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ARTICLE

Effect of the Novel Radiant Zone Drying Method on Anthocyanins and Phenolics of Three Blueberry Liquids

Moumita Chakraborty,[†] Mark Savarese,[‡] Eileen Harbertson,[†] James Harbertson,[†] and Kerry L. Ringer*,[†]

[†]School of Food Science, Washington State University, 24106 North Bunn Road, Prosser, Washington 99350, and [‡]Columbia PhytoTechnology, LLC, 101 Parallel Avenue, Dallesport, Washington 98617

The Radiant Zone dryer (RZD) is a novel drying method designed to dry liquid food products into powders. The impact of RZD on the phytochemical content of three blueberry liquid products (extract, juice, and puree) was examined. Comparative analysis between liquid and dried products revealed no statistically significant changes in the total anthocyanins (extract liquid/powder, 11.7/11.2 mg/g of dry weight; juice liquid/powder, 2.7/2.5 mg/g of dry weight; puree liquid/powder, 1.7/1.6 mg/g of dry weight, quantified as cyanidin 3-glucoside equivalents) and total phenolics (extract liquid/powder, 97.1/113.1 mg/g of dry weight; juice liquid/powder, 16.6/17.4 mg/g of dry weight; puree liquid/powder, 8.3/6.2 mg/g of dry weight, quantified as gallic acid equivalents). Total antioxidant activity also showed no significant variation between wet and dried products. The high-performance liquid chromatography−diode array detector (HPLC−DAD) analysis of the products exhibited a similar profile of 13 glycosylated anthocyanins. This study demonstrates that the novel RZD produces high-quality products because the retention of anthocyanins and phenolics during dehydration using RZD is the same as that for freeze drying. The RZD method of operation and its advantages over other dryers is also discussed.

KEYWORDS: Antioxidant activity; anthocyanins; blueberry; dehydration; freeze drying; phenolics; HPLC−UV DAD; Radiant Zone dryer; RZD

INTRODUCTION

Berries have a gamut of biomedical applications, and recent human and animal research has shown the potential of blueberries in disease applications (*1*−*4*). Consumption of blueberries, including in many cases, the consumption of blueberry powder, has been associated with increased levels of postprandial antioxidant capacity in the blood plasma of humans (*1*); improvement of ischemic stroke outcomes (*2*), and overcoming the genetic predisposition to Alzheimer's disease in rodents (*3*); and reduced levels of plasma lipids in pigs (*4*). The beneficial effects of blueberries are believed to be contributed mainly by the anthocyanins and other flavonoids (reviewed in refs *5* and *6*). In comparison to most other berries, blueberries have higher antioxidant activity and anthocyanin content (*7*). Consequently, there is a large consumer demand for fresh blueberries as well as their products.

Blueberries belong to the family Ericaceae, genus *Vaccinium*. They are mainly grown in a temperate climate, and North America is considered to be the major producer, contributing greater than 50% of the total world commercial production of blueberries (*8*). Because blueberries are seasonal crops and their shelf life as a fresh product is short, excess fresh berries have to be either frozen or otherwise processed. Because maintaining frozen products may be cost-prohibitive, there is a growing interest in developing cost-effective preservation methods capable of minimizing the degradation of anthocyanins in processed berry products (i.e., powders). The growing body of literature supporting the health benefits of blueberries has provided the impetus to produce berry-derived nutritional supplements and food ingredients in a dried powder form, which retain the nutritional content of the original fruit.

The main goals of drying food products are to extend shelf life and reduce packaging, handling, transportation, and storage costs associated with raw food (*9*). Dehydration of liquids into powders allows for long-term and relatively inexpensive storage as compared to frozen fruit, juices, or purees. Additionally, manufacturing of powders provides an alternative use for overproduced fruit and for the production of value-added products.

Pureeing, juicing, and dehydration of blueberries can result in losses of anthocyanins and phenolics because of enzymatic degradation (*10*−*12*), oxygenation (*13*), pH effects (*13*), and thermal treatment (*12*, *14*, *15*). Losses also occur during juice processing, with substantial amounts of both anthocyanins and polyphenolics remaining in press cake (*16*). Furthermore, the addition of high concentrations of drying aids or carriers, such as maltodextrin, during drying of fruit liquids reduces the nutritive value of resulting powders (*17*−*20*). This is particularly true in the case of fruit juices, which may require drying aid additions of as much as 75% of the dry matter content (*21*). Commercially available dehydration methods for liquid applications include spray, freeze, drum, air, Refractance Window, and a novel

*To whom correspondence should be addressed. Telephone: 509-786-9324. Fax: 509-786-9370. E-mail: kringer@wsu.edu.

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method, Radiant Zone drying (RZD). To the authors' knowledge, little to no research has been conducted on the processing of blueberry liquids to dried powders. Herein, we have described and used the novel and patented RZD developed by Columbia PhytoTechnology, LLC (Dallesport, WA) to produce three blueberry powders from puree, juice concentrate, and an extract with no to minimal carrier additions. This is the first research conducted using this drying system. Total phenolics, total anthocyanins, total antioxidant activity, and the high-performance liquid chromatography (HPLC) profile of the anthocyanins present in the liquid and the Radiant Zone dried products are compared. Physical characteristics, including moisture content and water activity, are also discussed as well as the mode of operation of the RZD.

MATERIALS AND METHODS

Chemicals. All solvents used were HPLC-grade and purchased from Sigma-Aldrich (St. Louis, MO). Phenolic and antioxidant standards were purchased from Sigma Aldrich. Anthocyanins were purchased from Extrasynthese (Cedex, France) (cyanidin-3-galactoside, cyanidin-3-glucoside, delphinidin-3-glucoside, peonidin-3-glucoside, malvidin-3-galactoside, and malvidin-3-glucoside).

