

Potential of Agricultural Residues from *Musa acuminata* (Cavendish) Peel: Study on Physicochemical Properties and Thin-Layer Drying Characteristic

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Abstract

Musa acuminata (Cavendish) peel is a waste product of limited values that is generated in large quantities and caused detrimental environmental issues in long term if there are no alternative solutions. This primary residue corresponds to 40 % of the fruit weight with a broad natural antioxidant such as polyphenols that will be valuable to the food industry application. This study aimed to investigate the physicochemical characteristics and solvent extraction for high polyphenols recovery between unripe and ripe peel following the drying characteristic and quantification analysis. The physicochemical characteristics of Cavendish peel showed significant differences at different ripening stages, thus effect the solvent extraction towards antioxidant compounds and activities. An aqueous extract of unripe peel was the best solvent for higher phenolic, tannin and flavonoid content compared to ripe peel. The 40 °C of drying treatment will preserve higher tannin content than other temperature and eleven profile of polyphenols had been detected using HPLC including tannic acid as a lead compound. The results from this study can be used for further isolation and purification of tannin to the possible application as functional food ingredients due to its antioxidants benefits and conversion of this residues as valuable is necessary.

Keywords: Physicochemical, Extraction, Drying, Cavendish peel, Antioxidant, Tannin, HPLC

Introduction

Banana is one of the world's important crops which are producing over 130 countries. A total of 115 million tons of banana were made in the year 2018 mainly in Asia (54 %), America (26 %) and Africa (17 %) and this tropical fruit are well known being consumed from worldwide because of its year-round production availability [1]. *Musa acuminata* is one of the most abundant bananas in Malaysia and the Cavendish cultivar is a popular for international trade due to its high demand exported to various countries. Export and local consumption of Cavendish banana is rising and becoming the largest fruit crop with high export value. However, the plantation area faces several challenges as the fruit rejection increases up to 20 % due to failure in the sorting process. Cavendish bananas are harvested during the unripe stage for export purposes and incorporated into the discarded fruit due to agricultural residues or waste. The fruits that did not meet the standard quality for commercialization, such as abnormal shape, prematureness size and those with damaged or spoiled areas, will cause microbial contamination of the bunch and be rejected. As the production of *M. acuminata* (Cavendish) increases due to export and local consumption, the rate of fruit rejection also increases rapidly. In Malaysia, the rejected banana fruits are approximately 30 % of total production and do not meet its standard quality commercialization [2]. The percentage of discarded bananas varies about 10 to 13 % of production and is usually used for animal feed, but most producers prefer to leave such residues to decompose outdoors [3].

The underutilization of agricultural residues eventually leads to severe environmental problems. When decomposed, these residues may produce noxious gases such as hydrogen sulfide and ammonia,

posing a severe environmental hazard [4]. There are limitations in the plantation level, especially in establishing a proper collecting facility for the banana to be sorted according to their quality, stored and a handling system to prevent the loss of rejected banana fruits with damaged areas [5]. Without a proper agricultural waste management practice, enormous amounts of valuable untapped commodities are lost and caused severe ecological damage. Another challenge is to overcome the problem related to the long-term storage of banana residues. Banana residues are highly biodegradable due to their richness in organic matter and high moisture content, leading to material instability and being degraded easily by exposure to microbes. Banana agricultural residues are important with a promising future known by their abundance, centralized position and availability.

The physicochemical characteristic of fruit is one of important evaluations in ripening process. Ripening process induces the changes of the structural, physical, chemical, nutritional, biochemical or enzymatic composition of fruits. The relationship between banana ripening and fruit peel phytochemicals is essential for selection of material for further recovery and extraction process. Physicochemical and antioxidant properties of banana peel are significantly changed through different ripening stages and the degradative changes were describe as example like chlorophyll breakdown, starch hydrolysis and cell degradation in the cell of fruits [6]. Extraction and drying are the main step that must be carried out in order to obtain the substantial ingredients or a product with certain acceptable moisture content for storage purpose in food industry.

Objective of this study was to characterize the physicochemical properties, select the best solvent for extraction, evaluate the thin-layer drying characteristic and quantification through HPLC. Physicochemical characteristics and solvent extraction contributed as a preliminary study to determine the differences and select the best one among the unripe and ripe peel for drying and quantification analyses. The extraction process contributed to the effect of solvents with different polarities on the antioxidant extract for both peels, reflecting the best solvent that gives a high value of antioxidant content. The drying characteristic of a banana peel's thin-layer also characterized in this study with different temperature exposure (40, 50, 60 and 70 °C) by giving different effects on the drying characteristic and tannin composition. This study revealed that the drying, extraction and quantification process from aqueous extracted peel could emphasize the possibility of entire exploitation of the unripe peel part as agricultural residues which are rich in antioxidant compounds and potentially used as functional food ingredients. The utilization of low-cost agricultural residues could be expanded to all possible industries to achieve sustainable technology and reduced environmental problems. It could provide an additional source of income for the farmers and processing industries without adversely affecting the soil fertility or caused environmental pollution.

