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Impact of drying processes on properties of polyphenol-enriched maple sugar powders

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Abstract

The aim of this research was to develop a natural food ingredient based on maple sugar powders (MSP) enriched in polyphenols. By incorporating 0.01% (wt/vol) of hot water extract (hot water extraction: 90°C and 1 hr; bark/water, 1/10 wt/vol) from sugar and red maple bark into substandard quality maple syrup, the latter was enriched by 13–20% in total phenolic content (TPC). The mixtures (syrup and extracts) were dehydrated using freeze-drying (FD: at −36°C for 15 hr and subsequently at 30°C for 10 hr) or vacuum double-drum drying (VDD: at 80°C and 660 Torr) to obtain the powders. Influence of drying processes on TPC, antioxidant capacity, and physical properties of powders was studied. Both drying processes caused a decrease in TPC and antioxidant capacity of MSP. Nevertheless, bark extracts contributed to higher TPC (8–10%) and antioxidant capacity (>40%) compared to control MSP. The moisture content of VDD powders (0.63–0.71%, dry basis) was significantly lower than that of FD powders (4.10–4.40%, dry basis). MSP produced by FD were amorphous and those produced by VDD crystalline. FD powders had instant-like properties (dissolution time of 12–13 s), whereas those produced by VDD were less cohesive (Hausner ratio, 1.13–1.21), with excellent flowability.

Practical Applications

Consumers are increasingly attracted by natural food products. Canada is the world major producer of maple syrup, a nutritious natural sweetener exclusively obtained from maple trees sap. Unfortunately, a "very dark" color syrup is accumulated as surplus in large quantity in Canada as it is considered of substandard quality. In this research, freeze-drying (FD) and vacuum double-drum drying (VDD) techniques were studied to produce maple sugar powders (MSP) from this substandard surplus syrup. This syrup was additionally enriched in polyphenols by adding hot water extracts from maple barks. The obtained polyphenol-enriched MSP have shown interesting qualities for application as natural sweeteners, such as free flowing or instant-like powder. Our results indicate that FD and VDD are suitable techniques for substandard syrup conversion into value-added maple product. MSPs have a huge potential

Abbreviations: CI, Carr's index; DPPH, 2, 2-diphenyl-1-picrylhydrazyl; FD, freeze-drying; FD:MSP + RBX, freeze-dried maple sugar powder with red maple bark extract; FD:MSP + SBX, freeze-dried maple sugar powder with sugar maple bark extract; FD:MSP, freeze-dried maple sugar powder; GAB, Guggenheim–Anderson–de Boer; HR, Hausner ratio; MSP, maple sugar powders; RBX, red maple bark extract; SBX, sugar maple bark extract; SEM, scanning electron microscopy; TPC, total phenolic content; VDD, vacuum double-drum drying; VDD:MSP + RBX, vacuum double-drum dried maple sugar powder with red maple bark extract; VDD:MSP + SBX, vacuum double-drum dried maple sugar powder with sugar maple bark extract; VDD:MSP, vacuum double-drum dried maple sugar powder.

of application as natural food ingredients of instant drinks, cereal mix, cookies, and energy bars.

1 | INTRODUCTION

Growing consumers' proclivity toward natural foods has led research on identifying diverse sources of natural foods, particularly plant-based ones. Maple trees, notably the sugar maple and red maple, are socially and economically appreciated North American forest species because of their use as traditional medicine (bark) and food (maple syrup). As traditional medicine, maple bark has been used by Native Americans to treat several ailments by bark infusion (Arnason, Hebda, & Johns, 1981). Bark extracts of these species have been reported to contain dietary polyphenols such as gallic-acid derivatives, lignans, and flavonoids. The major polyphenols in maple bark were found to be maplexins and ginnalins (about 15.6%, wt/wt), which belong to the family of gallotannin with 1,5-anhydroglucitol as carbohydrate moieties (Geoffroy, Meda, & Stevanovic, 2017). Gallotannins are generally recognized as safe by the Food and Drug Administration (FDA) at the concentration ranging from 10 to 400 ppm as food ingredients (Maqsood, Benjakul, & Balange, 2012). Beside polyphenols, the crude maple bark extracts were reported to present a wide array of organic and inorganic nutrients beneficial to human health (Bhatta, Ratti, Poubelle, & Stevanovic, 2018). Therefore, maple bark extracts have been determined as promising therapeutic and potent antioxidant activities (Bhatta et al., 2018; González-Sarrías, Li, & Seeram, 2012; Royer, Diouf, & Stevanovic, 2011).

Maple syrup is widely consumed, obtained by evaporating the sap of sugar and red maple trees. It is mainly composed of sugars (primarily sucrose at 65–67%, fructose, and glucose), and other nutrients (<1%) such as minerals, organic acids, and polyphenols (Ball, 2007). The presence of polyphenols is well-appreciated in syrup, even though they are found at low concentration (0.0015% wt/vol, St-Pierre et al., 2014). The polyphenols found in syrup have also shown potential antioxidant, anticancer, α-glucosidase enzyme inhibitory, and anti-inflammatory effects (Apostolidis, Li, Lee, & Seeram, 2011; González-Sarrías, Li, Seeram, & Gonza, 2012; Thériault, Caillet, Kermasha, & Lacroix, 2006).

Maple syrup is predominately produced in Canada (71% of world production), which contributes about 494 million dollars to country's economy (Agriculture and Agri-food Canada, 2018). Despite of important successes of maple industry, it faces serious challenges due to the important volume of the surplus maple syrup, estimated to be more than 38% of annual syrup production in 2017 (Agriculture and Agri-food Canada, 2018). Syrup is classified into four grades based on its color; golden, amber, dark, and very dark (Canadian Food Inspection Agency, 2016). A "very dark" colored syrup is considered to be substandard and not consumed widely as table syrup. As a result, huge quantities of very dark syrup are accumulated as surplus each year. Therefore, valorization of surplus syrup is a current need of the maple industry. One possible avenue is by enriching this substandard grade with polyphenols-rich maple bark extracts. The application of polyphenol-enriched maple syrup can be then enhanced by dehydrating syrup to produce a free-flowing maple sugar powder (MSP).

Drying of sugar-rich foods such as maple syrup is a process involving several problems. The high hygroscopicity of simple sugars, the increase in solubility with temperature, a low glass transition temperature of sugars (fructose, glucose, and sucrose; T_g = 5, 31, and 62°C, respectively [Y. H. Roos, 1993], and the stickiness problem in the drying equipment (B. R. Bhandari, Datta, & Howes, 1997) are some of the obstacles to overcome. Recently, we have applied freeze-drying (FD) to produce dried maple syrup powder with instant-like properties (Bhatta, Stevanovic, & Ratti, 2019). However, the dilution of maple syrup at 20 °Brix was required to successfully produce a powder. Additionally, the obtained powder displayed satisfactory to poor flowability. Vacuum double-drum drying (VDD) is another technique that is mostly used to dry pastes or viscous liquids such as maple syrup (Daud, 2006). It operates under vacuum but high operating temperatures make it possible to dry foods faster than by FD. It may also preserve the molecules sensitive to oxidation due to the use of vacuum and shorter processing times. Many foods, such as mango puree, jackfruit juice, molasses and honey, mashed potatoes, and other starchy foods have been dehydrated using drum-drying technique (Caparino et al., 2012; Daud, 2006; Pua et al., 2010). However, there is no scientific report available in literature about dehydration of maple syrup by vacuum double-drum dryer. The choice of drying methods can greatly affect the final quality of powder. Moisture content, surface morphology, size, density, and microstructure (crystalline or amorphous) of powder are important quality parameters influencing their functional properties including dissolution, flowability, and so forth (B. Bhandari, 2013).

Therefore, the objective of the present study was to incorporate polyphenol-rich maple bark extracts to substandard syrup and perform drying of the mixture using FD and VDD techniques, so as to produce polyphenol-enriched MSP with improved functional properties.

2 | MATERIALS AND METHODS

2.1 | Chemical and reagents

High-performance liquid chromatography (HPLC) grade methanol, acetonitrile, ethyl acetate, formic acid, and sodium carbonate were purchased from Fischer Scientific (Fair Lawn, NJ). Folin–Ciocalteu reagent, 1,1-diphenyl-2-picrylhydrazyl (DPPH), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (trolox), and gallic acid were purchased from Sigma–Aldrich (St. Louis, MO). All other chemicals and reagents used were of analytical grade.

2.2 | Sample preparation

2.2.1 | Hot water extraction of maple barks

Plant samples (sugar maple and red maple bark) were provided by Levaco, Inc. (Quebec, Canada). Samples were air-dried and ground to 250–500 μm particle size as previously mentioned (Geoffroy, Fortin, & Stevanovic, 2017). Hot water extraction of maple barks was done following the method previously used (Bhatta et al., 2018). The concentration of extractives in the filtrate was calculated by oven-dry method at 105 ± 2°C and expressed as mg extractives/ml filtrate. The filtrate was kept at −20°C for further use. The extractives from sugar maple and red maple bark are named as sugar maple bark extract (SBX) and red maple bark extract (RBX), respectively, throughout this article.

2.2.2 | Addition of maple bark extracts to maple syrup

Maple syrup (MS) was provided by Levaco, Inc., Canada. Syrup samples used for this study were determined 66.63 ± 0.21 °Brix (Pocket refractometer, PAL-2, Atago, Japan) and 560 nm wavelength light transmission of 10.02 ± 0.32% (Cary 50 UV–vis spectrophotometer, Varian, Inc., Palo Alto, CA), glycerol as reference, hence classified as "Very dark color and Strong taste" (Canadian Food Inspection Agency, 2016). Hot water maple bark extracts were added to maple syrup as to make the final concentration of extract in syrup of 0.01% wt/vol (based on toxicology results obtained from a previous study [Bhatta et al., 2018]). Hereafter, pure maple syrup without extracts will be denoted as MS (control), while maple syrup with sugar and RBX as MS + SBX and MS + RBX, respectively.

