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Characterization of Sugar from *Arenga pinnata* and *Saccharum officinarum* sugars

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Abstract

The study was carried out to characterize the physicochemical properties, antioxidant activities and the volatile compounds of sugars from *Arenga pinnata* and *Saccharum officinarum*. Refined cane sugar exhibited the highest L^* value, whereas jaggery powder showed the lowest L^* value ($p<0.05$). The solubility ranged from 99.18% to 99.57%. The proximate composition and chemicals properties were significantly ($p<0.05$) varied among different sugar samples. The highest moisture content (4.11%), crude fat (0.11%), crude fiber (0.02%) and reducing sugar (9.31%) were found in aren sugar. Highest amount of ash content (1.19%), crude protein (0.28%), titratable acidity (0.50%) and vitamin C (6.62 mg/100 g) were found in jaggery powder. As control, refined cane sugar contain significant amount of carbohydrate (99.95%), total soluble solid (90.00 °Brix) and water activity (0.55 aw). The pH values of all samples ranged from 4.14 to 6.65. The maximum DPPH radical scavenging activity and TPC were found in jaggery powder with values 4170 µg of GAE/g and 46.98% respectively. The volatile compounds detected were 5-hydroxymethylfurfural,2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one, aminoacethydrazine, hydroxyacetic acid, hydrazine, acetic acid, [S-(R^*, R^*)]-2, 3-butanediol, 2, 3-dihydro-3, 5-dihydroxy-6-methyl-4H-pyran-4-one and 6-acetyl-á-d-mannose. The quality data from this characterization can be used to indicate the standard of *A. pinnata* and *S. officinarum* sugars.

Introduction

Sugar is a basic food carbohydrate primarily comes from sugar cane, sugar palm and sugar beet. There are various types of sugar categorized by their use and their characteristics. Aren sugar is a type of sugar made by boiling the sweet sap harvested from the stalk of male inflorescent of *Arenga pinnata*. The nira sap of the inflorescence from the sugar palm trees was used to make traditional sugar blocks which called aren sugar or locally known as gula kabong/enau (Ishak *et al*., 2013). Aren sugar is believed to be more nutritious than sugar extracted from sugarcane. It contains minerals and vitamins that are not found in the refined cane sugar (Ishak *et al*., 2013).

Jaggery powder is form from raw sugarcane juice, a tropical grass from a group of Saccharum species which stores sucrose in its stem. It is produced from old or traditional systems of sugar production method in which evaporation takes place in an open pan and syrup produced is thick enough to solidify on cooling. This traditional sugar is operated less intensive on a semi-industrialized scale and not fully commercialized cultivation and processing (Johari, 1994). Jaggery powder contains all the food substances in sugarcane and value much higher than refined sugar, thus making it as a healthier alternative sweetener (Unde *et al*., 2011).

Refined cane sugar was preferred than aren sugar and jaggery powder in daily use due to its purity (Nayaka *et al.*, 2009). It imparts sweetness to food and beverage without unwanted taste (Wojtezak *et al*., 2012). However, refined cane sugar has little nutritional value and the concern of increasing consumption of refined cane sugar on health impact has been increased (Cheeseman, 2004).

Naknean and Meenune (2011) revealed that there was an increase in antioxidant activity of concentrated palm sugar syrup that freshly heated on a wood fire stove which was produced in Songkhla Province, Thailand is highly correlated with the amount of increases in Maillard reaction products, caramelization products and phenolic content.

Although studies on some characteristics and antioxidant activity of certain sugars have been mentioned but no information on characteristics and antioxidant activity of Aren sugar produced in Malaysia has been systematically reported. Thus this research aimed to characterize the physiochemical properties, antioxidant activities and the volatile compounds of

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sugars from *A. pinnata* and *S. officinarum.*

Materials and Methods

Sample collection and preparation

Aren sugar was traditional foodstuff and obtained at local market in Melaka, Malaysia. Refined cane sugar and jaggery powder were purchased from local supermarket (Bangi, Selangor, Malaysia) with the same sugar manufacturer. Sugar samples were vacuum packed in aluminium bag (500 g/bag) and kept at -20°C until used within 1 week. Refined cane sugar will be acted as a control sample.

Determination of color

The color measurement of the samples was carried out using a colorimeter (Ultrascan Pro, Hunter Lab, USA). The rates of lightness *(L^*)*, redness *(a^*)* and yellowness *(b^*)* of sugar samples were measured. (Naknean *et al*., 2010).

