



Antioxidant Nano Phlorotannin Powder from Brown Algae *Sargassum serratum*: Spray Drying, Antioxidant Activities, Physic-Chemical Characterization

Dang Xuan Cuong^{1*}

¹*Nha Trang Institute of Technology Application and Research, Vietnam Academy of Science and Technology, Nha Trang 650000, Khanh Hoa, Vietnam.*

Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

Article Information

DOI:10.9734/JPRI/2020/v32i930484

Editor(s):

(1) Dr. Mohamed Fathy, Assiut University, Egypt.

Reviewers:

(1) Mutwale Kapepula Paulin, University of Kinshasa, Democratic Republic of the Congo.

(2) Henry Mwangi, Kenyatta University, Kenya.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/57412>

Original Research Article

Received 28 March 2020

Accepted 04 June 2020

Published 18 June 2020

ABSTRACT

Introduction: Phlorotannins are bioactive-value polymers existing in brown algae and useful for pharmaceuticals and functional food. Therefore, the study focused on the spray drying conditions survey, the evaluation of antioxidant activities, and physico-chemical characterization of antioxidant nano phlorotannin powder prepared from brown algae *Sargassum serratum*.

Methods: To survey the effect of spray drying conditions (carriers, carrier-to-solution ratio, compressed air pressure, liquid feed speed, inlet air temperature) on antioxidant activities (total antioxidant, reducing power, DPPH free radical scavenging), and physico-chemical (solubility degree, moisture, particle morphology, and bulk density) of antioxidant phlorotannin powder from brown algae *Sargassum serratum* commonly growing in the Vietnam sea area.

Results: The optimum spray drying condition consisted of the carrier-to-solution ratio of 10%, compressed air pressure of 0.8 bar, the liquid feed speed of 10 ml min⁻¹, and the inlet temperature of 110°C. At the optimization condition, the antioxidant activity of phlorotannin powder possessed total antioxidant (4.347 ± 0.018 g ascorbic acid equivalent 100⁻¹ g DP), reducing power activity (9.390 ± 0.024 g FeSO₄ equivalent 100⁻¹ g DP), DPPH free radical scavenging activity ((70.02 ±

0.26%), physico-chemical of antioxidant phlorotannin powder consisting of moisture content ($5 \pm 0.5\%$), phlorotannin content (2.268 ± 0.010 g phloroglucinol equivalent 100^{-1} g DP), solubility degree (100%), and bulk density (<1 g/ml). Phlorotannin content and antioxidant activities were affected by the spray drying condition ($p < 0.05$) and a strong correlation to each other ($R^2 > 0.9$). Antioxidant phlorotannin particles possessed nanometer size and the morphology of irregular and microspheres.

Conclusion: Antioxidant nano phlorotannin powder could be useful as functional food and pharmaceuticals.

Keywords: Antioxidants; phlorotannin; powder; seaweed; spray drying.

1. INTRODUCTION

Phlorotannins are common secondary metabolites compounds that exist in the outer cortical layer of brown algae thalli from 0.4% to 3.0% of the dried algal [1] and non-toxic antioxidant biological polymers [2]. Phlorotannins structures are diverse, because they have four linkage styles from basic units (phloroglucinol), for example, phenyl, ether, and dibenzodioxin [3,4]. Phlorotannin is the largest group of natural pigments in brown algae, evaluated as sources of a functional food [5-7] because of their bioactive diversity. For example, antioxidant capacity [6,8,9], anti-inflammatory [6,10], anti-allergic [11], anti-proliferative and anti-diabetic [12], anti-HIV-1 [13], antitumoral [14], antithrombotic and profibrinolytic [15]. Phlorotannin improves against free radical within the human body, the replacement of synthetic antioxidants that cause the diseases in the human [16]. The experiment showed almost phlorotannin dissolve in ethanol and methanol in comparison to another solvent such as aqueous, non-polar solvent, or non-strong polar solvent. The thing caused the limit of application for phlorotannin into functional food, and pharmacy.

Nowadays, there are many methods for solvent movement, such as concentration, spray drying, lyophilized, but spray drying still is the most efficient method for the economy and application, such as longer shelf-life, lower moisture content, and lower shipping cost. Brown algae *Sargassum serratum* was detected for the first time in Vietnam [17,18] and evaluated to possess high phlorotannin content and good bioactivity, although they grow commonly in the Vietnam sea. The technique control of phlorotannin powder preparation from brown algae will support the efficient use and application of phlorotannins and high-value products increasing from production processing of fucoidan and alginate.

Therefore, the impact of different spray drying conditions on phlorotannin content, antioxidant activity (total antioxidant activity, reducing power, and DPPH free radical scavenging), and a correlation between factors were found. Physico-chemical such as solubility degree, moisture, particle morphology (surface and size), and bulk density was also analysed for best antioxidant activity powder.

2. MATERIALS AND METHODS

2.1 Solution Preparation for Spray Drying

The solution preparation for spray drying contained 550 mL of the sample solution and 257.5 mL of aids solution. Where in:

A sample solution: Brown algae *Sargassum serratum* N.H.Dai (2002) found commonly grown in Nha Trang Bay, Vietnam was washed clearly using seawater and dried at the velocity of 2 m s^{-1} and non-sunlight until the moisture of 19%. Dried algae then ground into a powder and soaked at the temperature (43°C), time (33 hours), and algae-to-solvent ratio ($27:1$, v w⁻¹). The extract was in turn collected by using filtration through the membrane Whatman No 4. and concentrated until phlorotannin content (3 ± 0.05 g phloroglucinol equivalent), total antioxidant activity (6.70 ± 0.02 g ascorbic acid equivalent), reducing power activity (20.80 ± 0.20 g FeSO₄ equivalent), and free radical scavenging activity ($87.25 \pm 1\%$ per 500 mL. The concentrated then stored in black bottles at 4°C temperature.

The aids solution (AS): The different spray drying aids (SDA) in other ratio was dissolved into 250 mL of water with 2.75 mL of tween 80 and vortexed for 15 minutes at 1.500 rpm for collecting the solutions of the aid.

The homogenization of the sample solution (550 mL) and the aids solution (257.5 mL) at 2.500 rpm for collecting the drying solution.

2.2 Experiment Design

Effect of inlet factors of drying processing such as types of spray drying aids (maltodextrin, glucose, and saccharose), drying aids-to-solution ratio (2%, 4%, 6%, 8%, 10%, 14%), pump pressure (0.4 bar, 0.6 bar, 0.8 bar, 1.0 bar), pump speed (10 rpm, 20 rpm, 30 rpm, 40 rpm, 50 rpm), and inlet temperature (110°C, 120°C, 130°C, 140°C, 150°C, 160°C) on phlorotannin content and antioxidant activities (total antioxidant activity, reducing power activity, and DPPH free radical scavenging activity) was designed according to the method of many factors fix and one-factor run [19]. The physico-chemical characterization such as moisture content, phlorotannin content, solubility degree, and bulk density were evaluated in the powder having the highest antioxidant phlorotannin content.

2.3 Determination of Phlorotannin Content

Phlorotannin content (TPC) was quantified according to the Folin-Ciocalteu's method and using a standard phloroglucinol [20]. One mL of 10% Folin-Ciocalteu was added to 300 µL extract and kept the mixture for 5 minutes and adding 2 mL of 10% Na₂CO₃ for the vortex. The compound was then incubated for 90 minutes in the dark and measured the absorbance at 750 nm by the UV-Vis Spectrophotometer Jen Way 6400/ 6405.

