Physicochemical properties of coarse palm sap sugars as natural alternative sweetener

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ABSTRACT

Palm sap sugar is a natural sweetener used as a sucrose replacement due to its potential for creating food products with distinctive characteristics. The physicochemical properties of several coarse palm sugars were investigated. In this study, coarse coconut sugars (CCS1, CCS2) and coarse palm sugars (CPS1, CPS2, and CPS3) of Indonesian origin from different producers were investigated. Coarse pure sucrose was used as the reference sample. The results showed that moisture content of palm sap sugars was higher than that of sucrose. While crude protein, reducing sugars and ash were only present in the palm sap sugars. Maillard reaction and caramelization which occur during sugar production were responsible for the dark color of palm sap sugars. Due to the presence of moisture, crude protein, reducing sugars, and ash as impurities, the melting and glass transition temperature of palm sap sugars were lower than those of sucrose. Moreover, particle densities and particle sizes of palm sap sugars were lower and less uniform, respectively, when compared to those of sucrose. The presence of relatively high moisture and reducing sugars as hygroscopic material may be responsible for the presence of "wet" layers sticking to the surface of palm sap sugar crystals, visualized using scanning electron microscopy. The variation on the physicochemical properties of palm sap sugars can be attributed to the raw materials and processing methods used by the sugar producers.

1. Introduction

Palm sap sugar (PSS) is an alternative sweetener made from the nectar/sap tapped from the flowers of several species of palm tree, such as sugar palm (*Arenga pinnata*), palmyra palm (*Borassus flabellifer*), nipa palm (*Nypa fruticans Wurmb*) and coconut palm (*Cocos nucifera*) that has the potential to be incorporated in food products as a substitute for sucrose. This sugar which is commonly used in many traditional foods in South-East and South Asian regions has an important role in color and flavor development of different food products (Arcieri, 2014; Ho et al., 2007; Hori & Purboyo, 1991; Purnomo, 2007; Tomomatsu et al., 1996). Moreover, PSS is also claimed to have health benefits due to its low glycemic index (35–42), its antioxidants, vitamin and mineral contents (Arcieri, 2014; Philippine Coconut Authority, 2016; Trinidad et al., 2010; Victor and Orsat, 2018; Waldrop and Ross, 2014). It is abundantly produced in coconut-planting regions, mainly in Indonesia and the Philippines, where coconut trees are also grown (Anonymous, 2010). Its commercial use may result in economic benefits. To ensure that the

utilization of palm sugar can yield products with good quality characteristics, knowledge about the physicochemical properties of this sugar should be obtained.

The physicochemical characteristics of PSS are affected by their raw materials (nectar/sap) and processing techniques (Phaichamnan et al., 2010; Purnomo, 2007; Saputro, Van de Walle, & Dewettinck, 2019). Aside from this, the form of the sugars (syrup, solid, coarse/powder) also determines their properties. Several studies have been done by researchers which mainly focused on the production and chemical characterization of palm sugar syrup and molded palm sugar (Apriyantono et al., 2002; Ho et al., 2008; Naknean et al., 2009, 2013; Phaichamnan et al., 2010; Saputro, Van de Walle, & Dewettinck, 2019). The study on the physicochemical characteristics of coarse PSS has not been done yet. Therefore, the aim of this research was to study the physicochemical properties of several coarse PSS.

Physicochemical analyses, such as moisture, fat, crude protein, reducing sugars, particle density, particle size distribution and thermal behavior were carried out. Color and microstructural visualization were

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also done to support the results of the aforementioned analyses.

2. Materials and methods

2.1. Raw materials

Two types of PSS, namely coarse coconut sugar (CCS1, CCS2) and coarse palm sugar (CPS1, CPS2, and CPS3) with relatively big crystal size were purchased from Sari Nira Nusantara CV (Yogyakarta, Indonesia). The samples were produced by 5 different producers. As a reference, coarse pure sucrose (CS) was obtained from Tiense Suikerraffinaderij (Tienen, Belgium).

To produce coarse PSS, the sap/nectar is boiled with agitation until crystalline sugar is formed. In this process, the duration, temperature and agitation method applied highly influence the degree of crystallinity and moisture left in the product. Afterwards, drying is required to evaporate moisture present in the final sugar.

2.2. Analytical methods

2.2.1. Sucrose and reducing sugars content

Sucrose and reducing sugars content were determined using gas chromatographic analysis, following the method described by De Wilde et al. (2005), after an aqueous extraction from samples. Prior to the extraction, phenyl-ß-ᴅ-glucopyranoside (6 mg/mL, (Sigma-Aldrich, Bornem, Belgium)) was added as an internal standard. After 30 min of incubation at 60 °C, Carrez I: 15% potassium hexacyanoferrate (5 mL, (Merck, Darmstadt, Germany)) and Carrez II: 30% zinc sulphate (5 mL, (Chem-Lab, Zedelgem Belgium)) were added. This solution was then filtered using Whatman No. 42 filter paper (Sigma-Aldrich) followed by drying of 1 mL of the filtered solution under nitrogen. The residue was derivatized by adding hydroxylamine hydrochloride (100 µL, (UCB, Brussels, Belgium)) and hexamethyldisilizane (100 µL, (Chem-Lab)) and trifluoraaceticacid (10 µL, (Chem-Lab)). A Varian 3380 gas chromatograph equipped with a flame-ionization detector (Varian Instrument Group, Walnut Creek, CA, USA) was used for sugar separation. The parameters used were as follows: stationary phase: 5% phenyl methylpolysiloxane, column: 30 m, 0.32 mm, 0.25 µm (Agilent Technologies, Palo Alto, CA, USA), mobile phase: He at 1 mL/min, injector temperature: 250 °C; detector temperature: 340 °C; injection volume: 1 µL; temperature program: 180 °C for 1 min, ramp at a rate 15 °C/min to 290 °C. The calculation of sucrose and reducing sugars concentration were based on the peak area of the measured sugars and the internal standard. Measurements were done in triplicate.