Determination of solubility

Solubility of sample was determined by modification of Naknean *et al.*, (2010). About 1 g of sample (refined cane sugar, aren sugar and jaggery powder) and 100 ml of distilled water were transferred into a beaker. The mixture was centrifuged at 3500 rpm for 20 min at 24°C by using centrifugal (Centrifuge S800, KUBOTA, Japan). The solution was filtered through pre-weighed filter paper (Whatman, No. 1) using a Buchner funnel and immediately dried in oven at 105°C for at least 7 hours. The percentage of solubility value was calculated by weight difference.

Determination of pH, titratable acidity (TA) and total soluble solid (TSS)

The pH, TA and TSS were determined according to AOAC method (1990). The pH value was measured by pH meter (3505 pH Meter, Jenway, UK). The instrument was calibrated using standard buffer solutions at pH 4 and 7. The titratable acidity was measured by dissolved 10 g of sample with 100 mL of distilled water. The homogenate was titrated with 0.1 M NaOH. The volume of base required to make the pH of the homogenate to pH 8.1 (end-point) was measured. The result was calculated as a percentage of lactic acid.The total soluble solid (°Brix) were measured using a hand Refractometer (Atago N1 Brix 0~32%, Japan).

Determination of water activity

The water activity of sample was measured at room temperature using a water activity meter (Aqualab Water Activity Meter, Decagon, Washington, USA).

Determination of vitamin C and reducing sugar content

The vitamin C and reducing sugar content was measured according to AOAC method (2012).

Analysis of proximate content

The moisture, ash, crude protein, crude fat and crude fibre were determined according to AOAC (2012). The carbohydrate content of samples was measured using 'by difference' method according to AOAC method (2012). Samples were analysed in triplicate.

% of Carbohydrate = 100% – (% moisture + % ash + % protein + % fat + % fiber)

Sample preparation and extraction

Samples were extracted using modification method adopted by Azlim *et al*. (2010). About 20 g of sample (refined cane sugar, aren sugar and jaggery powder) and 400 mL of methanol solvent was added into the beaker. The mixture was stirred with magnetic stirrer for 1 hour at room temperature. The mixture was filtered (Whatman No. 4) through Buchner funnel. The solvent in the extract were removed under reduced pressure at 40°C using rotary evaporator (Laborota 4000 Efficient Eco, Heidolph. Germany).

Determination of DPPH radicals scavenging activity

The free radical-scavenging activity of samples on DPPH radical was carried out according to the procedure described by Azlim *et al.* (2010) with slight modification. DPPH solution was prepared by dissolving 0.0024 g DPPH powder into 100 ml methanol. About 0.01 g of refined cane sugar, aren sugar and jaggery powder were added to 10ml of methanol to give concentration of 1 mg/ml. Then, 2 ml of sample aliquot was added into 2 ml of DPPH in methanol. The mixture was mixed with vortex and allowed to stand at room temperature in the dark for 30 minutes. The absorbance of the resulting solution was measured at 517 nm using a spectrophotometer (Thermo Spectronic GENESYS 20 Visible Spectrophotometer, Thermo Scientific, USA). The negative control was prepared in the same manner by replacing sample to methanol. Trolox solution was used to establish a standard curve. DPPH radical scavenging activity was expressed as mg Trolox equivalent (Trolox)/g dried sample. The scavenging capacity of sample was calculated by the following equation:

$$\text{Scavenging activity (\%)} = \frac{A_{blank} - A_{sample}}{A_{blank}} \times 100$$

Determination of total phenol content (TPC)

The total phenol content of sample was determined by Folin–Ciocalteu method with slightly modification from Azlim *et al.* (2010). Fiolin reagent was prepared by dissolving 10 ml of Folin-Ciocalteu into 90 ml distilled water. About 0.01 g of refined cane sugar, aren sugar and jaggery powder was added to 10ml of methanol to give concentration of 1 mg/ml. Then, 1 ml of sample aliquot was added into 5 ml of Folin-Ciocalteu reagent and allowed to stand at room temperature in the dark for 5 min. Then, 4 ml of sodium carbonate solution (70 g/l) was added. The mixture was incubated for 1 hour and 30 min in the dark at room temperature and then the absorbance was measured at 765 nm with spectrophotometer (Thermo Spectronic GENESYS 20 Visible Spectrophotometer, Thermo Scientific, USA). The blank solution contained methanol instead of sample. Gallic acid was used as standard. The standard calibration curve was prepared using gallic acid standard. The total phenol content was expressed as micrograms of gallic acid equivalent (GAE) per gram sample.