2.2.3 | Polyphenol identification by HPLC–MS

To determine polyphenol in syrup by HPLC–MS, samples were treated following the methods described in the literature with slight modifications (Kermasha, 1995; St-Pierre et al., 2014). Ten milliliters of maple syrup samples were dissolved in 50 ml of water. Then, 250 μL of gallic acid (5 mg/ml) was added to the sample as external standard. Subsequently, the resulting solution was extracted with ethyl acetate in three successive extractions using the volumes of 50, 25, and 25 ml. The organic fractions obtained from three successive extractions were evaporated in a rotary evaporator (Rotavapor R-215, Buchi Labortechnik AG, Flawil, Switzerland) at a temperature of 45°C. The dried extract was dissolved in 1.5 ml of 80% aqueous methanol and filtered using a 0.45 μM syringe filter before performing the HPLC analysis. HPLC analyses were performed on Agilent 1100 series HPLC (Agilent Technologies, Inc., Santa Clara, CA) equipped with a quaternary pump system, an autosampler, a column compartment, and a diode-array detector (DAD). A Zorbax SB-C18 column (250 mm × 4.6 mm, 5 μm) was used for the separations. The solvent system consists of mobile phase A, water/acetonitrile/formic acid (94/5/1, vol/vol/vol), and mobile phase B, water/acetonitrile/formic acid (69/30/1, vol/vol/vol) (Thériault et al., 2006). The elution gradient was: 100–87% A from 0 to 5 min, 87–35% A from 5 to 45 min, isocratic (35% A) from 45 to 55 min, 35–0% A from 55 to 56 min, 0–100% A from 56 to 64 min, and then kept constant for 10 min for equilibration before another injection. Ten microliters of sample was injected, the flow rate was 0.7 ml/min, and column temperature was set at 30°C. The DAD detection was set at 280 nm. HPLC analysis was coupled to Agilent 6210 series high-resolution mass spectrometer with Time-of-Flight (MS–TOF), equipped with an electrospray ionization interface. The analysis was performed in negative mode (ESI–). The parameters applied were gas temperature, 325°C; drying gas, 5 L/min; nebulizer pressure, 30 psig; capillary voltage, 4,000 V; cone voltage, 65 V; skimmer, 60 V; and fragmentor, 70 V. Data acquisition was achieved using the MassHunter Workstation software (Version B.02.00, Agilent Technologies, Inc.).

2.3 | Drying experiments

FD of syrup samples were done by following the previously formulated protocol for syrup only (Bhatta et al., 2019). Briefly, a freeze dryer (Freeze Mobile 24, Virtis Company, Inc., Gardiner, NY) equipped with a Unitop 400 L (Virtis Company, Inc.) drying chamber was used. Maple syrup was diluted to 20 °Brix and poured in Petri dishes to a sample-thickness of 3 mm. Then, samples were frozen at −40°C overnight before FD. The FD experiment was done by setting the shelf temperature at −36°C for 15 hr and successively at +30°C for 10 hr. The freeze-dryer condenser was operated at −90°C and vacuum was maintained below 30 mTorr. Freeze-dried MSP without extract (control), with SBX, and with RBX will be indicated as FD:MSP, FD:MSP + SBX, and FD:MSP + RBX, respectively. The FD samples were ground with spatula on flat surface until no lump of powder was noticed.

A laboratory-scale vacuum double-drum dryer (Buflovak Group, Buffalo, NY) such as the one depicted in Figure 1 was used to produce powder of polyphenol-enriched maple sugar. Vacuum double-drum dryer (VDD) was comprised of two metal drums that were internally heated by steam at 12 psig and operated under fixed vacuum of 660 Torr. Nip gap (clearance between two drums) was adjusted at

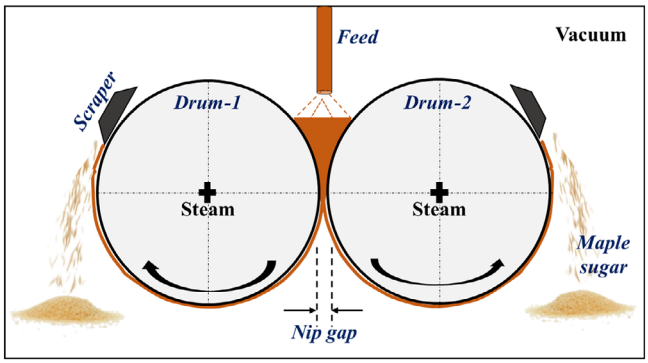

FIGURE 1 Schematic diagram of vacuum double-drum dryer (VDD) used for the development of maple sugar powder. Drum-1 and Drum-2 were internally heated with steam; vacuum was applied in the chamber

0.03 mm for allowing maple syrup to flow when drum rotates. From preliminary experiments, the rotational speed of drum was selected to obtain the homogenous dried maple sugar (less than 5% moisture content, dry basis). Maple syrup was fed with the aid of suction (created by vacuum) over the nip area. A constant feed level was maintained by adjusting the feed flow rate with the valve. A thin layer of maple syrup initiated to dry in approximately three fourth of the revolution of the drums. The dried maple sugar was scraped off from the drum surface using the in-built scrapers. The initial and final drum surface temperature measured by infrared thermometer (RAYMT6U, Raytek, QC, Canada) was 80 ± 5 and 103 ± 2°C, respectively. The obtained maple sugars were the mixture of maple big to small flakes, rolls, and powder. For further analysis, only flakes and powders were considered. Most of the big flakes were crumbled to small flakes or coarse granules when they were vacuum-packaged. As a result, VDD samples were mixture of coarse granules and powders. Vacuum double-drum dried MSP without extract (control), with SBX, and with RBX will be labeled as VDD:MSP, VDD:MSP + SBX, and VDD:MSP + RBX, respectively.

Each drying experiment was conducted three times. MSP was vacuum packed and then stored at 4°C for future analysis.

2.4 | Analyses of sample

2.4.1 | Sugar composition

Sugar compositions of samples were determined by HPLC with refractive index (HPLC–RI) following the method previously used (Bhatta et al., 2018). Column and detector used for sugar analysis was Sugar-Pak-I (6.5 × 300 mm; Waters, MA) and refractive index detector (Hitachi L-7490), respectively. Sugar compositions were quantified using sucrose, glucose, and fructose as standard as expressed in milligram per gram sample on dry basis (mg/g dry sample).

2.4.2 | Total phenolic content and antioxidant activity

The total phenolic content (TPC) was determined by the Folin–Ciocalteu method in 96-well plates using the method described in literature (Zhang et al., 2006). Briefly, 20 μL of standards or samples were mixed in 100 μL of Folin–Ciocalteu reagent (diluted, 1:10 vol/vol in water). After 5 min, sodium carbonate (80 μL, 75 g/L) was added to each well and kept in the dark for 30 min before the absorbance was read at 760 nm using microplate spectrophotometer (X Mark, Bio-Rad Laboratories, Hercules, CA). The analysis was performed in triplicate. Gallic acid was used for the standard calibration curve and the results are expressed in milligram gallic acid equivalent per gram of sample on dry basis (mg GAE/g dry sample).

Antioxidant activity of samples was determined by the radical scavenging capacity of the samples against 2, 2-diphenyl-1-picrylhydrazyl (DPPH). DPPH analysis was performed in 96-well microplate as described by (Geoffroy, Fortin, et al., 2017) with slight modification. Briefly, a volume of 100 μL of Trolox (standard) or samples (20 mg/ml) was mixed with 150 μL DPPH (40 mg/ml in methanol). The mixture was subsequently incubated at room temperature in the dark for 30 min before the absorbance was read at 517 nm with microplate spectrophotometer (X Mark, Bio-Rad Laboratories). Trolox (0 to 250 μmol/L) was used for the standard curve and the results were reported in μmol trolox equivalents per gram sugar on dry basis (μM TE/g dry sample).

2.4.3 | Moisture content

Moisture content in MSP was determined by vacuum-oven dry method (Park & Bell, 2004).

2.4.4 | Density, Hausner ratio, and Carr's index

Bulk density was determined by weighing about 1 g (m_s) of sample in 10 ml graduated cylinder and recording the volume occupied by the powder (V_b). For determining the tapped density, the cylindrical glass tube with constant mass of powder (m_s) was repeatedly dropped from the vertical distance of 14 ± 0.5 mm high manually until negligible difference in volume between succeeding measurements were recorded (V_t). The powder bulk (ρ_b) and tapped densities (ρ_t) were then calculated using Equations (1) and (2), respectively.

$$\rho_b = \frac{m_s}{V_b} \quad (1)$$

$$\rho_t = \frac{m_s}{V_t} \quad (2)$$

Hausner ratio (HR) and Carr's index (CI) indicates the cohesiveness and flowability of powder, respectively. HR (Equation 3) and CI (Equation 4) were calculated using the measured value of bulk and tapped densities of a powder as follows:

$$HR = \frac{\rho_t}{\rho_b} \quad (3)$$

$$CI = 1 - \left(\frac{\rho_b}{\rho_t}\right) \times 100\% \quad (4)$$

2.4.5 | Dissolution time

The dissolution test was modified from (Quek, Chok, & Swedlund, 2007). In brief, about 0.5 g of sample was dissolved in 10 ml of water in mini-beaker using magnetic stirrer (Thermix 210 T, Fisher, Edmonton, AB, Canada), stir set at number 4. The dimension of magnet was 12.8 × 3.4 mm (L × diameter). The dissolution time (in seconds) was recorded when the dried sample was fully reconstituted by visual observation.

2.4.6 | Color determination

Color of the sugar samples was measured with a CR-300 Chroma colorimeter (Konica Minolta, Tokyo, Japan), referring to color space CIE

$L^*a^*b^*$, where L^*, a^*, and b^* signifies color brightness, red parameter, and yellow parameter, respectively. Chroma value indicates the color intensity or saturation of the sample and it was calculated using the formula, $(a^{*2} + b^{*2})^{1/2}$. Results are presented as averages of three measurements.