Blueberry Preparation for Drying. For blueberry puree, whole frozen blueberries were generously provided by Trout Lake Farm (Trout Lake, WA). A mixture of the highbush blueberry varieties Duke, Bluecrop, Earlyblue, Jersey, Legacy, Reka, 1613-A, Rubel, Olympia, and Berkeley were used. Berries (68 kg) were thawed and pureed using a Quadro Comil (Waterloo, Ontario, Canada), and the solids content (17.4%) was determined; 20% (w/w) puree solids of both M100 maltodextrin and cornstarch (GPC, Muscatine, IA) were added (40% of the dried weight is carrier). The mixture was remilled to a fine consistency and diluted with ~10% water to 20% solids on a weight basis for application to the drying surface. The product thickness was 1.58 mm. Product thickness was determined by calculating the volume of the liquid product applied to the dryer in the given width and length of the drying area and was verified using a precision ruler to be approximately 1 mm for all products. The product width was 100.3 cm. Blueberry juice concentrate, 65 °Brix, was provided by Milne Fruit Products (Prosser, WA). Rice-trin 35 (maltodextrin derived from rice with a dextrose equivalence of 35) (Primera Foods, Cameron, WI) was solubilized in water and added at 20% (w/w) solids in the juice concentrate (20% of dried weight is rice-trin). The concentrate was diluted to 45% moisture/55% solids, for application to the dryer. The product was applied to the dryer at a width of 96.5 cm.

Blueberry extract, 30% solids and 6.88 g of sugar/100 g on a wet basis, was provided by Milne Fruit Products (Prosser, WA). The extract is manufactured from the pomace remaining after blueberry juicing using a proprietary process. The extract was applied directly to the applicator without the addition of a carrier or dilution. The product was applied at a width of 93.8 cm.

RZD Method. A pilot-sized RZD, model number RZD-410-Z5P (U.S. Patent 6,539,645, Columbia PhytoTechnology, LLC, Dallesport, WA), was used for the experiments. The pilot system is a continuous belt system with a drying area of 122 cm wide × 457.2 cm long, which is divided into five temperature zones. Zones 1−4 are 76.2 cm in length, and zone 5 is 152.4 cm in length. A final length of the belt is unheated and allows the product to cool prior to removal and packaging. The product was heated from below using $^1/_2$ in. × 48 in. at 40 W/in. infrared radiant heaters (Glo-Quartz, Menor, OH). The desired product temperature in each zone was set by the operator, and an infrared thermocouple sensor (IRt/c, Exergen Corporation, Watertown, MA) placed at the midpoint of each zone and 30 cm above the product was used to measure the product temperature during drying. Using a patented control loop, a controller and relay are used to regulate the heat to achieve the product temperature set point. The average air volume through the dryer for the experiments was 4400 cfm. Each drying experiment was run at least 3 times, and samples were collected from the applicator (liquid) and at the product removal assembly (powder). Samples were stored frozen (−20 °C) until analysis. Temperature profiles and time in each zone are shown in **Table 1**.

Table 1. Temperature Profiles for Drying Blueberry Extract, Juice, and Puree

zone number	temperature set point (°C)	actual temperature (°C)	time in each zone (s)	time in dryer (min)[a]	MC (%)[b]
		Extract			
1	65.5	64	72		
2	74	74	72		
3	79	80	72		
4	87	86	72	8	4.7
5	88	88	144		
cooling			53		
		Juice			
1	65	66	50		
2	74	75	50		
3	82	80	50		
4	88	84	50	6	1.0
5	88	87	100		
cooling			36		
		Puree			
1	65.5	63	91		
2	79	78	91		
3	85	80	91		
4	90	91	91	10	4.0
5	90	83	182		
cooling			67		

[a] Time in the dryer includes product cooling. [b] MC = final moisture content of the dried powder.

Belt velocities were 1.06 cm/s for extract, 1.52 cm/s for juice concentrate, and 0.84 cm/s for puree. For each product, samples were scraped from the belt during drying to determine moisture loss over time. Water activity (A_w) was measured to monitor product dryness using an Aqualab, Series 3 (Decagon Devices, Pullman, WA). Powder was placed in the sample cup to cover the bottom of the cup, and water activity measurement was taken according to the instructions of the manufacturer.

Determination of Physical Characteristics. The moisture content of the blueberry products was measured by placing approximately 0.1 g of material into a forced-air dryer at 70 °C. The change in weight was measured at an interval of 4 h until no change in weight loss was observed. All results take into account the respective moisture content of the liquids and powders.

Sample Preparation. Because of the solubility in water of the juice concentrate and extract, the liquid and dried samples were dissolved using acidified (1% citric acid) water and directly analyzed for total anthocyanins and total phenolics at the appropriate dilution. The juice concentrate and extract were extracted for HPLC analysis of anthocyanins as described below in the Extraction of Anthocyanins. Because the puree was not water-soluble, it was extracted as described below for both spectrophotometric quantification and HPLC analysis of anthocyanins. For total phenolics analysis, the puree was extracted with 50% methanol. Briefly, on the basis of the percent moisture, methanol was added to 0.5 g of liquid puree (or the equivalent amount of powder based on percent solids) to achieve 50% aqueous methanol. The mixture was homogenized (TissueMiser, Fisher Scientific) for 2 min, allowed to extract overnight under gentle shaking, and centrifuged at 1500*g* for 10 min, and the supernatant was removed. The procedure was repeated twice more with 50% aqueous methanol. The supernatants were combined and evaporated under reduced pressure at 40 °C using a Buchi rotary evaporator until a drop of liquid remained and then brought to a uniform volume with acidified water.