Sample preparation and extraction

Samples of refined cane sugar, aren sugar and jaggery powder were extracted using method adopted by Quinn *et al.* (2007) with slight modification. The method modified was developed as follow: 20 g of sample and 50 mL of dichloromethane solvent was added into the beaker. The mixture was stirred with magnetic stirrer for 3 hours at room temperature. The mixture was filtered (Whatman No. 1) through Buchner funnel. The solvent in the extract were removed under reduced pressure at 45°C using rotary evaporator (Laborota 4000 Efficient Eco, Heidoph, Germany). The extracts were filled in the vials and stored at 4°C until further uses. This method conducted prior to extract a mixture from all samples, ready to be analysed using GC in order to profile components of volatile compounds present in refined cane sugar, aren sugar, jaggery powder.

Determination of volatile compounds

Volatile compounds present in the sugar samples were carried out using Gas Chromatography – Mass Spectrometry Analysis by modification method of Ho *et al.* (2007, 2008). The volatile compounds of extract were identified using GC-MS (TRACE TM ULTRA Gas Chromatography, Thermo Scientific, USA) with db5 capillary column (30m x 0.25mm x i.d., 0.25μm film thickness). Flow rate of helium carrier gas was 1.0 mL/min. The injector temperature was 240ºC. The oven temperature was programmed from 60ºC to 240ºC at 6ºC/min with initial and final hold times of 5 min and 10 min respectively using splitless injection mode. Volatile compounds were identified with a quadropole mass selective detector. Mass spectral ionization was set at 180ºC. The mass spectrometer was operated in the electron ionization mode at a voltage of 70 eV. Volatile compounds were identified by comparing the mass spectra and retention time data with those of authentic compounds supplemented with data from MS library. The name, molecular weight and structure of the compounds of the test materials were ascertained.

Statistical analysis

All samples were analyzed in triplicate for each analysis except for reducing sugar and volatile compounds. Reducing sugar analysis was analyzed in duplicate while volatile compounds identification was analyzed in one time. Minitab statistical software (version 16) was used to conduct one-way ANOVA method in order to get the mean and standard deviation. Tukey's comparison test purposely for determination of significant differences among values of different sugar samples. Statistical significance was defined to be at a level of $p<0.05$.

Result and Discussion

Color

Table 1 shows the color parameter *(L^*, a^*, b^*)* investigated under CIE Lab system for refined cane sugar, aren sugar and jaggery powder. The results of color *(L^*, a^*, b^*)* were varied depending on types of sugar. Among all samples, the refined cane sugar had the highest L^* value ($p<0.05$). The difference in a^* and b^* values were noticeable in all samples ($p<0.05$).

Generally, the color of sugars could be found in light yellow to dark brown, depending on type of raw materials, heating process (temperature and time) and chemical process. In short, aren sugar and jaggery powder were appeared in yellow-brown to brown color, except for the refined cane sugar which appeared in white as shown in Table 1. Higher temperature exerted may lead to increasing amount of reducing sugar that will be reacted with amino acid during Maillard reaction thus produce brown pigment or melanoidin which contributed to dark brown color (Naknean and Meenune, 2011). The different color of all samples might result from the difference in type of plants raw material, temperature and heat as well as manufacturing process. (Naknean and Meenune,

Table 1. Physical properties of refined cane sugar, Aren sugar and jaggery powder

Property / Sample	L*	a*	b*	Solubility (%)
Refined cane sugar (control)	84.23^{a}±0.76	-0.36^{a}±0.01	5.36^{a}±0.03	99.57^{a}±0.31
Aren sugar	57.71^{b}±0.78	7.43^{b}±0.25	17.45^{b}±0.17	99.35^{a}±0.15
Jaggery powder	44.26^{c}±0.26	6.12^{c}±0.14	8.08^{c}±0.28	99.18^{a}±0.42

Table 2. Chemical properties of refined cane sugar, Aren sugar and jaggery powder

