copper (Cu) and manganese (Mn), was performed through application of atomic absorption spectrometry. The antioxidant activity was determined by application of the ferric reducing antioxidant power assay. The results showed that there was a change in composition of sucrose and fructose in palm sap to sucrose, glucose and fructose in palm sugar. Glucose and fructose content during the production process decreased. However, the sucrose content increased. The highest sucrose content was observed at 90 min of heating, which was 90.35% of all constituent saccharides. Regarding mineral content, Fe was the most abundant, and was found to be present at a level of 132.39 mg/kg at 90 min. The highest antioxidant capacity of 179.99 mg of ascorbic acid/kg sample was observed after 90 min of heating during palm sugar production.

Keywords: Palm sap, Brown sugar, Sucrose, Glucose, Fructose, Minerals, Antioxidants

1. Introduction

Arenga pinnata has been utilised traditionally in Indonesia as a multipurpose plant. For example, Arenga fruit, which is known locally as *kolang-kaling,* is consumed as a dish for breakfast during fasting months. The fibre of Arenga is used as a material for making rope. Villagers use Arenga leaves to make the roofs of traditional homes. The trunk is composed of starch, which is an important source of carbohydrate, and the sap is the raw material for brown sugar [1].

Arenga brown sugar is consumed similarly to sugar from cane. It provides nutrition for humans, and it offers advantages over cane sugar. The macro- and micronutrients in Arenga brown sugar are of greater nutritional value than those that are found in cane sugar [2]. Moreover, Arenga brown sugar has a lower glycaemic index than cane sugar. In addition, consumption of Arenga brown sugar aids in the digestion of starch [3].

Arenga brown sugar is generally produced in Indonesia through use of a traditional, simple method. The sap is tapped from the trees overnight and must be processed as soon as possible to prevent degradation of the sucrose. The sap is filtered to remove debris and poured into a large pan. Then the sap is heated on a firewood furnace for several hours at a temperature above 100 °C until it is concentrated and generates a caramel aroma. Two reactions occur during this process: the Maillard reaction and caramelisation [4]. These two reactions are responsible for the change in nutritive value of the sugar, particularly in glucose, fructose and sucrose composition, that occurs during the sap heating. The colour of Arenga sap changes from colourless to dark brown during the heating process [5].

The high temperature that is applied during sap processing produces brown sugar that contains reduced sucrose, which is produced by an inversion reaction. The formation of hydroxymethylfurfural is also favoured by use of high temperature conditions. A long processing period of approximately four hours leads to more thorough caramelisation and a greater proportion of completed Maillard reactions. Use of spray-drying technology could improve the sugar quality because of the short time of crystallisation; however, use of spray dryers can lead to the sugar sticking to the walls of the machines [6,7].

The aim of this investigation of traditional Arenga sugar production was to study the effect of the processing period on the sugar in terms of glucose, fructose, sucrose and mineral content, and regarding changes in antioxidant activity.

2. Materials and methods

2.1 Materials

Arenga sap and brown sugar were obtained from a traditional factory in Lebak, Banten, Indonesia.

2.2 Sugar analysis through application of high performance liquid chromatography

Fructose and glucose contents were analysed by application of high performance liquid chromatography (HPLC) with a refractive index or ultraviolet detector [8]. Glucose, fructose and sucrose were analysed by use of an HPLC detector of type SPD-10A, which incorporated an ultra-violet/visible (UV-VIS) detector (Shimadzu Corp., Kyoto, Japan). The mobile phase of the isocratic elution was 85% acetonitrile at a flow rate of 1 mL/min. The column temperature was maintained at 40 ˚C and the UV wavelength that was employed was 190 nm.

2.2.1. Preparation of standard

A stock reference standard was produced by mixing 0.5 g sugar in 50 mL distilled water in a volumetric flask. The mixture was shaken until it was homogeneous. Different concentrations of sugar standard mixture were used for quantification. A microlitre of solution was injected into the HPLC column.