Extraction of Anthocyanins. Anthocyanins were extracted from the extract, juice concentrate, and puree according to the protocol described by Guisti and Wrolstad (*22*), with some modifications. The weighed sample was macerated with 5 mL of acidified methanol (~0.1% formic acid) using a homogenizer (Tissue Miser, Fisher Scientific) for 2 min, kept overnight under gentle shaking, and centrifuged at 1500*g* for 5 min at 4 °C.

The supernatant was collected in a round-bottom flask. The extraction was performed with additional quantities of 5 mL of acidified methanol until the material was colorless. The combined supernatant was dried in a Buchi rotary evaporator and kept at 40 °C until a drop of liquid remained. The residue was resuspended in acidified water. The C_{18} Sep-Pack column (Waters) was activated through the successive application of 5 mL of acidified methanol and 5 mL of acidified water into the cartridge. The resuspended material (1 mL) was introduced into the column through a syringe, and the column was washed twice with 2 mL of water. Anthocyanins were eluted by washing the cartridge with acidified methanol. Methanol was evaporated in a rotary evaporator, and the residue was dissolved in 1.5 mL of acidified water. Prepared samples were stored at −35 °C until used for HPLC.

Determination of Total Anthocyanins. Anthocyanin quantification was performed by the pH differential method (*23*). Samples were diluted to the appropriate level by pH 1.0 and 4.5 buffer, so that the absorbance of the sample at the $\lambda_{vis\text{-}max}$ is within the linear range of the spectrophotometer (< 1.2 AU). Absorbance was measured at 520 and 700 nm in a Du 600 series single-beam UV/vis Beckman spectrophotometer. Total anthocyanins were calculated using the cyanidin-3-glucoside molar extinction coefficient of 26 900 and a molecular weight of 449.2. Resultant values were expressed in milligrams of cyanidin 3-glucoside equivalents per gram of dry weight. All samples were weighed and analyzed in triplicate, with three separate readings taken for each sample.

Determination of Total Phenolics. Total phenolic content was measured according to the Folin−Ciocalteau method (*24*), with some modification (*25*). Briefly, 1 mL of the previously solubilized juice concentrate or extract or the blueberry puree extracted as described above was mixed with 1 mL of 0.25 N Folin−Ciocalteau reagent; 1 mL of 1 N sodium carbonate was added followed by 7 mL of deionized water. The mixture was allowed to incubate for 60 min at room temperature. Absorbance was measured at 700 nm. Results are reported in milligrams of gallic acid equivalents per gram of dry weight using a gallic acid standard curve. Brix measurements of liquids to be assayed were taken to determine if a correction factor should be used. No correction factor for sugar was required. All samples were weighed and analyzed in triplicate, with three separate readings taken for each sample.

HPLC−Diode Array Detector (DAD) Analysis of the Anthocyanins. The HPLC method for the anthocyanin screening was adapted from Downey et al. (*26*), with slight modifications. A total of 25 μL of the extracted samples were analyzed using an Agilent 1100 series quaternary pump, coupled with diode array and multiple wavelength detectors. Separation was carried out using a C-18 SS Wakosil (150× 4.6 mm, 3 μm packing, SGE, Ringwood, Australia) column protected by a SGE C-18 guard column. Mobile-phase A (10% formic acid in water) and mobile-phase B (10% formic acid in methanol) at the flow rate of 1 mL/min were run under the following gradient conditions: 0 min, 10% B; 14 min, 29% B; 16 min, 32% B; 18 min, 41% B; 18.1 min, 30% B; and 29 min, 41%. Anthocyanins are quantified in terms of cyanidin-3-glucoside, and results are reported as milligrams per gram of dry weight.

Determination of Total Antioxidant Capacity (TAC). To determine the TAC, samples were tested employing a proprietary assay (www.columbiaphytotechnology.com). Briefly, the extract and juice concentrate liquid and powder samples were solubilized in water and diluted to the appropriate level, and the ability of the sample to scavenge the superoxide radical using Electro-Ox (proprietary equipment) was determined and compared to Trolox. The puree sample prepared for total phenolics (aqueous methanol) was analyzed for TAC. Additionally, the samples prepared for HPLC analysis of anthocyanins using acidified methanol were assayed for their ability to scavenge superoxide. All samples were weighed and analyzed in triplicate. A Trolox standard curve was generated, and results are reported in millimoles of Trolox equivalents per gram of dry weight.

Statistical Analyses. The standard deviation (SD) and correlation coefficient were deduced using Microsoft Office Excel 2007 (Redmond, WA). The unpaired t test was performed to compare the means using GraphPad Quick Calculator (http://www.graphpad.com/quickcalcs). Differences at $p = 0.05$ were considered significant. All data were reported as means ± SD.

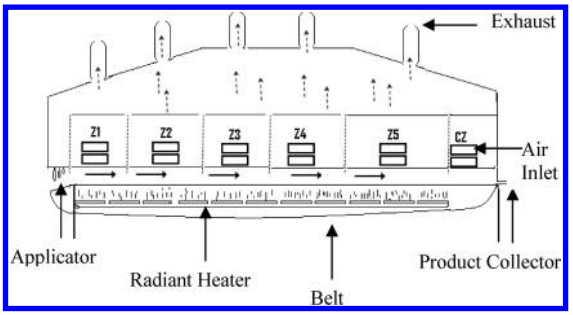

Figure 1. Schematic diagram of the RZD. Solid arrows indicate the direction of the product flow, from wet to dry. Z, zone; CZ, cooling zone.