2.4.7 | X-ray diffraction analyses

The crystallinity of maple sugars was analyzed with a powder X-ray diffractometer (Siemens/Bruker, Karlsruhe, Germany). The powder samples were prepared in 0.5 mm diameter capillary glass tube (Charlessupper Company, Natick, MA). Samples were measured under operational conditions of 40 kV and 40 mA using Co ($K\alpha_{1+2}$) radiation and scanned at a diffraction angle (2θ) between 0 and 50° with a step angle of 0.02° and scan rate of 2θ/0.5 s.

2.4.8 | Powder morphology

The morphology of powder samples was examined by scanning electron microscopy (SEM, JSM-6360 Version 1.0, JEOL, Inc., Peabody, MA) operated at an accelerating voltage of 20 kV. The samples were mounted on stubs and coated with thin layer of gold before analysis. All micrographs were photographed at a magnification of ×100, ×300, and ×1,000 at scale bar of 50 and 10 μm, respectively. Micrographs of ×100 were used to estimate the powder particle size using Image J software version 1.52i (National Institutes of Health, Bethesda, MD). Micrographs were accessed with ImageJ software and calibrated to set the scale of image from pixels to μm, following the method previously used (Bhatta et al., 2019). The particle size was measured using the particle analyze tool. The sizes of at least 50 particles was measured and averaged. The results are expressed as average ± *SD*.

2.4.9 | Sorption isotherm

FD and VDD maple sugars (without bark extracts) were studied for their sorption characteristics. About 0.5 g of sample in duplicate at room temperature over various saturated salt solutions (LiCl, CH_3COOK, $MgCl_2$, NaBr, NaCl, and KCl of water activities, 0.11, 0.22, 0.33, 0.58, 0.75, and 0.86, respectively) was kept in desiccators. Sample weight was measured initially and after 3 days, and then at every day during 1 week until constant weight, as mentioned by (Farahnaky, Mansoori, Majzoobi, & Badii, 2016). The equilibrium moisture content was then determined by vacuum-oven drying method.

The Guggenheim–Anderson–de Boer (GAB) model (Equation 5) was applied to fit the experimental data of sorption isotherm of MSP.

$$\frac{X}{X_m} = \frac{CKa_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \quad (5)$$

where X is the equilibrium moisture content (kg H_2O/kg dry solid), X_m is the monolayer moisture content (kg H_2O/kg dry solid), C and K are constants related to the heat of sorption of the monolayer and multilayer region, respectively. The model was fitted to experimental data using regression equation wizard in SigmaPlot 12.5 (Systat Software, Inc., San Jose, CA).

2.5 | Statistical analysis

Analyses of the physicochemical properties of MSP obtained by FD and VDD were performed in triplicate, unless otherwise stated. The values are presented as the Mean ± *SD*. Significant differences among the sample with and without bark extracts as well between the two drying methods were determined by one-way ANOVA (SigmaPlot 12.5, Systat Software, Inc.) followed by Tukey's test at $\alpha = 0.05$.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of polyphenol-enriched maple syrup

The TPC of MS, MS + SBX, and MS + RBX were found to be 8.04 ± 0.31, 9.09 ± 0.21, and 9.62 ± 0.44 mg GAE/g syrup (on dry basis), respectively. This corresponds to an average TPC increase in syrup by 13.05 and 19.65% for SBX and RBX, respectively. Accordingly, antioxidant capacity of MS (17.43 ± 4.72 μM TE/g syrup, in dry basis) increased by an average of 21 and 43% with SBX (21.10 ± 0.39), and RBX (25.00 ± 1.32), respectively. Overall, addition of maple bark extracts, notably red maple bark extract, enriched syrup significantly in polyphenolic content and antioxidant activities.

Figure 2 highlights the ESI (–) chromatogram of ethyl acetate extracted maple syrup (MS, control; Figure 2a), syrup with SBX (MS + SBX; Figure 2b) and with red maple bark extract (MS + RBX, Figure 2c). Polyphenolic compounds were identified based on their mass spectra and HPLC (UV–vis at 270 nm) results, and compared with the available mass spectra data reported in literature on maple products (Geoffroy, Meda, et al., 2017; Liu, Rose, DaSilva, Johnson, & Seeram, 2017; St-Pierre et al., 2014). The identified compounds are summarized in Table 1. From results presented in Table 1 and Figure 2a, indicate that phenolic acids and lignans were the major polyphenols present in maple syrup, which were also previously reported in the literature (Liu et al., 2017; St-Pierre et al., 2014). All three syrup samples were determined to contain 17 compounds in common; however, four additional phenolic compounds (Peaks 1, 4, 5, and 7) were identified in MS + RBX (Figure 2c and Table 1). These compounds were identified to be maplexin A (retention time, t_R = 7.768 min; Peak 1), Ginallin 3,6 (t_R = 10.118 min, Peak 4), Maplexin D (t_R = 10.426 min, Peak 5), and Ginnalin A (t_R = 11.887, min Peak 7). Previous studies have also reported the presence of these four phenolic compounds in the hot water extract of red maple bark and buds (Geoffroy, Meda, et al., 2017; N. R. Meda et al., 2017).

It is interesting to note that there is no Peak 7 (Ginnalin A) in the chromatograms related to the pure maple syrup, nor in the chromatogram obtained for the syrup enriched in SBX. It is, on the other hand,

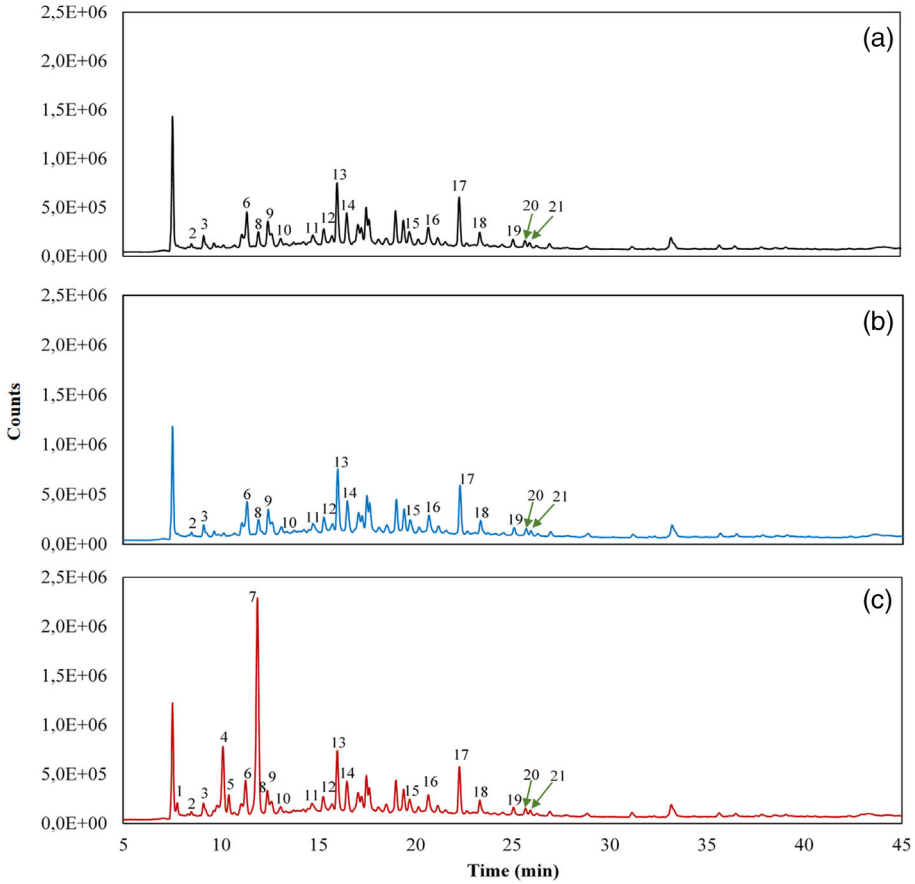

FIGURE 2 ESI(−) chromatogram of ethyl-acetate extracts of (a) maple syrup (MS, control); (b) maple syrup with sugar maple bark extract (MS + SBX); (c) maple syrup with red maple bark extract (MS + RBX). Compound names are listed in Table 1

the major peak in the chromatogram obtained for maple syrup enriched with RBX.

3.2 | Properties of MSP

3.2.1 | Sugar composition

The sugar compositions of maple syrup samples were MS (sucrose, 975.26 ± 1.21; glucose, 37.26 ± 0.25; fructose, 22.09 ± 1.59 mg/g dry sample), MS + SBX (sucrose, 985.04 ± 1.21; glucose, 38.25 ± 0.14; fructose, 22.85 ± 1.40 mg/g dry sample), and MS + RBX (sucrose, 976.57 ± 2.30; glucose, 38.05 ± 0.15; fructose, 21.05 ± 0.58 mg/g dry sample). From the above result, it was found that the sucrose content increased significantly in MS with the addition of SBX. Similarly, glucose content in syrup significantly increased with the addition of SBX as well as RBX. It can be due to the presence of sugars in SBX (sucrose, 10.94 ± 0.11; glucose, 5.28 ± 0.04; and fructose, 5.56 ± 0.03 g/100 g dry extract) and in RBX (sucrose, 5.58 ± 0.08; glucose, 3.51 ± 0.06; and fructose, 4.50 ± 0.92 g/100 g dry extract) (Bhatta et al., 2018). However, no significant change ($p > .05$) in fructose content was noticed for all syrup samples. The sugar composition of FD and VDD powder is presented in Table 2. No significant difference in sucrose content was observed among FD sugar powder samples. On the contrary, MSP + SBX produced from VDD demonstrated the highest sucrose content among all the samples. This could be due to the combined effect of high temperature in VDD and high sucrose content in MS + SBX syrup sample.