2.2.2. Preparation of sample

Ten grams of sample were ground to decrease the particle size and were inserted into a 125 mL Erlenmeyer flask, to which 50 mL of distilled water was added. The mixture was sonicated for 10 min. The solution was filtered and concentrated through use of a rotary evaporator. The concentrate was diluted to a 10 mL solution, which was injected into the HPLC column.

2.3. Analysis of minerals

The mineral content was analysed through use of atomic absorption spectrometry (AAS) in the same way as has been described for analysis of iron (Fe), copper (Cu), potassium (K) and sodium (Na) in grapes [9], 11 elements in dates [10] and various minerals in palm sugar, Arenga sugar and cane sugar [11]. In this experiment, Fe, Cu, zinc (Zn) and manganese (Mn) were analysed by use of an AAS machine type 200 series A (Agilent Technologies Inc., Santa Clara, USA).

Sample that weighed 2-5 g was added to 10 mL of 1:1 ratio nitric acid. The mixture was mixed gently while covered by a watch glass. Afterward, the mixture was heated at 95 ˚C in a reflux condenser for 10-15 min. After cooling, 5 mL of nitric acid was added and the mixture was heated again for 30 min under reflux. Then, the mixture was evaporated below its boiling point until 5mL of solution remained. The sample was cooled and added to 2 mL deionised water and 3 mL of 30% hydrogen peroxide (H_2O_2). The mixture was covered with a watch glass and heated until bubbles appeared but to below its boiling point. Ten ml of H_2O_2 30% was gradually added. The sample was cooled again and then 5ml of hydrochloric acid (HCl) was added, followed by 10 mL of deionised water. The sample was covered with the watch glass and heated under reflux for 15min below its boiling point. The mixture was cooled and diluted to a total of 100 mL by the addition of deionised water. The solution was filtered through filter paper (Whatman). The filtrate was ready for AAS analysis.

2.4. Analysis of antioxidants

The ferric reducing antioxidant power (FRAP) assay was performed to determine the total activity of antioxidants. In principle, the FRAP method employs a colorimeter at wavelength 593 nm to identify the blue colour of ferrous ions (Fe(II)), which result from the reaction between antioxidants and ferric-tripyridyltriazine (Fe(III)-TPTZ). The FRAP method is used frequently to determine levels of antioxidants in plants. The advantages of the FRAP method are its low cost, ease of reagent preparation, its simplicity and its robustness [12]. The antioxidant capacity of Arenga sap during production of traditional brown sugar was discovered by application of the FRAP method as follows:

Five milligrams of extract were diluted in 5 mL of 96 % ethanol. A pipette amount of 1ml of the solution was added to 1 mL of 0.2 M phosphate buffer and 1ml of 1% potassium ferricyanide ($K_3Fe(CN)_6$).The solution was incubated for 20min at 50 °C. After incubation, 1 mL of trichloroacetic acid was added and the resultant solution was centrifuged for 3 min at 3000 rpM. From the top layer, 1 mL was removed by pipette and this sample was inserted into a reaction flask. Distilled water (1mL) and 0.5 mL of ferric chloride ($FeCl_3$, 0.1%) were added. The solution was left to stand for 10 min and the absorbance at 720 nm was subsequently measured. Oxalic acid was used as a blank test. A calibration curve was produced by dissolution of ascorbic acid at various concentrations. The FRAP unit is mg equivalent ascorbic acid/g extract.

3. Results and discussion

3.1 Analysis of sugar content

Arenga sap has a high content of sucrose and amino acids, which are important precursors for the synthesis of new volatile components. The heating process causes the Maillard reaction and the consequential release of amino acid substrates, which catalyse sucrose conversion into reactive components of monosaccharides [4]. Brown sugar production traditionally involves conditioning by heat treatment for a long period. During the heating of the sap sample, the intensity of the brown colour increased, as the glucose and fructose content decreased [5]. The changes in content of sucrose, glucose and fructose are presented as HPLC chromatograms, as shown in Figures 1 and 2.

