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EFFECTS OF SPRAY DRYING ON ANTIOXIDANT CAPACITY AND ANTHOCYANIDIN CONTENT OF BLUEBERRY AND GRAPE BY-PRODUCTS

presented by

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Major Professor's Signature

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EFFECTS OF SPRAY DRYING ON ANTIOXIDANT CAPACITY AND ANTHOCYANIDIN CONTENT OF BLUEBERRY AND GRAPE BY-PRODUCTS

By

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ABSTRACT

EFFECTS OF SPRAY DRYING ON ANTIOXIDANT CAPACITY AND ANTHOCYANIDIN CONTENT OF BLUEBERRY AND GRAPE BY-PRODUCTS

By

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The degradation of nutraceutical components caused by spray drying of cull blueberry extract and grape pomace extract was investigated. Samples collected before and after spray drying were tested for antioxidant capacity using Oxygen Radical Absorbance Capacity ($ORAC_{FL}$) and Total Phenolics; and for individual anthocyanidins. In Study 1, the maximum ratio of fruit solids to maltodextrin was determined to be 30:70 using a pilot-scale spray dryer. Maltodextrin was also found to have a protective effect on the nutraceutical components during spray drying. There was significantly higher retention of nutraceutical components with increased levels of maltodextrin. In Studies 2 and 3, the air inlet temperature of the spray dryer was kept constant for all runs at 150°C, with varying outlet temperatures of a)80 and b)90°C. The degradation of nutraceutical components was not significantly different at the two selected outlet temperatures. $ORAC_{FL}$ reduction for blueberry and grape samples after spray drying was 66.3 – 69.6% and 5.9 – 14.7%, respectively. After spray drying, total phenolics reduction for blueberry and grape samples was 8.2 – 17.5% and 8.3 – 19.2%, respectively. Individual anthocyanidin reduction for blueberry and grape samples was 50 – 70% and 30 – 60%, respectively. The experimental spray dried powders compared favorably to commercial blueberry powders.

DEDICATION

To my wonderful mom, Kwan Ling Ng, for your selfless sacrifice and unconditional love. You are the heart of the family. Thank you for raising me to be the person I am and believing in me. I hope to grow up to be just like you: resilient and wise. To my younger brother Miles Ma for being so fun and loving. I am glad that we are still close despite the age difference and years apart from each other. I hope I have set a good example to you. To my dad Long Sang Ma for being my inspiration. We all miss you so dearly and there is not one day that we do not think about you. Thank you for leaving us the sweetest memories.

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Introduction

Anthocyanins are naturally occurring compounds that are widely distributed in nature. They are responsible for the color ranges of fruits and vegetables from red at pH values below 4, to colorless at pH 4-4.5 and to blue at pH 7 and above. In Greek, Anthos means flower and kyáneos means purple. Many fruits and vegetables are found to have very high anthocyanin content. Historically, anthocyanins have been used to produce natural food colorants which add attractive attributes to food. Research has also shown numerous health benefits that are associated with their antioxidant, anti-carcinogenic and anti-inflammatory properties (Kong et al., 2003). Incorporating anthocyanins in the food system can also contribute to improving the nutritive value of foods by preventing lipid and protein oxidation (Kähkönen et al., 2001)

Blueberries and grapes contain large amounts of anthocyanins. Blueberries were ranked to have the highest antioxidant capacity among the fruits and vegetables tested (Prior et al., 1998). Annually, there are around 0.75 – 3 million pounds of cull blueberries in the United States. Cull blueberries, which consist of under and over-ripe blueberries, are unmarketable and are discarded. Grape pomace is obtained after the processing of grapes into wines and juices. It consists mainly of skins, seeds, leaves and twigs and cellulose, which is used as the pressing aide. In Michigan, grape pomace is also thrown away. This results in the discarding of valuable anthocyanins present in these materials. Extracting these valuable anthocyanins to produce a value-added low cost fruit powder, which could be used as an ingredient in designer foods, would

be profitable because of the reduced raw material costs. In 1978, Clydesdale and others were the first to utilize grape pomace to produce a spray dried grape powder, which could be used as a food colorant (Threlfall et al., 2005).

Anthocyanins are highly unstable and susceptible to heat and light. The combination of heat and oxygen causes the most detrimental effects on anthocyanins (Nebesky et al., 1949). Typically, the production of a fruit powder requires heat to evaporate the water from the fruit juices, and a grinding mechanism to convert the product to a powder form. Spray drying is a one-step processing method for the production of powder because it eliminates the grinding step. Freeze drying is the least detrimental but most costly treatment to anthocyanins because the water in the fruit juices are sublimed under refrigerated vacuum. Freeze drying produces a product of highest quality.

The objectives of this research were to determine:

1. The maximum ratio of blueberry solids to maltodextrin when spray dried using a Marriott Walker Corporation (Birmingham, MI, USA), model 5.7-T-1-C, pilot -scale spray dryer.
2. The extent of degradation of the nutraceutical components of blueberry and grape by-products after spray drying.
3. How well the experimental spray dried fruit powders compared to some commercial blueberry powders.

1. LITERATURE REVIEW

1.1 Common Drying Methods for Fruits and Vegetables

Drying involves the removal of moisture from foods to retard microbial growth and thus prevent spoilage. Drying offers a shelf-stable product and thus increases the availability of many seasonal commodities year-long. It also reduces the weight and volume of the food stuff, thereby minimizing packaging, storage and transportation costs. When drying fruit products, it is important to preserve as much of the product's nutritive value, flavor and color as possible. Some common drying means for fruit based products are solar drying, fluidized bed drying, drum drying, hot air drying, freeze drying and spray drying.

Solar drying is one of the most ancient methods used for drying food products. The advantages of open-air sun drying are that it is a free and nonpolluting energy source. However, there are many drawbacks: it is unreliable due to uncertainty of weather conditions such as temperature and humidity, thus translating to difficulties to control the drying process; it requires large area; there is possibility of insect infestation and degradation of nutrients caused by exposure to light and large amounts of oxygen (Imre 1995).

Fluid bed drying is commercially used for granular materials. It provides an even flow of fluidized particles and avoids overheating of heat-sensitive products. When drying granular products, the drying gas suspends the material. The particle size of the material should be in the range of 20 μm to 10 mm. Finer particles tend to lump together due to cohesive forces (Hovmand 1995).

During drum drying, the product is usually in fluid or slurry form, and is dried on the surface of internally heated rotating drums. It is a relatively inexpensive technique. Due to operating variables such as the uniformity of the application of the material to the drum dryer, the quality of the dried product can be easily affected. Furthermore, drum drying does not produce a product with uniform particle size. Further processing methods such as grinding may be necessary (Moore 1995).

Cabinet dryers, tunnel dryers and belt-trough dryers are designed based on hot air drying technique. During hot air drying, heated air is brought into close proximity with the wet material and convection is mainly involved (Jayaraman et al., 1995).

Freeze drying produces dried food of the highest quality in terms of flavor, aroma and nutritive value. During freeze drying, the moisture in the product is removed as a vapor by sublimation from its frozen state by vacuum. The shape and structure of the food stuff is often maintained after freeze drying and is easily rehydrated when water is added at a later time. However, due to its slow drying rate and the use of vacuum, freeze drying is an expensive process (Liapis et al., 1995).

1.2 Spray Drying

Spray drying is used for drying liquid food products. It involves the atomization of the liquid feed in a hot, dry medium, and the end product is in powder form. Fruit juices, pulps and pastes can be spray dried with the addition

of additives. These spray dried powders are generally hygroscopic and thermoplastic (Jayaraman et al. 1995). Atomization, spray air mixing and moisture evaporation and separation of dry product from the exit are the three processing steps that constitute spray drying (Filkova et al., 1995). Figure 1 shows the setup of the spray dryer in the Michigan State University Dairy facility.

1.2.1 Principles of Spray Drying

Spray drying as indicated above, transforms a fluid into a dried product in a single process. A rotating wheel or nozzle is used to atomize the fluid where the droplets come in immediate contact with a hot medium. This results in rapid evaporation which maintains a low droplet temperature and hence the application of high temperature is possible without affecting the product drastically. Thus, spray drying is suitable for the drying of heat-sensitive products (Filkova et al. 1995).

The most important operation in spray drying is atomization because it determines the energy required to form the spray and also the size distribution of the droplets, which has direct correlation with the particle size of the final product. The most commonly used atomizers are the rotary wheel and the pressure nozzle single fluid atomizers (Filkova et al. 1995).

At the bottom of the drying chamber, the dry powder is collected. Powder separators such as cyclones separate the dry product from the heating medium at high efficiency and then the powder is collected. Air and particles inside the spray dryer whirl in a spiral pattern down the cyclone, where the spray dried

particles are collected and leave the cyclone, leaving clean air flowing upwards which can escape from the top (Filkova et al. 1995).

1.2.2 Issues and Concerns during Spray Drying

During spray drying, it is important to acknowledge that there is a potential danger of explosion and fire hazards. When the temperature of the air-product mixture reaches a flammability limit, when the oxygen content is high and if flammable liquids are present, fire hazards exist.

When spray drying fruit juices and other sugar rich liquids, stickiness of the powders on the spray dryer wall is one of the major problems. The stickiness problem is due to the low glass transition temperature (T_g) of sugars. At the glass transition temperature, the amorphous food polymer is transformed to a viscous liquid or the rubbery state; and at around 10-20^{o}C higher than the glass transition temperature, the amorphous food substances exhibit stickiness problems. To improve the stickiness problems, a high molecular weight material such as maltodextrin can be added to increase the glass transition temperature. Spray dryer designs that can help improve the stickiness issues include the incorporation of a vibrated fluid bed and installation of air brooms that rotate slowly close to the chamber walls (Jaya et al., 2002; Jaya et al., 2005).