Materials and methods

Plant materials and sample preparation

The ripe Cavendish banana was collected from Ladang Puchong UPM, Serdang. While, the unripe Cavendish banana with green colour of peel also collected from Ladang Puchong UPM, Serdang and local supplier at Batu Caves, Selangor that was harvested approximately 3 months after the plant had flowered. The raw material was prepared by washed the banana fruit carefully, manually peeled and ready to be used for next analysis.

Chemicals and reagents

The Folin-Ciocalteu's phenol reagent, sodium carbonate, methanol, ethanol and acetone were procured from R&M Chemicals (R&M Marketing, London, UK). The 2,2-Diphenyl-1-picrylhydrazyl (DPPH) radical, 2,2-azino-bis (3-ethylbenzothiazoline)-6-sulfonic acid (ABTS), potassium persulfate, aluminium chloride, tannic acid, rutin, trolox and gallic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Throughout the experiment, all the chemicals used as analytical grade and stock solutions were prepared using purified deionized water from the Mill-Q system (Millipore, Bedford, MA). Chemicals with HPLC grade such as methanol, acetonitrile, catechin, epigallocatechin gallate, caffeic acid, syringic acid, rosmarinic acid, cinnamic acid, myricetin and kaempferol were obtained from R&M Chemicals (R&M Marketing, London, UK), Extrasynthese (Genay Cedex, France) and Sigma-Aldrich (St. Louis, MO, USA).

Physicochemical analyses of banana peel

Physical characteristics

The physical characteristics analysis of unripe and ripe Cavendish banana consisted of thickness and mass measurements. The thickness of both peels were measured using a calliper and the result was

expressed in millimetres (mm). Mass of the fruits for both ripening stages were measured in gram using an analytical balance.

Mechanical characteristic

A mechanical analysis in term of hardness measurement for unripe and ripe Cavendish banana peels were measured using a texture analyser (TA-XT Plus Texture Analyzer, Stable Micro System, Scarsdale, NY) and controlled by a PC-based data acquisition card in a personal computer with a 2.0 mm diameter of cylindrical probe. The peel was placed on the surface plate with a distance between a cylindrical probe and sample surface at 6.0 mm. The value of maximum puncture force for each sample was employed and measured using a cylindrical probe at a return speed of 20.0 mm/s, a pre-test (1.0 mm), test (1.0 mm) and post-test (10.0 mm). Maximum force required to puncture the peel through the probe penetration was recorded by the analyser with respective time. The hardness value was derived from the force deformation curve in Newton (maximum peak of the first penetration) versus time [7].

Chromatic characteristic

The chromatic properties of unripe and ripe Cavendish peels were determined by lab calorimeter equipment of Hunter Lab UltraScan PRO Spectrocolorimeter (Hunter Associate Laboratory Inc., Reston USA.). The sample (peel) was placed inside a glass optical cell and direct to the L*a*b hunter colorimeter measurement which differentiated according to the pre-calibrated chromatic value. The chroma and hue angle were calculated using the equation as shown below (1) and (2);

$$\text{Chroma} = \sqrt{(a^*)^2 + (b^*)^2} \quad (1)$$

$$\text{Hue angle} = \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (2)$$

Chemical characteristic

The chemical characteristics including ash, pH and titratable acidity content were analysed for both Cavendish peels. The ash content was determined through an oven-dried by following previous method [8]. Titratable acidity and pH content of the peels were determined and measured using a pH meter (Mettler-Toledo (HK) MTCN Limited, Hong Kong).

Moisture content

The unripe and ripe Cavendish peel were weighed for 0.5 g and allowed to dry in an oven at 105 °C for 3 h (Memmert, Model 100 - 800, Germany) by following the previous method [8]. The samples were removed from the oven, cooled in a desiccator and weighted until a constant value was obtained. The final mass and the total loss were calculated. Next, the moisture content (%) and moisture ratio were calculated using the following Eqs. (3) - (4);

$$\text{Moisture content (\%)} = \frac{\text{loss weighted (g)}}{\text{sample used (g)}} \times 100 \quad (3)$$

$$\text{Moisture ratio} = \frac{\text{initial moisture content (\%)}}{\text{moisture content at any time (\%)}} \times 100 \quad (4)$$

Solvent extraction

The sample was prepared by following previous study and dried using an oven prior extraction process (Memmert, Model 100 - 800, German) [9]. Solvents with different polarities were selected in this study to evaluate their effect towards total extracted polyphenol content such as aqueous, methanol, ethanol, acetone and mixture of these organic solvent with aqueous at 80 % concentration. The solvent extraction was performed by mixing 1.0 g of the sample with the 10.0 mL of solvent. Next, the mixed solution had left for 24 h at room temperature in a shaker incubator for extraction based on previous method [10]. The crude extract was filtered, subjected to oven-dried until a constant mass was reached and stored at -4 °C for subsequent experimental analysis. The experimental data were compared between different ripening stages (unripe and ripe Cavendish peels) with various polarities of solvent used to evaluate the total extracted phenolic, flavonoid, tannin and antioxidant activities. Selection of the best solvent based on the maximum value of extracted antioxidant compounds and activities among the peel. The results were presented as the mean value of triplicates \pm standard deviation (SD).