Property / Sample	pH	Titratable acidity (%)	Total soluble solid (°Brix)	Water activity (a_w)	Vitamin C (mg/100g)	Reducing sugar (%)
Refined cane sugar (control)	6.65^{a}± 0.09	0.02^{a}± 0.00	90.00^{a}± 0.00	0.55^{a}± 0.01	0.64^{a}± 0.01	2.30^{a}± 0.06
Aren sugar	5.50^{b}± 0.03	0.09^{b}± 0.00	73.33^{b}± 5.77	0.50^{a}± 0.04	1.76^{b}± 0.38	9.31^{b}± 0.12
Jaggery powder	4.14^{c}± 0.05	0.50^{c}± 0.02	80.00^{b}± 0.00	0.51^{a}± 0.01	6.62^{c}± 0.61	5.40^{c}± 0.06

extraction and heating of the cane juice, which could be derived from oxidation of phenolic compounds; caramelization of sucrose, glucose and fructose; Maillard reaction and alkaline decomposition of sucrose (Guerra and Mujica, 2008). The different regional practices such as clarifying agents or additives used and storage practices also gave varying degree of color (Naknean and Meenune, 2011).

Solubility

In the presence of polar molecules such as sugars and water, these interactions are dominated by hydrogen bonding (Joupplia, 2006). Sugar is generally very soluble in water at room temperature (Coultate, 1993).The result of the solubility in Table 1 showed no significant difference among these three samples ($p>0.05$).

Normally, crystalline solids can hold less water than amorphous solids. This is due to the amorphous noncrystalline material that can form hydrogen bond with water internally, not just on the surface, which is the only way water can interact with perfect crystals (Bell and Labuza, 2000). In this case, sucrose would crystalline by a disruption such as seeding which could reduce the percentage of solubility (Asadi, 2007). High in reducing sugar content led to the hygroscopic of the sugars made it easy to crystalline (Naknean and Meenune, 2011).

pH and titratable acidity

The total acidity was calculated based on the lactic acid equivalence. Since, lactic acid is the main organic acid presented in palm sap (Taipaiboon and Loetkitsomboon, 2004). Aren sugar and jaggery powder had significantly ($p<0.05$) high percentage of acidity but lower pH than refined cane sugar because aren sugar and jaggery powder syrup contained high level of sugar content which acted as a food in providing an environment for microorganisms to grow. Thus, there was sugar fermentation process on the palm sap and cane syrup in which microorganism's activity occurred during traditional sugar production in a large open pan. The reduction in pH values occurring in the Maillard reaction was due to the formation of organic acids such as formic acid and acetic acid (Brands and Van Boekel, 2002; Lertittikul *et al*., 2007).

Besides, these variations of pH and acidity can be used for indicating food safety. They might be due to the effects of sugar fermenting process, which is based on activity caused by microorganisms. Microorganism contamination is responsible for the low pH and high total acidity of cane juice and palm sap sugar syrup. Moreover, during postproduction, syrup also could be contaminated by microorganisms from the air, equipment and packaging (Dumont *et al.*, 1993).

Total soluble solid

As shown in Table 2, total soluble solid for refined cane sugar had significantly ($p<0.05$) highest at 90.00±0.00 °Brix, followed by jaggery powder and aren sugar at 80.00±0.00 and 73.33±5.77 °Brix respectively. The results of total soluble solid were showed significant different among the samples ($p<0.05$).

The refined cane sugar after concentration contained 92% dissolved solid which was sucrose and only 8% was non-sugars showed that inorganic ash, suspended matter and any impurities presence were removed which left only sucrose content (Kent,

Table 3. Proximate composition of refined cane sugar, Aren sugar and jaggery powder

Property / Sample	Moisture content (%)	Ash content (%)	Crude protein content (%)	Crude fat content (%)	Crude fiber content (%)	Carbohydrate content (%)
Refined cane sugar (control)	0.03^{b}±0.01	0.01^{b}±0.00	0.00^{a}±0.00	0.00^{b}±0.00	0.01^{b}±0.00	99.95^{b}±0.01
Aren sugar	4.11^{a}±0.08	0.47^{a}±0.07	0.00^{a}±0.00	0.11^{a}±0.02	0.02^{a}±0.00	95.29^{a}±0.11
Jaggery powder	3.56^{c}±0.13	1.19^{c}±0.04	0.28^{b}±0.01	0.06^{c}±0.01	0.01^{b}±0.00	94.96^{c}±0.16

2007) that contributed to the high total soluble solid for refined cane sugar. Also, moisture content of sugar was directly affected the total soluble solid. From Table 3, the value of moisture content for refined cane sugar was the lowest due to the conditioned or aging of the refined cane sugar to achieve moisture equilibrium with surrounding atmosphere. Thus, the total soluble solid was higher for refined cane sugar compared to aren sugar and jaggery powder (Naknean and Meenune, 2011).