Figure 1: Michigan State University Dairy plant spray dryer schematic

1.3 Anthocyanins

1.3.1 Structure of Anthocyanins

Anthocyanin pigments are responsible for the red, purple and blue colors of many fruits, vegetables, flowers and several other plant storage organs. (Mcghie et al., 2003) They are a subclass of flavonoids. Anthocyanins are formed through photosynthesis and glycolysis (Mazza et al., 1993). They are glycosylated polyhydroxy and polymethoxy derivatives of 2-phenylbenzopyrylium cation, which is the flavylium cation shown in Figure 2 (Brouillard 1982). Anthocyanins are glycosides and acylglycosides of anthocyanidins. (Wang et al., 1997) In their anthocyanoside form, anthocyanidins are bound to glucose. They can also be found in proanthocyanidins, which are polymers of anthocyanins. There are six significant anthocyanidins found in fruits and vegetables (Francis 1989). These six important anthocyanidins are: delphinidin, cyaniding, malvidin, pelargonidin, peonidin and petunidin (Figure 3).

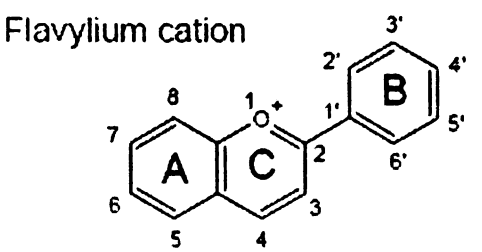
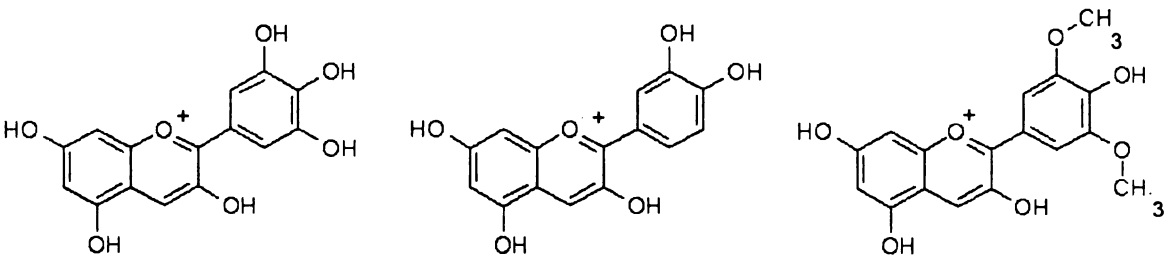
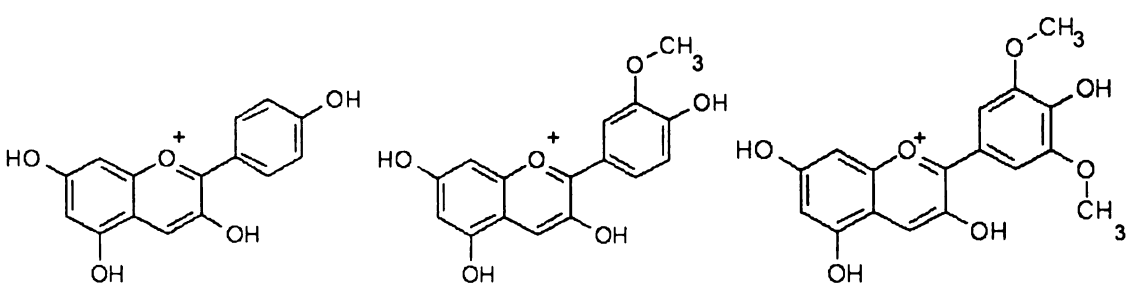


Figure 2: The flavylium cation



Delphinidin Cyanidin Malvidin



Pelargonidin Peonidin Petunidin

Figure 3: The six most important naturally occurring anthocyanidins found in fruits and vegetables

1.3.2 Impact of pH on anthocyanin Stability

pH affects the stability of anthocyanins. They are more stable in acidic solutions than in alkaline solutions with high pH values. According to Brouillard (1982), at different pH values, the ionic nature of the anthocyanins enables the changes of the molecule structure, which in turn results in different colors and hues and various pH values.

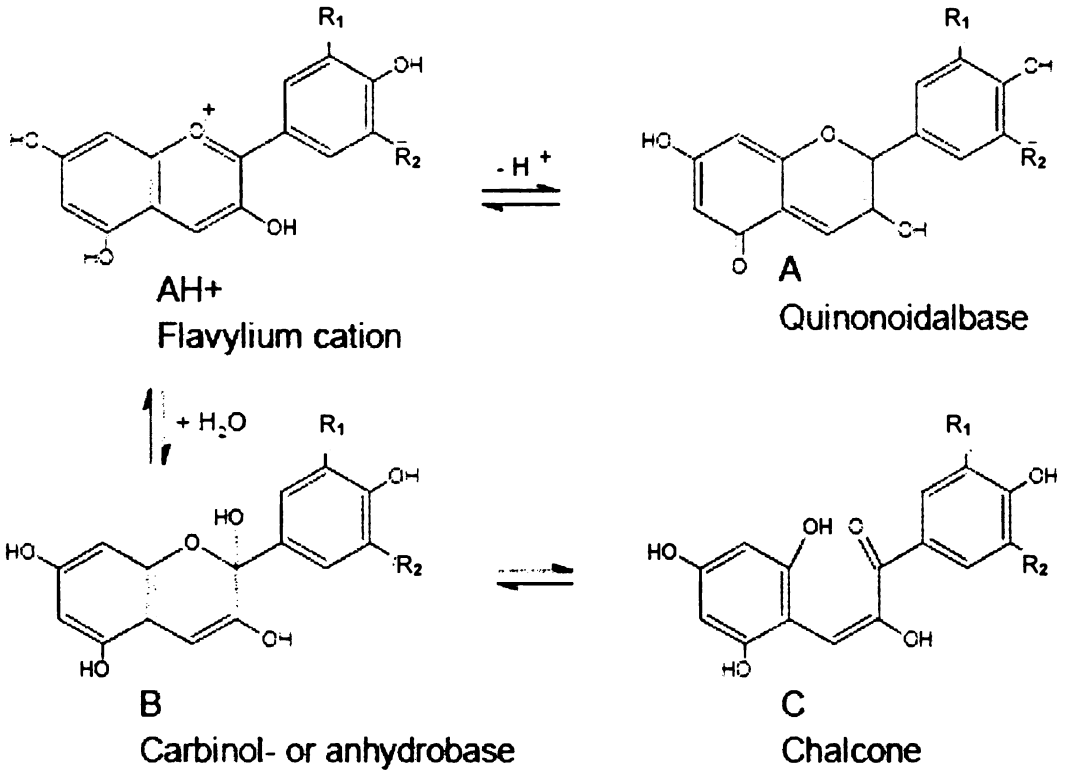


Figure 4: pH equilibrium forms of anthocyanins

According to Brouillard (1982), in acidic solutions, anthocyanins exist in the four difference equilibrium species: the quinoidal base, the flavylium cation, the carbinol or pseudobase (hemiketal) and the chalcone (Figure 4). At very acidic conditions, the flavylium cation AH+ is predominant and appears as the red color. As the flavylium is hydrated by nucleophilic attack of water, the carbinol or pseudobase is formed. In the carbinol form, the anthocyanin appears as colorless due to pH increase. A rapid proton loss from the flavylium cation takes place as the pH shifts higher and the quinoidal form is formed, where the anthocyanins appear as blue hues.

Therefore, depending on the pH, they appear in the hues in the range from orange-red to red to purple. At pH values of 1-3, the pigments will be in the form of the flavylium cation and appear as red to orange color. At pH values between 4 – 4.5, they exist as the colorless carbinol and yellowish chalcone forms. At pH 7.0 and above, they exist as the quinoidal form and appear as blue colored. These reactions are pH dependent and are reversible. The flavylium cation form is more stable and less sensitive to degradation. Hence, anthocyanins are more stable in low pH. Metal ions, heat, pH values > 4, sulfites and oxygen are some factors that can accelerate anthocyanin breakdown. (Wrolstad 2000)

1.3.3 Impact of Temperature on Anthocyanin Stability

Temperature affects anthocyanin stability. Anthocyanin degradation rate increases as temperature rises during processing and storage (Palamidis et al., 1978). By acid hydrolysis of the glycosidic bonds of cyaniding-3-glycosides at pH 2, and heating at 100°C, it was found that the rate of the loss of the glycosyl moieties of the anthocyanin was similar the rate of the loss of red color (Adams 1973). Research has shown that anthocyanin degradation follows first order kinetics (Markakis et al., 1957; Adams 1973; Ahmed et al., 2004). Thermal degradation of anthocyanins can be hindered by decreasing pH as well as removing oxygen (Markakis et al. 1957; Daravingas et al., 1968).

1.3.4 Impact of Oxygen on Anthocyanin Stability

The most detrimental condition for anthocyanins is the combination of elevated temperature in the presence of oxygen (Nebesky et al. 1949). Oxygen induced anthocyanin degradation can be classified by direct oxidative mechanism and/or, through indirect oxidation. In indirect oxidation, the oxidized constituents of the media react with the anthocyanins to form colorless or brown products (Jackman et al., 1987). Peroxyradicals are oxygen radicals, and can also react with anthocyanins. In this case, anthocyanins act as the antioxidant, which can neutralize the peroxyradicals and lead to health benefits (Rossetto et al., 2004).