3.2.2 | TPC and antioxidant activity

Table 2 summarizes the TPC and antioxidant activity of MSP obtained from FD and VDD process. Drying resulted in a significant decrease in TPC value of powders, by an average of 13–20% and 8–16.7% for FD and VDD, respectively, when compared with initial TPC of syrup samples obtained upon addition of bark extracts. Despite at the higher temperature applied in VDD than in FD, the powders produced by VDD were determined to have somewhat higher TPC (7.40–8.01 mg GAE/g dry sugar) than those obtained by FD (6.97–7.64 mg GAE/g dry sugar). High temperatures in VDD could have caused the cleavage of the glycoside bonds in phenol-glycosides, releasing phenols. As a result, more phenolics become available to form a complex with the Folin's reagent for TPC determination, compared to the FD sample. Similar results were reported in the literature for heat-treated *Citrus unshiu* peels and Shiitake extracts, where TPC was found to increase with higher temperatures during the treatment (Choi, Lee, Chun, Lee, & Lee, 2006; Jeong et al., 2004). Jeong et al. (2004) identified that low molecular weight phenolic compounds such as vanillic acid, ferulic acid, and so forth were newly formed after the heat treatment of citrus peel extract.

Regardless of the type of drying process used, the powders containing bark extracts had higher TPC than the control (MSP). In particular, MSP + RBX presented significantly higher ($p < .05$) TPC than control. This is in agreement with previous results from LC–MS (Section 3.1). Interestingly, among the dried syrup TPC values, VDD:MSP + RBX represented similar TPC ($p > .05$) determined for pure maple syrup (8.04

TABLE 1 Major polyphenols identified in ethyl-acetate extracts of maple syrup samples

Peak	Retention time (min)	High-resolution mass spectroscopy (–)	Mass (g/mol)	Calculated mass (g/mol)	Molecular formula	Compounds identification
1	7.768	315.0722	316.0809	316.0794	$C_{13}H_{16}O_9$	Maplexin A
2	8.500	167.035	168.0441	168.0423	$C_8H_8O_4$	Vanillic acid
3	9.139	109.0295	110.0385	110.0368	$C_6H_6O_2$	Catechol
4	10.118	467.0831	468.0921	468.0904	$C_{20}H_{20}O_{13}$	Ginnalin 3,6
5	10.426	467.0831	468.0926	468.0904	$C_{20}H_{20}O_{13}$	Maplexin D
6	11.365	137.0244	138.0332	138.0317	$C_7H_6O_3$	Catechaldehyde
7	11.887	467.0831	468.0925	468.0904	$C_{20}H_{20}O_{13}$	Ginnalin A
8	11.955	109.0295	110.0384	110.0368	$C_6H_6O_2$	Catechol
9	12.445	151.0401	152.0490	152.0473	$C_8H_8O_3$	Vanillin
10	13.101	515.1923	516.2023	516.1995	$C_{27}H_{32}O_{10}$	Leptolepisol
11	14.754	179.035	180.0440	180.0423	$C_9H_8O_4$	Caffeic acid
12	15.743	419.1711	420.1815	420.1784	$C_{22}H_{28}O_8$	Lyoniresinol
13	16.009	377.1606	378.1702	378.1679	$C_{20}H_{26}O_7$	*threo*-guaiacylglycerol-β-O-4′-dihydroconiferylalcohol
14	16.499	377.1606	378.1704	378.1679	$C_{20}H_{26}O_7$	*erythro*-guaiacylglycerol-β-O-4′-dihydroconiferylalcohol
15	19.721	361.1657	362.1759	362.1729	$C_{20}H_{26}O_6$	Secoisolariciresinol
16	20.702	403.1398	404.1493	404.1471	$C_{21}H_{24}O_8$	Lignanes derivatives
17	22.296	585.2341	586.2439	586.2414	$C_{31}H_{38}O_{11}$	Acernikol
18	23.351	585.2341	586.2439	586.2414	$C_{31}H_{38}O_{11}$	Neolignanes derivatives
19	25.062	613.2291	614.2395	614.2363	$C_{32}H_{38}O_{12}$	Lignanes derivatives
20	25.677	583.2185	584.2287	584.2258	$C_{31}H_{36}O_{11}$	Buddlenol E
21	25.918	809.3026	810.3131	810.3099	$C_{42}H_{50}O_{16}$	Lignan derivatives

Abbreviation: HRMS, high-resolution mass spectroscopy.

TABLE 2 Total phenolics, antioxidant activity, and sugar compositions of maple sugar powders

Process	Sample	TPC (mg GAE/g dry sample)	DPPH (μM TE/g dry sample)	Sugar compositions (mg/g dry sample)		
				Sucrose	Glucose	Fructose
FD	MSP	6.97 ± 0.07^{bcf}	8.20 ± 3.04^{a}	863.95 ± 2.55^{a} (95%)	32.93 ± 0.22^{a} (3%)	18.73 ± 0.15^{a} (2%)
	MSP + SBX	7.26 ± 0.23^{ce}	10.63 ± 1.13^{a}	872.06 ± 1.81^{a} (95%)	33.01 ± 0.76^{a} (3%)	18.54 ± 1.32^{a} (2%)
	MSP + RBX	7.64 ± 0.17^{ae}	11.99 ± 1.50^{a}	865.06 ± 3.55^{a} (95%)	30.69 ± 0.11^{cd} (3%)	18.34 ± 1.06^{a} (2%)
VDD	MSP	7.40 ± 0.03^{def}	7.90 ± 2.93^{a}	826.13 ± 0.66^{b} (95%)	31.05 ± 0.60^{bd} (3%)	18.40 ± 0.47^{a} (2%)
	MSP + SBX	7.59 ± 0.33^{ae}	10.28 ± 1.09^{a}	894.92 ± 1.03^{a} (95%)	33.78 ± 0.18^{a} (3%)	18.86 ± 1.27^{a} (2%)
	MSP + RBX	8.01 ± 0.32^{a}	11.57 ± 1.45^{a}	834.60 ± 0.12^{a} (95%)	32.35 ± 0.09^{ad} (3%)	17.43 ± 0.53^{a} (2%)

Notes: Values represent mean ± *SD*. Means with difference superscript letters in columns are significantly different by Tukey's test ($p < .05$).
Abbreviations: FD, freeze-drying; GAE, gallic acid equivalent; MSP, maple sugar powders; RBX, red maple bark extract; TE, trolox equivalent; TPC, total phenolic content; VDD, vacuum double-drum drying.

± 0.31 mg GAE/g syrup, in dry basis). Thus, an addition of RBX to syrup (0.01% wt/vol) seems to compensate for the negative effect of the drying process itself on phenolic content causing its reduction.

The results of antioxidant activities of MSP determined by DPPH assay are shown in Table 2. Similarly to TPC results, decrease in antioxidant activity was noticed when syrup samples were dried by FD and VDD. MSP containing bark extracts were determined to have higher antioxidant activity than of the control. MSP with RBX had the highest antioxidant activity among studied sugar powders. However, the results were neither statistically significant ($p > .05$) among syrup with bark extracts added, nor between the studied drying processes.

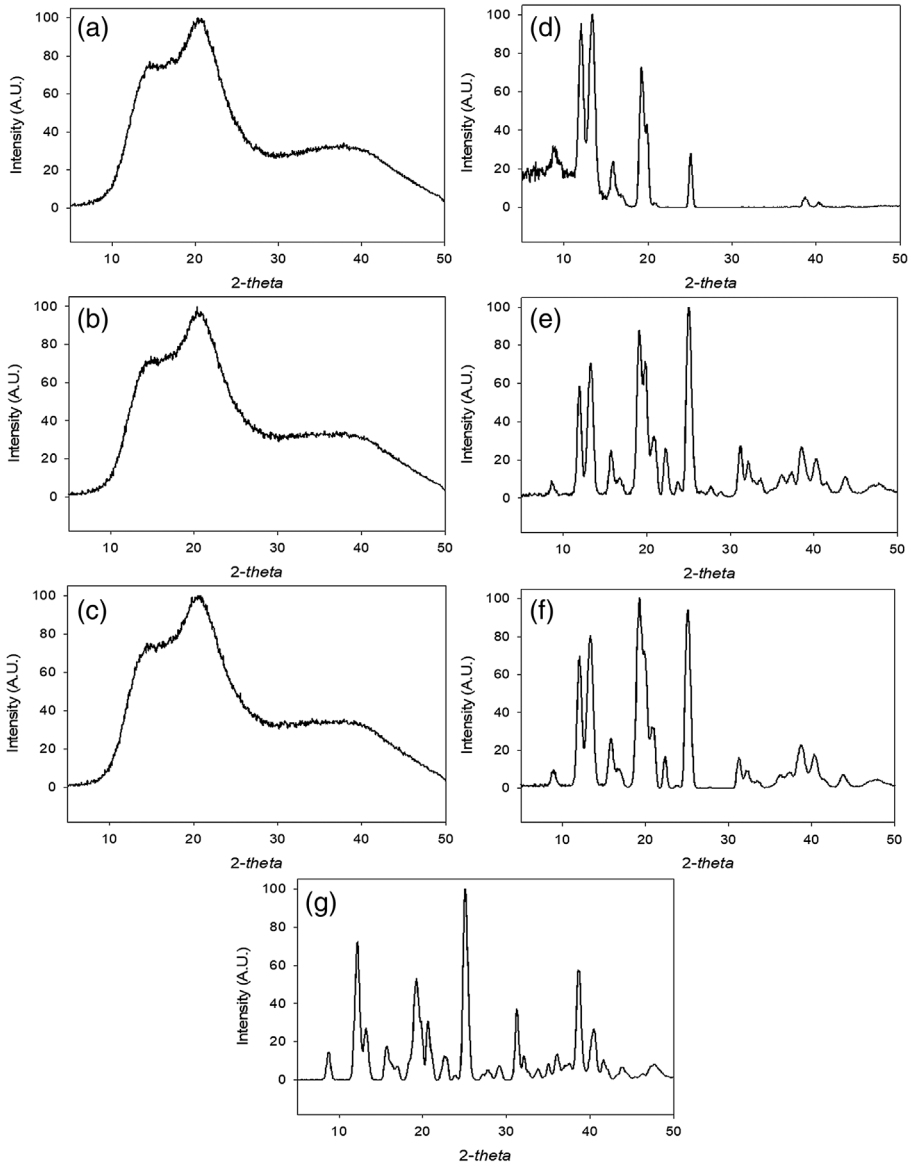

FIGURE 3 X-ray diffractograms of maple sugar powders achieved from FD (a–c) and VDD (d–f) methods. (a) FD:MSP; (b) FD:MSP + SBX; (c) FD:MSP + RBX; (d) VDD:MSP; (e) VDD:MSP + SBX; (f) VDD:MSP + RBX; and (g) powdered sucrose crystal for the reference. FD, freeze-drying; MSP, maple sugar powders; RBX, red maple bark extract; VDD, vacuum double-drum drying