Water activity

The water activity (a_w) values for refined cane sugar was 0.55±0.01, for aren sugar was 0.50±0.04 and for jaggery powder was 0.51±0.01 as tabulated in Table 2. The result was indicated no significant different among the samples ($p>0.05$). Water activity (a_w) is an intrinsic product characteristic that most influences the microbial ecology of a sugar-rich product. The moisture content and water activity highly used to control the shelf life of sugar during storage as water could increase stickiness of the sugar, increase microbial deterioration and biochemical degradation reaction (de Rodriguez, 2004). The result of water activity for these three sugars was considered stable which was in about 0.50 as most of the water would be removed during boiling or evaporation process in the sugar manufacturing. Therefore, sugar with water activity in this range would not encourage the growth of bacteria especially osmophilic type which normally grew at water activity in the range of 0.65-0.80 (Naknean and Meenune, 2011).

The moisture content of refined cane sugar was marked as the lowest, 0.03±0.01% but it had the highest water activity, 0.55±0.01 aw compared to aren sugar and jaggery powder. Since water activity value refers to free water that can promote microbial deterioration and biochemical degradation reaction. Guerra and Mujica (2008) concluded that different commercial granulated cane sugar had different water activity value.

Vitamin C

From this study, jaggery powder has the highest vitamin C content which was 6.62±0.61 mg/100g, followed by Aren sugar at 1.76±0.38 mg/100g and refined cane sugar at 0.64±0.01 mg/100g. All of samples are statistically significant at ($p<0.05$). The experimental vitamin C content obtained for refined cane sugar was higher than the vitamin C content reported by Rao *et al.* (2009) which was 0.0046 mg/100g. While for the experimental vitamin C content obtained for jaggery powder was lower than the vitamin C content (7.00mg/100g) as stated by Singh *et al.* (2013).

The refined cane sugar gave the lowest vitamin C content because of the refining process occurred which separated the molasses from sugar crystals and the vitamin C content was removed together with the molasses. Molasses was component that contained different types of vitamin and mineral. Jaggery powder was sugar that contained molasses and there was no separation of molasses from sucrose crystals as like refined cane sugar. Thus, jaggery powder had high level of vitamin C compared to refined cane sugar and aren sugar. Aren sugar contained less

Table 4. Antioxidant properties of refined cane sugar, Aren sugar and jaggery powder

Property / Sample	DPPH radical scavenging activity (%)	Total phenol content (µg of GAE/g)
Refined cane sugar	0.16[a]±0.14	20.24[a]±0.00
Aren sugar	28.86[b]±0.49	1943.00[b]±58.30
Jaggery powder	46.98[c]±0.27	4170.00[c]±57.70

vitamin C content compared to jaggery powder could be due to high heating temperature and time might destroy the vitamin C in the palm syrup as vitamin C was very heat labile (Sansouci, 2014).

Reducing sugar

The wide range reducing sugar content of refined cane sugar, aren sugar and jaggery powder from 2.30-9.31% was noticeable ($p<0.05$). Martins *et al*. (2001) reported that during heating in the manufacturing process, especially at high temperature and long heating time, it could accelerate the hydrolysis of sucrose yielding reducing sugars. However, high reducing sugar content presented in sugar also influences the browning color of sugar afterward, due to the Maillard reaction (Naknean and Meenune, 2011).

Aren sugar was traditional produced by evaporating the juice in a large opened pan under heating with the wood fired stove until the concentrated paste was obtained (Naknean *et al.*, 2013). Those aren sugar and jaggery powder had higher reducing sugar content than refined cane sugar. Thus, low reducing sugar in refined white cane sugar compared to aren sugar and jaggery powder may be due to the chemical refining process which can eliminate the reducing sugar. In addition, (Phaichamnan *et al.*, 2010) reported that the difference of total sugar and reducing sugar contents might be due to the effect of contamination from micro-organisms in sugar. The microrganisms can convert sucrose to glucose and fructose (invert sugar) and finally to organic acids or alcohols (Willits *et al*., 1976).

Proximate content

The Table 3 below showed the result of proximate content of moisture content, ash content, crude protein content, crude fat content, crude fiber content and carbohydrates content for refined cane sugar, aren sugar and jaggery powder.