2.4 Determination of Antioxidant Activity

2.4.1 Total antioxidant activity

Total antioxidant activity (TA) was determined by the reduction of Phosphate-Mo (VI) to Phosphate Mo (V) [21] with the ascorbic acid standard. 100 µL extract diluted by 900 µL of distilled water, then shaken with 3 mL of solution A (0.6M sulfuric acid, 28 mM sodium phosphate, and 4 mM ammonium molybdate), and kept for 90 minutes at 95°C. The absorbance measurement of the compound was at a wavelength of 695 nm.

2.4.2 Reducing power

Reducing power was determined based on the reduction of iron (III) to iron (II) with FeSO₄ standard [18]. 0.5 mL phosphate buffer (pH 7.2) and 0.2 mL of 1% K₃[Fe(CN)₆] was added to 500 µL extract, in turn, and kept at 50°C for 20 minutes. 500 µL of 10% CCl₃COOH, 300 µL of distilled water, and 80 µL of 0.1% FeCl₃ were then added to the mixture, in turn and shaken.

The absorbance measurement was determined at a wavelength of 655 nm.

2.4.3 Free radical scavenging DPPH

Free radical scavenging DPPH was determined based on electron-transfer that produces a violet solution in ethanol [20]. 200 µL, 400 µL, 600 µL, 800 µL, and 1000 µL of extract were poured into each of test-tube, in turn, and added the 3 mL of DPPH (25 mg L⁻¹) into each test-tube, called the test sample. The blank sample was similar to the test sample but replaced 3 ml of DPPH by 3 ml of 96% ethanol. The control sample was similarly the blank sample but replaced the extract with DPPH, respectively. All test-tubes were kept in the dark under room temperature for 30 minutes before the absorbance measurement at a wavelength of 550 nm. The percent of free radical scavenging DPPH was calculated the following equation:

$$A\% = \left[1 - \left(\frac{A_{sample} - A_{blank}}{A_{control}} \right) \right] \times 100\%$$

In here: A sample: the absorbance of the test sample at 550 nm

A control: the absorbance of the control sample at 550 nm

A blank: the absorbance of the blank sample at 550 nm

UV-Vis Spectrophotometer Jen Way 6400/ 6405 machine was used to measure.

2.5 Determination of Physico-Chemistry Characterization

2.5.1 The particle morphology

The particle morphology of powder was observed by using scanning electron microscopy (SEM) (FEI, QUANTA 250 FEG).

2.5.2 The bulk density

The powders were poured into a 10 mL graduated cylinder without any pressure and weighed the powders weigh. The bulk density (pb) of powder was determined based on the sample weight-to-volume ratio [22].

2.5.3 Solubility degree

5 g of antioxidant phlorotannin powder was suspended in 50 mL of distilled water at ambient

temperature, stirred for 1 min, and kept for 30 min at 37°C. The mixture was then centrifuged at 1500 rpm at 4°C for 10 min and separated the supernatant that dried at 105°C until constant weight, named A (g). Solubility degree calculation was based on the ratio of A and 5 g.

2.5.4 Fourier-transform infrared spectroscopy and differential scanning calorimetry of powder

2.5.4.1 Fourier-transform infrared spectroscopy

FTIR spectrum analysis was on the machine Tensor 37 (Brucker, Germany) with the spectrum range of 7,500 to 370 cm^{-1} and beamsplitter of standard KBr. The extended spectral range with a near and middle infrared detector was from 15,000 to 370 cm^{-1} .

2.5.4.2 Differential scanning calorimetry

DSC spectrum of antioxidant phlorotannin powder were measured and calculated on the machine (DTA/ DSC/TGA) Labsys Evo S60/58988.

2.6 Data Analysis

Remove outlier values by using Dulcan method. Statistic, ANOVA and regression analysis using MS. Excel software. Figures were exhibited by Origin 8.0 software. Experiments were repeated intriplicate (n=3).

3. RESULTS AND DISCUSSION

3.1 Effect of Spray Drying Conditions

3.1.1 Effect of drying aids

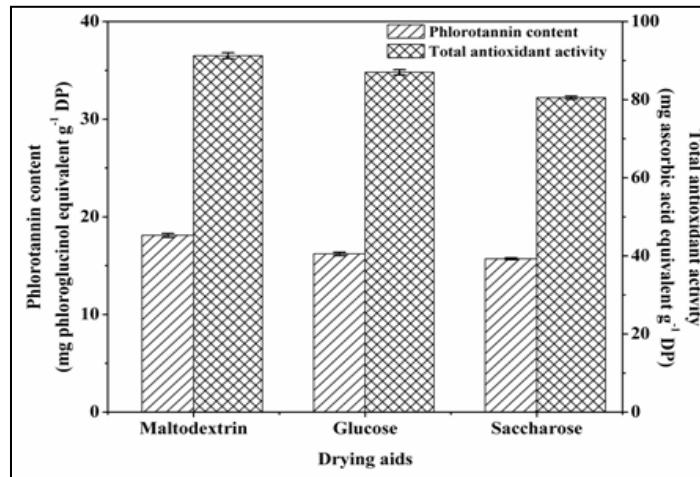
Phlorotannin content and antioxidant activity of brown algae powder got the highest value as used maltodextrin, 1.81 ± 0.13 g phloroglucinol equivalent 100^{-1} g powder and $(3.65 \pm 0.1$ g ascorbic acid equivalent 100^{-1} g powder (Fig. 1a), 7.92 ± 0.18 g FeSO_4 equivalent 100^{-1} g powder and $(67 \pm 1.05\%)$ (Fig. 1b), respectively, and was decreased in the order: maltodextrin/ saccharose/ glucose ($p < 0.005$). Phlorotannin content and antioxidant activity of brown algae powder were strongly impacted by drying aids ($p < 0.005$).

One of the reasons causing statistical significance in the drying aids efficiency was the

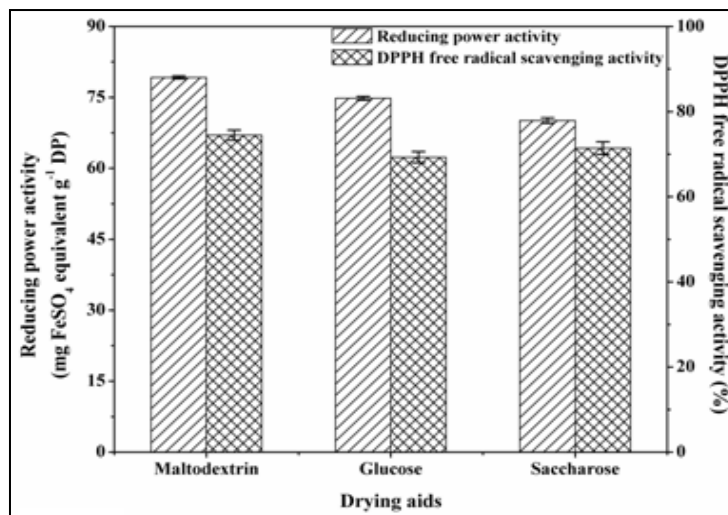
difference in drying aids structure. Maltodextrin has three to 17 of D-glucose units with the primary linkage of $\alpha(1\rightarrow4)$ glycosidic and a branch structure. Saccharose only consisted of glucose and fructose in their molecules. The molecular weight and the hydrogen groups of glucose are the least. The hydrophobic tail and the hydrophilic head of tween 80 linked to phlorotannin and maltodextrin, respectively, through hydrogen linkage for microparticles formation that depended on many hydroxyl groups and molecular weight of drying aids. Maltodextrin has the most groups of hydrogen and the highest molecular weight. Therefore, the ability of spatial network formation of maltodextrin is better than one of the other drying aids (saccharose, glucose) for wrap and linkage of phlorotannin through tween 80 (polysorbate 80). Maltodextrin was also used in spray drying for the polyphenol-rich extract of apple [23], the bioactive substances-rich extract of cactus, and was the most effective for the protection of pigments and the restriction of antioxidant activities decline of terrestrial plant antioxidants [24], but non-notices on maltodextrin use for phlorotannin powder. The current study showed maltodextrin had a good effect on the drying aid of antioxidant pigment from terrestrial plant and brown algae. Phlorotannin content in powder was higher than polyphenol content of tomatoes powder (12.24 mg gallic acid equivalents 100^{-1} g DP) [25] and lower than polyphenol content of tea-green powder (200.37 ± 0.9 mg gallic acid equivalents g^{-1} DP) [26].