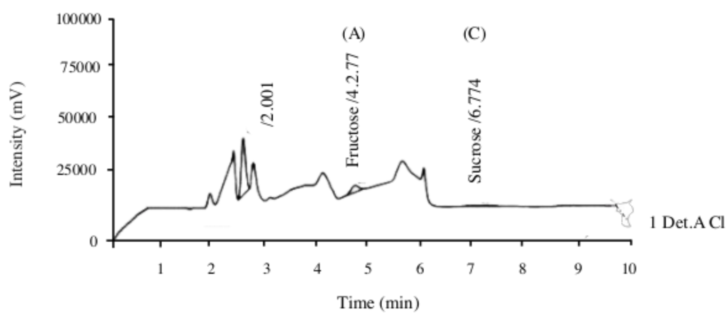

Figure 1 HPLC chromatogram of palm sap of mono-and disaccharides in *Arenga pinnata*.

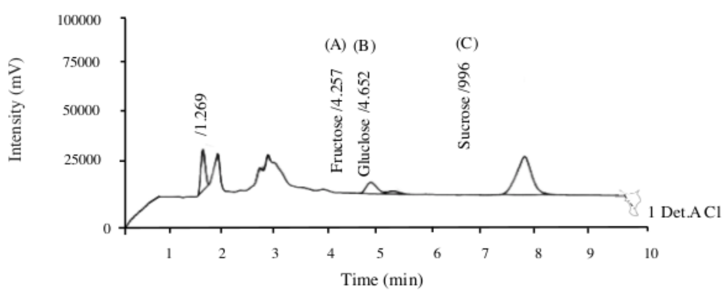

Figure 2 HPLC chromatogram of mono- and disaccharides that were found in the brown sugar that was produced by heating Arenga sap at 120 °C.

The Arenga sap contained sucrose as the majority component, with small amounts of glucose and fructose. A sweetener that contains a high content of sucrose is a healthy sugar as compared with synthetic sweetener. Sucrose has a reduced effect on obesity compared with glucose and starch [13]. Figure 1 shows that the Arenga sap from Lebak, Banten, contained only sucrose and fructose. The mono- and di-saccharides in the brown sugar that were produced by heating at 120 ˚C were fructose, glucose and sucrose. They are identified in Figure 2.

Table 1 Types of carbohydrate and their composition in palm sap and brown sugar produced at 120 ˚C.

Sample	Mono-and di-saccharide profiles		
	Fructose	Glucose	Sucrose
Palm sap	18	-	5
Brown sugar	13	4	63

Sucrose is an important requirement of the human body and is commonly used as a food sweetener. Sucrose is a disaccharide that has pharmaceutical functions and is a healthy dietary component [14]. Sucrose degradation occurs during the high-temperature processing of Arenga sap. During this degradation process, coloured and colourless products are produced that are important for the sugar industry. Sucrose degradation is caused not only by heating, but also by the presence of acid [15]. Sucrose (chemical formula $C_{12}H_{22}O_{11}$) contains glucose and fructose. Sucrose is found naturally in various plants such as sugar cane [16]. Other studies have mentioned that degradation or hydrolysis of sucrose can occur during microbial fermentation of palm sugar. Invertase enzymes hydrolyse sucrose into glucose and fructose [13,17].

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \quad (1)$$

In this study, changes were observed in the mono- and di-saccharide components of palm sugar, as sucrose and fructose were converted to sucrose, fructose and glucose. These results are shown in Table 1. Changes were also observed in the composition of carbohydrates every 30 min during the process.