2.2.2. Moisture content

The moisture content of the dissolved sugars was automatically determined using the Karl-Fisher titration method using a 719 Titrino instrument (Metrohm, Herisau, Switzerland), following a method described by Saputro, Van de Walle, Aidoo, et al. (2017) in a previous study. Hydranal titrant 5 reagent (Riedel de Haen, Seelze, Germany) and hydranal solvent (Riedel de Haen) were used.

Approximately 25 mL of hydranal solvent (Riedel de Haen) was poured into a beaker attached to the instrument. Afterwards, start button was pressed and Hydranal titrant 5 reagent (Riedel de Haen, Seelze, Germany) was automatically added. flowed to the beaker glass. After OK sign appeared, ̰1 gr of sugar was put into the beaker. Subsequently, enter button was pressed. After ̰5 min, the result appeared on the screen of the instrument. This result was calibrated with the result of water as a sample. The instrument indicated when ~1 g of sugar should be added and a result was generated in ~5 min. Water was used to calibrate the instrument. Measurements were done in triplicate.

2.2.3. Crude protein content

The protein content of the sugars was determined using the Kjeldahl method (Egan et al., 1981) and the results were calculated using a conversion factor of 6.25. Approximately 0.5 g of sugar was digested by heating to boiling 10 mL concentrated H_2SO_4 (Sigma-Aldrich). K_2SO_4 (Sigma-Aldrich) as a catalyst was added to the sugar prior to digestion. The digestion was finished when a bright green color appeared. Afterwards, samples were placed in a distillation apparatus. The digest was subsequently distilled to release the ammonia. In the last step, the distillate was titrated using 0.05 N HCl (Sigma-Aldrich). Measurements were done in triplicate.

2.2.4. Ash content

The ash content of the sugars was determined using a muffle oven (Williams, 1984). Approximately 5 g of sugar was placed in a crucible and heated at ~200 °C on a heating plate to allow full carbonization. Afterwards, the sample was put in a muffle oven (Thermo Scientific, Langenselbold, Germany) for at least 4 h at 500 °C. The residue left in the crucible was the ash. Measurements were done in triplicate.

2.2.5. Fat content

The fat content of the sugars was determined using the Weibull method (Egan et al., 1981). Approximately 5 g of sugar was boiled with 25% HCl for 15 min. Afterwards the sample solution was filtered using Whatman No. 42 filter paper (Sigma-Aldrich) and washed with hot water (80–100 °C). The filter paper was then dried at the temperature of 100 °C and placed into a Soxhlet apparatus (Thermo Scientific) and was subsequently extracted with ̰200 mL petroleum ether (Sigma-Aldrich) for 4 h. The solvent was then evaporated using an evaporator to precipitate the fat. Measurements were done in triplicate.

2.2.6. Solubility

The solubility test was done in a water bath (Memmert, Schwabach, Germany) that was set at 22 °C by quantifying the amount of sugar that can be completely dissolved in 40 mL distilled water. The sugar was added into distilled water and was subsequently agitated using an automatic stirrer. Once the sugar solution reached its supersaturation point which was indicated by the inability of water to further dissolve the sugar, the test was stopped. This method was developed by the authors. Measurements were done in triplicate.

2.2.7. Particle density and bulk density

The particle density was measured using a pycnometer. Approximately 10 g of sugar was put into a 25 ml pycnometer. Afterwards, the pycnometer was filled with hexane (Sigma-Aldrich) with a density of 0.659 g/mL at 25 °C, in which the sugar is assumed to be completely insoluble. The weight of the displaced hexane can then be determined, and subsequently the volume of sugar can also be calculated. This method was developed by the authors. Measurements were done in triplicate.

The bulk density of the sugars was analyzed using a PT-N powder tester (Hosokawa Iron Works, Osaka, Japan). During the measurement, sugars were gently poured into the hopper of the instrument which then automatically transferred it into a cup below the hopper. A scraper was used to manually level the sugar mound in the cup. This process was done carefully to create a flat surface with the same level as the edge of the cup. The bulk density of the powder was determined by measuring the ratio of mass to the volume occupied by the sugar.

2.2.8. Color

The color of the sugars was measured with a colorimeter (Minolta Model CM-2500D Spectrophotometer, Tokyo, Japan) following a method described by Saputro, Van de Walle, Aidoo, et al. (2017). The SCE-mode (specular light excluded) values were measured and the color parameters were expressed in $L*a*b*$ color space system where $L*$ represents lightness (luminance ranging from 0 (black) to 100 (white)), $a*$ represents green to red, and $b*$ represents blue to yellow. Measurements were done in triplicate.