RESULTS AND DISCUSSION

RZD of Blueberry Products. A pilot version of the novel and patented drying system, the RZD, was used herein to produce the powders. This is the first report of the RZD being used in research to date. The RZD is a continuous system, whereby the product is applied to a transparent belt and is conveyed through a drying chamber (**Figure 1**). Radiant heat is directed from below (and in some cases above) the product. Steam is removed by pulling air over the product through side air inlets in a hood that covers the drying surface. The air is then exhausted through an overhead venting system. The drying chamber is divided into several independently programmable temperature zones. Infrared sensors monitor the product temperature and directly modulate heat input to maintain the set point of each zone. The product is cooled in a final zone prior to removal. The temperature set points for the blueberry products ranged from 65 to 90 °C and required between 5 and 10 min for drying depending upon the product (**Table 1**). The time for which the products were kept under high temperature (80−90 °C) varied from approximately 3 to 5 min. The loss of moisture/change in water activity over the length of the RZD is illustrated for each of the three blueberry products (**Figure 2**). The extract and juice concentrate show a typical loss of moisture on drying curve (*9*), with the majority of the moisture loss occurring in the first zone (50−72 s). In contrast, the puree shows a relatively constant rate of moisture loss throughout the drying process, possibly because of the presence of the blueberry skin and pulp found in this unpurified, whole blueberry product that may require higher temperatures or longer drying times to remove bound water.

Effect of RZD on Total Anthocyanins and Total Phenolics. The stability of anthocyanins and the rate of their degradation are influenced by temperature (*14*, *27*−*29*). Samples were taken of the three liquid blueberry products and the corresponding dried powders as described in the Materials and Methods to determine the effect of RZD on the phenolic and anthocyanin components. Anthocyanins were quantified by both the pH differential method (**Table 2**) (*23*) and HPLC (**Table 3**) (*26*), with results reported as milligrams of cyanidin-3-glucoside equivalents per gram of dry weight. For the pH differential method, the maximum amount of anthocyanin was obtained in the blueberry extract products followed by juice concentrate and puree. For HPLC quantification, the same pattern was found but the total anthocyanin content obtained by HPLC was higher than that of the pH differential method. This type of discrepancy has previously been reported (*30*, *31*). Although the HPLC quantified data are generally higher in comparison to the results obtained using the pH differential method, the results are typically well-correlated (*31*). In this case, for the powdered extract, juice concentrate, and puree, results were 1.4, 2.1, and 1.9 times greater, respectively, for the HPLC method than the results obtained from the pH differential method. The extract and juice concentrate

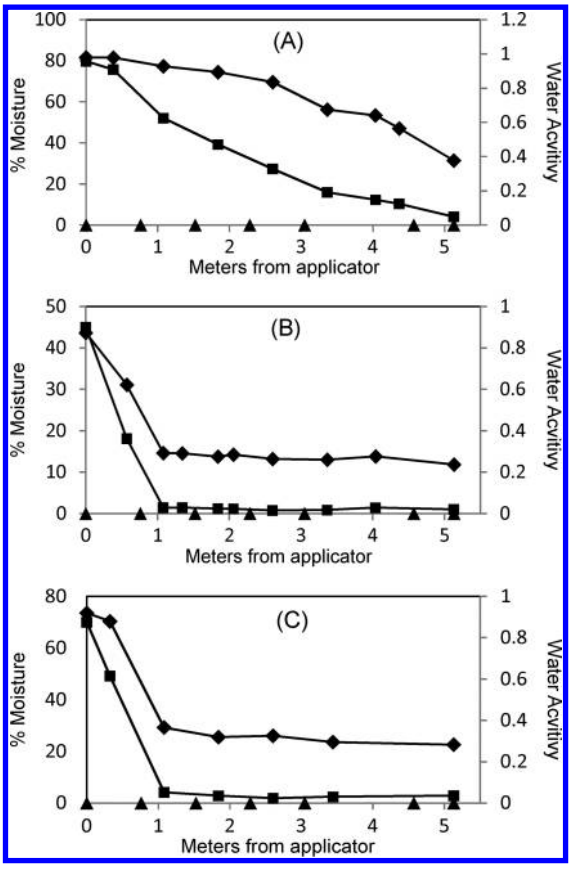

Figure 2. Loss of moisture/decrease in water activity as (A) blueberry puree, (B) juice concentrate, and (C) extract move through the RZD. (▲) Beginning and end of each zone, (■) % moisture, and (◆) water activity.

Table 2. Total Phenolics and Total Anthocyanins of the Blueberry Extract, Juice, and Puree before and after RZD[a]

	total anthocyanins (mg of cya-3-glu equiv/g of DW)		total phenolics (mg of GAE/g of DW)	
blueberry products	liquid	powder	liquid	powder
extract	11.7 ± 0.4	11.2 ± 1.7	97.1 ± 5.4	113.1 ± 7.6
juice	2.7 ± 0.3	2.5 ± 0.2	16.6 ± 0.8	17.4 ± 1.1
puree	1.7 ± 0.2	1.6 ± 0.3	8.3 ± 0.1	6.2 ± 0.8

[a] Data presented as means ± SD. An unpaired *t* test was conducted to compare the means of the liquid and powder for each sample type (sample types were not compared to each other), and the means are not significantly different ($p < 0.05$). Cya-3-glu equiv, cyanidin-3-glucoside equivalents; DW, dry weight; GAE, gallic acid equivalents.

samples were solubilized in acidified water and directly analyzed using the pH differential method, whereas the puree was solvent-extracted prior to analysis. All three samples underwent solvent extraction prior to HPLC analysis to remove impurities. Although total quantities of anthocyanins were lower using the pH differential method, the analysis is relatively facile and rapid for the samples that do not require solvent extraction.

Similar to the anthocyanin results, total phenolics (**Table 2**) were found to be maximal in the blueberry extract followed by juice concentrate. Most notably, there was no statistical difference between the total anthocyanins or total phenolics between the liquid samples and the powder samples after RZD.