1.3.5 Health Benefits of Anthocyanins

Free radicals are atoms or groups of atoms with an unpaired electron, which form reactions with oxygen. It has been shown that free radicals cause oxidative damage to lipids, proteins, and nucleic acids. Some examples of free radicals include: hydrogen peroxide, hydroxyl ions, superoxide, nitric acid and triplet oxygen. Antioxidants are molecules that donate electrons to the free radicals and therefore terminate reactions caused by free radicals. An example of the generation of free radicals in the body is cellular respiration, which is an oxygen-dependent metabolic reaction in the mitochondria.

The benefits of consuming a diet rich in fruits and vegetables has been widely acknowledged by the public. Natural antioxidants are primarily polyphenolic compounds such as anthocyanins, flavonols, flavones, isoflavones,

flavonones, and catechins that occur naturally in fruits and vegetables. Many of these compounds show high antioxidant properties and are believed to reduce the risks of a number of degenerative diseases, such as cancer, cardiovascular diseases, cataracts and macular degeneration and neurodegenerative diseases. (Halliwell 1994; Yu 1994; Kamei et al., 1995; Meiers et al., 2001).

Studies have shown that antioxidants retard oxidation of low density lipoproteins (LDL) (Laplaud et al., 1997; Satue-Garcia et al., 1997). They have also been shown to reduce cardiovascular diseases (CVD). Hypertension and atherosclerosis reduce the flexibility of capillary walls, leading to reduced blood flow. Delphinidin, an anthocyanidin, induces similar vasorelaxation properties to that of red wine polyphenols (Andrimbeloson et al., 1998). Anthocyanins are also found to reduce urinary tract infections by inhibiting *Escherichia coli* from adhering to the epithelial cells in the urinary tract (Howell et al., 1998).

Due to their health benefits and attractive color, there is an increasing trend of replacing synthetic colorants with natural pigments such as anthocyanins in the food industry. However, the stability of these natural food colorants is often affected by temperature, oxygen, water activity, and light (Clydesdale et al., 1978; Main et al., 1978). Main and others (1978) reported the use of spray drying as a means to produce shelf-stable anthocyanins. Freeze drying and drum drying are also other methods to manufacture anthocyanins; and amongst the above methods, freeze drying is considered the best way to dry and preserve these sensitive pigments, although it is also the most costly (Cai et al., 2000).

1.4 Background of Blueberries

Blueberries belong to the *Vacciniums* species and they are native to the United States. In Europe, blueberries are known as bilberries. Highbush (*V. corymbosum* L.), lowbush (*V. angustifolium* Aiton) and rabbiteye (*V. ashei* Reade) are the three major categories of blueberries in the United States (Eck 1988; Kalt et al., 1999). Michigan and New Jersey have become the largest blueberry producing states due to their climatic conditions, which favor the growth of blueberries. Blueberries can be grown for one month straight at temperatures between 7.2 to 24°C (Eck 1988). Annually, there are approximately 40 million pounds of blueberries produced in Michigan, which accounts for 32% of the nation's production (approximately 150 million pounds). Around 0.5 – 2% of the blueberries harvested are culls, which are considered unmarketable and are discarded. That translates to around 0.01 – 0.1 million pounds discarded in Michigan and 0.3 – 3 million pounds thrown away in the United States.

Using artificial selection, highbush blueberries are produced as unique varieties whereas lowbush blueberries are grown wild. Same as lowbush berries, bilberries in Europe are also grown wild and the commercial product of these two varieties contain a mixture of genotypes (Kalt et al. 1999). According to Ballington et al., belonging to the *Vacinnium* subgenera *Myrtillus*, bilberries contain anthocyanins in both their peel and flesh. Anthocyanins are only found in the peels of highbush, lowbush and rabbiteye cultivars, which belong to the subgenera *Cyanococcus*. Only of 15% of blueberries reach the fresh market.

The remaining blueberries end up in the frozen or canned sector (Moore 1994). Blemished and undesirable blueberries would end up in the wine or juice industry.

Blueberries did not gain much importance in the scientific community until Prior et al (1998) measured the oxygen radical absorbance capacity (ORAC), total phenolics and total anthocyanins of blueberries and reported it to be one of the richest sources of phytonutrients and to have the highest antioxidant capacity amongst all the fruits and vegetables studied.

1.5 Background of Grapes

Being one of the world's largest fruit crop, 65 million metric tons of grapes are produced each year (Mazza 1995). The United States alone produces over 7,828,000 tons of grapes and of that, around 7,825,000 tons are utilized. 995,000 tons are utilized as fresh and the remaining 6,830,000 tons are processed as into wine, juice, dried and canned fruit (USDA – NASS 2006).

Grapes belong to the genus *Vitis* and the *V. vinifera* species of the Vitaceae family is the most important anthocyanin containing fruit crop in the world (Timberlake et al., 1982). According to Mazza (1995), over 95% of the grapes produced are of the *V. vinifera* species. This variety is characterized by a relatively thick skin which is bound to a firm pulp and is sweet throughout.

The most prevalent species in North America include *V.* labrusca, commonly known as concord grapes, and *V. rotundifolia* species, commonly known as muscadine grapes. In the Great Lakes region of the United States and Canada,

V. labrusca grapes are most commonly grown; and the *V. rotundifolia* are grown in the southeast regions of the United States, from North Carolina to eastern Texas.

Historically, there has been great interest in extracting anthocyanin pigments from grapes as food colorants and "enocyanin", a commercial food colorant that was produced in the 1800s. Clydesdale et al (1978) recognized grape wastes as an excellent source of anthocyanin pigments which could possibly utilized as a food colorant source. Clydesdale extracted anthocyanins from the Concord grape filter trim (tartrate sludge), which was obtained from Welch Foods, Inc., and spray dried using maltodextrin (Morrex 1918, 10 – 13 DE) as a carrier agent.

Grape pomace is generated after the processing of grape wines and juices. Its main composition include skins, seeds, stems and cellulose, which is used as pressing aide. It has been used as livestock feed and fertilizer for soil, and the remaining material is treated as waste. Like Clydesdale's study in 1978, valuable anthocyanins could also be extracted from grape pomace and then spray dried to use as a food ingredient, not only to add attractive color to foods, but also to add nutritive value to food products.

1.6 Analysis of Antioxidant Capacity

It has been established that dietary antioxidants, such as phenolic compounds, vitamins E and C, and carotenoids, are effective in preventing oxidative stress related diseases such as inflammation, cardiovascular diseases, cancer and other age-relating disorders. Therefore, there is an increasing

interest in studying antioxidant capacity of the foods we consume. It is difficult to separate each antioxidant compound for analysis individually due to the complexity of the food system and the possible synergistic effects amongst the antioxidant compounds in the food matrix. (Huang et al., 2005)

1.6.1 Folin-Ciocalteu's Assay

The Folin-Ciocalteu's assay is also known as the Total Phenolics assay. It has been used for many years to measure total phenolics in natural products through the use of a spectrophotometer (Singleton et al., 1965). The mechanism of this reaction is an oxidation reduction reaction. The original Folin-Ciocalteu's assay was developed in 1927 for the measurement of tyrosine. The assay measured the oxidation of phenols by a molybdotungstate reagent and yields a colored product at absorption wavelengths of 745 – 750 nm. Although this reaction is simple and precise, it is slow at low pH. Using molybdotungstphosphoric heteropolyanion reagent, which reduced phenols more precisely at λ_{max} of 765 nm, Singleton and Rossi improved the assay. The advantages of the Folin-Ciocalteu's assay are that it is a straightforward method used for characterizing and standardizing plant samples. However, the mechanism is interfered by a number of substances, in particular sugars, aromatic amines, ascorbic acid and other enediols and reductones. Other nonphenolic organic substances such as adenine, adenosine, benzaldehyde, glycine, etc. react with the Folin-Ciocalteu's reagent. Some inorganic substances

such as sodium phosphate react with the reagent and give misleading results of elevated phenolic content. (Prior et al., 2005)

1.6.2 Oxygen Radical Absorbance Capacity ($ORAC_{FL}$)

ORAC measures antioxidant inhibition of peroxyl radical induced oxidations by 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) and thus reflects the classical chain breaking antioxidant activity by hydrogen atom transfer. Peroxyl radical reacts with a fluorescent probe to yield a non-fluorescent product, which can be monitored easily by measuring fluorescence in the function of time with incubation at 37°C. Prior et al. (2005) illustrated the reaction as follow:

$$R\text{-}N{=}N\text{-}R \xrightarrow{O_2} N_2 + 2ROO^{\cdot}$$

$ROO^{\cdot}$ + fluorescent probe $\rightarrow$ ROOH + oxidized probe (loss of fluorescence)

$$ROO^{\cdot} + AH \rightarrow ROOH + A^{\cdot}$$

$$ROO^{\cdot} + A^{\cdot} \xrightarrow{fast} ROOA$$

Initially, the reaction was carried out using β-phycoerythrin (β-PE), which is a protein isolated from *Porphyridium cruentum*, as the fluorescent probe. However, due to its inconsistency from lot to lot, there was variable reactivity to peroxyl radicals and hence, inconsistent results for the $ORAC_{PE}$ assay. Furthermore, since β-PE is not photostable: it can be photobleached subsequent to exposure to excitation light (Ou et al., 2001).