2.2.9. Particle size distribution (PSD)

The PSD of the sugar was analyzed using a Malvern Mastersizer S Long Bench (Malvern Instruments Ltd., Malvern, Worcestershire, UK) equipped with a 1000 F lens, following a method described by Saputro et al. (2017b, 2019a) with a slight modification. This lens can measure sugar particle size ranging from 5 to 3500 μm. The refractive index for sugar measurement was set at 1.54. Additional devices consisting of a vibrating hopper (MS-64, Malvern) to circulate the coarse sugar were installed with the air pressure set at 2 bar. Approximately 100 g of sugar was used in each measurement. D(v,0.9), D(v,0.5), D(v,0.1), D(4,3) and D(3,2) and span representing a percentile of 90, 50 and 10%, volume-weighted mean, Sauter diameter (mean of volume to surface area ratio) and distribution width (width between the biggest and smallest particles), respectively were automatically obtained from the instrument. Measurements were done in triplicate.

2.2.10. Thermal behavior

Thermal behavior of the sugars was investigated with a Q1000 differential scanning calorimeter (DSC) equipped with a refrigerated cooling system (TA Instruments, New Castle, DE, USA), following a method described by Saputro, Van de Walle, Aidoo, et al. (2017) with a slight modification. To obtain the melting profile,~2 mg of the sugar was hermetically sealed in an aluminum cup. Afterwards, the sample was equilibrated at 20 °C followed by heating to 200 °C at 5 °C/min.

To measure the glass transition temperature, the sample in a sealed pan was equilibrated at 20 °C followed by heating at a rate of 5 °C/min until the sample melted completely. Afterwards, the sample was quickly cooled to −40 °C at a rate of 5 °C/min and finally reheated at a rate of 5 °C/min to 210 °C. Melting peaks calculated by the software were characterized by onset temperature (°C), maximum melting temperature (°C) and enthalpy (J/g). The glass transition was characterized by onset (°C), midpoint (°C), offset (°C) and specific heat (ΔCp) (J/(g·°C)). Measurements were done in triplicate.

2.2.11. Microstructural images

The surface morphology of sugars was visualized using a JSM-7100 F TTLS LV TFEG-SEM (scanning electron microscopy) (Jeol Europe, Zaventem, Belgium), following a method described by Saputro et al. (2017b). This process was done under high vacuum and at an accelerating voltage of 3 keV. The samples were vitrified in liquid nitrogen and transferred to a PP3000T device (Quorum Technologies, Newhaven, East Sussex, UK) at −140 °C. To remove frost, in this device, the samples were allowed to sublime for 15 min at −70 °C, followed by sputtering a thin platinum film on the sugars surface.

2.3. Data analysis

Statistical analysis was done using the Statistical Package for the Social Sciences (SPSS) 22.0 software (SPSS Inc., Chicago, IL, USA). The physicochemical properties of sugars were subjected to one-way analysis of variance (ANOVA) at the 5% significance level. Testing for homogeneity of variances was done using the Levene Test. The Tukey test was used to determine differences among samples. In case variances were not homogeneous, the Games–Howell test was done. Principal component analysis (PCA) was used to visualize the relationships between chemical and physical properties of the sugars.

3. Results and discussion

3.1. Chemical properties of palm sap sugars

3.1.1. Sucrose and reducing sugars content

The amount of reducing sugars as the Maillard reactions precursor in PSS could be influenced by the progress of the Maillard reactions during sugar production. The amount of fructose and glucose in sap/nectar decreased as the degree of Maillard reactions increased (Apriyantono

Table 1
Chemical composition of sampled palm sap sugars (dry matter basis).

Sugar	Moisture (%)	Protein (%)	Ash (%)	Sucrose (%)	Reducing sugars	
					Fructose (%)	Glucose (%)
CCS1	1.8 ± 0.1[cd]	1.2 ± 0.0[c]	2.0 ± 0.0[d]	85 ± 2[ab]	2.4 ± 0.1[b]	1.2 ± 0.1[b]
CCS2	1.9 ± 0.1[d]	0.8 ± 0.0[b]	1.5 ± 0.0[c]	82 ± 5[a]	2.7 ± 0.1[c]	2.0 ± 0.0[c]
CPS1	1.7 ± 0.1[c]	1.6 ± 0.0[e]	2.0 ± 0.0[d]	84 ± 2[a]	1.4 ± 0.0[a]	0.7 ± 0.0[a]
CPS2	1.0 ± 0.1[b]	0.5 ± 0.0[a]	0.3 ± 0.0[b]	95 ± 6[b]	1.3 ± 0.1[a]	1.3 ± 0.1[b]
CPS3	2.4 ± 0.1[e]	1.3 ± 0.0[d]	2.1 ± 0.0[f]	79 ± 4[a]	3.3 ± 0.2[d]	2.0 ± 0.1[c]
CS	0.3 ± 0.0[a]	n.d.	0.0 ± 0.0[a]	100	n.d.	n.d.

Mean values ± standard deviations from triplicate analysis.
Different superscripts in the same column indicate significant differences ($P < 0.05$) among samples.
n.d.: not detected.

et al., 2002; Ho et al., 2008; Naknean et al., 2009). However, the conversion of sucrose to fructose and glucose during sugar production (Phaichamnan et al., 2010) should also not be neglected. Table .1 shows that fructose and glucose were only present in PSS and in varying amounts. Lactose and maltose, which are commonly present in milk and starch, respectively (Beckett, 2009; Lees & Jackson, 1973) were not found in the PSS.