3.1.2 Effect of the maltodextrin-to-drying solution ratio (MDS)

Phlorotannin content of powder got 1.008 ± 0.02 g phloroglucinol equivalent 100^{-1} g powders and 1.792 ± 0.043 g phloroglucinol equivalent 100^{-1} g powder, respectively when 2% of MDS ratio and 14% of MDS ratio was used (Fig. 2a). When maltodextrin aids were 2%, the total antioxidant activity of phlorotannin powder corresponded to 2.928 ± 0.05 g ascorbic acid equivalent 100^{-1} g powders (Fig. 2a), reducing power activity of 4.919 ± 0.062 g FeSO_4 equivalent 100^{-1} g powders (Fig. 2b). When the maltodextrin-to-drying solution ratio increased to 14%, the total antioxidant activity of phlorotannin powder corresponded to 3.653 ± 0.06 g ascorbic acid equivalent 100^{-1} g powders, and reducing power activity of 7.516 ± 0.061 g FeSO_4 equivalent 100^{-1} g powders.

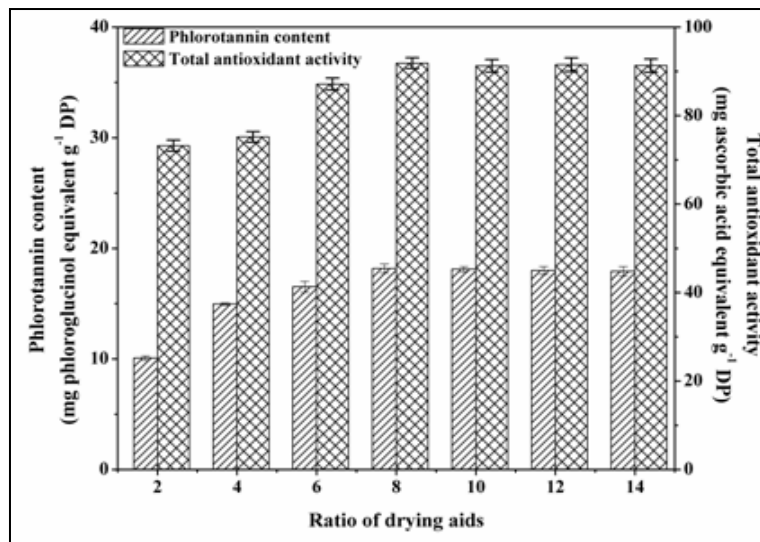


(a)

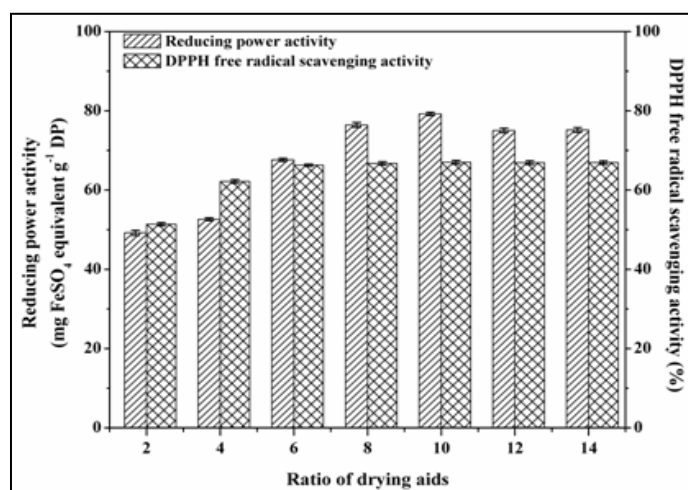


(b)

Fig. 1. Changes in phlorotannin content and antioxidant activities of brown algae extract powder according to drying aids



(a)



(b)

Fig. 2. Changes in phlorotannin content and antioxidant activities of brown algae extract powder according to drying aids ratio

Phlorotannin content and antioxidant activity of the powder was strongly affected by the maltodextrin/solution ratio ($p < 0.05$) and the highest value as 10% MDS ratio. Phlorotannin content increased by 45% when the MDS ratio increased from 2% to 10% and decreased by 1% as 14% MDS was, compared to 10% MDS. Total antioxidant and reducing power activity of phlorotannin powder were correspondingly increased by 24.66% and 61.02% as using of 10% maltodextrin aids, compared to 2% maltodextrin aids. The total antioxidant activity was not significantly different, and reducing power activity was decreased by 5.1% when the MDS ratio was more than 10%. The highest and lowest value of DPPH free radical scavenging activity was when 10% and 2% of MDS was, respectively (Fig. 2b). A low MDS ratio caused less formation of microparticles. When maltodextrin content increased too high, the viscosity of the solution was increased and difficult dry processing, described on the drying of Gac powder by Kha [27]. Quek et al. (2007) showed that the maltodextrin content affected the dry powder characteristics of watermelon juice and recovery yield that stuck in a drying chamber and cyclone as non-use of maltodextrin[28]. The MDS ratio was strongly related to phlorotannin content and antioxidant activity of powder ($R^2 > 0.81$) that changed according to the non-linear model of level 2 with the maximum peak at 10% of MDS ratio.

3.1.3 Effect of compressed air pressure

Phlorotannin content of powder was varied from 1.73 ± 0.017 to 1.91 ± 0.015 mg phloroglucinol

equivalent 100^{-1} g DP. Phlorotannin content, total antioxidant activity, reducing power activity, and DPPH free radical scavenging of powder got the highest value, corresponding to 1.940 ± 0.021 g phloroglucinol equivalent, 4.080 ± 0.012 g ascorbic acid equivalent (Fig. 3a), 8.870 ± 0.025 g FeSO₄ equivalent, $(69.98 \pm 0.19)\%$ (Fig. 3b), respectively for 100 g DP as a compressed air pressure of 0.8 bar. The value of target functions was increased by 7.18%, 11.78%, 12.03%, and 0.02%, respectively, compared to that of prepared powder in compressed air pressure of 0.6 bar. Phlorotannin content, total antioxidant activity, reducing power activity, and DPPH free radical scavenging of powder was decreased to 1.912 ± 0.015 g phloroglucinol equivalent 100^{-1} g DP, 3.967 ± 0.09 g ascorbic acid equivalent, 7.970 ± 0.023 g FeSO₄ equivalent, and $(69.98 \pm 0.19)\%$ for 100 g DP, respectively at the compressed air pressure of 1.0 bar.