Ou et al (2001) showed that the fluorescein (FL) (3',6'-dihydroxyspiro[isobenzofuran-1[3*H*],9'[9*H*]-xanthen]-3-one) probe is preferred over β-PE due to its stability and reduced reactivity. After identification by LC/MS, it is determined that the oxidized products of FL induced by peroxyl radicals follow ac classical hydrogen atom transfer mechanism. (Prior et al. 2005)

The reaction mixture consists of AAPH, as the radical generator; a fluorescent probe, such as β-PE or more commonly nowadays, fluorescein; antioxidant samples at appropriate dilutions or Trolox, which is a vitamin E analogue and exhibits antioxidant properties, as the control which are buffered in sodium phosphate buffer solution (Cao et al., 1999). The samples are incubated at 37°C and fluorescence is measured every minute until the reaction goes to completion. The higher the antioxidant capacity of a product, the longer it takes for the reaction to go to completion. Data reduction from the ORAC assay is achieved by calculating the area under the kinetic curve (AUC) and net AUC ($AUC_{sample} - AUC_{blank}$), using the trapezoidal rule and obtaining a standard curve by plotting the concentrations of Trolox against AUC for calculation of the Trolox equivalents of a sample using the standard curve. ORAC results are often reported as Trolox equivalents. Trolox is a vitamine E analogue and is a known antioxidant. Data are reported as micromoles of trolox equivalents (TE) per gram or liter of sample (μmol of TE/g or μmol of TE/L)

1.6.3 High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) with UV-Vis or diode array detectors (DAD) is the most studied methods for separation and quantification of anthocyanins. The most powerful method for identification of individual anthocyanins is, however, HPLC coupled with a mass spectrometer (MS). One of the major challenges for quantifying individual anthocyanins is the lack of existing anthocyanin standards. As of year 2003, there are more than 400 naturally existing anthocyanins reported and they consist of one of six aglycones glycosylated with various sugar substitutes (Kong et al. 2003). There are only a few anthocyanin references that are commercial available.

Acid hydrolysis can be performed to reduce the complex anthocyanin glycosides to six major anthocyanidins: delphinidin, cyanidin, petunidin, peonidin, pelargonidin and malvidin, for easy quantification. The advantages of acid hydrolysis of anthocyanins are that it greatly simplifies the profile of anthocyanins and the anthocyanidins aglycones can be completely separated. Therefore, it is possible to accurately quantify individual anthocyanidins. The HPLC analysis without hydrolysis is very useful for the control of product quality and the identification of raw materials. Both methods are precise and can be applied to any plant extracts. (Zhang et al., 2004)

2. MATERIALS AND METHODS

2.1 Plant Material

2.1.1 Cull Blueberries

Cull blueberries were collected from True Blue Farms in Grand Junction, Michigan. Cull blueberries include under and over ripe blueberries and range from 0.5 – 2% of the total volume of blueberries harvested in Michigan (Dave Trinka, personal correspondence, 2005). At True Blue Farms, the blueberries were sorted using a color sorter. Annually, there are one million pounds of cull blueberries discarded. The cull blueberries were stored in 30 pound boxes in the Michigan State University Food Science Pilot Plant freezer (room 124D) at -15°C until extraction for spray drying.

2.1.2 Grape Pomace

Grape pomace is the residue remaining when grapes are processed for wine making. They consist of mainly the pulp, peel, seeds, stalks and pressing aide, which is usually cellulose. Concord grape pomace was collected from St. Julian Winery in Paw Paw, MI. The grape pomace was packed in 30 pound boxes and stored at -15°C until extraction for spray drying.

2.2 Extraction of Anthocyanins

Simple alcohols such as methanol and ethanol, and acetone combined with small amounts of concentrated acids, usually hydrochloric acid or glacial acetic acid, are typically used to optimize the extraction of anthocyanins (Prior et

al. 1998). Insufficient evaporation of alcohols prior to spray drying will impose a fire hazard. The lower limit of flammability of ethanol, methanol and acetone are 3.3, 6.0 and 2.15% (v/v) respectively (Markowski et al., 1995). If alcohol were to be used for extraction, they should be lower than the lower limit of flammability in air to ensure safety. Furthermore, evaporation of alcohol adds to production cost of the low-cost added-value spray dried fruit powders. The method below was used for the extraction of anthocyanins from the cull blueberries and grape pomace.

Anthocyanins from both cull blueberries and grape pomace were extracted in the exact same manner. Cull blueberries or grape pomace was added to 1% citric acid at a 1:3 ratio and heated to 100°C for 30 minutes in a steam jacketed kettle. While heating, the kettle was covered with foil to minimize evaporation. After heating, the material was strained and the extract collected. The collected extract was then put through the Vibrecon separator, unit number 97179 (Southwestern Wire Cloth Inc., Tulsa, OK). The Vibrecon is equipped with a 100 mesh screen to allow the retention of only very fine particles to prevent the clogging of the nozzle during spray drying. The solids content of the extract was then determined using Sartorius MA 30 moisture meter (Edgewood, NY, USA). Maltodextrin (Maltrin-M100 Grain Processing Corporation, Muscatine, IA, USA) was added using a mechanical mixer model C2 with 1/8 horsepower and 1725 rpm (Lightnin Mixing Equipment Co. Inc. Rochester, NY, USA) at three determined levels of blueberry solids to maltodextrin of 5:95, 10:90 and 30:70 (w/w).

2.3 Spray Drying

The pilot plant spray dryer used in the Michigan State University Dairy Plant is from Marriott Walker Corporation (Birmingham, MI, USA), model 5.7T-1-C. Its dimensions are 1.73 meters interior diameter and 3.05 meters chamber height and 1.26 meters cone height.

The drier is a single-stage tower drier with a cyclone and a product receiver cyclone for the conveying system. The product was held in a balance tank, and went through a high-pressure pump up to the spray nozzle. The air heating system was direct gas-fired and the air was filtered before going into the heating chamber.

The spray dried powder and process air exit out the bottom of the drier into the air/powder transfer duct, which carries it to the main cyclone. At the bottom of the cyclone is a rotary airlock. The process air was then removed via the exhaust fan, which maintained a small vacuum throughout the system. After the airlock, the product can be collected, or sent through a small cooler/conveyor system to be cooled, and then recovered from the product receiver cyclone, which also has a rotary airlock. The conveying air is also removed through the exhaust fan.

The feed was preheated to approximately 60°C with constant stirring and then transferred to the balance tank of the spray dryer. For study 1, which was an initial study to determine the maximum ratio of blueberry solids to maltodextrin, the spray drying conditions were kept constant for each run with air inlet temperature at 140 – 150°C and air outlet temperatures of 75 - 85°C.

Individual runs of blueberry solids to maltodextrin ratios of 5:95, 10:90 and 30:70 were performed. Samples were collected before and after spray drying for analyses.

For study 2, the effects of spray dryer outlet temperatures on nutraceutical content of blueberry by-products were analyzed. The feed was also preheated to around 60°C prior to spray drying. The air inlet temperature was kept constant at 150 – 155°C and the air outlet temperature varied. Duplicate runs of air outlet temperatures of approximately a)80°C and b)90°C were performed with the blueberry solids to maltodextrin ratio constant at 30:70.

For study 3, the effects of spray dryer outlet temperatures on nutraceutical content of grape by-products were analyzed. The feed was also preheated to around 60°C prior to spray drying. The air inlet temperature was kept constant at 150±5°C and the air outlet temperature varied. Duplicate runs of air outlet temperatures of around a)80°C and b)90°C were performed with the grape solids to maltodextrin ratio constant at 30:70.

For study 4, five commercial blueberry powders were compared to randomly chosen blueberry and grape powders produced in the above studies. Oxygen radical absorbance capacity, total phenolics and individual anthocyanins of the powders were analyzed and compared on a per gram fruit powder basis.

2.4 Particle Size Analysis

Particle size of the powders obtained after spray drying were estimated using different mesh-size sieves (W. S. Tyler Co., Mentor, OH). Mesh-size

sieves ranging from Number 200 (75 microns) to Number 425 (32 microns) were used for testing.

2.5 Oxygen Radical Absorbance Capacity ($ORAC_{FL}$)

Fluorescein sodium salt, 2,2'-Azobis(2-amidinopropane) dihydrochloride (AAPH) and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were purchased from Sigma-Aldrich (St. Louis, MO). Black-sided, special optics clear bottom plates (part # 3615) were obtained from Corning (Corning, NY).

2.5.1 Sample and Reagent Preparation

The ORAC assay was perform as described by Huang *et al* (2002) where 0.414 g AAPH was dissolved in 10 mL 75 mM phosphate buffer (pH 7.4) to obtain a final concentration of 153 mM. The AAPH was prepared fresh daily. The fluorescein stock solution of 4×10^{-3} mM was prepared in 75 mM phosphate buffer (pH 7.4) and stored wrapped in foil and placed in the refrigerator. Fresh fluorescein stock solution should be remade every three months. Prior to analysis, a fluorescein working solution is made daily by diluting the fluorescein stock solution 1:1000 with 75 mM phosphate buffer (pH 7.4). The trolox standards were prepared by dissolving 0.25 g trolox in 500 mL of the 75mM phosphate buffer (pH 7.4) to give a 1.89×10^{-3} M stock solution. The stock solution was diluted prior to each analysis with the same phosphate buffer to 6.25, 12,5, 25, 50 and 100 µM working solutions.

2.5.2 Experimental Setup for $ORAC_{FL}$

The exterior wells of the plate were filled with 300µL of water, while the interior wells were used for experimental analyses. 150 µL of working sodium fluorescein solution was added to all experimental wells; to the blank wells, 25 µL of 75 mM phosphate buffer (pH 7.4) was added; to the standard wells, 25 µL of trolox dilutions were added and to the sample wells, 25 µL of appropriate sample dilutions was added. The plate was then incubated for 30 minutes at 37°C in the FLx800 Multi-Detection Microplate Reader (Biotek Instruments, Winooski, VT, USA) after which reactions were initiated by the addition of 25 µL of AAPH solution that was freshly prepared. The microplate reader was controlled by the Biotek Gen5 software where it was programmed to shake the microplate automatically for 10 seconds prior to each reading. Detection parameters were set at 485 nm, 20 nm bandpass, excitation filter and a 528 nm, 20 nm bandpass, emission filter. The fluorescence was monitored kinetically and recorded every 1 minute and 30 seconds.