3.2.3 | Microstructure of powder

Figure 3 depicts the X-ray diffractograms of powders produced by FD and VDD. For amorphous material, the diffractograms patterns are large and disperse due to disorderly arranged molecules, whereas XRD patterns of crystalline material shows sharp and defined patterns indicating that the molecules are present in a highly ordered state. As seen from Figure 3, powders obtained from FD (Figure 3a–c) were amorphous in nature and there was no observable effect of the type of bark extract added (Figure 3b,c). This could be explained by low mobility of solutes in frozen state, lacking enough energy to rearrange in a more ordered, crystalline form (Palzer, Dubois, & Gianfrancesco, 2012). It is reported that FD of sucrose solutions and other sugar-rich foods such as mango powder, produced usually an amorphous powders (Caparino et al., 2012; Harnkarnsujarit & Charoenrein, 2011; Y. Roos & Karel, 1991).

The X-ray diffractograms of powders obtained by VDD has the characteristic crystalline pattern (Figure 3d–f). A significant effect of addition of bark extract on crystallinity has been noticed in terms of XRD patterns. VDD:MSP (control, in Figure 3d) presented lesser sharp peaks (indicating the presence of amorphous and crystalline states) as presented for VDD:MSP + SBX (Figure 3e) and VDD:MSP + RBX (Figure 3f). The sharper peaks observed in diffractograms of VDD:MSP + SBX compared to VDD:MSP + RBX can be associated to their difference in sugar composition, discussed in Section 3.2.1. The sucrose added through extracts may have contributed to the initiation of sugar crystallization during the VDD process. The crystallinity of powders obtained from VDD could also be related to the high drying temperature. During experiment, the drum surface temperature increased from 75°C (before vacuum is applied) to 105°C (by the end of experiment), therefore increasing the product temperature. An increase in the difference of product temperature and glass transition temperature (T_g) of sucrose (62°C, [Y. H. Roos, 1993]) may have lowered viscosity, finally resulting in the formation of crystals during VDD process. Similarly to our results, Islam and Langrish reported that increase in $T - T_g$ initiated the crystallization of lactose during spray drying, which was explained by the William–Landel–

Ferry theory (Islam & Langrish, 2010; Islam, Sherrell, & Langrish, 2010). Above T_g, the food materials change from glassy to rubbery state that results in decrease in system viscosity and thus allowing for the rearrangement of molecules to form crystals. The pattern of the VDD diffractograms, particularly for powder containing bark extracts, were comparable to that of pure sucrose powder (included for comparison, Figure 3g).

3.2.4 | Morphology and particle size

The morphology of sugar powder particles was studied by SEM. Figure 4 illustrates the morphology of powders obtained by FD (Figure 4a–f) and VDD (Figure 4g–l). As seen in Figure 4a–c, particles of FD powders presented smooth flat surface with elongated shape and no homogeneity. Similar results were reported for freeze-dried blackberries and date powders (Franceschinis, Salvatori, Sosa, & Schebor, 2014; Seerangurayar, Manickavasagan, Al-Ismaili, & Al-Mulla, 2017). Porous-like structure can also be observed on the magnified images (×1000) (Figure 4d–f), characteristic of freeze-dried food powders (Palzer et al., 2012). The particle size ranges of FD powders were determined to be between 113 ± 82.7 and 131 ± 73.5 μm, similar to the results reported for FD date powders (Seerangurayar et al., 2017). The particles of FD:MSP powder (113 ± 82.7 μm) was relatively smaller than those of powder with bark extracts, 131 ± 73.5 and 114 ± 82.2 μm for FD:MSP + SBX, and FD:MSP + RBX, respectively. The presence of sugars in bark extracts in different proportion could have resulted in discrepancies in the particle size.

On the other hand, VDD powders also displayed irregular particles with rough and grainy surfaces (Figure 4g–l for the magnification of ×300 and ×1,000, respectively). VDD:MSP powder showed islands of grains (Figure 4g,j), these grains (sugar crystals) are found to be surrounded by amorphous sugars (liquid/glass like). This is similar to the XRD pattern observed of VDD:MSP (Section 3.2.3), indicating the presence of both amorphous and crystalline states. VDD powders with maple bark extracts (MS + SBX, Figure 4h,k, and MS + RBX, Figure 4i,l) have considerably different particle morphology and size distribution from the control (MSP, Figure 4g,j). For instance, the surface of VDD:MSP + SBX particles has remarkably textured appearance due to the presence of sucrose crystals in larger proportion than in VDD:MSP + RBX and VDD:MSP. It is also observed that the surfaces of some particles of VDD powders were smooth, while rough and corrugated on other side (clearly visible in Figure 4i). The smooth surface could be due to the direct contact of sample with drum surface, which is a common characteristic of VDD. Similar observation was reported when mango powder was produced by double-drum drying (Caparino et al., 2012).

In comparison to FD, powders obtained by VDD presented smaller particle size, ranging between 58 ± 23.3 and 94 ± 60.4 μm. Among VDD powder, the particle size of VDD:MSP + SBX was smaller (58 ± 23.3 μm) than VDD:MSP + RBX (94 ± 60.4 μm) and VDD:MSP (83.1

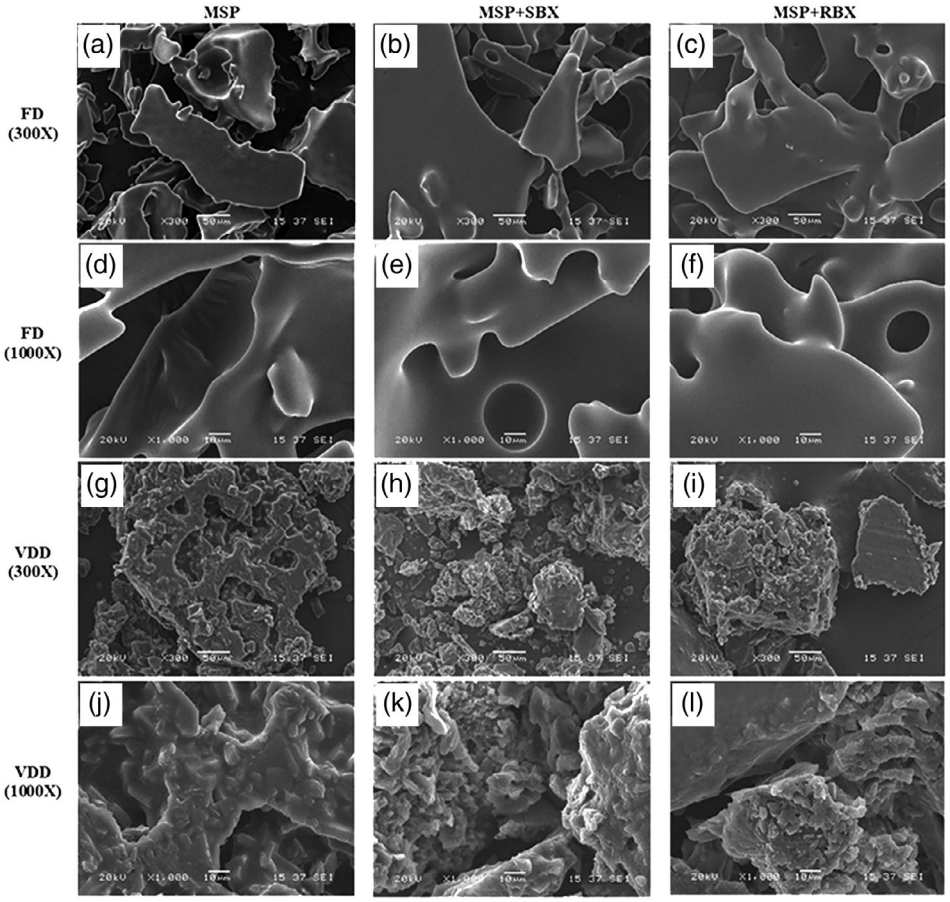

FIGURE 4 Morphologies of maple sugar powder achieved from FD (a–f) and VDD (g–l) using scanning electron microscopy. ×300 (a–c for FD:MSP, FD:MSP + SBX, and FD:MSP + RBX, respectively; g–i for VDD:MSP, VDD:MSP + SBX, and VDD:MSP + RBX, respectively); and ×1,000 (d–f for FD:MSP, FD:MSP + SBX, and FD:MSP + RBX, respectively; j–l for VDD:MSP, VDD:MSP + SBX, and VDD:MSP + RBX, respectively). FD, freeze-drying; MSP, maple sugar powders; RBX, red maple bark extract; VDD, vacuum double-drum drying

± 66.7 μm). Besides sucrose, SBX was reported to be rich in complex sugars (oligo/poly-saccharides) (Bhatta et al., 2018). The presence of sucrose may have assisted sucrose crystallization (as discussed in Section 3.2.3), but further growth of crystals may have been disturbed by the presence of complex sugars in SBX. It has been described in the literature (Hartel & Shastry, 1991) that the presence of macromolecules such as proteins, oligosaccharides, and dextrans can inhibit the growth of sucrose crystal and influence the mode of attachment of sugar molecules to the crystal lattice when such macromolecules are absorbed to crystal surface. Overall, FD and VDD produced MSP with different surface morphology and particle size that may affect their functional properties such as dissolution and flow characteristics.