Phlorotannin content, total antioxidant activity, reducing power activity, and DPPH free radical scavenging of powder was affected by compressed air pressure ($p < 0.05$) and changed as the change of compressed air pressure. The correlation between phlorotannin content and antioxidant activities were ($R^2 > 0.8$), and the close relation between compressed air pressure and target functions was also recorded ($R^2 > 0.75$). Phlorotannin content and antioxidant activities of powder were changed according to the non-linear model of level 2, and got the maximum point at a compressed air pressure of 0.8 bar, except for DPPH free radical scavenging activity because this activity had the model of

linear change. The difference in each organic material leading compressed air pressure was used differently in spray drying processing. The compressed air pressure was adequate from 0.6 – 1.4 bar for spray drying [29,30], except for spray drying of leaves extract Piper betle (4 bar), described by Lee [31], antioxidant powder from *Tinospora cordifolia* leaf (45 psi (3.103 bar)) [32]. The compressed air pressure, particle weight, and powder weight in the container also affected recovery yield. Moving microparticles in the cyclo were affected by at least two forces (the earth's gravitational and the inertial force) that due to the fogging speed and thrust of the compressed air. Microparticles were blown out of the cycle when the earth's gravitational forces are smaller than the inertial force (thrust of the compressed air), and it found for less powder weight. The larger the weighted particle is, the

larger the earth's gravitational force for particle weight. The faster nozzle rotates, the smaller fog particles, and this happens as an increase of pumping speed, and the contact areas between fog particles and hot air increased. When microparticle weight is too small, they cannot be able to overcome the thrust of the compressed air to reach the container, collected powder weight in the condition is less than that in lower compressed air pressure.

3.1.4 Effect of feed flow rate

The phlorotannin content, antioxidant activities, and powder weight got the highest and the lowest value at 10 ml min^{-1} (rpm) and 50 rpm, respectively. When feed flow rate was at 10 rpm, phlorotannin content, total antioxidant activity, reducing power, and DPPH free radical

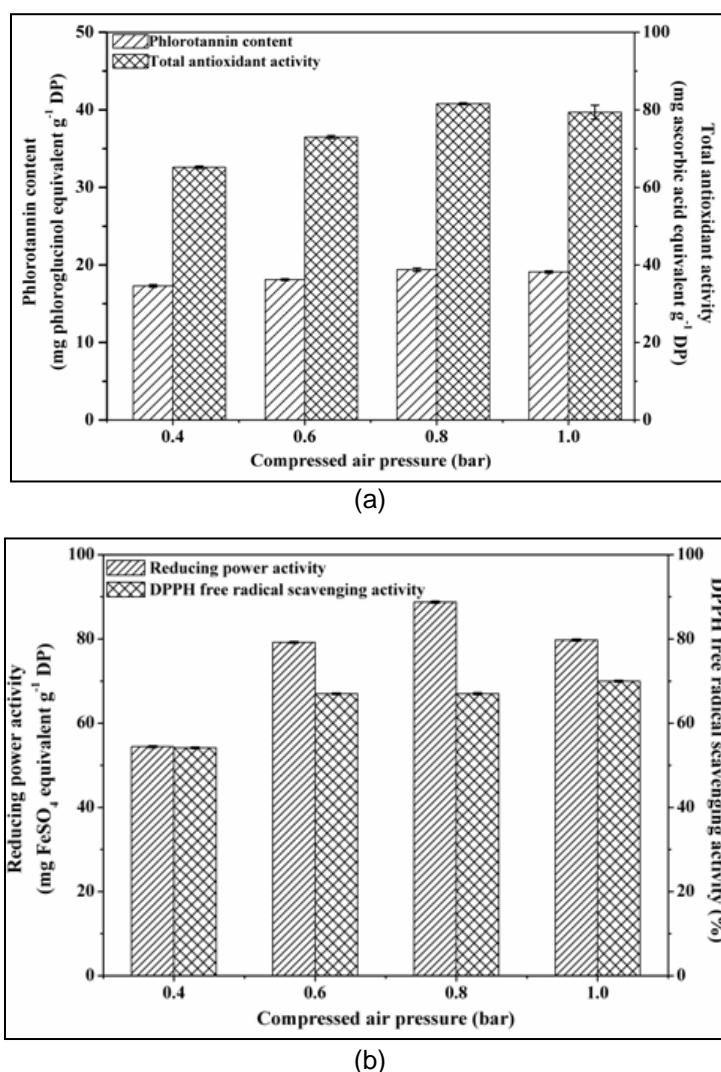


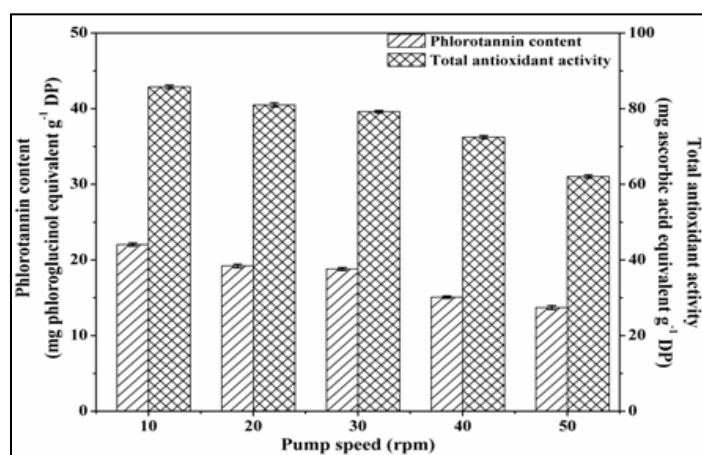
Fig. 3. Changes in phlorotannin content and antioxidant activities of brown algae extract powder according to pump pressure

scavenging activity corresponded to 2.203 ± 0.020 g phloroglucinol equivalent, 4.287 ± 0.023 g ascorbic acid equivalent, 10.021 ± 0.026 g FeSO_4 equivalent, and $(67.01 \pm 0.24)\%$ per 100^{-1} g DP, respectively. The lowest value of DPPH free radical scavenging activity corresponded $(66.92 \pm 0.11)\%$ (Fig. 4b). Pumping speed affected phlorotannin content, antioxidant activities, and collected powder weight ($p < 0.05$) that decreased as the increase of feed flow rate. Phlorotannin content decreased to 87% and 62,14% as the feed flow rate of 20 rpm and 50 rpm, respectively, compared to the pumping speed at 10 rpm. Total antioxidant activity corresponded to 94% and 72.36% as the feed flow rate of 20 rpm and 50 rpm, respectively, compared to the feed flow rate at 10 rpm. The reducing power of the powder was decreased by 13% and 37.33% as feed flow rate at 20 rpm and 50 rpm, respectively, compared to the feed flow rate at 10 rpm. The correlation

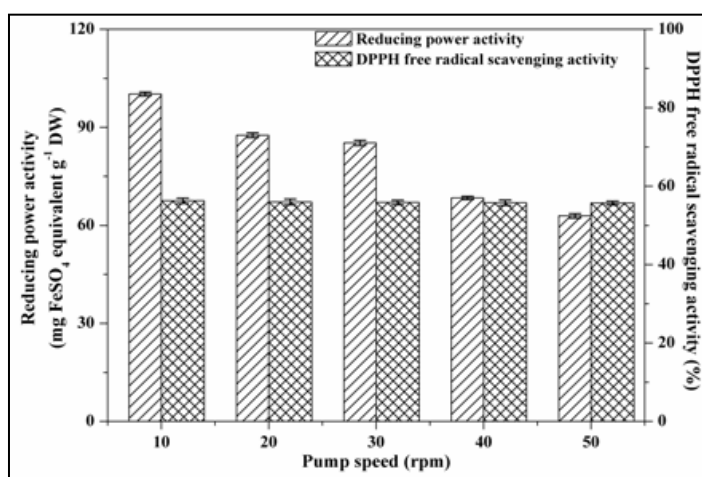
between feed flow rate and phlorotannin content, antioxidant activities, and weight of powder was good ($R^2 > 0.92$; $F > F_{\text{crit}}$) and a negative correlation, and the reverse is a positive correlation between phlorotannin content and antioxidant activities. The increase of feed flow rate caused more fog number, higher humidity in cycle, the longer the drying time of the dewdrops. The difference in extract caused various liquid feed rates, for example, polyphenol (quercetin and vanillin) microencapsulation (10 mL min^{-1}) [33] and polyphenol extract of green tea (3 mL min^{-1}) [34].