2.5.3 Data Analysis of $ORAC_{FL}$

ORAC values were computed according to Cao and Prior (1999). The net area under the curve (AUC) of the standards and samples were calculated using the trapezoidal rule as shown in equation 1.

$$AUC=\left(\frac{R1}{2}+R2+R3+...+R_{n-1}+\frac{Rn}{2}\right)\Delta t \qquad \text{(Eq. 1)}$$

Where R1 is the fluorescence reading at the initial time of the reaction and Rn is the final measurement of fluorescence. Δt is the time difference between each reading.

The net AUC is determined by $AUC_{sample} - AUC_{blank}$ and the standard curve was obtained by plotting the trolox concentrations against the net AUC of different trolox concentrations. The ORAC values of the samples could then be calculated automatically using the Biotek Gen5 software by interpolating the sample's net AUC against the trolox standard curve, with the dilution factor taken into account. Results are generally expressed as trolox equivalents (TE) μmol TE / g sample or μmol TE / mL sample.

2.6 Folin-Ciocalteu's Assay

2.6.1 Preparation of saturated sodium carbonate solution

50 grams of sodium carbonate was added to 200 mL of deionized water. The solution is stirred and heated until the sodium carbonate was completely dissolved. The solution was then filtered and stored at room temperature until precipitation of crystals occurs. The sodium carbonate solution was stored for further use.

2.6.2 Preparation of Gallic Acid Stock solution

1000 ppm of gallic acid stock solution was prepared by weighing 0.5g gallic acid and dissolving it in 500 mL deionized water. 0.5 mL ethanol or the use of a sonicator can help dissolution of gallic acid. The stock solution can be stored in an amber glass container in the refrigerator for up to 3 months. Fresh working standards using the gallic acid stock solution were prepared for each analysis.

2.6.3 Preparation of Gallic Acid Standards for Analysis

The gallic acid stock solution was brought to room temperature before use. Five standards were prepared fresh in a test tube each time of analysis:

25 ppm 0.5 mL stock solution brought to 20 mL with DI water

50 ppm 0.5 mL stock solution brought to 10 mL with DI water

100 ppm 1.0 mL stock solution brought to 10 mL with DI water

150 ppm 1.5 mL stock solution brought to 10 mL with DI water

200 ppm 2.0 mL stock solution brought to 10 mL with DI water

2.6.4 Analysis of Total Phenolics

In blank test tube, 0.5 mL of DI water was pipetted; 0.5 mL of gallic acid standards were added to corresponding test tubes and 0.5 mL of diluted samples were added to subsequent test tubes. To each test tube, 8.8 mL of DI water, 0.2 mL Folin-Ciocalteu's reagent and 0.5 mL of sodium carbonate solution were added and the contents were vortexed. The intensity of the blue color of each

test tube was measured at 750 nm and 765 nm using a LKB Biochrom Ultrospec II spectrophotometer (Cambridge, United Kingdoms) after one hour.

Linear regression of the absorbance data for the gallic acid standards vs. gallic acid concentration was performed and the resulting graph, along with the absorbance data for the diluted samples, was used to calculate the concentration of total phenolics in ppm for each sample. The results were then corrected for the dilution factor and results are expressed as gallic acid equivalents (GAE) mg GAE / g sample or mg GAE / mL sample.

2.7 Analysis of Individual Anthocyanidins

2.7.1 Anthocyanidin Preparation

1 mL Extract samples or diluted powder samples were combined with 0.25 mL 12.1 N HCl and 0.25 mL distilled water in a screw-cap test tube to achieve a 2 N final concentration. The capped test tube was heated in a boiling water bath for 30 minutes. Then it was cooled in an ice bath before centrifugation. The Sorvall RT 6000B Refrigerated Centrifuge (Du Pont, Wilmington, DE, USA) was set at 3000 rpm for 10 minutes.

2.7.2 Solid Phase Extraction

C_{18} Sep-Pak cartridge (Vac 6cc, Waters, Milford, MA, USA) was activated with 5 mL ethyl acetate, followed by 5 mL acidified methanol (0.1% hydrochloric acid, v/v) and lastly with 5 mL acidified water (0.1 % hydrochloric acid, v/v). 1 mL of centrifuged hydrolysate was applied to the activated C_{18} Sep-Pak cartridge

and the anthocyanidins were washed with 5 mL of acidified water, 5 mL of ethyl acetate, which elutes polyphenolics other than anthocyanidins, and the anthocyanidins were recovered by 5 mL of acidified methanol. The acidified methanol elutant was evaporated using a rotary evaporator (Laborata 4002 digital, Heidolph Instruments, Cinnaminson, NJ, USA) to dryness at 35°C. It was then redissolved in 1 mL acidified methanol for subsequent analysis.

2.7.3 High Performance Liquid Chromatography

2.7.3.1 HPLC Parameters

The HPLC is equipped with a 717plus autosampler, 2487 Dual λ Absorbance Detector and 1500 Series HPLC Pump (Waters, Milford, MA, USA). Sample injections were set at 20 µL and absorbance was measured at 520 nm. The flow rate was set at 1 mL/min and the temperature was ambient. Breeze Software 3.3 was used for monitoring the experiment.

2.7.3.2 HPLC Analysis of Anthocyanidins

Prior to analyses by HPLC, the samples were filtered using 0.2µm Millipore syringe filters directly into HPLC vials. Anthocyanidins were separated using Agilent Zorbax Eclipse XDB-C18 column (4.6 x 250mm, 5µm) and it was protected by a Agilent Zorbax High Pressure Reliance Cartridge Guard-Column (4.6 x 12.5mm, 5µm) (Santa Clara, CA, USA)column. Solvent A: 100% acetonitrile and solvent B: 1% phosphoric acid, 10% acetic acid 5% acetonitrile (v:v:v). The software was set to follow 30 minutes linear gradient from 0 – 30%

solvent A. Anthocyanidin reference standards delphinidin chloride, cyanidin chloride, peonidin chloride and malvidin chloride were purchased from Sigma-Aldrich (St. Louis, MO, USA); petunidin chloride was purchased from Extrasynthèse (Genay Cedex, France)

According to the manufacturer's suggestion, the anthocyanidin standard curves were prepared by dissolving delphinidin chloride in methanol; cyanidin chloride was dissolved in 5% hydrochloric acid in 80% ethanol; malvidin chloride was dissolved in 95% ethanol; and petunidin chloride was dissolved in methanol acidified with 0.1% hydrochloric acid. All samples were dissolved at 1 mg / mL solvent. Appropriate dilutions were then made using the solvent recommended to generate a standard curve.

2.8 Particle Residence Time in Spray Dryer Estimation

The maximum time (t_{max}) that each particle spent in the spray dryer can be estimated using the following equations:

$$H_1 = L_1 W_1 \qquad \text{(Eq.2)}$$

$$H_2 = L_2 W_2 \qquad \text{(Eq. 3)}$$

L = BTU/lb water evaporated (psychrometric chart from Proctor & Schwartz)

W = lb water / lb dry air (psychrometric chart from Proctor & Schwartz)

Heating rate of air (BTU / hr) from natural gas = gas flow (ft^3/hr) * 1020 (assumed fuel value of natural gas = 1020 BTU/ft^3 (Eq. 4)

$$\dot{m}_{dry\ air} = \text{dry air mass flow rate} = \frac{\text{Heating Rate of Air from natural gas}}{(H_2 - H_1)} \qquad \text{(Eq.5)}$$

V_2 = air flow rate in the spray dryer (psychrometric chart from Proctor & Schwartz)

$$\bar{u} = \frac{V_2\left[\frac{ft^3}{lbm\ dry\ air}\right]\dot{m}_{dry\ air}\left[\frac{lbm\ dry\ air}{hr}\right]}{A_{cross\ section}\left[m^2\right]} \qquad \text{(Eq. 6)}$$

$$t_{max} = \frac{\text{height of verticle section}}{\text{average velocity}} = \frac{h}{\bar{u}} \qquad \text{(Eq. 7)}$$

The t_{max} value of any particle spent in the spray drying chamber, cone and pipes should be calculated separately and then summed for the total maximum residence time estimation for a particle in the spray dryer. The height of the vertical section of the spray drying chamber is 3.05m with a diameter of 1.93m. The cone has a height of 1.79m and the length of the pipe section is 7.01m with a 0.15m diameter.

2.9 Rate Constant Determination of Anthocyanin Degradation

The rate of anthocyanin degradation has been found to follow a first-order reaction (Sastry et al., 1952). An overall constant for anthocyanin degradation (k) could therefore be computed using the following equation

$$\frac{C}{C_0} = e^{-kt} \qquad \text{(Eq. 7)}$$

Where $\frac{C}{C_0}$ is the retention of anthocyanins after spray drying and t is obtained from Equation 7.

3. RESULTS AND DISCUSSION

3.1 Study 1: Spray Drying of Cull Blueberries with Varying Levels of Maltodextrin

Table 3.1.1 Spray drying conditions and data for cull blueberry extract containing varying levels of maltodextrin.

Ratio of Blueberry solids to Maltodextrin	5:95	10:90	30:70
Feed Temp (°C)	60	60	60
Air inlet Temp (°C)	145±5	145±5	145±5
Air outlet Temp (°C)	75±5	75±5	75±5
Specific gravity	1.632	1.567	1.011
Feed weight (lbs)	42.20	35.78	31.50
Bowl Feed Rate (cm / min)	0.37	0.33	0.98
Powder weight (lbs)	10.84	4.32	2.16
Feed total solids (%)	29.24	17.99	6.98
Feed moisture (%)	70.76	82.01	93.02
Powder moisture (%)	6.84%	7.50%	8.08%
Powder solids (%)	93.16%	92.50%	91.92%
Calculated sample Solids (lbs)	12.34	6.44	2.20
Solids in powder (lbs)	10.10	4.00	1.99
Yield (%)	81.84	62.08	90.32

Table 3.1.1 shows the spray drying conditions and additional data collected in this study. Three different levels of maltodextrin were mixed into the extracted blueberry extract at the following percentages: 95%, 90% and 70%. Samples with 50:50 blueberry solids to maltodextrin were also spray dried but was unsuccessful due to the sticky issues in the spray dryer, which caused clogging and termination of the run.