Effect of RZD on the Anthocyanin Profile. A total of 14 glycosylated anthocyanins (**Table 3**) were identified in the blueberry extract, juice, and puree by matching the retention time and spectra with that of authentic standards along with comparing the elution sequence to the published data (*32*). The HPLC−DAD chromatogram at 520 nm of blueberry extract liquid and powder are illustrated (**Figure 3**) and are typical of the chromatograms for juice and puree. To avoid the chromatogram shifting error while comparing the retention time, samples were spiked with the standards. No qualitative differences in the anthocyanin profiles of the blueberry products were seen after RZD of the three blueberry products.

Effect of RZD on TAC and Correlation with Phenolics and Anthocyanins. As expected from the total phenolic and anthocyanin data, TAC of the liquid products also showed no statistical difference with the Radiant Zone dried powder (**Table 4**). The blueberry juice concentrate and extract samples that were solubilized in water had higher TAC than the acidified methanol extracted samples likely because of the presence of other water-soluble antioxidants that were not extracted with methanol and/or the losses of phenolic compounds that may occur during the extraction process. Mean values of TAC for the crude extracts showed positive correlation with total phenolics of the three powder products, and mean values of TAC for the acidified methanol extracts also showed positive correlation with both spectrophotometric and HPLC quantification of total anthocyanins, with correlation coefficients, r, of 0.9999, 0.9998, and 0.9916, respectively, and $p < 0.01$ for each of the comparisons. Similar strong positive correlations have been found between phenolic content and antioxidant activity (*33*), and considering the potent superoxide scavenging ability of the anthocyanins found in blueberry (*34*), it is not surprising that there is a correlation between total anthocyanins and antioxidant activity using an assay that employs superoxide.

Physical Characteristics of Powders. The water activity and the percent moisture of the three powders were analyzed and were 0.28 and 4.7% for the extract, 0.24 and 1% for the juice concentrate, and 0.38 and 4% for the puree. Typical specifications for the moisture content for powders for the nutritional and food industry are < 5%. The values obtained herein are within this range.

This is the first report of the effect of RZD on the anthocyanin and phenolic content, and to the authors' knowledge, this is the first report of dehydration of different blueberry liquids into powders. The three forms of blueberry (puree, extract, and juice concentrate) showed no significant change in the content of anthocyanins or phenolics after drying, indicating that the RZD is a suitable drying technology for preserving the antioxidants of berries or processed fruit liquids in dried powders that may subsequently be used for food ingredients or nutraceuticals. The data presented herein does not account for losses that may have occurred during preprocessing of the blueberry products. It has been well-documented that degradation of anthocyanins and phenolics occurs during processes such as juicing, pureeing, and pasteurization (*12*, *15*, *16*, *35*) as well as during dehydration (*14*, *36*, *37*). Dehydration of whole fresh blueberries using a cabinet dryer at 90 °C for 90 min, 70 °C at 120 min, or 50 °C at 120 min resulted in a loss of total anthocyanins of 41−49% (*14*). Freeze drying of whole marionberries resulted in no losses of phenolics, whereas a significant loss was seen for air-dried marionberries (*36*). In the same study, there was a significant loss of phenolics in freeze-dried whole strawberries. In contrast, freeze drying of whole strawberries resulted in no losses of total anthocyanins (*37*). Conventional and vacuum drying decreased the quantities of these two groups of phytochemicals, with lower losses seen with vacuum−microwave drying.

The hygroscopicity and thermoplastic properties of fruit liquids, particularly juices (and juice concentrates), typically requires the addition of carriers to facilitate dryness and reduce stickiness (*20*, *38*, *39*). A reduction in final powder moisture is

Table 3. Anthocyanins Detected in the Blueberry Liquids (Extract, Liquid, and Puree) and Radiant Zone Dried Powders[a]

	blueberry products (mg of cya-3-glu equiv/g of DW)					
	extract		juice		puree	
anthocyanins	liquid	powder	liquid	powder	liquid	powder
1. del-3-gal[b]	0.99 ± 0.13	1.12 ± 0.11	0.57 ± 0.01	0.66 ± 0.14	0.44 ± 0.08	0.31 ± 0.03
2. del-3-glu	0.55 ± 0.07	0.61 ± 0.09	0.12 ± 0.00	0.14 ± 0.02	0.12 ± 0.12	0.09 ± 0.00
3. cya-3-gal	0.29 ± 0.04	0.34 ± 0.05	0.21 ± 0.00	0.24 ± 0.05	0.23 ± 0.04	0.18 ± 0.00
4. del-3-ara	1.34 ± 0.20	1.51 ± 0.20	0.39 ± 0.01	0.45 ± 0.10	0.29 ± 0.04	0.19 ± 0.03
5. cya-3-glu	0.24 ± 0.03	0.26 ± 0.04	0.06 ± 0.00	0.07 ± 0.01	0.10 ± 0.02	0.07 ± 0.00
6. pet-3-gal	0.90 ± 0.12	0.99 ± 0.16	0.42 ± 0.01	0.48 ± 0.10	0.40 ± 0.07	0.28 ± 0.02
7. cya-3-ara	0.40 ± 0.06	0.47 ± 0.08	0.12 ± 0.00	0.14 ± 0.03	0.13 ± 0.02	0.08 ± 0.00
8. pet-3-glu	0.63 ± 0.08	0.72 ± 0.12	0.10 ± 0.00	0.13 ± 0.02	0.22 ± 0.04	0.16 ± 0.01
9. peo-3-gal	0.21 ± 0.03	0.26 ± 0.04	0.09 ± 0.00	0.11 ± 0.02	0.06 ± 0.01	0.04 ± 0.00
10. pet-3-ara	0.83 ± 0.12	0.95 ± 0.19	0.24 ± 0.00	0.27 ± 0.06	0.21 ± 0.03	0.14 ± 0.02
11. peo-3-glu	TA	TA	ND	ND	TA	TA
12. mal-3 gal	3.35 ± 0.46	3.93 ± 0.61	1.36 ± 0.03	1.56 ± 0.33	1.02 ± 0.21	0.70 ± 0.03
13. mal-3-glu	1.54 ± 0.17	1.83 ± 0.26	0.32 ± 0.00	0.37 ± 0.08	0.60 ± 0.10	0.41 ± 0.02
14. mal-3-ara	1.99 ± 0.29	2.37 ± 0.41	0.60 ± 0.02	0.70 ± 0.15	0.46 ± 0.10	0.30 ± 0.00
total	13.3 ± 2.4	15.4 ± 1.8	4.6 ± 0.1	5.3 ± 1.1	4.3 ± 0.8	3.0 ± 0.1