3.1.5 Effect of inlet air temperature

Phlorotannin content, total antioxidant activity, reducing power, DPPH free radical scavenging of the powder got the highest value, corresponding to 2.268 ± 0.010 g phloroglucinol equivalent, 4.347 ± 0.018 g ascorbic acid



(a)



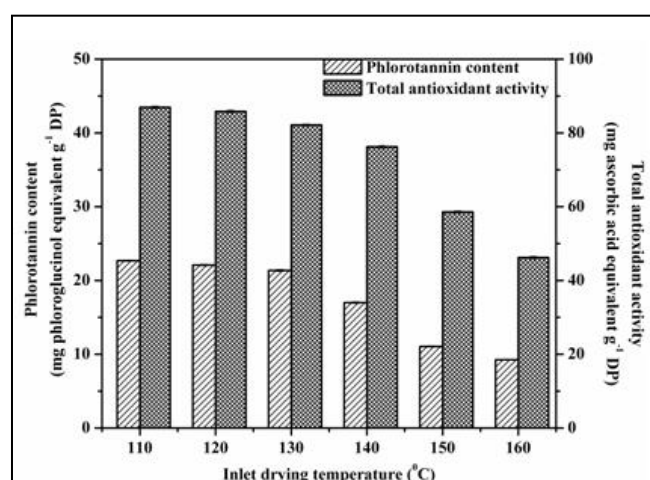
(b)

Fig. 4. Phlorotannin content and antioxidant activities of brown algae extract powder at different pump speeds

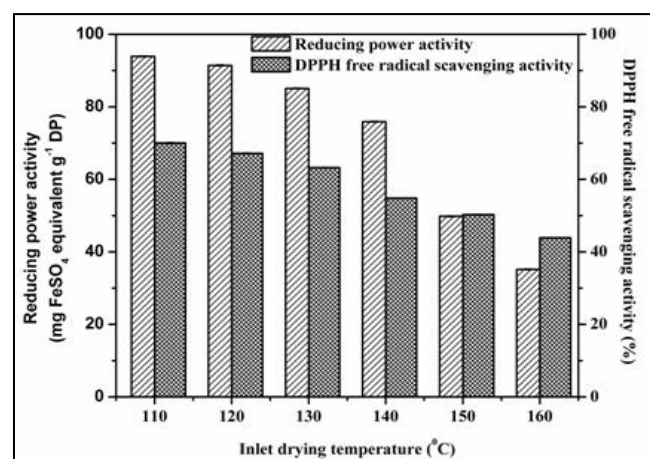
equivalent, 9.390 ± 0.024 g FeSO_4 equivalent, and $(70.02 \pm 0.26)\%$ per 100 g DP, respectively, at the inlet air temperature of 110°C . Total antioxidant activity and reducing power activity of powder were decreased by 46.84% (2.311 ± 0.020 g ascorbic acid equivalent 100^{-1} g DP) and to 62.59% (3.513 ± 0.024 g FeSO_4 equivalent 100^{-1} g DP) in comparison to the inlet air temperature of 110°C . DPPH free radical scavenging activity of powder got the lowest value at the inlet air temperature of 160°C and was 37.28% in comparison to the inlet air temperature of 110°C (Fig. 5b). At the inlet air temperature of 160°C , phlorotannin content, total antioxidant activity, and reducing power also got the lowest value.

The inlet air temperature affected phlorotannin content and antioxidant activities of powder ($p < 0.05$). Phlorotannin content of powder at various

inlet air temperature was statistically significant, and the difference also happened for antioxidant activities. The inlet air temperature increased to 160°C , phlorotannin content of powder was decreased by 59.26%, compared to the inlet air temperature of 110°C . The changes in phlorotannin content and antioxidant activities complied to the linear equation when the inlet air temperature was altered from 110°C to 160°C and had a close correlation with each other ($R^2 > 0.87$; $F > F_{\text{crit}}$). The moisture diffusion rate at the particle surface and inside particles were relatively balanced. Microparticles formation happened rapidly, phlorotannin content and antioxidant activity of microparticles were good, found at the inlet air temperature of 110°C . When the inlet air temperature was above 110°C , phlorotannin content and antioxidant activities decreased, the surface of microparticles was drier, even burnt, compared to the inlet air



(a)



(b)

Fig. 5. Effect of inlet drying temperature on phlorotannin content and total antioxidant activity of powder

temperature of 110°C. Inlet air temperature in the current study was lower than for bayberry polyphenols extract (150°C) [35] and polyphenol-rich grape marc extract (140°C) [36]. The difference in extract characteristics and polyphenol characteristics caused various input air temperature. Bayberry polyphenols and polyphenol-rich grape marc extract contained mainly water [35,36], phlorotannin extract consisted of ethanol and water. The evaporation temperature of ethanol is lower than that of water, caused by rapid particle formation. In the current study, lower drying temperature led to less electricity cost for drying temperature.

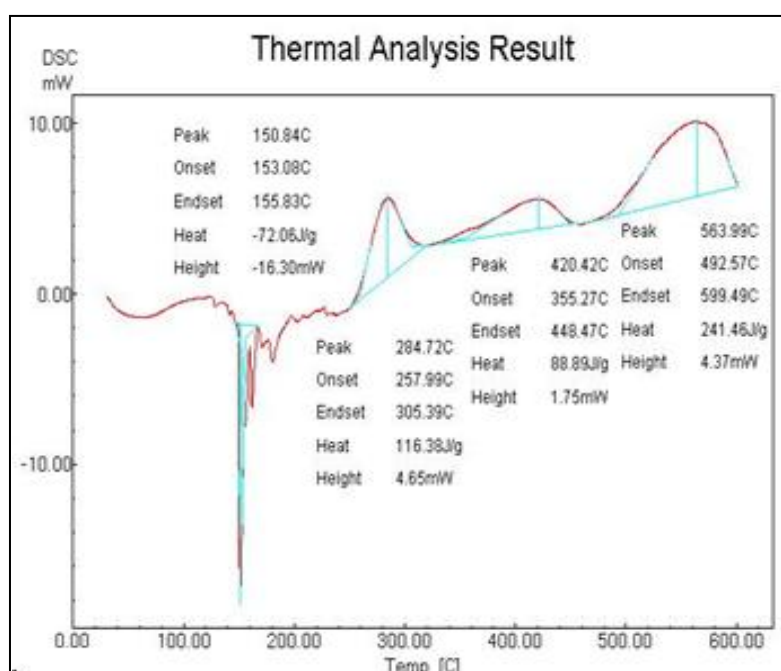
3.3 Physico-chemical Characterization

3.3.1 Fourier-transform infrared spectroscopy and differential scanning calorimetry of powder

3.3.1.1 Differential scanning calorimetry

The temperature zone of sub-T relaxation, glass transition, crystallization, melting and decomposition exhibited very clear based on the notice of Qiuju et al. [37]. The sub-T relaxation of phlorotannin powder occurred before T_g point. The glass transitions (T_g) determination of antioxidant phlorotannin powder was to base the heating curve change from onset to the endpoint of them that occurred located 67.12°C and the