The feed temperature was kept constant at 60°C and the air inlet and outlet conditions were maintained as closely as possible at 145±5°C and 75±5°C respectively. This allows the examination of how maltodextrin impacts the antioxidant properties of the final spray dried product.

The decreasing weight of powder obtained as the maltodextrin level decreased was due to the fact that maltodextrin was added as a ratio to the blueberry solids in the extract. Therefore, at higher maltodextrin levels, more powder would be obtained.

The yield was satisfactory (>80%), except for 10:90 which showed only ~62%. This may be due to remaining powder in the spray dryer. A ~90% yield obtained for the 30:70 run seemed rather high and it may be due to the carry over of the remains from the 10:90 run. Due to time and money constraints, the spray dryer was not switched off and cleaned under sanitation standard operating procedures prior to each run, and this might have caused carry over of the powder from run to run.

3.1.1 Particle Size Analysis

For the spray dried blueberry powder containing 5:95 ratios of blueberry solids to maltodextrin, the particle size ranged approximately from 53 – 63 microns, corresponding 270 and 230 mesh size sieves, respectively. For the spray dried blueberry powder containing 10:90 ratios of blueberry solids to maltodextrin, the particle size ranged approximately from 38 –45 microns, corresponding 400 and 325 mesh size sieves, respectively. For the spray dried blueberry powder containing 30:70 ratios of blueberry solids to maltodextrin, the particle size ranged approximately from 32 – 45 microns, corresponding 450 and 325 mesh size sieves, respectively.

There was a clear trend showing an increase in particle size as the level of maltodextrin increased. This may be due to the agglomeration of maltodextrin around the blueberry solids. Literature shows spray dried whole milk powder to have a particle size ranging from 0.3 to 100 microns (Aguilar et al., 1994). When compared to the blueberry powder that contained 95% maltodextrin, the blueberry powder containing 90% maltodextrin showed a ~28% decrease in mean particle size, and the powder containing only 70% of maltodextrin showed a ~40% decrease in particle size.

3.1.2 Oxygen Radical Absorbance Capacity

Prior to spray drying, samples of the 5:95, 10:90 and 30:70 blueberry extract were collected and analyzed for $ORAC_{FL}$. When the results were converted to per gram blueberry solids basis, it exhibited no significant difference between the three samples when examined using the Tukey's Test. The averages of the three extract samples were: 924.23, 913.17 and 906.13 μmol TE / g blueberry solids (extract) for 5, 10 and 30% blueberry solids respectively. Literature shows 2441 – 2792 μmol TE / g blueberry extract (dry basis) (Ou et al. 2001). Literature values show a higher $ORAC_{FL}$ value because high quality blueberries were used, as opposed to cull blueberries, which were used for this study and Study 2.

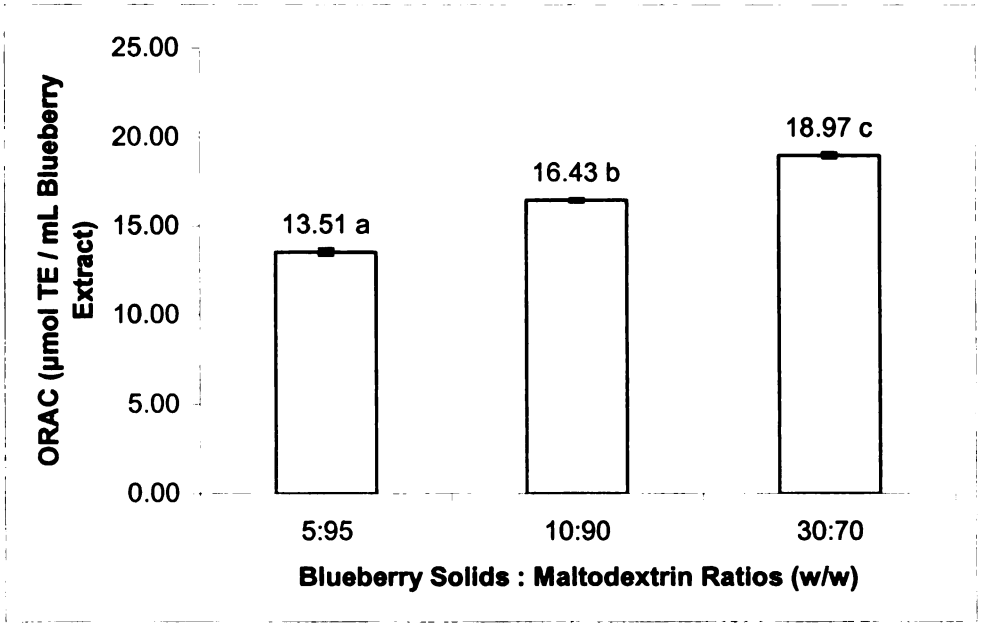


Figure 3.1.2.1 ORAC values per gram of blueberry extract containing different levels of maltodextrin

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

**Results are expressed as micromoles of Trolox Equivalents per milliliters of Blueberry Extract (µmol TE / mL Blueberry Extract)

The $ORAC_{FL}$ value can also be expressed per milliliter of blueberry extract (Figure 3.1.2.1). The $ORAC_{FL}$ value of the blueberry extracts that contained 5%, 10% and 30% of blueberry solids before spray drying were significantly different. With an increased percentage of blueberry solids per milliliter of blueberry extract, an increase in the $ORAC_{FL}$ value was detected. It was expected that the extract that contained the highest percentage of blueberry solids would show the highest $ORAC_{FL}$ value.

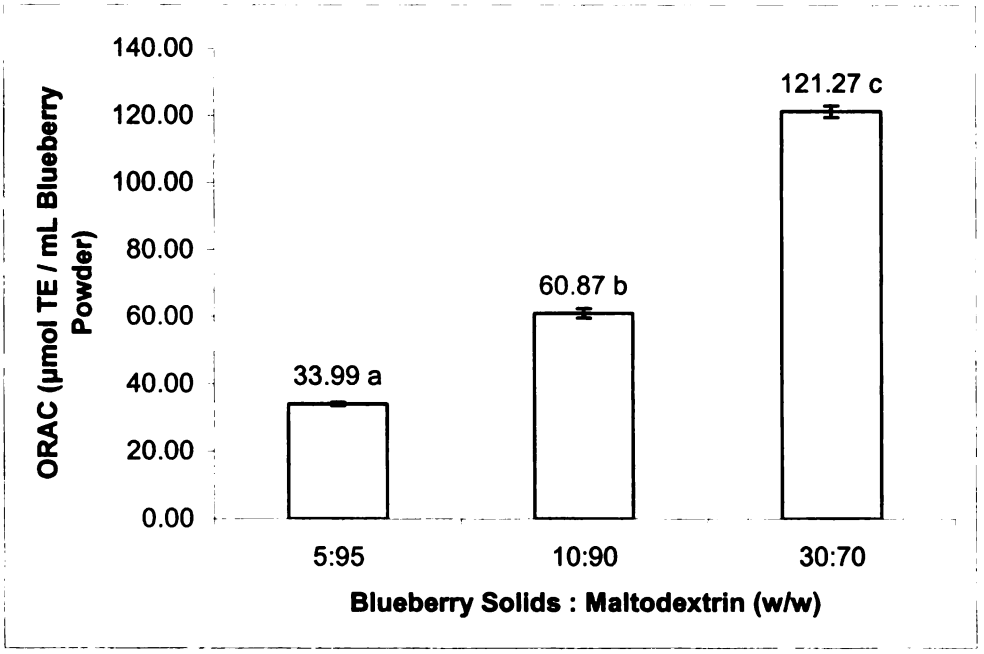


Figure 3.1.2.2 ORAC values per gram of blueberry powder containing different levels of maltodextrin

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

**Results are expressed as micromoles of Trolox Equivalents per gram of Blueberry Powder (µmol TE / g Blueberry Powder)

After spray drying the blueberry powders containing 5, 10 and 30% of blueberry solids were analyzed for $ORAC_{FL}$ per gram blueberry powder basis (Figure 3.1.2.2). The trend obtained was the same as the samples before spray drying, with the sample containing the least percentage of blueberry solids expressing the lowest $ORAC_{FL}$ value.