[a] Data presented as means ± SD. An unpaired *t* test was conducted to compare the means of the totalanthocyanins of the liquid and powder for each sample type (sample types were not compared to each other), and the means are not significantly different ($p < 0.05$). Cya-3-glu equiv, cyanidin-3-glucoside equivalents; DW, dry weight; TA, trace amount; ND, not detected. [b] Anthocyanins are numbered to correspond with peaks in **Figure 3**.

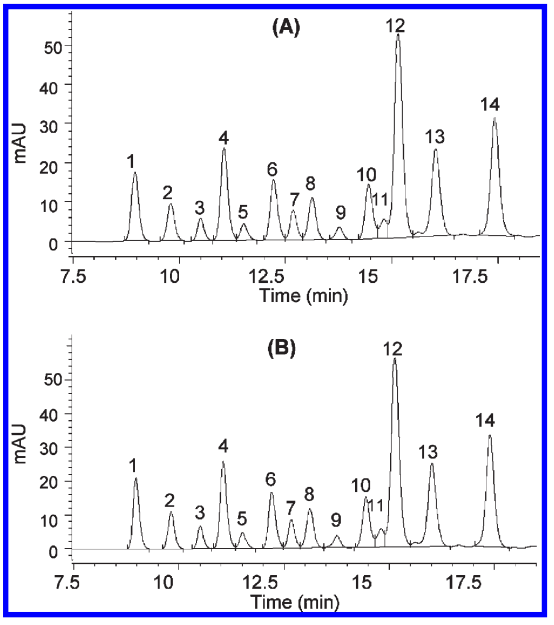

Figure 3. HPLC profiles of blueberry anthocyanin present in (A) blueberry extract liquid and (B) Radiant Zone dried powder. Anthocyanins are 1, delphinidin-3-galactoside; 2, delphinidin-3-glucoside; 3, cyanidin-3-galactoside; 4, delphinidin-3-arabinoside; 5, cyanidin-3-glucoside; 6, petunidin-3-galactoside; 7, cyanidin-3-arabinoside; 8, petunidin-3-glucoside; 9, peonidin-3-galactoside; 10, petunidin-3-arabinoside; 11, peonidin-3-glucoside; 12, malvidin-3-galactoside; 13, malvidin-3-glucoside; and 14, malvidin-3-arabinoside.

necessary to maintain the glass transition temperature of the powder to room temperature or above (*38*). The addition of a carrier, however, dilutes the nutritive value of the powder. Carrier percentages in the range of 35−45% were required for spray drying of blackcurrant, apricot, and raspberry juice to minimize the product loss to 20% (*20*). Spray drying of orange without carrier addition resulted in no product produced, and the material adhered to the interior of the dryer (*39*). With the addition of maltodextrin (unknown amount), dry orange powder (< 5%) was achieved, but the yield did not exceed 35%. The moisture content of freeze-dried and Refractance Window dried strawberry

Table 4. TAC of Blueberry Products (mmol of TE/g of DW)[a]

	water		acidified methanol	
solvent	liquid	powder	liquid	powder
extract	23.58 ± 1.03	22.34 ± 1.25	7.02 ± 0.58	7.57 ± 0.66
juice	2.81 ± 0.41	3.18 ± 0.40	0.99 ± 0.06	1.05 ± 0.05
puree	0.56 ± 0.03[b]	0.60 ± 0.04[b]	0.68 ± 0.1	0.70 ± 0.04

[a] Data presented as means ± SD. An unpaired *t* test was conducted to compare the means of the TAC of the liquid and powder for each sample type (sample types were not compared to each other), and the means are not significantly different ($p < 0.05$). TE, Trolox equivalents; DW, dry weight. [b] Aqueous methanol extracted puree was used because the puree was not water-soluble (described in Materials and Methods).

puree without a carrier exceeded 9% moisture, and with the addition of 70% carrier, moisture contents of 3.9% (freeze) and 5.7% (Refractance Window) were achieved (*40*). In this study, dry, nonsticky powders (< 5% moisture, A_w < 0.4) were produced with minimal carrier additions, 0, 20, and 40% for extract, juice, and puree, respectively, and with only minor product losses (data not shown). These quantities of carriers are lower than those previously reported for fruit purees and concentrates and were not optimized to a minimum content in this study. Ongoing research has shown RZD capable of producing low moisture, flowable powder with no carrier additions (Wu and Ringer, unpublished results). The thin layer of liquid applied to the RZD promotes rapid and sufficient drying, and the final cooling zone enables the product to cool below the glass transition temperature prior to removal and packaging, resulting in minimal powder losses.