Moisture content

In Table 3, the result for moisture content of refined cane sugar differed significantly ($p<0.05$) among the samples. Refined cane sugar had the lowest moisture content, followed by jaggery powder and aren sugar. The moisture content in sugar was largely depended on the heating temperature, heating time and total soluble solid. The higher the heating temperature and longer the heating time during production process would reduce the water content from the sugars (Naknean *et al*., 2010). The value of total soluble solid for refined cane sugar was the highest, followed by jaggery powder and aren sugar (Table 2). The higher the total soluble solid, the lower the moisture content thus contributed to the lowest moisture content of refined cane sugar.

Besides, the refined cane sugar was conditioned after drying to allow moisture stabilization which led to low percentage of moisture content. Conditioning process was the removal of bound to free moisture in which the film saturated syrup surrounding the outside of the crystal formed supersaturated solution deposited on the surface of the crystals when dried above room temperature. The sugar was then cooled and aged, water was released during this syrup phase crystallization (Kent, 2007).

Ash content

Ash content could be used to measure the total mineral content by oxidation organic matters in sugars. The result of ash content in Table 3 was showed significant different among the samples ($p<0.05$). The ash content for refined cane sugar was the lowest, followed by aren sugar and jaggery powder. This was because refined cane sugar undergone refining process where the raw sugar would pass through a bed of activated carbon to remove inorganic ash.

While for the jaggery powder, the highest ash content was due to the presence of the molasses in the jaggery powder in which molasses contained 10-15% of ash by weight. Also, non-sugar substances such as insoluble solid might concentrate on the molasses which contributed to the higher ash content (Payet *et al.*, 2005). Aren sugar contained little amount of ash content was due to the some of the minerals retained during the production process (Hacking, 1986).

Crude protein content

The results of crude protein content for refined cane sugar and aren sugar shows no significant

different ($p>0.05$) but they were significant different with jaggery powder ($p<0.05$). Kjeldahl method basically was used to determine crude protein content, however determined the total nitrogen in sugar as well. Thus, the higher crude protein content in jaggery powder might be related to nitrogen content as jaggery powder contained molasses. The total nitrogen in cane molasses was in the range of 0.5-1.6% which might contribute to the crude protein content for jaggery powder (Kristiansan, 2002).

In general protein acts as a substrate of Maillard reaction that occurring during the production of palm sugar syrup. High protein content presented in oil palm sap influenced on the quality of palm sugar syrup afterward (Naknean *et al.*, 2010). In addition, microorganisms may use protein as a carbon source or as a nitrogen source for their metabolism and genetic material (Adams and Moss, 1995). High heating temperatures and times could accelerate the Maillard reaction that is responsible for lower protein content (Wang *et al*., 2006).

Crude fat content

For crude fat content, refined cane sugar had 0.00±0.00%, aren sugar had 0.11±0.02% and jaggery powder had 0.06±0.01%. There was no crude fat content found in refined cane but little found in jaggery powder and aren sugar. This might due to the small quantity of groundnut/mustard oil was sprinkled during the evaporating/boiling of cane juice and palm syrup in a large pan to prevent excess frothing as well as for easily flowing of hot cane juice or palm syrup during transferring from one container to another (Rao *et al.*, 2009).

Crude fibre content

According to the nutrition facts, the fiber content present in sugar is supposedly zero as fiber and most of the other nutrients in the plant are removed during refining process. However, some crude fiber with lower value was derived during this study ranged from 0.01% to 0.02%. The result of crude fiber content in Table 3 was showed no significant different between refined cane sugar and jaggery powder ($p>0.05$) but they showed significant different with aren sugar ($p<0.05$).

The little crude fibre content in these three sugars could be relate to the fibre residue left during cane extraction and palm sap collection that was not filtered through properly in the manufacturing process which led to the existing of crude fibre (Duyff, 2011). Poorly clarified juice caused inorganic materials and polysaccharides passed into the clear juice and sugar as well if there was no further purification step taken place. The polysaccharides presence in the sugars which was not removed during experiment would be considered as crude fibre content (Kent, 2007).

Carbohydrates content

The result of carbohydrates content presented in Table 3 was indicated significant different among refined cane sugar, aren sugar and jaggery powder at 99.95±0.01%, 95.29±0.11% and 94.96±0.16% respectively ($p<0.05$). The carbohydrate content was highest for refined cane sugar compared to aren sugar and jaggery powder as most of the composition of refined cane sugar was made up of sucrose and there was very little of organic matter. The carbohydrate content of aren sugar and jaggery powder was almost the same as they were other nutrients in these two sugars other than sucrose (Rao *et al*., 2009). The higher carbohydrates content in sugars was due to the simple carbohydrate units, glucose could form long chain polymer molecules either in linear or branched such as starch, cellulose, and dextran. Indigenous sugarcane polysaccharides were removed from fresh cane juice but starch and dextran were occluded within the crystals and distributed throughout (Kent, 2007).