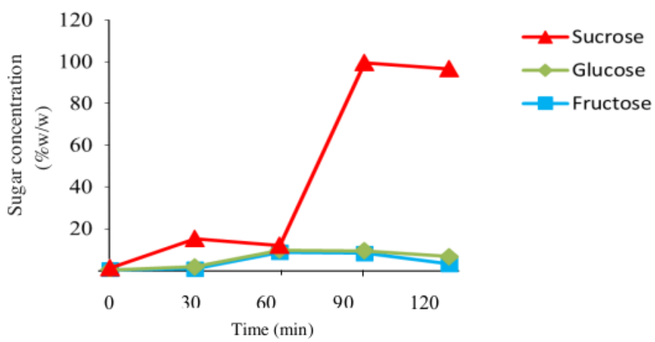

Figure 3 Changes in sucrose, glucose and fructose content of palm sap during processing into brown sugar.

The longer the production process of the palm sugar was continued, the higher the temperature that the sugar reached. The high temperature favoured the formation of compounds that produced the caramel aroma and sweet taste, which are characteristic of palm-sugar products. The products resulted from the Maillard reaction, which occurs on heating for 2 h at 110 ˚C [4]. Maillard's reaction occurs during heating or prolonged storage and is one of the processes that leads to deterioration of the quality of stored food [18]. Maillard's reaction is that between amino acids and reducing sugars such as glucose and fructose. It is affected by temperature. The reaction produces various flavours, odours, and brownish colours in food [19]. Figure 3 shows that at 90 min of sap processing, the glucose and fructose contents began to decrease. This may indicate the start of the Maillard reaction. The sucrose content increased and the highest content of 90.35% was obtained after 90 min because of water evaporation. The fast Maillard reaction resulted from fructose hydrolysis, whereas sucrose was not hydrolysed [20].

3.2 Analysis of mineral content

Analysis of the mineral nutrient and inorganic contaminant content has an important role in the improvement of data on nutritional quality and food safety [21]. In this study, the analysis of the mineral content of palm sap during the production of palm sugar was performed and the results are presented in Figure 4.

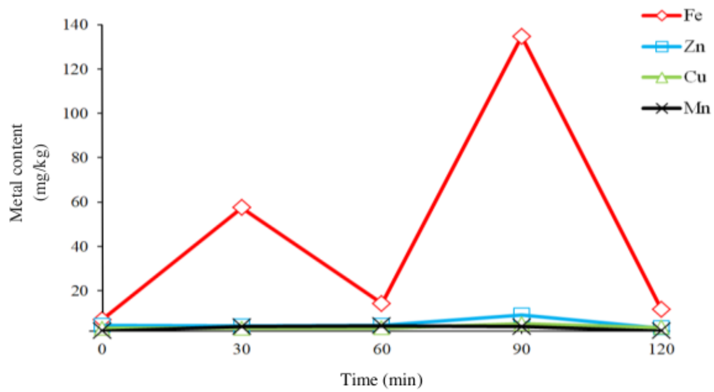

Figure 4 Changes in mineral content during processing of palm sap into brown sugar**.**

Analysis was carried out on the amounts of Fe, Zn, Mn, Cu, lead (Pb) and cadmium (Cd) that were measured during the traditional production of palm sugar. The results show that an organic farming system, which produces organic sugar, results in improved metal mineral content. Other studies have shown that the nutritional content of food is not only affected by cultivation, but also by soil, climate and culture [21]. The method of production of palm sugar also affects the mineral content, the production of which, through open-pan cooking, freeze drying and vacuum evaporation, has been reported in the literature [22]. These results showed that the highest percentage of ferrous metal (Fe) was obtained through vacuum evaporation (28.20%), followed by freeze drying (26.31%) and open-pan cooking (12.75%). The previous study concluded that control of the temperature to achieve a slow rise led to maintenance of the iron content. Iron functions as a chelate ion (Fe^{2+}) and is associated with antioxygenic activity.

In the current study, the Fe, Zn, Cu and Mn content of the sap was analysed, and the corresponding content of the sugar during production at between 30 and 120 min of heating was studied. The results show that the greatest mineral content was of Fe after 90 min; this mineral was found to be present at 132.39 mg/kg sample. This was in agreement with previous studies that a high Fe content was obtained at low temperatures and after a short heating period [22]. When palm sugar from Lebak-Banten is produced traditionally by an open-heating method, the temperature is not controlled, but other studies have reported that at 90 min, sap processing by the traditional method shows temperature ranges from 100 $^{\circ}$C to 110 $^{\circ}$C [4].