width of the clear transition. The midpoint T_g and the endpoint T_g of antioxidant phlorotannin powder were 100.21 and 117.54°C. According to Agata et al. T_g values of carbohydrate-protein systems were higher than single disaccharides consisting of lactose and trehalose [38], and the current study showed T_g temperature values of the phlorotannin-maltodextrin system were lower than β -lactoglobulin-vitamin A-trehalose and β -lactoglobulin-cholecalciferol-lactose powder [38]. The difference in T_g could be from the different solvent using before the spray drying, described the T_g temperatures of foods depending on their moisture content and chemical compositions [39-41]. The temperature zone of crystallization, melting and destroying appeared in turn to the peak of 1, 2 and 3 from left to right. The onset, midpoint, and endpoint of crystallization temperature (T_c) corresponded to 153.08°C, 150.84°C, and 155.83°C, respectively. The temperature zone belongs to the exotherm zone (give up heat) (Fig. 6a). The melting of antioxidant phlorotannin powder occurred in the temperature zone from 257.99°C (onset temperature) to 305.39°C (endpoint temperature), named the melting temperature (T_m). The destruction of antioxidant phlorotannin and their linkages to maltodextrin appeared beginning at 355.27°C and finishing at 448.47°C. The full destruction of antioxidant phlorotannin powder was in the temperature zone from 492.57°C to 599.49°C.



(a)

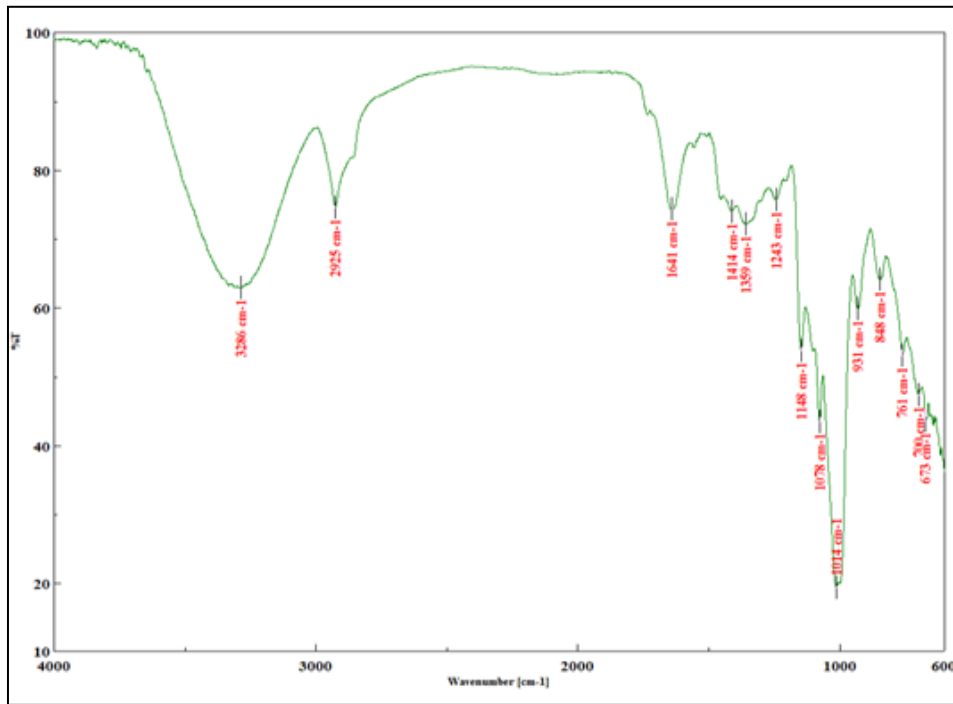


Fig. 6. Differential scanning calorimetry and fourier-transform infrared spectroscopy of phlorotannin powder

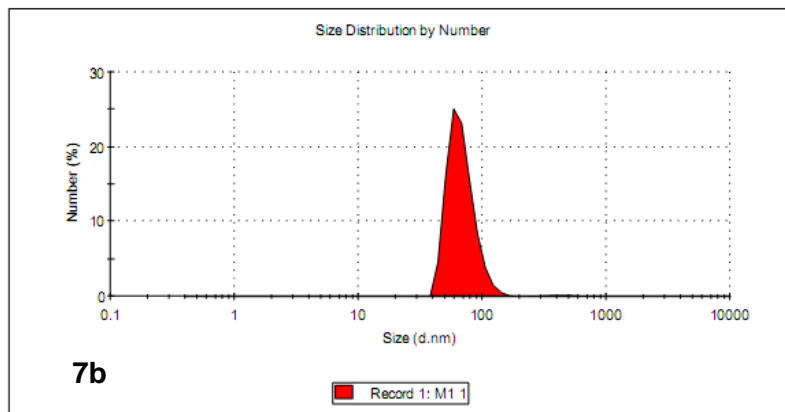
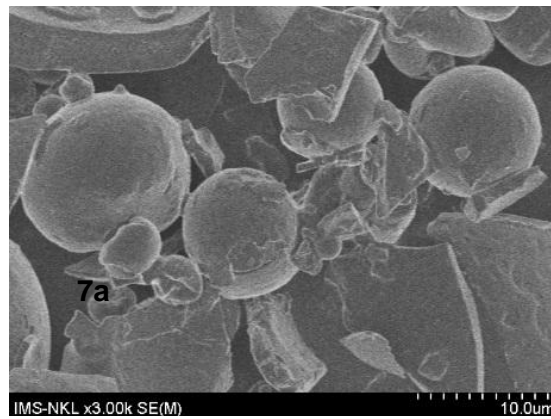


Fig. 7. The morphology and the size of antioxidant phlorotannin particles

3.3.1.2 Fourier-transform infrared spectroscopy

The results showed that different peaks appeared in FTIR spectrum of antioxidant phlorotannin powder, for example, 3286 cm^{-1} , 2925 cm^{-1} , 1641 cm^{-1} , 1414 cm^{-1} , 1359 cm^{-1} , 1243 cm^{-1} , 1148 cm^{-1} , 1078 cm^{-1} , 1014 cm^{-1} , 931 cm^{-1} , 848 cm^{-1} , 761 cm^{-1} , 700 cm^{-1} , and 673 cm^{-1} . The peak 3286 cm^{-1} related to the hydroxyl stretching vibration and H-bonding [42]. The peak 2925 cm^{-1} exhibited the CH and C-H stretching vibration belonging to the group of methoxy compounds (2928 cm^{-1}), described by Rengasamy et al. [43] and John [42] and C-H asymmetry stretching (2937 cm^{-1}) [44]. The peak 1641 cm^{-1} exhibited the stretching of carbonyl groups (C=O), noticed by Rengasamy et al. [43] and Senthilkumar et al. [45]. According to Mayra et al., C-C stretch (in-ring) of phenolic groups from 1500-1400 cm^{-1} [46] and in the current study, the peak 1414 cm^{-1} occurred. The peak 1359 cm^{-1} belonged to the stretching of C-O groups (1383 cm^{-1}), found in a previous study [47]. Basing on the peak 1243 cm^{-1} showed the COO- (C-O) stretching [48]. The sulfonate radicals appeared in antioxidant phlorotannin powder, exhibited via the peak 1148 cm^{-1} [42] (Fig. 6b). The peak 1078 related to the vibration of hydroxyl groups [47]. The C-F stretch found in the spectrum FTIR (the peak 1014 cm^{-1}) exhibiting aliphatic fluoro compounds existence in phlorotannin structure. The stretching of =C-H and =CH₂ presented in the spectrum FTIR via the peak 931 cm^{-1} , described by Showkat et al. (2018) on gallic acid (951.87 cm^{-1}) [49]. The C-H groups at the sites para of aromatic ring exhibited in the peak 848 cm^{-1} [42]. The peak 761 cm^{-1} showed occurring the C-H groups of aromatic phenyl. The C-H bend (rocking) of -C≡C-H was from 700-610 cm^{-1} and in the current study, the peak 700 cm^{-1} and the peak 673 cm^{-1} presented [50].