3.1.2. Moisture content

Table .1 shows that coarse coconut sugar (CCS1, CCS2) and coarse palm sugar (CPS1, CPS2, CPS3) had significantly higher ($P < 0.05$) moisture content than that of coarse pure sucrose (CS). CPS 2 showed significantly lower ($P < 0.05$) moisture content than other PSS and CPS3 had the highest moisture content among all sugars.

Different drying techniques used by either small-scale industries or farmers result in different levels of moisture (Phaichamnan et al., 2010). Moreover, the applied grinding process to the dried sugars to reduce the particle size of the sugar may also create amorphous parts which are hygroscopic, contributing to a higher moisture absorption. Therefore, the moisture content of PSS was significantly higher ($P < 0.05$) than that of pure crystalline sucrose and varied among samples (Table .1). During distribution, hermetic packaging is required to avoid further moisture absorption from the environment. High moisture levels produce agglomerations of the sugar particles, reducing the quality of coarse palm sugar.

3.1.3. Crude protein content

Crude protein/amino acids are present not only in the sap/nectar, but also in PSS (Ho et al., 2008; Purnomo, 2007). As can be seen in Table .1, the results showed that crude protein was present in coarse coconut sugar (CCS1, CCS2) and coarse palm sugar (CPS1, CPS2, CPS3), in contrast to sucrose (CS). Different crude protein contents among PSS may be due to different composition of the sap/nectar as well as the time and temperature used during PSS production. These factors determine the degree of Maillard reaction that occurred.

3.1.4. Ash content

PSS contains various minerals, such as phosphorus, potassium, calcium, magnesium, and iron (Arcieri, 2014; Philippine Coconut Authority, 2016). Thus, to be able to roughly quantify them, ash content analysis was done. As stated by Marshall (2010), ash content represents the total minerals present in foods. Table .1 shows that PSS, in contrast with sucrose, contained relatively high ash indicating the presence of higher amounts of minerals. CCS1, CPS1 and CPS3 showed higher ash content than CCS2 and CPS2, while there was no ash present in sucrose,

Table 2
Physical properties of palm sap sugars.

Sugar	Solubility (%)	Bulk Density (g/mL)	Particle Density (g/cm^3)	Color		
				L*	a*	b*
CCS1	69.8 ± 0.3[b]	0.6 ± 0.0[a]	1.52 ± 0.01[a]	48 ± 1[c]	18 ± 1[c]	67 ± 3[c]
CCS2	69.8 ± 0.3[b]	0.6 ± 0.0[d]	1.53 ± 0.01[a]	48 ± 1[c]	16.5 ± 0.2[c]	62 ± 1[b]
CPS1	69.7 ± 0.5[b]	0.7 ± 0.0[c]	1.56 ± 0.01[bc]	38.2 ± 0.2[a]	20 ± 1[b]	62 ± 1[b]
CPS2	67.0 ± 0.3[a]	0.7 ± 0.0[c]	1.56 ± 0.01[bc]	37 ± 1[a]	20.7 ± 0.2[b]	60 ± 1[b]
CPS3	69.9 ± 0.1[b]	0.6 ± 0.0[b]	1.54 ± 0.01[ab]	41.8 ± 0.3[b]	17 ± 1[c]	62 ± 2[b]
CS	66.3 ± 0.1[a]	0.9 ± 0.0[e]	1.57 ± 0.01[c]	95.2 ± 0.1[d]	0 ± 0[a]	1.1 ± 0.3[a]

Mean values ± standard deviations from triplicate analysis.
Different superscripts in the same column indicate significant differences ($P < 0.05$) among samples.

indicating its high purity. The presence of impurities affects the degree of PSS crystallinity (Saputro et al., 2017b).

3.1.5. Fat content

Fat content analysis was carried out to verify that fat was not present in PSS. Fat was not detected in the samples.

3.2. Physical properties of palm sap sugars

3.2.1. Solubility

As can be seen in Table .2, CCS1, CCS2, CPS1, CPS2 and CPS3 had significantly higher ($P < 0.05$) solubility than sucrose, CS. This can be attributed to the presence of minerals, reducing sugars, crude proteins, and moisture in PSS (Asadi, 2006; Lees & Jackson, 1973; Qian et al., 2010; Sun et al., 2012). Theoretically, pure sucrose has a solubility of 66.5% at room temperature (20 °C) (Hartel et al., 2011). Changes in the molecular interaction between the solutes and the water due to the presence of impurities might be responsible for the increase in solubility (Asadi, 2006; Hartel & Shastry, 1991; Lees & Jackson, 1973). Apart from the impurities, some amount of amorphous sugar which can be generated during PSS production also increases the solubility to some extent. Amorphous sugar is less physically stable than the crystalline sugar which might explain these results (Qian et al., 2010; Sun et al., 2012).

3.2.2. Particle density and bulk density

It can be seen in Table .2 that the trends in particle density and bulk density of the sugars were similar. The higher the particle density, the higher the bulk density. Sucrose (CS), which had similar particle size distribution to PSS (CPS1, CPS2) (Table .3), had a higher bulk density than CPS1 and CPS2. These results emphasized that PSS are bulkier than sucrose.

3.2.3. Color

During PSS production, Maillard reactions and caramelization take place as indicated by the formation of brown colored sugar, with the color becoming darker as the heating time increases (Apriyantono et al., 2002; Ho et al., 2008; Naknean et al., 2009; Naknean & Meenune, 2011).