Antioxidant properties

Plant-derived foods especially the raw and unprocessed fruits and vegetables are often associated with high content in polyphenols. Phenolic compounds are always associated with antioxidant properties that are able to scavenge free radicals. Thus, the antioxidant properties of DPPH radical scavenging activity and total phenol content (TPC) for refined cane sugar, aren sugar and jaggerry powder was studied.

DPPH Radical scavenging activity

The analytical results for DPPH radical scavenging activity and total phenol content of refined cane sugar, aren sugar and jaggery powder are displayed in Table 4. The result of DPPH radical scavenging activity was showed significant different among the samples ($p<0.05$), gave out the highest percentage for jaggery powder, followed by aren sugar and refined cane sugar respectively.

The higher percentage scavenging activity of aren sugar and jaggery powder were coincidental with the higher reducing sugar, intermediate browning product, browning intensity and total phenolic content as compared to refined cane sugar. DPPH is one of compounds that possess a proton free radical with a characteristic absorption, which decreases significantly on the exposure to proton radical

scavenging. (Yamaguchi *et al.*, 1998).

Previous studies conducted by Lertittikul *et al.* (2007) and Benjakul *et al.* (2005a, 2015b) reported that Maillard reaction products (MRPs) and caramelization products (CPs) from fructose showed the highest radical-scavenging activity, compared with glucose. The reduction of alcoholic DPPH solution in the presence of a hydrogen-donating antioxidant is due to the formation of the non-radical form, DPPH-H. When the DPPH-radical is scavenged by antioxidants through the donation of hydrogen to form a stable DPPH-H molecule, the color is changed from purple to yellow (Shon *et al*., 2003). However, sugar consists primarily of sucrose containing glucose and fructose. Therefore, the higher the reducing sugar the greater the percentage scavenging activity was observed.

In addition, Haghparast *et al.* (2013) reported that intermediates or the final brown polymer could function as hydrogen donors. From the results, aren sugar and jaggery powder can function as antioxidant through the donation of hydrogen atom especially jaggery powder which exhibited the highest DPPH radical scavenging activity. The antioxidant activity of phenolic compounds is clearly related to free radical-scavenging and hydrogen-donation ability (Kukuc *et al*., 2007).

Total phenol content

The total phenol content for refined cane sugar, aren sugar and jaggery powder was 20.24±0.00 µg of GAE/g, 1943.00±58.30 µg of GAE/g and 4170.00±57.70 µg of GAE/g respectively. All samples were found statistically significant at $p<0.05$. The result of total phenol content as stated by Nayaka *et al*. (2009) in refined cane sugar and jaggery powder as well as stated by Amin (2010) in commercial palm syrup was very close. Since DPPH radical scavenging activity was strongly related to total phenol content, the total phenol content was increased with the increasing of DPPH radical scavenging activity as shown in Table 4.

Based on a study conducted by Harish *et al*., (2009) on antioxidant activity of jaggery sugar observed that jaggery powder had the higher total phenol content than refined cane sugar in which both manufactured by using the same source, sugarcane juice. This was probably due to the minimal chemical processing in the manufacture of jaggery powder and aren sugar which retains more polyphenols. The dark brown color of jaggery powder basically resulted from phenolic compound's oxidation proved that there were phenolic compounds present in jaggery powder while the white color of refined cane sugar showed that most of the phenolic compounds had been removed during clarification and carbonation steps.

Moreover, the presence of phenolic compounds in aren sugar was occurred naturally. (Naknean *et al.*, 2010). The phenolic compounds impart color as well as taste to the sugar and its removal is an important problem associated with sugar manufacture (Godshall *et al.*, 2002). The different techniques used in sugar processing to remove color and impurities affect the amount of polyphenols in sugars and this may explain the low phenolic content of white refined sugars.

Volatile compounds analysis

Volatile compounds of refined cane sugar, aren sugar and jaggery powder studied by gas chromatography mass spectrometry (GCMS). The result showed that there were 2 volatile compounds found in refined cane sugar and aren sugar while 4 volatile compounds were found in jaggery powder.