Yield recovery

The yield of the crude extract for each solvent was determined based on the mass difference of the dried extract. The volume of crude extract was oven-dried at 40 °C (Memmert, Model 100 - 800, Germany) until it reached a constant mass. The yield of extractable crude extract was calculated according to Eq. (5);

$$\text{Yield (\%)} = \frac{\text{mass of dried extract (g)}}{\text{sample used (g)}} \times 100 \quad (5)$$

Analysis of antioxidant content and activities

The total phenolic, tannin, flavonoid content and antioxidant activities (DPPH and ABTS) were determined using the method described by previous study [9].

Drying characteristic of banana peel

The unripe Cavendish peel was selected for the drying characteristic experiment and being collected, washed, manually peeled and cut the peel into slices. The sliced peel was placed in the crucible and put on dryer tray at selected different drying temperatures (40, 50, 60 and 70 °C) with 65 % relative humidity. The reduction in moisture content during the drying process was recorded at every 15 min [11]. The drying process was stopped until the moisture content of sample reached about 10 to 15 % (wet base) as the reduction in moisture content was no longer observed by the calculation. The limit of drying temperature for current study was selected to be maximum at 70 °C, since 90 % of the antioxidant activity is reduced at 75 °C [12]. The experiment results were presented as the mean value of triplicates ± standard deviation (SD).

Extract preparation for HPLC analysis

The sample of aqueous extract was prepared by carrying out the acid hydrolysis treatment with modification [13], prior to the HPLC analysis to remove any remaining residues in the extract. The extract was mixed with 12.0 mL of deionized water, 8.0 mL of methanol, followed by 5.0 mL of 6 M HCl and placed in a circulating water bath with 960 W, 50 Hz 830-S1 (Protech, Tech-Lab Manufacturing Sdn. Bhd, Selangor, Malaysia) at 90 °C for 2 h. Next, the final volume was adjusted to 50 mL with the absolute methanol, filtered using a 0.45 µm nylon membrane and transferred to HPLC autosampler vials. The standard solutions were prepared by dissolving 1.0 mg of the sample in methanol and aqueous solution. The prepared mobile phase solution, standard and sample solution were filtered through a 0.45 µm nylon membrane and degassed with ultrasound before use.

Identification of bioactive compound by high performance liquid chromatography (HPLC)

The HPLC analysis was performed on an LC system (Open Lab CDS ChemStation Rev.) comprising with 2 Agilent 1290 Infinity Pumps (G4220A), an autosampler (G4226A) with cooler (G1330A) and Agilent 1290 infinity diode array detector (DAD, G4212A) (Agilent®, CA, USA) with modification [14]. The column used for the chromatographic separation was a Zorbax Eclipse Plus C₁₈ (1.8 µm, 150×2.1 mm²) (Agilent Technologies, Palo Alto, CA, USA). Acetonitrile and acidified water (0.5 % formic acid, v/v) were used as mobile phases for A and B, respectively and the gradient was set as follows: 0 min, 95 % B; 10.0 min, 65 % B; 15.0 min, 35 % B; 18.0 min, 95 %; initial conditions. The detection with diode array detector (DAD) was performed at a wavelength of 280 nm with 25 °C of column temperature. The flow rate was set to 0.50 mL/min throughout the gradient with 10.0 µL of injection volume in the HPLC system. Data acquisition and analysis were done using an Open Lab CDS ChemStation Rev. C01.03 with 1290 infinity 2D-LC solution add-on software with LCxLC Software for 2D-LC data analysis (GC Image LLC., Lincoln, NE, USA).

The chromatography peaks were confirmed by comparing its retention time with the corresponding standards that plotted using 5-point calibration curves and DAD spectra (280 nm). Tannic acid, gallic acid, catechin, caffeic acid, epigallocatechin gallate, syringic acid, rutin, rosmarinic acid, myricetin, cinnamic acid and kaempferol were used for the calibration curves. The calibration curves were prepared for each analysis and R² > 0.99 were obtained. All chromatography operations were carried out in triplicate.

Statistical analysis

Statistical analysis was performed with Minitab version 16 (Minitab Pty Ltd, Sydney). Each treatment was replicated 3 times and the results were reported as mean \pm standard deviation. The 1-way analysis of variance (ANOVA) model was performed by Turkey's test at $p < 0.05$ (confident level of 95 %) to determine the significant differences among the means of various sample treatments between the diverse groups.

Results and discussion

Physicochemical characteristic analyses of the unripe and ripe peel

The physicochemical properties of Cavendish banana were carried out to evaluate the differences between 2 ripening stages in term of their physical, mechanical, chromatic and chemical as showed in **Table 1**. The physical characteristics including pulp (%), peel (%), pulp/peel ratio and thickness had significant changes due to ripening process of banana fruit. The thickness of ripe Cavendish peel were lower than the unripe peel, but the pulp/peel ratio of unripe peel was significantly higher due to the ripening process. The mass of the ripe pulp increased significantly ($p < 0.05$) with a gradual decrease of the peel upon ripening. The mechanical characteristic with regard to hardness from the unripe peel was more rigid than ripe peel as the value of peak force (N) versus time (sec) graph that generated through the probe penetration against peel by texture analyser was significantly higher ($p < 0.05$) than the ripe peel. There were significantly changes in L*, a*, b*, chroma and hue angle values between unripe and ripe peel for chromatic characterisation as it indicated the green colour is darker than yellow (**Table 1**). Meanwhile, the chemical composition analyses of both peels indicated that the moisture content was reduced significantly ($p < 0.05$), but the ash content was significantly increased ($p < 0.05$) due to ripening progression. The unripe peel was slightly acidic as total titratable acidity significantly higher ($p < 0.05$) than the ripe peel, but had no significant ($p > 0.05$) effects on the pH value for either peel.