Color measurements showed that coarse PSS had more intensive brown color compared to sucrose which was indicated by a lower *L** and higher *a** and *b** values (Table .2). The variation in the color parameter values among PSS was associated with the degree of Maillard reaction of PSS.

The color differences among sugars can be seen in Fig. 1. CPS 1 and CPS2 had a darker color than CCS1, CCS2 and CPS3, while, in general, PSS were much darker than sucrose.

3.2.4. Particle size distribution (PSD)

PSD values can be used to describe the homogeneity of the sugar particles. It can be seen in Table .3 that the PSD values of PSS varied not only in terms of the largest size of the particle D (v,0.9), but also in terms of D (v,0.5), D (v,0.1), D (4.3), and D (3.2). The variation was attributed to the different methods of sugar production used by the farmers. Aside from this, particle agglomeration was highly likely to have occurred in the presence of relatively high moisture as well as reducing sugars (glucose and fructose) in the PSS which may be present in the amorphous phase, thus affecting the measured PSD. Moreover, coarse sucrose had more uniform particle size than PSS which can be seen from their span values (Table .3). The span value of CCS1, CCS2, CPS1, CPS2 and CPS3 were wider than that of CS indicating the presence of groups of big and small particles. As PSS is still traditionally produced by farmers without a proper sieving process which may explain these results. In general, it can also be seen that the D (v,0.9) value of sucrose was still in the range of the D (v,0.9) values of PSS.

3.2.5. Thermal properties

Sugar has important role in determining the quality attributes of foods in general. Therefore, understanding the state of the sugar is important. In a food matrix, sugar may be present in the crystalline or amorphous (glassy) state or a combination. During processing, sugar in confectionery formulations can undergo one or more phase transition, depending on the nature of the product (Hadjikinova & Marudova, 2016; Hartel et al., 2011).

Melting is an endothermic transition where the crystalline state transforms to the liquid state upon heating (Hadjikinova & Marudova, 2016). The presence of impurities, such as water and other chemical
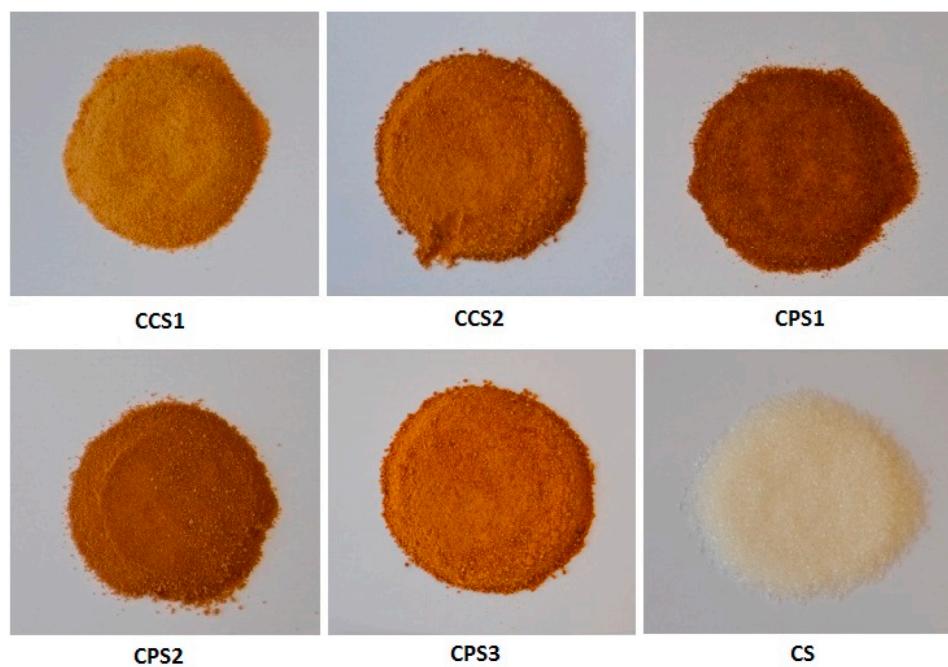
Table 3
Particle size distribution of palm sap sugar as compared to that of sucrose.
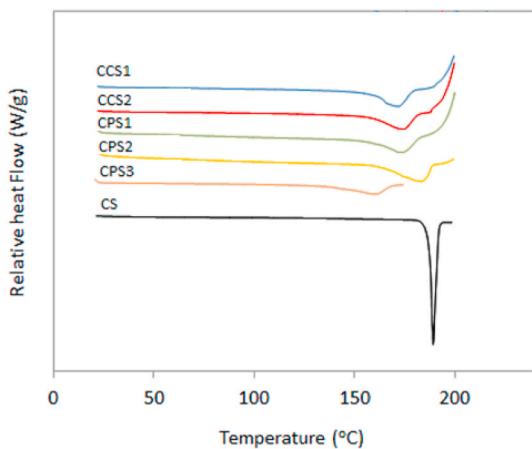
Sugar	Distribution Percentiles (μm)			Derived Diameter (μm)		Span (−)
	D(v, 0.9)	D(v, 0.5)	D(v, 0.1)	D(4,3)	D(3,2)	
CCS1	1200 ± 100[c]	550 ± 60[b]	170 ± 20[b]	640 ± 50[b]	270 ± 30[a]	2.0 ± 0.2[c]
CCS2	1100 ± 100[b]	420 ± 50[a]	122 ± 4[a]	550 ± 40[a]	210 ± 10[a]	2.5 ± 0.1[d]
CPS1	920 ± 80[a]	450 ± 30[a]	140 ± 20[ab]	500 ± 40[a]	220 ± 20[a]	1.7 ± 0.1[b]
CPS2	900 ± 100[a]	440 ± 20[a]	165 ± 1[b]	500 ± 40[a]	235 ± 2[a]	1.7 ± 0.2[b]
CPS3	1200 ± 20[b]	570 ± 10[b]	200 ± 3[c]	630 ± 10[b]	370 ± 10[b]	1.7 ± 0.0[b]
CS	920 ± 10[a]	500 ± 10[a]	220 ± 10[d]	540 ± 10[a]	370 ± 30[b]	1.4 ± 0.0[a]