Aminoacethydrazine and hydroxyacetic acid, hydrazine were the volatile compounds found in refined cane sugar. They gave ammonia-like flavor. This was mostly due to the chemicals used in the processing steps (Agteren *et al*., 1998). The relative peak percentage for aminoacethydrazine and hydroxyacetic acid, hydrazine was almost the same with 21.32% and 22.48% respectively.

The volatile compounds found in aren sugar were 5-hydroxymethylfurfural and 2, 3-dihydro-3, 5-dihydroxy-6-methyl-4H-pyran-4-one. Both were heterocyclic compounds from furans derivatives. 5-hydroxymethylfurfural was contributed to caramel-like and burnt sugar flavor. It was the products of caramelization by heating the carbohydrates in aren sugar. Degradation of carbohydrates would cause formation of furan. Furfural formation as heating with high temperature caused removal of hydroxyl group located in the alpha-position of the carboxyl group from 1, 2-enolic form which leads to the formation of 5-hydroxymethylfurfural (Naknean *et al*., 2010).

2, 3-dihydro-3, 5-dihydroxy-6-methyl-4H-pyran-4-one was the result from ring closure of a hexose. It was Maillard reaction product of glucose and glycine which giving a caramel-like odor and a slight astringent flavor (Flament, 2002). 5-Hydroxymethylfurfural was found to be the predominant volatile compounds in aren sugar with relative peak area of 97.96% which was much higher than 5-dihydroxy-6-methyl-4H-pyran-4-one with only 2.04%.

The volatile compounds found in jaggery powder were acetic acid, [S-(R^*, R^*)]-2, 3-butanediol, 2, 3-dihydro-3, 5-dihydroxy-6-methyl-4H-pyran-4-one and 6-acetyl-á-d-mannose. Acetic acid was derived

from the oxidation of ethanol produced by the fermentation of hexoses, pentoses and glycerol. In addition, the α-dicarbonyl compounds were unstable which were precursor for volatile compounds formation and undergo a cleavage reaction (at the C-C bond) resulting in acetic acid produced during the Maillard reaction (Jackson, 2008). [S-(R*, R*)]-2, 3-butanediol was the by-product of alcoholic fermentation. Most butanediol was formed by yeasts during the fermentation of carbohydrates (Storza, 2013). 2, 3-dihydro-3, 5-dihydroxy-6-methyl-4H-pyran-4-one contributed to caramel flavor (Flament, 2002) and 6-acetyl-á-d-mannose gave sweet taste. The relative peak area for acetic acid was considered high with 4.83% as compared to [S-(R*, R*)]-2, 3-butanediol, 2, 3-dihydro-3, 5-dihydroxy-6-methyl-4H-pyran-4-one and 6-acetyl-á-d-mannose with relative peak area of 0.73%, 0.39%, and 0.25% respectively.

However, according to Ho *et al.* (2008) and Asikin (2014), volatile compounds found for palm syrup of Arenga pinnata and cane brown sugar were furans and pyrazines from the Maillard reaction and caramelisation. Furan derivatives such as 2-furanmethanol, 2-furancarboxaldehyde and 2, 3-dihydro-3,5-dihydroxy-6-methyl-pyran-4-one were detected. Pyrazine derivatives were detected in palm syrup of Arenga pinnata and cane brown sugar such as 2, 3-dimethylpyrazine, 2, 5-dimethylpyrazine, and 2-ethyl-3,5- dimethylpyrazine. These pyrazines compounds gave flavors such as sweet and roast-like flavor (Naknean *et al*., 2010).

Conclusions

In this research, colour of aren sugar and jaggery powder resulted higher value for a^* and b^* while refined cane sugar recorded highest on L^*. Most acidic sugar founded was Jaggery powder (4.14) followed by Aren sugar (5.50) while refined cane sugar resulted on mostly neutral pH at 6.65. Refined cane sugar was recorded high value in TTS, vitamin C, and reducing sugar, followed by aren sugar and jaggery powder. Jaggery powder resulted on highest DPPH activity at 46.98% and total phenol content at 4170.00 (µg of GAE/g). Aren sugar and jaggery powder comprises of many useful minerals, vitamins and antioxidants may replace refined cane sugar as alternatives sweetener with antioxidant properties for food production and nutraceutical benefits. Further investigations can be carried out by conducting sensory evaluation to determine the acceptance of consumers towards aren sugar.

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