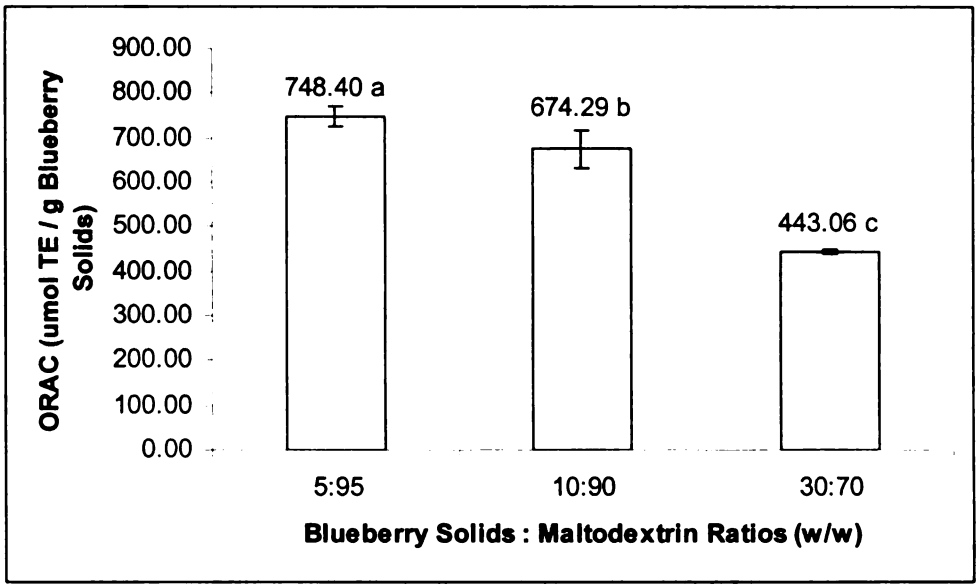


Figure 3.1.2.3 ORAC values per gram of blueberry solids containing different levels of maltodextrin during spray drying

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

**Results are expressed as micromoles of Trolox Equivalents per gram of Blueberry Solids (µmol TE / g Blueberry Solids)

When converted to per gram of blueberry solids, the spray dried powder showed an inverse trend where the sample that contained the least blueberry solids had a higher $ORAC_{FL}$ value and vice versa (Figure 3.1.2.3). The calculated percentage reduction in $ORAC_{FL}$ per gram of blueberry solids after spray drying was: 19%, 26% and 51% for samples that contained 5, 10 and 30% blueberry solids respectively.

3.1.3 Total Phenolics

Samples containing the different ratios of blueberry solids to maltodextrin were collected before spray drying and analyzed for total phenolics using the Folin-Ciocaulteu's assay. When the results were converted to per gram blueberry solids basis, it exhibited no significant difference among the three

samples when examined using the Tukey's Test. The averages of the three extract samples were: 37.58, 36.43 and 32.37 mg GAE / g blueberry solids for blueberry extract containing 5, 10 and 30% blueberry solids respectively. Literature shows that the mean of total phenolics for different cultivars of blueberries to be approximately 290.7 mg GAE / 100g fresh weight (Prior et al. 1998). Assuming blueberries contain ~5% solids, the total phenolic value found in literature would translate to around 58.14 mg GAE / g blueberry solids, which is higher than the values obtained for this study.

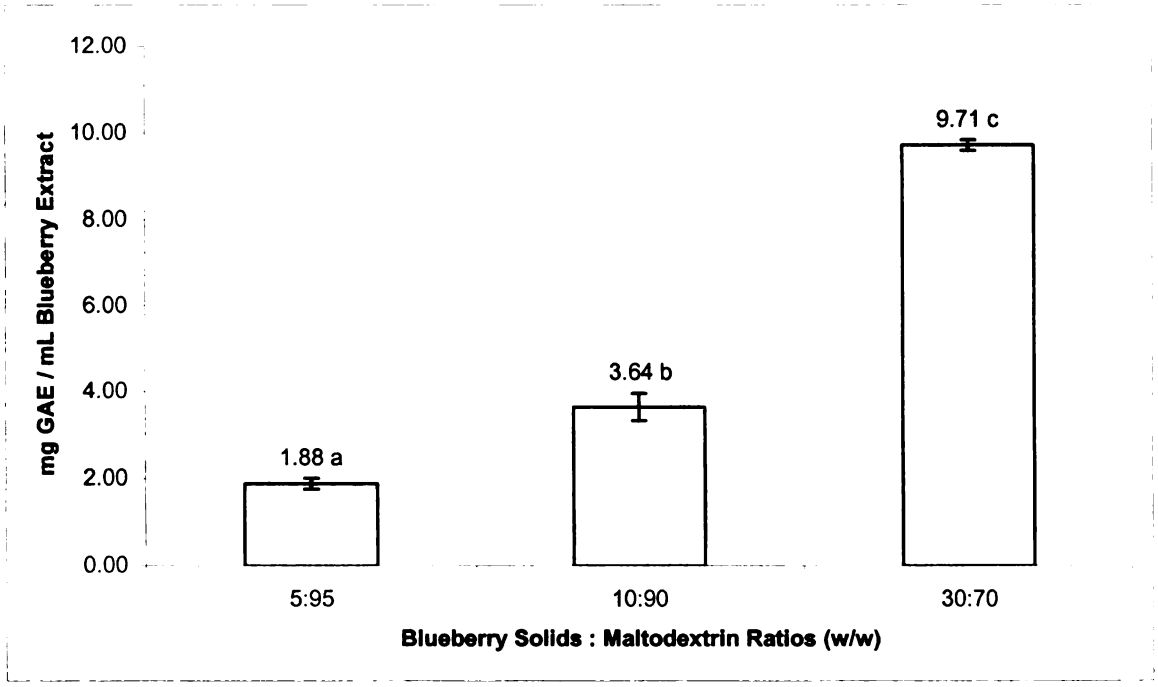


Figure 3.1.3.1 Total phenolics per milliliters of blueberry extract containing different levels of maltodextrin before spray drying, measured at 765nm
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)
** Results are expressed as Gallic Acid Equivalents per milliliters of Blueberry Extract (mg GAE / mL Blueberry Extract)

As seen in Figure 3.1.3.1, the total phenolics value of the blueberry extracts that contained 5%, 10% and 30% of blueberry solids before spray drying were

significantly different. With an increased percentage of blueberry solids per milliliter of blueberry extract, an expected increase in total phenolics value was detected.

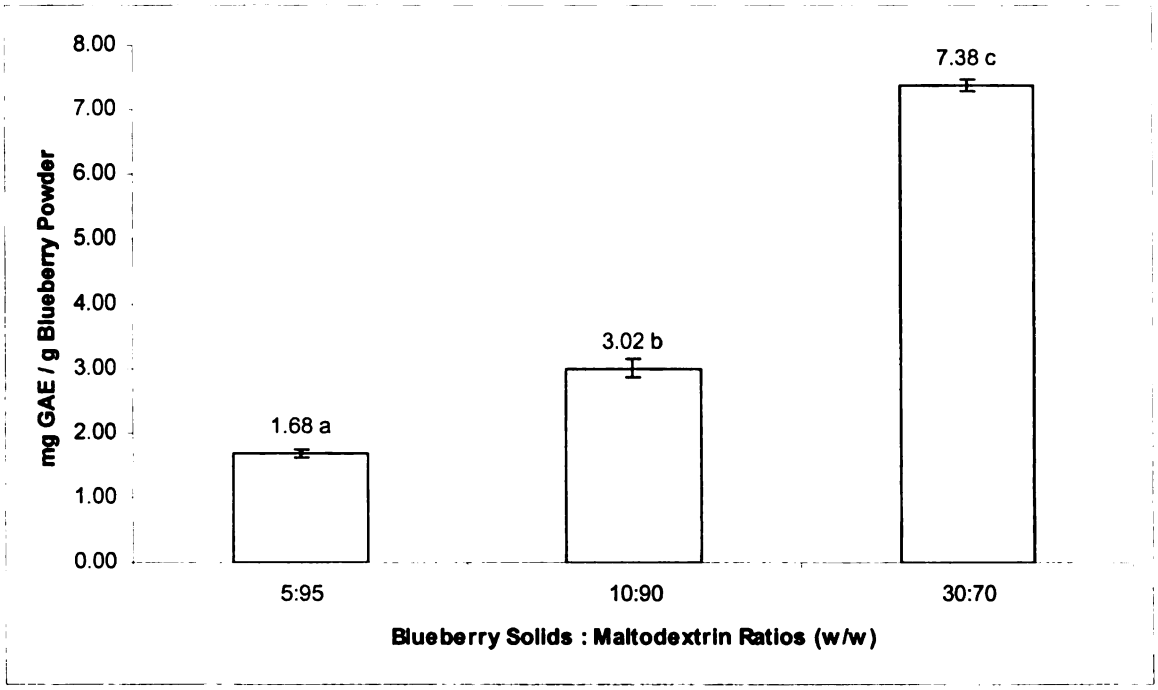


Figure 3.1.3.2 Total phenolics per gram of blueberry powder containing different levels of maltodextrin after spray drying, measured at 765nm

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

** Results are expressed as Gallic Acid Equivalents per gram of Blueberry Powder (mg GAE / g Blueberry Powder)

When analyzed for total phenolics, the same trend of $ORAC_{FL}$ appeared for the spray dried powder. The sample containing the least percentage of blueberry solids expressed the lowest total phenolic value (Figure 3.1.3.2)