Table 1 Physicochemical characteristics of unripe and ripe peel of *Musa acuminata* (Cavendish).

	Characteristics	Unripe peel	Ripe peel
Physical	Total mass of single fruit (g)	144.9 \pm 9.6 ^a	144.8 \pm 11.6 ^a
	Thickness (mm)	2.4 \pm 0.1 ^a	1.50 \pm 0.7 ^b
	Pulp (%)	47.9 \pm 7.7 ^a	65.2 \pm 8.4 ^b
	Peel (%)	52.1 \pm 9.2 ^a	34.8 \pm 5.8 ^b
	Pulp/peel ratio	1.0:1.1 ^a	1.8:1.0 ^b
Mechanical	Hardness of the peel (N)	13.0 \pm 2.7 ^a	2.4 \pm 5.3 ^b
Chromatic	L*	55.2 \pm 6.0 ^a	68.8 \pm 6.3 ^b
	a*	-6.6 \pm 1.6 ^a	5.3 \pm 0.34 ^b
	b*	21.7 \pm 5.0 ^a	33.7 \pm 2.7 ^b
	Chroma	22.7 \pm 5.2 ^a	34.1 \pm 2.6 ^b
	Hue angle	-73.0 \pm 1.5 ^a	81.1 \pm 1.3 ^b
Chemical	Moisture content (%)	91.0 \pm 0.1 ^a	88.6 \pm 0.1 ^b
	Ash (%)	1.1 \pm 0.1 ^a	1.7 \pm 0.1 ^b
	Total titratable acidity (mg/100ml)	18.0 \pm 0.1 ^a	26.0 \pm 0.1 ^b
	pH	5.5 \pm 0.1 ^a	5.8 \pm 0.1 ^a

Note: The data calculated in average, \pm standard deviation (n = 3) and the means value that do not share the same letter are significantly different ($p < 0.05$) between columns.

The physical characteristics of the peels differed and allowed the changes occur due to the osmotic transfer of moisture from the peel to pulp as a result, the sugar content increases during the ripening process [15]. This situation was contributed to the softening texture of the peel. The decrease in hardness properties of banana peel is due to the ripening process, as the structure of cell wall is altered for the degradation by the polygalacturonase enzymes, solubilization of pectin and starch [16]. The primary cell wall of the peel consists of a network from several polysaccharides, proteins, phenolic substances and the fruits are softened during ripening due to the changes in cell wall composition and structure. The banana peel contains

chlorophyll and carotenoid as the degradation of chlorophyll (green color) and increasing carotenoids (yellow color) during the ripening process had similar trends with the current study due to significantly different values each chromatic analysis. The ash content is generally an inorganic material which directly and indirectly associated to the absorption capacity of mineral salts at different stages as the white colour of ash formed represented inorganic constituents of the sample materials [17]. The ash contains organic sources such as sulphur and phosphorus from protein and the loss of volatile material in the form of sodium, chloride, potassium, phosphorus and sulphur occurs during ignition [18]. The moisture and ash were reduced during the ripening process due to the breakdown of carbohydrate and osmotic transfer from peel to the pulp. Also, the degradation of acidic compounds in the peel takes place during the ripening process. The physicochemical characteristics of unripe and ripe peel showed significant differences since different ripening stage expressed various elements and could affect the extractable component. The relationship between ripening and phytochemical content of the peel is essential for the selection and predetermined of further recovery materials by extraction process.

Effect of solvent extraction on antioxidant compounds

The results from **Figure 1** showed that the highest yield recovery was obtained from 80 % acetone extract of unripe peel compared to other solvents. The 80 % ethanolic extract for both Cavendish peels showed no significant difference for the yield recovery (**Figure 1**). The aqueous extract of unripe Cavendish peel contained the highest total phenolic than the ripe peel followed by 80 % of methanol and acetone (**Figure 1(b)**). While, insignificant difference of phenolic content from ripe peel was detected when using absolute or 80 % methanol and 80 % acetone for extraction. The aqueous extract also significantly higher in total flavonoid and tannin content ($p < 0.05$) for both unripe and ripe peel compared to other organic solvent used (**Figures 1(c) - 1(d)**). Extraction using methanol, ethanol, acetone, 80 % methanol and 80 % ethanol had no significant difference in flavonoid content of the ripe peel (**Figure 1(c)**). Total tannin content from aqueous extract of unripe Cavendish peel was significantly higher ($p < 0.05$) than the ripe peel and other solvents (**Figure 1(d)**). This is due to water-soluble phenolic compound of tannin that will degrade during ripening process since the unripe peel showed the highest value as this compound is related with astringency sensation [19].