Mean values ± standard deviations from triplicate analysis.
Different superscripts in the same column indicate significant differences ($P < 0.05$) among samples.

Fig. 1. The pictures of coarse palm sap sugars and sucrose.

Fig. 2. Melting point of palm sugar as compared to that of sucrose.

Table 4
Melting profile of palm sugar as compared to that of sucrose.

Sugar	Onset (°C)	Melting peak (°C)	Width (°C)	Enthalpy (J/g)
CCS1	161 ± 3[bc]	172 ± 1[b]	13 ± 1[b]	110 ± 10[b]
CCS2	157 ± 2[b]	174 ± 1[c]	15 ± 1[bc]	120 ± 10[b]
CPS1	158 ± 0.3[bc]	174 ± 1[bc]	16 ± 1[c]	118 ± 1[b]
CPS2	162 ± 0.2[c]	183 ± 0.2[d]	16.4 ± 0.3[c]	119 ± 1[b]
CPS3	138 ± 2[a]	160 ± 1[a]	21 ± 1[d]	88 ± 6[a]
CS	188 ± 0.2[d]	190 ± 0.4[e]	2.9 ± 0.1[a]	154 ± 2[c]

Mean values ± standard deviations from triplicate analysis.
Different superscripts in the same column indicate significant differences ($P <$ 0.05) among samples.

compounds, lowers the melting temperature of a substance (Beckett et al., 2006; Kedward et al., 1998; Roos, 1993; Roos & Karel, 1991). Fig. 2 shows the melting curve of the sugars. It can be seen that CCS1, CCS2, CPS1, CPS2 and CPS3 in general had a blunt, broad, and asymmetric peak with large width values, while coarse sucrose had a sharp and symmetric peak with small width value. Furthermore, it can be seen in Table .4 that PSS showed significantly lower ($P <$ 0.05) onset and melting peak temperatures than sucrose (CS). A higher content of impurities and moisture, which can act as plasticizer, in PSS were responsible for these results. Coarse sucrose (CS) which had a high purity had comparable melting temperature to sucrose studied by others with values within the range of 185–190 °C (Hurtta et al., 2004; Roos, 1993). Moreover, the enthalpy value of CS was higher than that of PSS, indicating that a higher energy was required to melt the sugar crystals. This further showed that sucrose had a higher amount of crystallinity than PSS. In the PSS, some amorphous regions were most likely formed during their production. Many food materials exist in a completely or partially amorphous state due to food processing (Kim et al., 2001; Liu et al., 2006; Meste et al., 2002).

Variation of the melting profile within PSS was attributed to the different level of impurities present in the sugars. For example, CPS3, which had a higher content of moisture, reducing sugars, crude protein and ash than other PSS, had the lowest melting temperature and enthalpy values (Table .4). The onset temperature for melting varied not only due to the presence of different amount of impurities, but also due to the different thermal contact between the sugar and the DSC pan (Saputro, Van de Walle, Aidoo, et al., 2017). In the same mass, sugar with small particle size has a wider surface contact with the DSC pan than sugar with big particle size. This creates different heat transfer rates from the DSC to the samples, resulting in different temperatures measured during thermal profiling.

Most of the pure solid sugars are in the crystalline state, while in impure sugar some amount of amorphous state may also be present (Kasapis, 2005). The amorphous state undergoes structural changes due to the presence of moisture and/or heat, resulting in undesirable events, such as stickiness, caking, and collapse. The amorphous state can exist either as a viscous fluid-like rubbery state or as a highly viscous glassy state with low molecular mobility (Hadjikinova & Marudova, 2016, Liu et al., 2006). The glass transition occurs when the glassy state converts to the rubbery state (or vice versa) (Ergun et al., 2010; Hadjikinova & Marudova, 2016; Lee et al., 2011; Meste et al., 2002). Amorphous sugar is highly hygroscopic and absorbs moisture from the environment, resulting in plasticization that lowers the glass transition temperature (Abbas et al., 2010). In the food matrix, for instance in chocolate, the

Table 5
Glass transition parameters of palm sugar as compared to that of sucrose.