3.3.2 The particle morphology, the bulk density, the moisture and the solubility degree of powder

The solubility degree of antioxidant phlorotannin powder was 100%, observed on all powder sample that dried at different conditions. Drying temperature, aids kind, and aids ratio did not affect the solubility degree of powder ($p > 0.05$). Drying temperature and aids kind correlated negatively to the bulk density of powder ($p < 0.05$) that was in the range of 0.53 to 0.67 g/ml, reported in a previous study [51,52]. The antioxidant phlorotannin particles possessed

different morphologies (irregular microcapsule and microspheres) (Fig. 7a). The moisture content of the antioxidant nano phlorotannin powder got $5 \pm 0.5\%$. Maltodextrin formed a hard wall outside the microcapsule. 99.2% and 0.8% of particles got an average size of 68.23 and 479.3 d.nm, respectively (Fig. 7b). The average size of antioxidant phlorotannin powder was 211.0 d.nm that got the average level in the size of nano polyphenol particles as reported in the previous studies (30 – 1300 d.nm) [53]. The nanosize of antioxidant phlorotannin powder in the current study was lower than the notice of Marco et al. [52] and did not find in the previous studies on phlorotannin powder.

4. CONCLUSION

Antioxidant nano phlorotannin powder from brown algae *Sargassum serratum* got the highest phlorotannin content and antioxidant activity with moisture content ($5 \pm 0.5\%$) at the optimum condition (10% carrier-to-solution ratio, 0.8 bar compressed air pressure, 10 ml min^{-1} liquid feed speed, and 110 °C inlet temperature), compared to other conditions. Nano phlorotannin correlated strongly and possessed antioxidant activities. Antioxidant nano phlorotannin powder dissolved fully into the water with their bulk density under 1 g/ml. 100% of phlorotannin powder (99.2% of powder size under 70 d.nm) possessed the nanoparticles and the irregular and microspheres morphology. The current study showed the characterization of the transition temperature (DSC) and the functional group (FTIR) of nanopowder but did not present NMR, DTA, TGA, and TEM. Different bioactivities, flow properties, and other bioactive substances attachment of antioxidant nano phlorotannin powder should be studied and evaluated in further studies. Antioxidant nano phlorotannin powder preparing from brown algae *Sargassum serratum* has the high potency of application into the field of the functional food and the pharmaceuticals as a bioactive material.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Toshiyuki S, Shigeo K, Yoichiro H, Masanori I, Kuniko Y, Takashi N. Local and chemical distribution of phlorotannins in brown algae. *J Appl Phycol*. 2004;16:291-296.
2. Marco N, Balz F, Joseph A, John F. Antioxidants and atherosclerotic heart disease. *N Engl J Med*. 1997;337:408-416.
3. Ragan M, Glombitza K. Phlorotannins, brown algal polyphenols. *Prog phycol Res*. 1986;4:130-230.
4. Nakamura T, Nagayama K, Uchida K, Tanaka R. Antioxidant activity of phlorotannins isolated from the brown alga *Eisenia bicyclis*. *Fish Sci*. 1996;62:923-926.
5. Toshiyuki S, Kanji I, Shigeo K, Hiromichi Y, Yoichiro H. Antioxidant activities of phlorotannins isolated from Japanese Laminariaceae. *J Appl Phycol*. 2007;20:255-261.
6. Kim A, Shin T, Lee M, Park J, Park K, Yoon N, Kim J, Choi J, Jang B, Byun D, Park N, Kim H. Isolation and identification of phlorotannins from *Ecklonia stolonifera* with antioxidant and anti-inflammatory properties. *J Agric Food Chem*. 2009;57:3483-3489.
7. WAJP W, Seok-Chun K, You-Jin J. Effect of phlorotannins isolated from *Ecklonia cava* on angiotensin I-converting enzyme (ACE) inhibitory activity. *Nutr Res Pract*. 2011;5:93-100.
8. Chew Y, Lim Y, Omar M, Khoo K. Antioxidant activity of three edible seaweeds from two areas in South East Asia. *LWT-Food Sci Technol*. 2008;41:1067-1072.
9. Toshiyuki S, Kanji I, Shigeo K, Hiromichi Y, Yoichiro H. Antioxidant activities of phlorotannins isolated from Japanese Laminariaceae. *J Appl Phycol*. 2007;20:705-711.
10. Kang K, Hwang H, Hong D, Park Y, Kim S, Lee B, Shin H. Antioxidant and antiinflammatory activities of ventol, a phlorotannin-rich natural agent derived from *Ecklonia cava*, and its effect on proteoglycan degradation in cartilage explant culture. *Res Commun Mol Pathol Pharmacol*. 2004:115-116.
11. Yoshimasa S, Kohji M, Takashi O, Makoto K, Hideomi A. Anti-allergic effects of the brown alga *Eisenia arborea* on Brown Norway rats. *Fish Sci*. 2008;74:180-186.
12. Felix N, Jennifer M, Victoria A, Derek S, Heather A, Gordon J. Anti-proliferative and potential anti-diabetic effects of phenolic-rich extracts from edible marine algae. *Food Chem*. 2011;126:1006-1012.
13. Artan M, Li Y, Karadeniz F, Lee S, Kim M, Kim S. Anti-HIV-1 activity of phloroglucinol derivative, 6,6'-bieckol, from *Ecklonia cava*. *Bioorganic Med Chem*. 2008;16:7921-7926.
14. Mayalen Z, Marie S, Veronique K. Antioxidant and antitumoural activities of some Phaeophyta from Brittany coasts. *Food Chem*. 2009;116:693-701.
15. Jong-Sup B. Antithrombotic and profibrinolytic activities of phloroglucinol. *Food Chem Toxicol*. 2011;49:1572-1577.
16. Kanti B, Syed I. Plant polyphenols as dietary antioxidants in human health and disease. *Oxid Med Cell Longev*. 2009;2:270-278.
17. Abbott I, J F, KJ McDermid. Taxonomy of economic seaweeds with reference to some Pacific species. La Jolla, CA: California Sea Grant College Program. 2002;281.
18. Vu NB, Dang XC, Phan TKV. Effects of extraction conditions over the phlorotannin content and antioxidant activity of extract from brown algae *Sargassum serratum* (Nguyen Huu Dai 2004). *Free Radicals and Antioxidants*. 2017;7(1):115-122.
19. Lynn DT. Pharmaceutical and medical device validation by experimental design. New York: Informa Healthcare USA, Inc; 2007.
20. Dang XC, Vu NB, Tran TTV, Le NH. Effect of storage time on phlorotannin content and antioxidant activity of six *Sargassum* species from Nhatrang Bay, Vietnam. *J Appl Phycol*. 2016;28(1):567-572.
21. Prieto P, Pineda M, Aguilar M. Spectrophotometric quantitation of antioxidant capacity through the formation of a phosphomolybdenum complex: specific application to the determination of vitamin E. *Anal Biochem*. 1999;269(2):337-341.
22. Jinapong N, Suphantharika M, Jamnong P. Production of instant soymilk powders by ultrafiltration, spray drying and fluidized bed agglomeration. *J Food Eng*. 2008;84:194-205.
23. Phisut N. Spray drying technique of fruit juice powder: some factors influencing the properties of product. *Int Food Res J*. 2012;19:1297-1306.