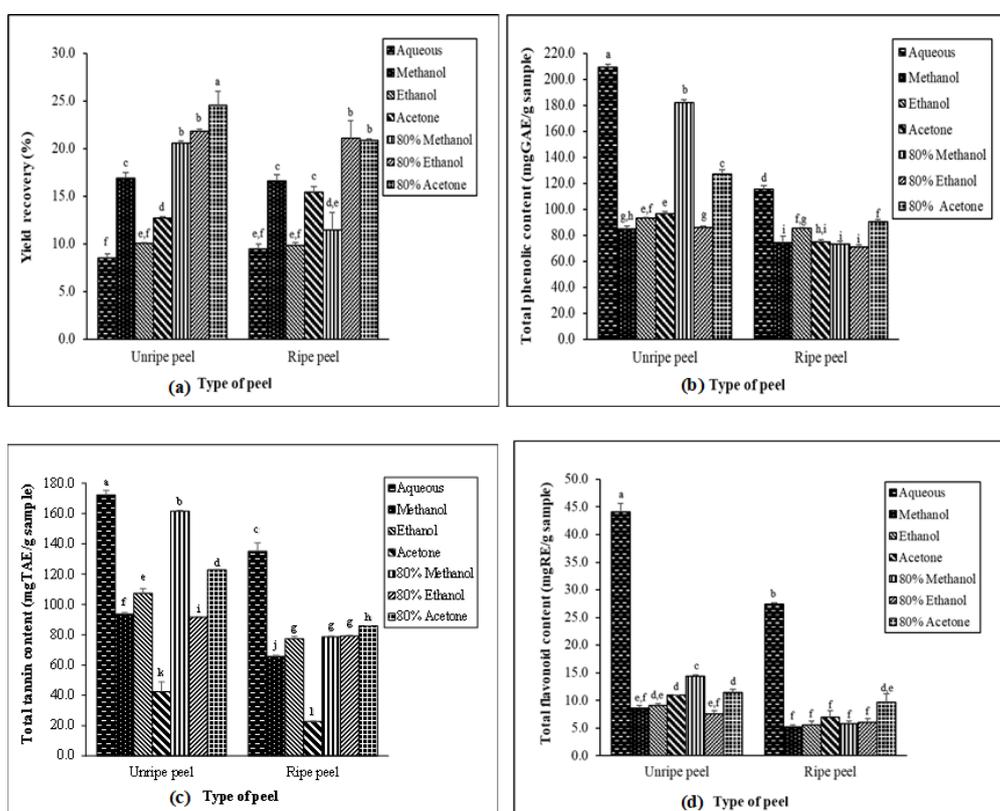


Figure 1 Effect of different solvent extraction on (a) yield recovery, (b) total phenolic, (c) tannin, and (d) between unripe and ripe Cavendish peel.

From all the antioxidant compound in present study such as phenolic, tannin and flavonoid, the aqueous extract showed the highest extracted content due to its solubility towards the antioxidant molecule [20]. Besides, most of the antioxidant compounds have a high solubility in aqueous, thus make it easily extracted out from the plant material. The result of this study proved that the unripe Cavendish peel contained a highest amount of antioxidant component such as phenolic, tannin and flavonoid content than the ripe peel, similar with previous study which found higher tannin content in the unripe peel [21]. However, instead of getting a low yield recovery from aqueous extract, this extract contained the highest antioxidant compounds and activities than other solvents. Thus, it was most effective solvent used for extraction and very good at insulating the charges of compounds from the peel due to the similarities between polarity of water and these antioxidants compounds. The difference type and polarity of solvent become an essential aspect in measuring antioxidant capacity as it can affect a single electron and hydrogen atom transfer [22].

Effect of solvent extraction on antioxidant activities

The antioxidant activity of unripe Cavendish peel exhibited higher ABTS and DPPH scavenging activity (%) than the ripe peel except for acetone extract. Aqueous extract from unripe peel exhibited higher ABTS scavenging activity (%) than the ripe peel but differed from the evaluation of DPPH assay. There was no significant difference ($p > 0.05$) in their antioxidant activity of unripe and ripe peel between the solvents for DPPH assay. This situation was contradicted with the previous study as the aqueous extract of unripe Cavendish peel is significantly higher than ripe peel as evaluated by DPPH assay [20]. It might seem due to other polyphenol compounds present in the ripe Cavendish peel extract that contributed a high percentage of scavenging activity. The ABTS scavenging activity of unripe peel for absolute methanol and ethanol extracted also showed no significant difference ($p > 0.05$) with the aqueous extract.

The antioxidant activity of polyphenol compound from unripe Cavendish peel as assessed by the ABTS assay was higher than the DPPH assay except for 80 % methanol and acetone. This phenomenon could be due to the steric accessibility of DPPH radicals as an active site in the middle of the structure, so that antioxidants hardly access DPPH radical sites [23]. Banana peel extract showed a remarkable effect in protecting cells from oxidative damage as additional phenolic compounds are presented in the peel compared to pulp residues [21]. These results were similar with previous study as the ripe and overripe of banana peel contained less antioxidant power with phenolic and flavonoid compound than unripe peel [24]. As solid-liquid extraction is separation process that involves the transfer of solutes from a solid to a liquid phase, the selection of solvent depends on several factors such as physicochemical properties, cost and toxicity as solvent like ethanol, aqueous and their mixtures are designated as “generally recognized as safe” (GRAS).