3.2.5 | Moisture content, color, and dissolution time of MSP

Moisture contents of FD and VDD MSP are presented in Table 3. No significant ($p > .05$) difference in moisture content was found between different powder samples if produced by the same drying process. However, a significant effect ($p < .05$) of drying processes on moisture content is found. The moisture content of FD MSP was in the range of 4.10–4.40% on dry basis. It is in agreement with the reported value (<5% in dry basis) of FD maple sugar (Bhatta et al., 2019). The moisture content of VDD powders was in the range of 0.63–0.71%, dry basis. Lower moisture content in VDD powders can be attributed to higher drying temperature in VDD (>80°C), providing greater driving force for moisture removal, than in FD. Similarly, the moisture content of mango powder obtained by double-drum drying (1.3%, dry basis) was reported to be lower than obtained by FD (Caparino et al., 2012). Generally, low moisture content is preferred for food powders to avoid caking and stickiness during handling and processing (Fitzpatrick, 2013).

Color of food powder is a very important attribute from the consumer's point of view. The color parameters ($L^*a^*b^*$) and Chroma value of powders produced by FD and VDD are presented in Table 3. L^*-value was higher for FD powders (78.68–80.64) in comparison to VDD (72.16–73.20). This means VDD produced darker maple sugars than FD, probably due to the higher drying temperature during the process. Such effect has been confirmed on mango and jackfruit puree powder, in which high drying temperature process produced dark colored powder (Caparino et al., 2012; Pua et al., 2010). Maple syrup contains sucrose, glucose, and fructose (Ball, 2007). Therefore, brown color can be induced by Maillard reaction or caramelization due to the chemical reactions between sugars and proteins which are present both in maple syrup and in the extracts (Caparino et al., 2012; Pua et al., 2010). L^*-value of FD powders in this study is consistent with the values previously reported from our studies (Bhatta et al., 2019). Powder produced by VDD have shown significantly higher a^*- and b^*- values, indicating more redness and yellowness in color, respectively, than powders produced by FD (Table 3). Increase in redness of VDD powders can be associated to increase in browning or decrease in L^* value. At last, higher Chroma value or vividness was determined for VDD powders than for FD powders. Different surface morphologies could explain the differences in color parameters of MSP obtained by FD and VDD. As the color is measured by the amount of light reflected from the dried surface, therefore changes in surface morphology or porosity of FD and VDD powders have considerably affected the amount of light reflected (Ozkan, Cemeroglu, & Kirca, 2003; Palzer et al., 2012).

Table 3 shows the dissolution time of powders produced by FD and VDD. The dissolution characteristics of powder can provide an important information for its use as instant-powder. FD maple sugars dissolved significantly ($p < .05$) faster than VDD maple sugars. From Table 3, the dissolution time for FD maple sugars was less than 13 s, whereas it was around 29 s for VDD maple sugars. Dissolution time of MSP obtained by FD was comparable to the literature (Bhatta et al., 2019). Foods and food powders produced by FD are generally highly porous (discussed in Section 3.2.4) resulting in an increase of surface area for dissolution (L. Meda & Ratti, 2005; Palzer et al., 2012). Furthermore, FD powder is amorphous; therefore, it was easier to dissociate molecules compared to highly ordered crystalline VDD powder. Dissolution times of FD and VDD MSP with bark extracts were not significantly different ($p > .05$) from those for control. Skimmed milk powders that dissolve in less than 15 s is termed "instant" (Sharma, Jana, & Chavan, 2012). Therefore, FD powder showed instant-like property in this study. Dried syrup powders can be used as natural food ingredients, for example, in instant drinks, dairy powder mix, sweet snacks, beverage, ice cream, candy, and so forth.

TABLE 3 Moisture content, color, and dissolution time of maple sugar powders

				Color analysis			
Process	Sample	Moisture (% db)	Dissolution (s)	L^*	a^*	b^*	Chroma value
FD	MSP	4.40 ± 0.38^a	12.90 ± 1.0^b	78.68 ± 1.48^a	0.67 ± 0.02^b	17.07 ± 0.01^b	17.08 ± 0.01^b
	MSP + SBX	4.16 ± 0.74^a	12.80 ± 0.57^b	78.97 ± 0.03^a	0.99 ± 0.01^b	18.40 ± 0.01^b	18.42 ± 0.01^b
	MSP + RBX	4.10 ± 0.64^a	12.20 ± 1.75^b	80.64 ± 0.25^a	0.59 ± 0.07^b	16.83 ± 0.01^b	16.84 ± 0.01^b
VDD	MSP	0.63 ± 0.30^b	28.80 ± 3.51^a	73.20 ± 0.05^a	2.10 ± 0.02^a	22.75 ± 0.05^a	22.85 ± 0.04^a
	MSP + SBX	0.69 ± 0.05^b	28.80 ± 2.25^a	72.62 ± 1.08^a	1.86 ± 0.17^a	21.06 ± 0.42^a	21.14 ± 0.43^a
	MSP + RBX	0.71 ± 0.29^b	27.1 ± 2.20^a	72.16 ± 2.34^b	1.94 ± 0.45^a	21.97 ± 1.05^a	22.06 ± 1.08^a

Notes: Values represent mean ± *SD*. Means with difference superscript letters in columns are significantly different by Tukey's test ($p < .05$).
Abbreviations: db, dry basis; FD, freeze-drying; GAE, gallic acid equivalent; MSP, maple sugar powders; RBX, red maple bark extract; TE, trolox equivalent; TPC, total phenolic content; VDD, vacuum double-drum drying.

TABLE 4 Density and flow characteristics of maple sugar powders

Process	Sample	Bulk density (g/ml)	Tapped density (g/ml)	Hausner ratio	Cohesiveness	Carr's index (%)	Flow characteristic
FD	MSP	0.27 ± 0.01[a]	0.39 ± 0.00[a]	1.45 ± 0.03[a]	High	30.82 ± 1.43[a]	Fair
	MSP + SBX	0.27 ± 0.01[a]	0.39 ± 0.01[a]	1.48 ± 0.07[a]	High	32.13 ± 3.04[a]	Fair
	MSP + RBX	0.26 ± 0.01[a]	0.38 ± 0.01[a]	1.47 ± 0.06[a]	High	31.75 ± 2.62[a]	Fair
VDD	MSP	0.35 ± 0.01[b]	0.40 ± 0.01[a]	1.14 ± 0.02[b]	Low	12.34 ± 1.73[b]	Very good
	MSP + SBX	0.33 ± 0.02[b]	0.40 ± 0.01[a]	1.20 ± 0.04[b]	Low	16.78 ± 3.10[b]	Good
	MSP + RBX	0.33 ± 0.01[b]	0.40 ± 0.00[a]	1.22 ± 0.02[b]	Intermediate	17.69 ± 1.38[b]	Good

Notes: Values represent mean ± *SD*. Means with difference superscript letters in columns are significantly different by Tukey's test ($p < .05$).
Abbreviations: FD, freeze-drying; GAE, gallic acid equivalent; MSP, maple sugar powders; RBX, red maple bark extract; TE, trolox equivalent; TPC, total phenolic content; VDD, vacuum double-drum drying.

3.2.6 | Flowability of powder

The results on densities and calculated flowability of powders produced by FD and VDD are presented in Table 4. Addition of bark extracts resulted in no significant difference on powder densities and flowability when produced by the same drying process. Bulk densities of FD powders (0.26–0.27 g/ml) were significantly lower ($p < .05$) than those of VDD powders (0.33–0.35 g/ml). Similarly, the bulk density of FD mango powder was reported to be lower than drum-dried powder (Caparino et al., 2012). High bulk density of VDD MSP can be associated to its small particle size (presented in Section 3.2.4), which allows for the particles to rearrange in a lesser space. Similar tendency of increase in bulk density with decrease in particle size was observed for date syrup powders (Seerangurayar et al., 2017). Tapped density of MSP was higher than bulk density because tapping allowed the smaller particles to occupy the void spaces and thus achieve the dense packing conditions (Seerangurayar et al., 2017). The tapped densities of MSP obtained from the two drying processes were not significantly different ($p = .074$).

HR was calculated using the bulk and tapped density of powder, and the obtained values are presented in Table 4. According to the literature (Hausner, 1967), the cohesiveness of powder is considered high for HR values higher than 1.4, intermediate for the values between 1.2 and 1.4, and low for values lower than 1.2. The HR values of MSP produced by FD and VDD were 1.45–1.47 and 1.14–1.22, respectively. These values indicate that FD powders are highly cohesive, whereas VDD powders are low to intermediate in cohesiveness (Table 4). The HR value of FD MSP was comparable to a previous study (Bhatta et al., 2019). HR value is inversely related to powder flowability (Fitzpatrick, 2013).

The flowability of MSP produced by FD and VDD was characterized by CI, shown in Table 4. Based on CI, the powder's flowability is considered as very good for the value less than 15%, good flow by values between 15 and 20%, fair flow by values between 21 and 35%, bad flow by values between 36 and 45%, and very bad flow when values of CI is greater than 45% (Carr, 1965). The CI values of MSP produced by FD and VDD in this study are 30.82–32.13 and 12.34–17.69%, respectively. These values designate the fair flowability for FD powder, whereas good to very good flowability for VDD powders. Differences in flowability of FD and VDD powders can be explained by differences in previously discussed values of cohesiveness (HR values). Overall, powder produced by VDD demonstrated low cohesiveness and better flowability than powder produced by FD.