24. Renata V, Carlos R, Miriam D. Influence of emulsion composition and inlet air temperature on the microencapsulation of flaxseed oil by spray drying. *Food Res Int.* 2011;44:282-289.
25. Maruf A, Mst S, Koo-Bok C, Jong-Bang E. Effect of maltodextrin concentration and drying temperature on quality properties of purple sweet potato flour. *Food Sci Biotechnol.* 2009;18:1487-1494.
26. Susantikarn P, Donlao N. Optimization of green tea extracts spray drying as affected by temperature and maltodextrin content. *Int Food Res J.* 2016;23:1327-1331.
27. Kha TC, Minh HN, Paul D. Effects of spray drying conditions on the physicochemical and antioxidant properties of the Gac (*Momordica cochinchinensis*) fruit aril powder. *J Food Eng.* 2010;98(3):385-392.
28. Quek S, Chok N, Swedlund P. The physicochemical properties of spray-dried watermelon powder. *Chem Eng Process.* 2007;46:386-392.
29. Praveen K, Awang B. Antioxidant activity, total phenolic and flavonoid content of morinda citrifolia fruit extracts from various extraction processes. *Int J Eng Sci Technol.* 2007;2:70-80.
30. Anjali V, Satya VS. Spray drying of fruit and vegetable juices - A review. *Crit Rev Food Sci Nutr.* 2015;55:701-719.
31. Lee HT, Abdullah LC, K YP, A AR. Optimization of spray drying process parameters of Piper betle L. (Sirih) leaves extract coated with maltodextrin. *J Chem Pharm.* 2012;4(3):1833-1841.
32. Sarala M, Velu V, Anandharamakrishnan C, Singh R. Spray drying of *Tinospora cordifolia* leaf and stem extract and evaluation of antioxidant activity. *J Food Sci Technol.* 2012;49:119-122.
33. Dongxiao S, Sandhya S, Geoffrey I. Spray-drying microencapsulation of polyphenol bioactives: A comparative study using different natural fibre polymers as encapsulants. *Food Bioprocess Technol.* 2013; 6:2376-2388.
34. Wei-Qiang T, Di-Cai L, Yang-Xiao L, Jian-Guo J. Concentration and drying of tea polyphenols extracted from green tea using molecular distillation and spray drying. *Dry Technol.* 2011;29:584-590.
35. Zhongxiang F, Bhesh B. Effect of spray drying and storage on the stability of bayberry polyphenols. *Food Chem.* 2011; 129:1139-1147.
36. Moreno T, E dP, I N, S R-R, A M, C D, M S-B, M.J C. Spray drying formulation of polyphenols-rich grape marc extract: evaluation of operating conditions and different natural carriers. *Food Bioprocess Technol.* 2016;9:2046-2058.
37. Qiuju Z, Zhang Y, Montazerian M, Gulbitten O, John CM, Edgar DZ, Yuanzheng Y. Understanding glass through differential scanning calorimetry. *Chem Rev.* 2019;119(13):7848–7939.
38. Agata G, Karolina S, Ewa O-L, Joanna B, Magdalena W-W. Effect of composition and drying method on glass transition temperature, water sorption characteristics and surface morphology of newly designed β -lactoglobulin/retinyl palmitate/disaccharides systems. *J Therm Anal Calorim.* 2017;130:177-185.
39. Gońska A, Szulc K, Ostrowska-Ligeżka E, Wirkowska M, Bryś J. The influence of trehalose-maltodextrin and lactose-maltodextrin matrices on thermal and sorption properties of spray-dried β -lactoglobulin-vitamin D3 complexes. *J Therm Anal Calorim.* 2013;112:429-436.
40. Jakubczyk E, Ostrowska-Ligeżka E, Gondek E. Moisture sorption characteristics and glass transition temperature of apple puree powder. *Int J Food Sci Technol.* 2010;45:2515-2523.
41. Gońska A, Ostrowska-Ligeżka E, Szulc K, Wirkowska M. A differential scanning calorimetric study of β -lactoglobulin and vitamin D3 complexes. *J Therm Anal Calorim.* 2012;110(1):473-477.
42. John C. Interpretation of Infrared Spectra, A practical approach. In: Robert AM, editor. *Encyclopedia of Analytical Chemistry.* New York, United States. John Wiley & Sons; 2007.
43. Rengasamy RRK, Rajasekaran A, Perumal A. Fourier transform infrared spectroscopy analysis of seagrass polyphenols. *Current Bioactive Compounds.* 2011;7:118-125.
44. Hong Y, Joseph I, Manish M. Discriminant analysis of edible oils and fats by FTIR, FT-NIR and FT-Raman spectroscopy. *Food Chem.* 2005;93:25-32.
45. Senthilkumar S, Sivakumar T, Arulmozhi K, Mythili N. FT-IR analysis and correlation studies on the antioxidant activity, total phenolics and total flavonoids of Indian commercial teas (*Camellia sinensis* L.) - A novel approach. *International Research Journal of Biological Sciences.* 2017;6(3):1-7.

46. Mayra AP-C, Horacio G-R. Study by infrared spectroscopy and thermogravimetric analysis of Tannins and Tannic acid. *Rev latinoam quim.* 2011;39(3):107-112.
47. Luca P. *Advances in nanoparticles: Synthesis, characterization, theoretical modelling, and applications.* Switzerland: MDPI. 2020;144.
48. Mahendra KT, Alice B, Dahryn T, Harish S, Khemraj B, Snehasis J. Fourier transform infrared and ultraviolet-visible spectroscopic characterization of biofield treated salicylic acid and sparfloxacin. *Nat Prod Chem Res.* 2015;3:186-193.
49. Showkat AB, Tham SS, Mohammad NMI. Synthesis of molecular imprinting polymers for extraction of gallic acid from urine. *Chem Cent J.* 2018;12:19-26.
50. Yang R. *Analytical methods for polymer characterization:* CRC Press; 2018;319.
51. Poonam M, Anjali B, Dibyakant S. Physicochemical, functionality and storage stability of hog plum (*Spondia pinnata*) juice powder produced by spray drying. *J Food Sci Technol.* 2017;54(5):1052-1061.
52. Marco P, Bahar A, Alessandro AC, Alberto L, Rodolfo B, Patrizia P. Microencapsulation of phenolic compounds from olive pomace using spray drying: A study of operative parameters. *LWT-Food Sci Technol.* 2015;62(1):177-186.
53. Danijel DMcc, Dušanka APc, Steva MLc, Aleksandar ŽKc, Živoslav LTc, Viktor ANc, Mirjana BPc. Review: Application of polyphenol-loaded nanoparticles in food industry. *Nanomaterials.* 2019;9:1629-1650.

© 2020 Cuong; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:

<http://www.sdiarticle4.com/review-history/57412>