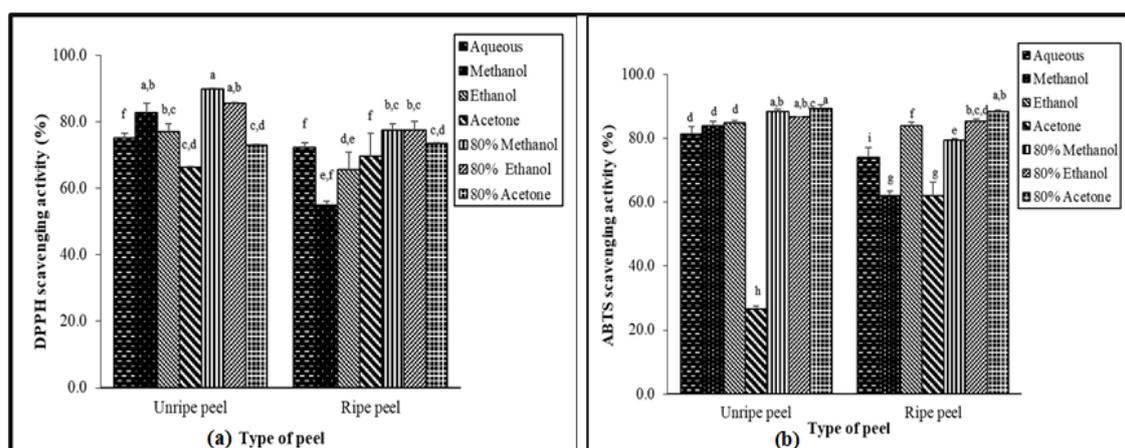


Figure 2 Effect of different solvent extraction on (a) DPPH and (b) ABTS scavenging activity between unripe and ripe Cavendish peel.

Banana peel extract is superior to free radical scavenging because polyphenols rich and high antioxidant activity indicated that antioxidants of different polarity were present in the extracts as assessed by other assays. Since aqueous extracted from unripe peel not showed the highest antioxidant activities compared to other organic solvents, the value was quite high, no huge differences and considered as green technology approach with reduction in solvent consumption in food industry application. This extract

potentially can be used for its rich-antioxidant production in the development of various functional foods and nutritional consumption. This study proved that the unripe Cavendish peel contained more antioxidants than the ripe peel such as phenolic, tannin, flavonoid and antioxidant activities. Thus, the extract has the potential to be used in the development of various functional foods. Banana peel extract is superior to free radical scavenging because it is rich in polyphenols and high antioxidant activity indicated that antioxidants of different polarity were present in the extracts as assessed by other assays [25]. However, instead of getting a low yield recovery from aqueous extract, this extract contained the highest antioxidant compounds and activities than other solvents. Hence, it was selected for the following recovery process for its antioxidant properties. The most effective solvent extraction for antioxidant properties from unripe banana peel was aqueous because it contained the highest polyphenol content. The aqueous extract was very good at insulating the charges of compounds from the peel due to the similarities between the polarity of water and these antioxidants compounds.

Thin-layer drying characteristic and effect on extracted tannin content

As the unripe Cavendish peel contained a higher antioxidant capacity than the ripe, it was selected for further drying characteristic analysis. The moisture ratio of unripe Cavendish peel with respect to drying time at different temperatures is shown in **Figure 3(a)**. The initial moisture content for all drying treatment of unripe Cavendish peel was analysed to be $90.9\% \pm 0.1$ and equivalent with 1.0 of moisture ratio (**Figure 3(a)**). The moisture ratio was decreased as the drying time increased and the moisture content dropped rapidly at the initial stage and then gradually decreased until it reached 10 to 15 % (wet base) (**Figure 3(a)**). During the first 45.0 min drying time, the higher moisture ratio was reduced to 79.0 %, consequently at 70 °C than the 60, 50 and 40 °C of the drying temperature (**Figure 3(a)**). A high drying temperature increases the drying rate and thus leads to a significant moisture loss due to driving force that initiative evaporation of water from peel as well as increases in surrounding temperature. The drying rate decreased continuously throughout the drying time and the ratio of moisture decreased exponentially with increasing drying time (**Figure 3(a)**). The drying condition with 70 °C started to achieve a 10 to 15 % moisture content at 105.0 min, which was faster than other treatments. It took the longest drying time for 40 °C drying condition to dry the peel until it achieved a constant moisture content in 10 to 15 %. There was no significant difference of moisture ratio at first 250.0 min of drying time for all drying temperatures. From the **Figure 3(a)**, it can be observed that the time elapse for drying banana peel decreases with increasing temperature, while the moisture ratio decreases incessantly with the drying time.