3.3 Analysis of antioxidant capacity

Antioxidants are important compounds for the maintenance of health because they function as free-radical scavengers. At appropriate levels in the human body, free radicals can trigger insulin sensitivity, which is positive for health. However, in excessive amounts, free radicals may attack healthy human cells. The human body produces antioxidants, but in not enough quantity to fight disease-causing free radicals. Therefore, it requires additional food intake to supply the required antioxidants [23]. The quantities of antioxidants that were found in the sap during the production of the palm sugar are presented in Figure 5.

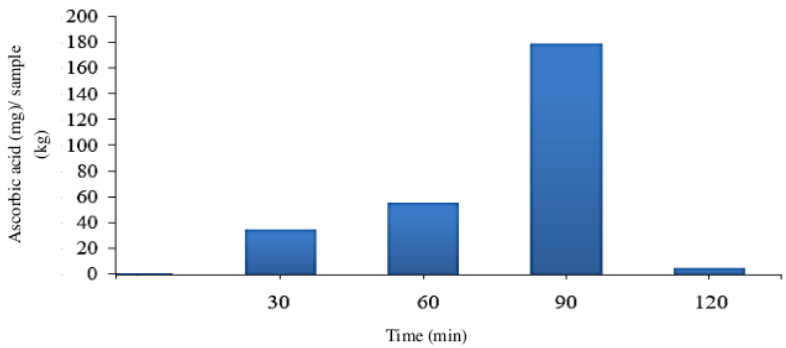

Figure 5 Antioxidant capacity during the processing of palm sap into brown sugar.

Phenols form the main group of antioxidants that is found in plants and fruits. A previous study found that the total amount of phenolic palm sugar that could be produced by spray drying was greater than that produced by vacuum drying, even though the required temperature was lower in the spray-drying method [4]. The greatest amount of antioxidant that was produced in our study was 179.99 mg ascorbic acid/kg sample, which was observed after 90 min of processing. The amount of antioxidant that was observed decreased as the heating process continued. This is because as heating continues, the temperature increases, and at high temperatures, the traditional sugar production process forms brown sugar due to caramelisation and the completion of the Maillard reactions [6,7]. The browning reaction, which occurs during production of palm and coconut sugar, starts at 105 °C and the reaction rate increases until production is completed [5]. The Maillard reaction results in: production of a brown pigment known as melanoidin, which has a distinctive colour and taste; production of volatile compounds that have a strong aroma and taste; production of reductants and antioxidants, which are reducing compounds that contribute to stabilisation of food and in the body, lower the risk of development of degenerative diseases; the development of mutagenic compounds, which are usually produced during long periods of storage; loss of essential amino acids such as lysine; and the development of compounds that cause protein cross-linkage [18]. The rates of these reactions may increase after 90 min of processing and near completion, which may be shown by the significant reduction in production of antioxidants at 120 min. The value of the antioxidants in Arenga sugar could be increased through the incorporation of other methods into the production process, such as freeze drying, vacuum evaporation and membrane ultra-filtration [4,6,7,23].

4. Conclusion

The mono- and disaccharide compositions of sap are changed from sucrose and fructose to sucrose, glucose and fructose during the process of sugar production from palm sap. Glucose and fructose content of the sugar decreased during the production process due to the Maillard reaction, while the sucrose content increased. The highest sucrose content that was observed in this study was 90.35% after 90 min of heating. Among the minerals that were found during the process, Fe was found to be the most abundant; the maximum amount of Fe was measured as 132.39 mg/kg sample, which was observed at 90 min of Arenga sap processing. Similarly, the greatest quantity of antioxidant (179.99 mg ascorbic acid/kg sample) was obtained after 90 min of sugar production. The caramelisation and Maillard reactions reduced the antioxidant production.

5. Acknowledgments

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