With more research being conducted on the health benefits of berries and the compounds within berries (i.e., anthocyanins), there is an increasing demand for high-quality nutraceutical ingredients. Drying of these types of products provides an alternative avenue for overproduced fruit and waste streams of the juicing industry. Moreover, extracts produced from blueberry pomace (waste stream of the juicing process) rich in anthocyanins can be dehydrated to produce a value-added product for encapsulation as a nutritional supplement. The RZD allows for dehydration of liquids in a thin film, allowing for short drying times and reducing the risk of the loss of heat-sensitive phytochemicals. Retention of anthocyanins and phenolics during dehydration using the pilot RZD is the same as that of

freeze-drying whole blueberries (in laboratory-size freeze dryers) (*36*, *37*), which has often been associated with producing the highest quality dried food products. Freeze drying is an expensive process, however, because of the slow drying rate and energy costs and, unlike the RZD, is typically a batch process (*41*). In contrast to the Refractance Window dryer, which applies a constant temperature to the product via a water bath (*42*), the zonal design of the RZD permits temperature adjustments throughout the drying process to optimize phytochemical retention and the temperature sensing prevents product temperatures from exceeding set points. Input of heat can be greater in the initial zones because of the heat of vaporization and reduced in the latter zones to retain heat-sensitive phytochemicals. We are currently conducting research on the effect of RZD on vitamin C retention in various fruits, production of powders with no carrier, as well as energy efficiency, throughput optimization, and minimizing nutrient losses during preprocessing to retain the majority of the initial fruit nutrition.

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LITERATURE CITED

(1) Prior, R. D.; Gu, L.; Wu, X.; Jacob, R. A.; Sotoudeh, G.; Kader, A. A.; Cook, R. A. Plasma antioxidant capacity changes following a meal as a measure of the ability of a food to alter *in vivo* antioxidant status. *J. Am. Coll. Nutr.* **2007**, *26* (2), 170–181.

(2) Sweeney, M. I.; Kalt, W.; Mackinnon, S. L.; Ashby, J.; Gottschall-Pass, K. T. Feeding rats diets enriched in lowbush blueberries for six weeks decreases ischemia-induced brain damage. *Nutr. Neurosci.* **2002**, *5*, 427–431.

(3) Joseph, J. A.; Denisova, N. A.; Arendash, G.; Gordon, M.; Diamond, D.; Shukitt-Hale, B.; Morgan, D. Blueberry supplementation enhances signaling and prevents behavioral deficits in an Alzheimer disease model. *Nutr. Neurosci.* **2003**, *6*, 153–162.

(4) Kalt, W.; Foote, K.; Fillmore, S. A. E.; Lyon, M.; Van Lunen, T. A.; McRae, K. B. Effect of blueberry feeding on plasma lipids in pigs. *Br. J. Nutr.* **2008**, *100*, 70–78.

(5) Kong, J. M.; Chia, L. S.; Goh, N. K.; Chia, T. F.; Brouillard, R. Analysis and biological activities of anthocyanins. *Phytochemistry* **2003**, *64*, 923–933.

(6) Zafra-Stone, S.; Yasmin, T.; Bagchi, M.; Chatterjee, A.; Vinson, J. A.; Bagchi, D. Berry anthocyanins as novel antioxidants in human health and disease prevention. *Mol. Nutr. Food Res.* **2007**, *51*, 675–683.

(7) Zeng, W.; Wang, S. Y. Oxygen radical absorbing capacity of phenolics in blueberries, cranberries chokeberries and lignonberries. *J. Agric. Food Chem.* **2003**, *51*, 502–509.

(8) United State Department of Agriculture. Economics, statistics, and market information system. U.S. Blueberry Industry, Economic Research Service, http://usda.mannlib.cornell.edu/MannUsda/viewDocumentInfo.do?documentID=1765.

(9) Barbosa-Cánovas, G. V.; Vega-Mercado, H. Introduction to dehydration of food. In *Dehydration of Foods*; Barbosa-Cánovas, G. V., Vega-Mercado, H., Eds.; Chapman and Hall: New York, 1996; p 3.

(10) Kader, F.; Rovel, B.; Girardin, M.; Metche, M. Mechanism of browning in fresh highbush blueberry fruit (*Vaccinium corymbosum* L.). Partial purification and characterization of blueberry polyphenol oxidase. *J. Sci. Food. Agric.* **1997**, *73*, 513–516.

(11) Kader, F.; Rovel, B.; Girardin, M.; Metche, M. Mechanism of browning in fresh highbush blueberry fruit (*Vaccinium corymbosum* L.). Role of blueberry polyphenol oxidase, chlorogenic acid and anthocyanins. *J. Sci. Food Agric.* **1997**, *74*, 31–34.

(12) Skrede, G.; Wrolstad, R. E.; Durst, R. W. Changes in anthocyanins and polyphenolics during juice processing of highbush blueberries (*Vaccinium corymbosum* L.). *J. Food Sci.* **2000**, *65*, 357–364.

(13) Kalt, W.; McDonald, J. E.; Donner, H. Anthocyanins, phenolics, and antioxidant capacity of processed lowbush blueberry products. *J. Food Sci.* **2000**, *65*, 390–393.

(14) Lohachoompol, V.; Srzednicki, G.; Craske, J. The change of total anthocyanins in blueberries and their antioxidant effect after drying and freezing. *J. Biomed. Biotechnol.* **2004**, *5*, 248–252.

(15) Brownmiller, C.; Howard, L. R.; Prior, R. L. Processing and storage effects on procyanidin composition and concentration of processed blueberry products. *J. Agric. Food Chem.* **2009**, *57*, 1896–1902.

(16) Lee, J.; Durst, R. W.; Wrolstad, R. E. Impact of juice processing on blueberry anthocyanins and polyphenolics: Comparison of two pretreatments. *J. Food Sci.* **2002**, *67*, 1660–1667.

(17) Jaya, S.; Das, H.; Mani, S. Optimization of maltodextrin and tricalcium phosphate for producing vacuum dried mango powder. *Int. J. Food Prop.* **2006**, *9*, 13–24.

(18) Chegini, G. R.; Ghobadian, B. Effect of spray-drying conditions on physical properties of orange juice powder. *Drying Technol.* **2005**, *23*, 657–668.

(19) Bhandari, B. R.; Datta, N.; Crooks, R.; Howes, T.; Rigby, S. A semi-empirical approach to optimize the quantity of drying aid required to spray dry sugar-rich foods. *Drying Technol.* **1997**, *15*, 2509–2525.