This phenomenon occurred because more heat evaporation of moisture from the banana peel occurred during a high temperature, since it accelerated the evaporation of the moisture near the surface better than the low temperature. It also associated with greater heat energy used to vaporises water molecule from the surface of the sample and lead to faster drying process [26]. Thus, the drying time could be reduced together with a high drying rate. If a low drying temperature used, the time required to remove the moisture content from the banana peel will be longer and could be a slow diffusion process.

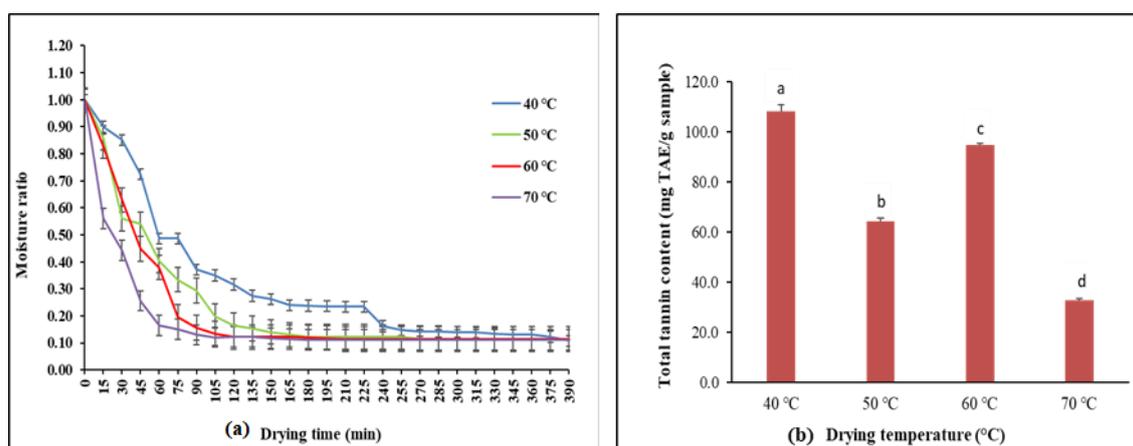


Figure 3 The unripe Cavendish banana peel at different drying temperature (a) moisture ratio versus drying time and (b) effect towards total tannin content.

Different drying temperature results in different extracted total tannin content from unripe Cavendish peel as shown in **Figure 3(b)**. When the peel was exposed to a high drying temperature up to 70 °C, the total extracted tannin content was reduced to be the lowest value (**Figure 3(b)**). The recovery of tannin content from the unripe Cavendish peel at 40 °C was the highest compared to the 50, 60 and 70 °C of drying conditions. The loss of antioxidant compounds like tannin probably due to the binding its compounds to other components such as protein or chemical structure and being altered [27]. The breakdown of hydrogen bond from tannin compound results in the lowest recovery value at maximum drying treatment and even higher than 70 °C. About 90 % of antioxidant activity will be reduced when the drying temperature at 75 °C and it also affects the tannin content as it contributed to the antioxidant activity [12]. This situation generally caused the natural depletion of antioxidants due to the instability from the heat drying temperature [28]. The denaturation of membrane porosity and cell protein improved the permeability of the cell wall and diffusivity of solvent, thus led to an increase in the extraction rate of the compound. Since high drying temperature reduced the drying time, this leads to poor product quality because of heat damage on surface and high energy consumption [29]. The drying temperature of 40 °C was the most appropriate drying treatment for high recovery total tannin content from unripe Cavendish peel.

Quantification of bioactive compound by the HPLC

The chromatographic profile of extracted unripe Cavendish peel using HPLC-DAD showed 11 peaks accordingly the amounts as follows: Tannic acid > rutin > catechin > myricetin > gallic acid > rosmarinic acid > cinnamic acid > syringic acid > epicatechin gallate > caffeic acid > kaempferol (**Figure 4**). The quantifications of each compound were shown in **Table 2**. Other peaks present could not be identified and detected by standards chromatography. Tannin compound such as tannic acid was the highest in quantity detected in unripe Cavendish peel extract as a lead compound. It could be seen that the amount of this compound was quite remarkable in the HPLC profile. This situation due to the tannin compound is supposed to be protected inside banana peel from being attacked by predators [30]. Studies showed that tannin is effective as therapeutic target for prevention of various diseases, antimicrobial and natural antioxidant by increase oxidative stability and active packaging materials as a nanocellulose-tannin based film potential in food industry [31-33]. These results were in line with green process definition terms as it could reduce energy consumption and the solvent amount by allowing the use of water as a solvent, renewable the natural resources and ensured a safe and high-quality extract to be applied in food industry.