3.2.7 | Sorption isotherm

The sorption isotherm curves of FD and VDD MSP at ambient temperature is presented in Figure 5. Only dried samples without bark

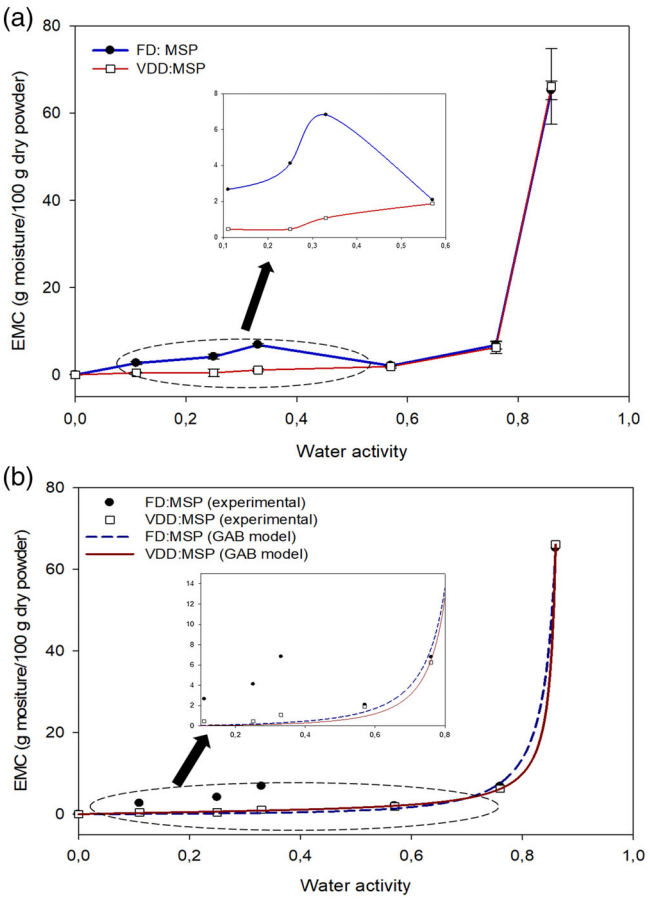

FIGURE 5 Sorption isotherm curve of FD and VDD maple sugar powder. (a) Experimental data; (b) curve fitted with GAB model. FD: MSP (filled circle); VDD:MSP (open square). EMC, equilibrium moisture content; FD, freeze-drying; MSP, maple sugar powders; RBX, red maple bark extract; VDD, vacuum double-drum drying

TABLE 5 The GAB model parameters of maple sugar powders from FD and VDD

GAB parameters	FD:MSP	VDD:MSP
X_m	0.0211	0.0082
K	1.130	1.148
C	0.168	3.200
R^2	0.9797	0.9999

Note: X_m, monolayer water content (g water/g dry solids).
Abbreviations: FD, freeze-drying; GAB, Guggenheim–Anderson–de Boer; MSP, maple sugar powders; VDD, vacuum double-drum drying.

extract were studied to understand the sorption characteristics of amorphous (produced by FD) and crystalline (VDD) MSP matrices. As expected from XRD results, MSP obtained from FD and VDD showed similarities in terms of characteristic isotherm curves for amorphous and crystalline sucrose, respectively (Mathlouthi & Rogé, 2003). The distinct differences in the two curves are observed in the encircled section of the Figure 5a. For FD:MSP, the equilibrium moisture content (EMC) increased abruptly from 0.11 to 0.36a_w, which was followed by decrease in EMC from 0.36 to 0.56a_w. The decrease in EMC can be associated with amorphous FD sucrose crystallization, since the molecular mobility of sucrose at higher water activity may have increased leading to the formation of sucrose crystals (Mathlouthi & Rogé, 2003). For VDD:MSP, one can note that the powder absorbs very little moisture over the range of 0.11 to 0.56a_w. However, both samples showed isotherm curves with similar characteristics with an exponential increase in EMC above 0.76a_w. Such exponential increase in EMC at high water activity (>0.76a_w) was also reported for crystalline sucrose and lactose powder (Bronlund & Paterson, 2004; Mathlouthi & Rogé, 2003). At high a_w, there is a phase transition from solid to solution, induced by water uptake from surrounding environment. The relative humidity at which the crystalline sucrose adsorbs water in large quantities from the atmosphere is often called deliquescence point (Palzer et al., 2012).

The fitted GAB model and its parameters for MSP obtained from different drying methods are presented in Figure 5b, and Table 5, respectively. The fitness of GAB model to describe the sorption isotherm was better for VDD:MSP (R^2 = .9999) than for FD:MSP (0.9797). Monolayer moisture content (X_m) refers to the amount of water strongly adsorbed to specific sites at the surface of food materials, and it is an important parameter for assuring food stability. The value of X_m was determined to be 0.021 (g water/g solid) and 0.008 for FD:MSP and VDD:MSP samples, respectively. The moisture contents of MSP (Table 2) obtained from both drying methods were below or similar to their respective X_m values, indicative of good product stability over time. In the present study, the value of K was found to be 1.13 and 1.14 for FD:MSP and VDD:MSP samples, respectively. The obtained K values are comparable to those determined for other sugar-rich dehydrated food products, ranging between 1.009 for freeze-dried mango pulp powder and 1.10–1.20 for vacuum-dried honey powder (Fongin, Kawai, Harnkarnsujarit, & Hagura, 2017; Nurhadi & Roos, 2016). Considering the studied sorption isotherms (Figure 5a), the obtained powders should be stored below 0.36a_w for FD:MSP, whereas below 0.56a_w for VDD:MSP, at ambient temperature, to avoid the physicochemical changes in powder.

4 | CONCLUSION

The addition of maple bark extracts to low quality maple syrup is an interesting way of valorizing the surplus of this substandard grade of syrup. The addition of sugar and red maple bark extracts at low level of 0.01% wt/vol resulted in syrup enrichment in polyphenols by 13 and 20% respectively. The LC–MS results confirmed the presence of 17 phenolic compounds in syrup and extract enriched syrup samples; however, four additional phenolic compounds were identified in syrup with RBX. Furthermore, in order to facilitate the distribution and to widen its application as natural food ingredients, syrup was successfully dehydrated using FD and VDD to produce free-flowing MSP. After drying of maple syrup with bark extracts, the obtained MSP were determined to have 8–10% higher TPC with RBX than the control. The differences in physicochemical properties of powders are mainly due to the differences in the drying method. FD produced amorphous and instant-like powder, whereas VDD produced crystalline powder with excellent flow characteristics. Apart from the effect of bark extracts on crystallinity of VDD powder, no significant differences were observed in terms of properties of powder such as moisture content, dissolution, densities, and flowability. Overall, MSPs have huge potential of use in instant foods, and as functional food ingredients, particularly for the development of natural food products. Future studies shall focus on the storage stability of polyphenols within different microstructural MSP matrices in order to enhance their use as natural ingredients.

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REFERENCES

Agriculture and Agri-food Canada. (2018). Statistical overview of the Canadian maple industry 2017. Retrieved from http://www.agr.gc.ca/resources/prod/doc/pdf/st_ovrv_maple_2017-eng.pdf

Apostolidis, E., Li, L., Lee, C., & Seeram, N. P. (2011). In vitro evaluation of phenolic-enriched maple syrup extracts for inhibition of carbohydrate hydrolyzing enzymes relevant to type 2 diabetes management. *Journal of Functional Foods*, *3*(2), 100–106. https://doi.org/10.1016/j.jff.2011.03.003

Arnason, T., Hebda, R. J., & Johns, T. (1981). Use of plants for food and medicine by native peoples of eastern Canada. *Canadian Journal of Botany*, *59*(11), 2189–2325. https://doi.org/10.1139/b81-287

Ball, D. W. (2007). The chemical composition of maple syrup. *Journal of Chemical Education*, *84*(10), 1647. https://doi.org/10.1021/ed084p1647

Bhandari, B. (2013). Introduction to food powders. In *Handbook of food powders: Processes and properties* (pp. 1–25). Cambridge, England: Woodhead Publishing Limited. https://doi.org/https://doi.org/10.1533/9780857098672.1

Bhandari, B. R., Datta, N., & Howes, T. (1997). Problems associated with spray drying of sugar-rich foods. *Drying Technology*, *15*(2), 671–684. https://doi.org/10.1080/07373939708917253

Bhatta, S., Ratti, C., Poubelle, P. E., & Stevanovic, T. (2018). Nutrients , antioxidant capacity and safety of hot water extract from sugar maple (*Acer saccharum* M.) and red maple (*Acer rubrum* L.) bark. *Plant Foods for Human Nutrition*, *73*(1), 25–33.

Bhatta, S., Stevanovic, T., & Ratti, C. (2019). Freeze-drying of maple syrup : Efficient protocol formulation and evaluation of powder physicochemical properties. *Drying Technology*, *0*(0), 1–13. https://doi.org/10.1080/07373937.2019.1616751

Bronlund, J., & Paterson, T. (2004). Moisture sorption isotherms for crystalline, amorphous and predominantly crystalline lactose powders. *International Dairy Journal*, *14*(3), 247–254. https://doi.org/10.1016/S0958-6946(03)00176-6

Canadian Food Inspection Agency. (2016). Colour classes of maple syrup. Retrieved from http://www.inspection.gc.ca/food/labelling/food-labelling-for-industry/maple-products/eng/1392414400422/1392414462687?chap=8

Caparino, O. A., Tang, J., Nindo, C. I., Sablani, S. S., Powers, J. R., & Fellman, J. K. (2012). Effect of drying methods on the physical properties and microstructures of mango (Philippine "Carabao" var.) powder. *Journal of Food Engineering*, *111*(1), 135–148. https://doi.org/10.1016/j.jfoodeng.2012.01.010

Carr, R. L. (1965). Evaluating flow properties of solids. *Chemical Engineer*, *18*, 163–168.