(20) Bhandari, B. R.; Senoussi, A.; Dumoulin, E. D.; Lebert, A. Spray drying of concentrated fruit juices. *Drying Technol.* **1993**, *11*, 1081–1092.

(21) Masters, K. *Spray Drying Handbook*, 4th ed.; George Goodwin: London, U.K., 1985

(22) Giusti, M. M.; Wrolstad, R. E. Characterization and measurement of anthocyanins by UV−visible spectroscopy. In *Handbook of Food Analytical Chemistry*; Wrolstad, R. E., Acree, T. E., Decker, E. A., Penner, M. H., Reid, D. S., Schwartz, S. J., Showemaker, C. F., Smith, D. M., Sporns, P., Eds.; John Wiley and Sons: New York, 2005; pp 19−31.

(23) Lee, J.; Durst, R. W.; Wrolstad, R. E. Determination of total monomeric anthocyanin pigment content of fruit juices, beverages, natural colorants, and wines by the pH differential method: Collaborative study. *J. AOAC Int.* **2005**, *88*, 1269–1278.

(24) Singleton, V. L.; Orthofer, R.; Lamuela-Raventós, R. M. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin−Ciocalteu reagent. *Method Enzymol.* **1998**, *299*, 152–178.

(25) Perkins-Veazie, P.; Collins, J. K.; Howard, L. Blueberry fruit response to postharvest application of ultraviolet radiation. *Postharvest Biol. Technol.* **2008**, *47*, 280–285.

(26) Downey, M. O.; Rochfort, S. Simultaneous separation by reverse-phase high-performance liquid chromatography and mass spectral identification of anthocyanins and flavonols in shiraz grape skin. *J. Chromatogr., A* **2008**, *1201*, 43–47.

(27) Kírca, A.; Cemeroğlu, B. Degradation kinetics of anthocyanins in blood orange juice concentrate. *Food Chem.* **2003**, *81*, 583–587.

(28) Kírca, A.; Özkan, M.; Cemeroğlu, B. Effects of temperature, solid content and pH on the stability of black carrot anthocyanins. *Food Chem.* **2007**, *101*, 212–218.

(29) Xu, S.-Y.; Wang, W.-D. Degradation kinetics of anthocyanins in blackberry juice and concentrate. *J. Food Eng.* **2007**, *82*, 271–275.

(30) Lee, J.; Finn, C. E. Anthocyanins and other polyphenolics in American elderberry (*Sambucus canadensis*) and European elderberry (*S. nigra*) cultivars. *J. Sci. Food Agric.* **2007**, *87*, 2665–2675.

(31) Lee, J.; Rennaker, C.; Wrolstad, E. R. Correlation of two anthocyanin quantification methods: HPLC and spectrophotometric methods. *Food Chem.* **2008**, *110*, 782–786.

(32) Lohachoompol, V.; Mary, M.; Srzednicki, G.; Craske, J. Determination of anthocyanins in various cultivars of highbush and rabbiteye blueberries. *Food Chem.* **2008**, *111*, 249–254.

(33) Velioglu, Y. S.; Mazza, G.; Gao, L.; Oomah, B. D. Antioxidant activity and total phenolics in selected fruits, vegetables, and grain products. *J. Agric. Food Chem.* **1998**, *46*, 4113–4117.

(34) Garcia-Alonso, M.; Rimbach, G.; Sasai, M.; Nakahara, M.; Matsugo, S.; Uchida, Y.; Rivas-Gonzalo, J. C.; De Pascual-Teresa, S. Electron spin resonance spectroscopy studies on the free radical scavenging

activity of wine anthocyanins and proanthocyanins. *Mol. Nutr. Food. Res.* **2005**, *49*, 1112–1119.
(35) Rossi, M.; Giussani, E.; Morelli, R.; Scalzo, R.; Nani, R. C.; Torregiani, D. Effect of fruit blanching on phenolics and radical scavenging activity of highbush blueberry juice. *Food Res. Int.* **2003**, *36*, 999–1005.
(36) Asami, D. K.; Hong, Y.-J.; Barrett, D. M.; Mitchell, A. E. Comparison of the total phenolic and ascorbic acid content of freeze-dried and air-dried marionberry, strawberry, and corn grown using conventional, organic, and sustainable agricultural practices. *J. Agric. Food Chem.* **2003**, *51*, 1237–1241.
(37) Wojdyło, A.; Figiel, A.; Oszmiański, J. Effect of drying methods with the application of vacuum microwaves on the bioactive compounds, color, and antioxidant activity of strawberry fruits. *J. Agric. Food Chem.* **2009**, *57*, 1337–1343.
(38) Roos, Y.; Karel, M. Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *J. Food Sci.* **1991**, *56*, 38–43.
(39) Chegini, R.; Ghobadian, B. Spray dryer parameters for fruit juice drying. *World J. Agric. Sci.* **2007**, *3*, 230–236.
(40) Abony, B. I.; Feng, H.; Tang, J.; Edwards, C. G.; Chew, B. P.; Mattinson, D. S.; Fellman, J. K. Quality retention in strawberry and carrot purees dried with Refractance Window™ system. *J. Food Sci.* **2001**, *67*, 1051–1056.
(41) Barbosa-Cánovas, G. V.; Ortega-Rivas, E.; Juliano, P.; Yan, H. Drying. In *Food Powders: Physical Properties, Processing, and Functionality*; Barbosa-Cánovas, G. V., Ed.; Kluwer Academic/Plenum Publishers: New York, 2005; p 285.
(42) Nindo, C. I.; Tang, J. Refractance Window Dehydration Technology: A novel contact drying method. *Drying Technol.* **2007**, *25*, 37–48.

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