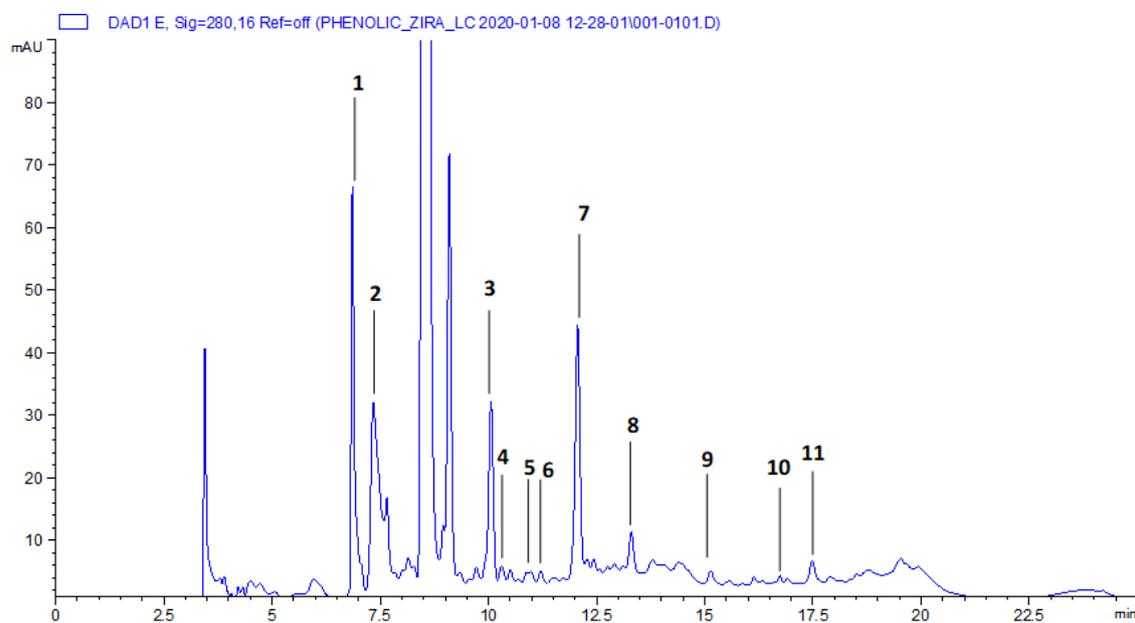


Figure 4 Identification of compounds for extracted unripe Cavendish peel based on the peak of high performance liquid chromatography, where peak 1= tannic acid, 2 = gallic acid, 3 = catechin, 4 = caffeic acid, 5 = epigallocatechin gallate, 6 = syringic acid, 7 = rutin, 8 = rosmarinic acid, 9 = myricetin, 10 = cinnamic acid and 11 = kaempferol.

Table 2 Bioactive compounds detected from unripe Cavendish peel of aqueous extract. Results are expressed as mean \pm standard deviation (n = 3).

No	Compounds	Standard's retention time (min)	Extract' retention time (min)	Content ($\mu\text{g/g}$ sample)	Equation of linear regression
1	Tannic acid	7.089	6.882	1551.210 \pm 4.9	y = 2.433x + 106.720 R ² = 0.9995
2	Gallic acid	7.330	7.335	17.298 \pm 1.9	y = 49.036x + 337.570 R ² = 0.9147
3	Catechin	9.807	10.057	191.719 \pm 4.0	y = 10.881x + 72.410, R ² = 0.9998
4	Caffeic acid	10.561	10.301	2.786 \pm 0.8	y = 114.19x - 2.0189, R ² = 0.9999
5	Epigallocatechin gallate	10.706	10.984	4.784 \pm 0.6	y = 12.072x + 17.991, R ² = 0.9998
6	Syringic acid	11.039	11.203	5.032 \pm 1.8	y = 69.411x - 18.623, R ² = 0.9997
7	Rutin	12.159	12.059	227.507 \pm 2.6	y = 12.395x + 122.190, R ² = 0.9997
8	Rosmarinic acid	13.573	13.298	7.249 \pm 1.1	y = 50.021x + 27.259, R ² = 0.9945
9	Myricetin	15.044	15.133	21.321 \pm 2.5	y = 19.997x - 9.235, R ² = 0.9891
10	Cinnamic acid	17.055	16.736	5.404 \pm 1.5	y = 15.031x + 1.921, R ² = 0.9999
11	Kaempferol	17.214	17.484	0.348 \pm 0.3	y = 63.601x + 3.018, R ² = 0.992

Conclusions

The current work explained the comparison of physicochemical properties for unripe and ripe peels as well as the impacts of different solvent such as aqueous, methanol, ethanol and acetone which have different polarities in order to select the best solvent for high antioxidant composition. Extraction process using aqueous as a solvent showed the highest value in the extracted phenolic, tannin and flavonoid content from unripe peel compared to other organic solvents used. As the drying operation influenced by the different drying temperature, 40 °C was the best drying condition to recover a high tannin content compared to 50, 60 and 70 °C. In addition, HPLC analysis revealed that 11 bioactive compounds were detected in chromatograph and tannic acid become the lead compound as it quite remarkable high in quantity. As the unripe Cavendish peel is economical and environmentally friendly due to its unique chemical composition and their availability in abundance, renewable nature and low cost, thus potentially contributes to enhance nutritional consumption among people by implementing aqueous extracted that rich in antioxidants with an environmentally friendly process. Creating products that turn waste materials into valuable ingredients seems requisite and needs to be prioritized. It would be feasible to fulfil the consume requirement for natural and preserved healthy food and lead the industry to a lower-waste agribusiness, increase the profitability of the industry and more value can be added to the banana industry and plantation.

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