Sugar	Glass Transition Temperature (Tg)			
	Onset (°C)	Midpoint (°C)	Offset (°C)	Δ Cp (J/(g·°C))
CCS1	54 ± 1^c	58 ± 1^d	61 ± 0^c	0.4 ± 0.04^{ab}
CCS2	54 ± 2^c	59 ± 2^d	63 ± 2^c	0.3 ± 0.01^a
CPS1	36 ± 1^a	40 ± 1^a	44 ± 1^a	0.6 ± 0.00^b
CPS2	46.9 ± 0.4^b	51 ± 1^c	54 ± 1^b	0.4 ± 0.00^{ab}
CPS3	41 ± 4^b	45 ± 3^b	48 ± 3^a	0.2 ± 0.00^a
CS	63 ± 1^d	67.0 ± 0.3^e	70 ± 1^d	0.3 ± 0.01^a

Mean values $\pm$ standard deviations from triplicate analysis.
Different superscripts in the same column indicate significant differences ($P < 0.05$) among samples.

presence of the amorphous state may create problems during chocolate processing and storage, especially with regard to the rheological and textural changes (Hanselmann, 2013). However, the presence of the amorphous state may increase the intensity of cocoa flavor (Beckett, 2009).

Due to the presence of glucose and fructose as well as moisture, the glass transition temperature of PSS were expected to be lower than that of sucrose, but higher than that of glucose and fructose. The glass transition temperature of a mixture is usually located between the glass transition temperatures of its components (Hadjikinova & Marudova, 2016; Liu et al., 2006; Seo et al., 2006). The measurement of glass transition temperature was initially done by directly heating the sugar samples to 200 °C. However, the glass transition could not be detected which may be attributed to relatively small amount of amorphous state present in PSS. Aside from this, the low sensitivity of the instrument may have contributed.

To roughly estimate the glass transition temperature of the PSS, a different method following the description of Liu et al. (2006) and Saavedra Leos et al. (2012) with slight modifications was chosen. This involved melting of the crystalline state followed by fast cooling to create the glass state. Afterwards, the glass transition temperature was measured through re-heating the sugar glass (Liu et al., 2006). The drawback of this method is that the thermal history of the sugars is changed. Moreover, caramelization may occur during the first heating, which results in the degradation of some sugar molecules and polymerization (Jiang et al., 2008), thus influencing the measured glass transition to some extent.

Regardless of molecule degradation and polymerization that may occur due to "heating-cooling-reheating" method, the glass transition temperature is influenced by heating rate, holding time, and the highest heating temperature (Jiang et al., 2008; Vanhal and Blond, 1999). Thus, the fixed glass transition temperature of a material is often difficult to determine. For instance, the glass transition temperature of sucrose reported by different authors varies between 62 and 75 °C (Hadjikinova & Marudova, 2016; Jiang et al., 2008; Vanhal and Blond, 1999).
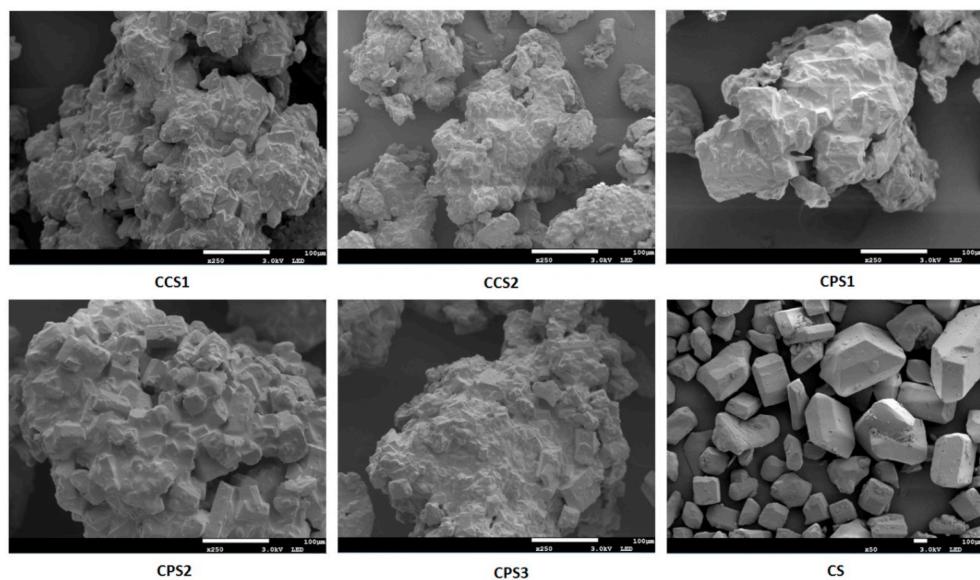
The glass transition takes place at a range of temperatures. Thus, in this study, the glass transition temperature is reported as the onset, midpoint and endpoint/offset temperature. Regardless of the thermal history of the sugars, the glass transition temperature of PSS were significantly lower than that of CS. It can be seen in Table .5 that CS had a glass transition temperature which was comparable to that of sucrose reported by Roos (1993) and Hartel et al. (2011) (62–72 °C). Variation of the glass transition temperature within PSS samples was attributed to the variations in the amount of impurities and different level of molecule degradation and polymerization that occur during the first heating. The specific heat (ΔCp) among samples were not significantly different ($p \geq 0.05$), with the specific heat of CPS1 being slightly higher than the other samples.