Choi, Y., Lee, S. M., Chun, J., Lee, H. B., & Lee, J. (2006). Influence of heat treatment on the antioxidant activities and polyphenolic compounds of shiitake (Lentinus edodes) mushroom. *Food Chemistry*, *99*(2), 381–387. https://doi.org/10.1016/j.foodchem.2005.08.004

Daud, W. R. W. (2006). Drum Dryers. In *Handbook of industrial drying: Third edition* (Vol. 28, pp. 1–12). Boca Raton, FL: CRC press. https://doi.org/10.1021/ie50313a003

Farahnaky, A., Mansoori, N., Majzoobi, M., & Badii, F. (2016). Physicochemical and sorption isotherm properties of date syrup powder : Antiplasticizing effect of maltodextrin. *Food and Bioproducts Processing*, *98*, 133–141. https://doi.org/10.1016/j.fbp.2016.01.003

Fitzpatrick, J. J. (2013). Powder properties in food production systems. In *Handbook of food powders: Processes and properties* (pp. 285–308). Cambridge, England: Woodhead Publishing Limited.

Fongin, S., Kawai, K., Harnkarnsujarit, N., & Hagura, Y. (2017). Effects of water and maltodextrin on the glass transition temperature of freeze-dried mango pulp and an empirical model to predict plasticizing effect of water on dried fruits. *Journal of Food Engineering*, *210*, 91–97. https://doi.org/10.1016/j.jfoodeng.2017.04.025

Franceschinis, L., Salvatori, D. M., Sosa, N., & Schebor, C. (2014). Physical and functional properties of blackberry freeze- and spray-dried powders. *Drying Technology*, *32*(2), 197–207. https://doi.org/10.1080/07373937.2013.814664

Geoffroy, T. R., Fortin, Y., & Stevanovic, T. (2017). Hot-water extraction optimization of sugar maple (*Acer saccharum* marsh.) and red maple (*Acer rubrum* l.) bark applying principal component analysis. *Journal of Wood Chemistry and Technology*, *37*, 1–12. https://doi.org/10.1080/02773813.2017.1279631

Geoffroy, T. R., Meda, N. R., & Stevanovic, T. (2017). Suitability of DPPH spiking for antioxidant screening in natural products: The example of galloyl derivatives from red maple bark extract. *Analytical and Bioanalytical Chemistry*, *409*(22), 5225–5237. https://doi.org/10.1007/s00216-017-0465-9

González-Sarrías, A., Li, L., & Seeram, N. P. (2012). Effects of maple (Acer) plant part extracts on proliferation, apoptosis and cell cycle arrest of human tumorigenic and non-tumorigenic colon cells. *Phytotherapy Research*, *26*(7), 995–1002. https://doi.org/10.1002/ptr.3677

González-Sarrías, A., Li, L., Seeram, N. P., & Gonza, A. (2012). Anticancer effects of maple syrup phenolics and extracts on proliferation, apoptosis, and cell cycle arrest of human colon cells. *Journal of Functional Foods*, *4*(1), 185–196. https://doi.org/10.1016/j.jff.2011.10.004

Harnkarnsujarit, N., & Charoenrein, S. (2011). Effect of water activity on sugar crystallization and β-carotene stability of freeze-dried mango powder. *Journal of Food Engineering*, *105*(4), 592–598. https://doi.org/10.1016/j.jfoodeng.2011.03.026

Hartel, R. W., & Shastry, A. V. (1991). Sugar crystallization in food products. *Critical Reviews in Food Science and Nutrition*, *30*(1), 49–112. https://doi.org/10.1080/10408399109527541

Hausner, H. H. (1967). *Friction conditions in a mass of metal powder*. University of California, Los Angeles: Polytechnic Inst. of Brooklyn.

Islam, M. I. U., & Langrish, T. A. G. (2010). An investigation into lactose crystallization under high temperature conditions during spray drying. *Food Research International*, *43*(1), 46–56. https://doi.org/10.1016/j.foodres.2009.08.010

Islam, M. I. U., Sherrell, R., & Langrish, T. A. G. (2010). An investigation of the relationship between glass transition temperatures and the crystallinity of spray-dried powders. *Drying Technology*, *28*(3), 361–368. https://doi.org/10.1080/07373931003641586

Jeong, S.-M., Kim, S.-Y., Kim, D.-R., Jo, S.-C., Nam, K. C., Ahn, D. U., & Lee, S.-C. (2004). Effect of heat treatment on the antioxidant activity of extracts from citrus peels. *Journal of Agricultural and Food Chemistry*, *52*(11), 3389–3393.

Kermasha, S. (1995). Determination of phenolic compound profiles in maple products by high-performance liquid chromatography. *Journal of Agricultural and Food Chemistry*, *43*, 708–716. https://doi.org/10.1021/jf00051a028

Liu, Y., Rose, K. N., DaSilva, N. A., Johnson, S. L., & Seeram, N. P. (2017). Isolation, identification, and biological evaluation of phenolic compounds from a traditional north American confectionery, maple sugar. *Journal of Agricultural and Food Chemistry*, *65*(21), 4289–4295. https://doi.org/10.1021/acs.jafc.7b01969

Maqsood, S., Benjakul, S., & Balange, A. K. (2012). Effect of tannic acid and kiam wood extract on lipid oxidation and textural properties of fish emulsion sausages during refrigerated storage. *Food Chemistry*, *130*(2), 408–416. https://doi.org/10.1016/j.foodchem.2011.07.065

Mathlouthi, M., & Rogé, B. (2003). Water vapour sorption isotherms and the caking of food powders. *Food Chemistry*, *82*(1), 61–71. https://doi.org/10.1016/S0308-8146(02)00534-4

Meda, L., & Ratti, C. (2005). Rehydration of freeze-dried strawberries at varying temperatures. *Journal of Food Process Engineering*, *28*(3), 233–246. https://doi.org/10.1111/j.1745-4530.2005.00404.x

Meda, N. R., Poubelle, P. E., & Stevanovic, T. (2017). Antioxidant capacity , phenolic constituents and toxicity of hot water extract from red maple buds. *Chemistry & Biodiversity*, *14*(6), e1700028. https://doi.org/10.1002/cbdv.201700028

Nurhadi, B., & Roos, Y. H. (2016). Water sorption and water plasticization behavior of vacuum dried honey. *International Journal of Food*

Properties, *19*(6), 1370–1380. https://doi.org/10.1080/10942912.2015.1081607

Ozkan, M., Cemeroglu, B., & Kirca, A. (2003). Effect of moisture content on CIE color values in dried apricots. *European Food Research Technology*, *216*, 217–219. https://doi.org/10.1007/s00217-002-0627-6

Palzer, S., Dubois, C., & Gianfrancesco, A. (2012). Generation of product structures during drying of food products. *Drying Technology*, *30*(1), 97–105. https://doi.org/10.1080/07373937.2011.622060

Park, Y. W., & Bell, L. N. (2004). Determination of moisture and ash contents of foods. In L. M. L. Nollet (Ed.), *Handbook of food analysis: Physical characterization and nutrient analysis* (Vol. 1, 2nd ed., pp. 55–82). New York: Marcel Dekker AG.

Pua, C. K., Hamid, N. S. A., Tan, C. P., Mirhosseini, H., Rahman, R. B. A., & Rusul, G. (2010). Optimization of drum drying processing parameters for production of jackfruit (*Artocarpus heterophyllus*) powder using response surface methodology. *LWT - Food Science and Technology*, *43*(2), 343–349. https://doi.org/10.1016/j.lwt.2009.08.011

Quek, S. Y., Chok, N. K., & Swedlund, P. (2007). The physicochemical properties of spray-dried watermelon powders. *Chemical Engineering and Processing: Process Intensification*, *46*(5), 386–392. https://doi.org/10.1016/j.cep.2006.06.020

Roos, Y. H. (1993). Melting and glass transitions weight carbohydrates of low molecular. *Carbohydrate Research*, *238*, 39–48.

Roos, Y., & Karel, M. (1991). Amorphous state and delayed ice formation in sucrose solutions. *International Journal of Food Science & Technology*, *26*(6), 553–566. https://doi.org/10.1111/j.1365-2621.1991.tb02001.x

Royer, M., Diouf, P. N., & Stevanovic, T. (2011). Polyphenol contents and radical scavenging capacities of red maple (*Acer rubrum* L.) extracts. *Food and Chemical Toxicology*, *49*(9), 2180–2188. https://doi.org/10.1016/j.fct.2011.06.003

Seerangurayar, T., Manickavasagan, A., Al-Ismaili, A. M., & Al-Mulla, Y. A. (2017). Effect of carrier agents on flowability and microstructural properties of foam-mat freeze dried date powder. *Journal of Food Engineering*, *215*, 33–43. https://doi.org/10.1016/j.jfoodeng.2017.07.016

Sharma, A., Jana, A. H., & Chavan, R. S. (2012). Functionality of Milk powders and Milk-based powders for end use applications — A review. *Comprehensive Reviews in Food Science and Food Safety*, *11*(5), 518–528. https://doi.org/10.1111/j.1541-4337.2012.00199.x

St-Pierre, P., Pilon, G., Dumais, V., Dion, C., Dubois, M. J., Dubé, P., … Marette, A. (2014). Comparative analysis of maple syrup to other natural sweeteners and evaluation of their metabolic responses in healthy rats. *Journal of Functional Foods*, *11*(C), 460–471. https://doi.org/10.1016/j.jff.2014.10.001

Thériault, M., Caillet, S., Kermasha, S., & Lacroix, M. (2006). Antioxidant, antiradical and antimutagenic activities of phenolic compounds present in maple products. *Food Chemistry*, *98*(3), 490–501. https://doi.org/10.1016/j.foodchem.2005.05.079

Zhang, Q., Zhang, J., Shen, J., Silva, A., Dennis, D. A., & Barrow, C. J. (2006). A simple 96-well microplate method for estimation of total polyphenol content in seaweeds. *Journal of Applied Phycology*, *18*(3–5), 445–450. https://doi.org/10.1007/s10811-006-9048-4

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