3.2.6. Microstructural images

Microstructural visualization of sugars showed that the surfaces of PSS, in contrast to sucrose, were covered with layers which induced the sugar crystals to stick to each other, creating agglomerates (Fig. 3). The presence of these layers may be due to the relatively high moisture content (Beckett, 2008), as well as the presence of hygroscopic materials such as fructose, glucose and amorphous sugar (Saputro et al., 2017b).
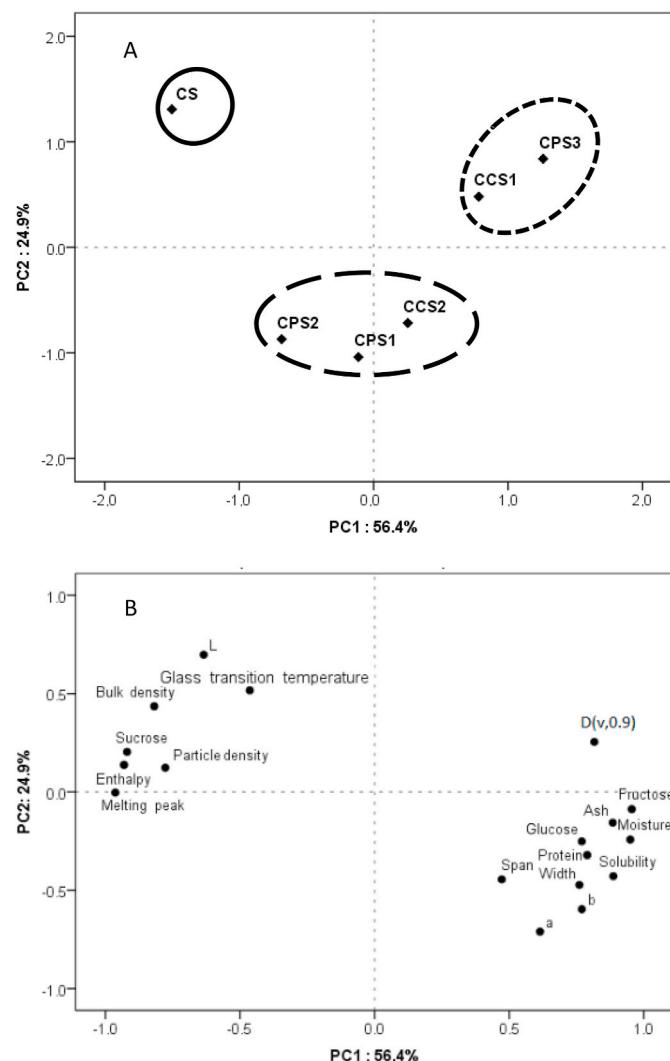
3.3. Relationships between chemical and physical properties of palm sap sugars

The relationships between chemical and physical properties of PSS was investigated using PCA. It can be seen in Fig. 4 that PCA explained more than 81% of the variance in the first two factors, namely PC1: 56.4% and PC2: 24.9%. It can be observed from Fig. 4 (A) that there were 3 clusters of sugar. The first cluster (CCS1 and CPS3) was characterized by high positive values of PC, and included high moisture, fructose, crude protein and ash content. Moreover, this cluster also showed high D (v,0.9), solubility and width values which can be

Scale bar represents 100 μm (CCS1, CCS2, CPS1, CPS2, CPS3) and 10 μm (CS).

Fig. 3. Surface morphology of sugars. Scale bar represents 100 μm (CCS1, CCS2, CPS1, CPS2, CPS3) and 10 μm (CS).

Fig. 4. PCA score plot (A) of physicochemical properties of sugars. PCA loading plot (B) of palm sap sugars and sucrose.

attributed to the presence of the aforementioned chemical compounds. The second cluster (CPS1, CPS2, CCS2) was characterized by relatively high negative values of PC2 and included high moisture, glucose, crude protein and ash content. In turn, these chemical compounds resulted in PSS with high solubility, span, width, and $a*$ and $b*$ values. The third cluster (CS) was characterized by high negative value of PC1 and high positive value of PC2 and included high sucrose content and $L*$ values. Due to its high purity, this cluster also showed high enthalpy values and melting and glass transition temperatures. Moreover, this cluster also showed high particle and bulk density. Fig. 4 (B) shows that, in general, the higher the chemical impurities (moisture, fructose, glucose, crude protein, ash), the lower the enthalpy values and melting and glass transition temperatures, bulk and particle density were observed. Moreover, the higher chemical impurities, the higher D (v,0.9), solubility, span, width, and $a*$ and $b*$ values were observed.

4. Conclusions

Several palm sap sugars had various physicochemical properties that could be attributed to the differences of the raw materials and processing methods used by the sugar producer. The degree of non-enzymatic reactions that occur during sugar production, namely Maillard reactions and caramelization, theoretically were responsible for the different level of crude protein and reducing sugars present in the PSS.

Further, these compounds together with the presence of moisture and minerals determine the level of PSS purity. Furthermore, in combination with thermal and mechanical processes used during sugar production, they defined the solubility, thermal behavior, particle density, and particle size distribution of coarse palm sugar. This study has shown that the physicochemical properties of PSS that varied with different processing histories have various physicochemical characteristics.

Compliance with ethics requirements

This article does not contain any studies with human or animal subjects.

CRediT authorship contribution statement

Arifin Dwi Saputro: Conceptualization, Methodology, Investigation, Formal analysis, Writing - review & editing. **Davy Van de Walle:** Methodology, Data curation, Writing - original draft, Formal analysis, Supervision. **Koen Dewettinck:** Methodology, Supervision, Writing - review & editing, Conceptualization.

Declaration of competing interest

The authors have no conflicts of interest to declare.

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