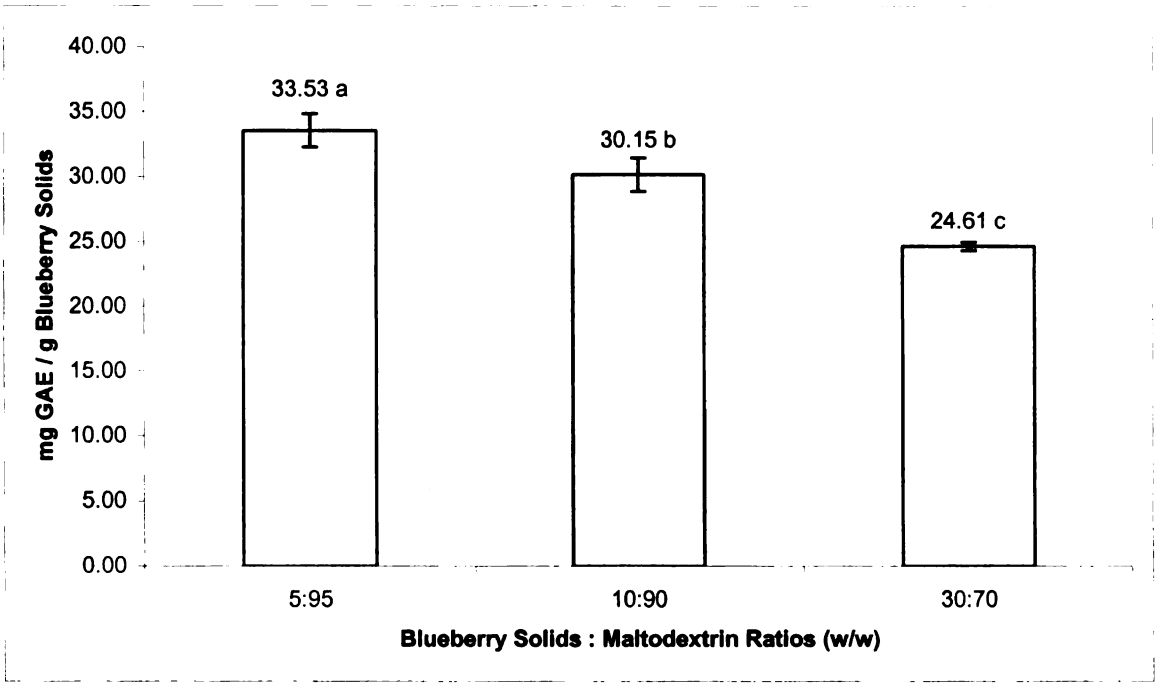


Figure 3.1.3.3 Total phenolics per gram of blueberry solids containing different levels of maltodextrin after spray drying, measured at 765nm

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

** Results are expressed as Gallic Acid Equivalents per gram of Blueberry Solids (mg GAE / g Blueberry Solids)

When converted to per gram of blueberry solids, the spray dried powder again showed an inverse trend where the sample that contained the least blueberry solids had a higher total phenolic value and vice versa (Figure 3.1.3.3). The calculated percentage reduction in total phenolics per gram of blueberry solids after spray drying was: 11%, 17% and 24% for samples that contained 5, 10 and 30% blueberry solids respectively.

3.1.4 High Performance Liquid Chromatography

High performance liquid chromatography was used to analyze five commonly found anthocyanidins in blueberries: delphinidin, cyanidin, petunidin,

peonidin and malvidin. Figure 3.1.4.1 shows a typical chromatogram obtained from blueberry samples, with the corresponding elution times of respective anthocyanidins.

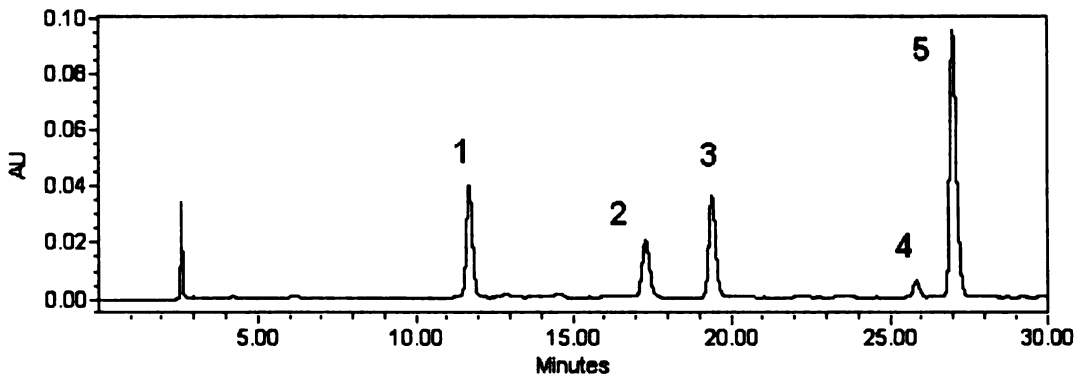


Figure 3.1.4.1 Typical chromatogram of anthocyanidins detected in blueberry samples. Corresponding anthocyanidin peak assignments: 1= delphinidin, 2 = cyanidin, 3 = petunidin, 4 = peonidin, 5 = malvidin

Table 3.1.4.1 Delphinidin determination of blueberry samples containing 5, 10 and 30% blueberry solids before and after spray drying

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg anthocyanidins / mL Blueberry Extract (Before Spray Drying)	µg anthocyanidins / g Blueberry Powder (After Spray Drying)	µg anthocyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg anthocyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of anthocyanidin[a]
5:95 Delphinidin	23.10±0.21	21.33±0.18	461.92±4.25 **A**	458.02±3.83 **A**	0.84%
10:90 Delphinidin	76.88±6.62	23.92±3.04	459.64±6.62 **A**	258.57±32.9 **B**	43.74%
30:70 Delphinidin	138.46±2.49	29.75±1.59	461.52±2.49 **A**	107.89±5.75 **C**	76.62%

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

Table 3.1.4.1 shows the values of delphinidin obtained from the three different spray dried blueberry samples containing different ratios of blueberry solids. When analyzed in both extract form (before spray drying) and powder

form (after spray drying), there was a significant difference in all three samples, with an increasing μg delphinidin detected per mL or g of sample respectively. When converted to per gram blueberry solids basis, no significant difference was found in the extract prior to spray drying; and the 5% blueberry solid sample showed the least degradation in delphinidin content. The samples expressed in per gram blueberry solids showed significant difference among all three powders. The percentage degradation of the samples is shown in Table 3.1.4.1. The sample that contained 95% maltodextrin showed the least degradation.

Table 3.1.4.2 Cyanidin determination of blueberry samples containing 5, 10 and 30% blueberry solids before and after spray drying

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	μg anthocyanidins / mL Blueberry Extract (Before Spray Drying)	μg anthocyanidins / g Blueberry Powder (Before Spray Drying)	μg anthocyanidins / g Blueberry Solids (Extract, Before Spray Drying)	μg anthocyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of anthocyanidin[a]
5:95 Cyanidin	3.53±0.33	1.70±0.09	70.64±6.57 **A**	36.47±2.01 **C**	48.37%
10:90 Cyanidin	6.94±0.91	3.28±0.92	69.42±9.07 **A**	35.46±0.84 **C**	48.92%
30:70 Cyanidin	25.81±1.76	4.95±0.43	86.05±5.87 **B**	17.95±1.57 **D**	79.14%

[a] Calculated from μg anthocyanidins / g Blueberry Solids before and after spray drying
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

Table 3.1.4.2 shows the values of cyanidin obtained from the three different spray dried blueberry samples containing different ratios of blueberry solids. When analyzed in both extract form (before spray drying) and powder form (after spray drying), there was a significant difference in all three samples, with an increasing μg cyanidin detected per mL or g of sample respectively. When converted to per gram blueberry solids basis, no significant difference was found in the extract prior to spray drying; and the 5% blueberry solid sample showed the least degradation in cyanidin content. However, no significant

difference was found in the sample containing 5% and 10% blueberry solids for cyanidin analysis. The percentage degradation of the samples is shown in Table 3.1.4.2 and the sample that contained 95% maltodextrin showed the least degradation.

Table 3.1.4.3 Petunidin determination of blueberry samples containing 5, 10 and 30% blueberry solids before and after spray drying

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg anthocyanidins / mL Blueberry Extract (Before Spray Drying)	µg anthocyanidins / g Blueberry Powder (After Spray Drying)	µg anthocyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg anthocyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of anthocyanidin[a]
5:95 Petunidin	3.44±0.12	3.22±0.34	68.73±2.40 **A**	61.61±2.28 **A**	10.36%
10:90 Petunidin	6.51±0.32	4.59±0.09	65.07±3.20 **A**	49.58±0.09 **B**	23.81%
30:70 Petunidin	19.26±0.68	7.16±0.80	64.20±2.26 **A**	25.95±0.80 **C**	59.58%

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

Table 3.1.4.3 shows the values of petunidin obtained from the three different spray dried blueberry samples containing different ratios of blueberry solids. When analyzed in both extract form (before spray drying) and powder form (after spray drying), there was a significant difference in all three samples, with an increasing µg petunidin detected per mL or g of sample, respectively. When converted to per gram blueberry solids basis, no significant difference was found in the extract prior to spray drying; however, there was a significant difference between the samples obtained after spray drying when expressed in per gram solids basis. The concentration of petunidin decreased with decreasing percent blueberry solids. The percentage degradation of the samples is shown in Table 3.1.4.3 and the sample that contained 95% maltodextrin showed the least degradation and vice versa.

Table 3.1.4.4 Peonidin determination of blueberry samples containing 5, 10 and 30% blueberry solids before and after spray drying

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg anthocyanidins / mL Blueberry Extract (Before Spray Drying)	µg anthocyanidins / g Blueberry Powder (After Spray Drying)	µg anthocyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg anthocyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of anthocyanidin[a]
5:95 Peonidin	0.80±0.09	0.34±0.01	16.07±1.73 **A**	7.30±0.17 **B**	54.57%
10:90 Peonidin	1.28±0.05	0.40±0.05	12.82±0.49 **A**	4.29±0.53 **C**	66.53%
30:70 Peonidin	3.94±0.42	0.78±0.08	13.12±1.40 **A**	2.82±0.29 **D**	78.51%

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

Table 3.1.4.4 shows the values of peonidin obtained from the three different spray dried blueberry samples containing different ratios of blueberry solids. When analyzed in both extract form (before spray drying) and powder form (after spray drying), there was a significant difference in all three samples, with an increasing µg peonidin detected per mL or g of sample respectively. When converted to per gram blueberry solids basis, no significant difference was found in the extract prior to spray drying; however, there was a significant difference between the samples obtained after spray drying when expressed in per gram solids basis. The concentration of peonidin decreased with decreasing percent blueberry solids. The percentage degradation of the samples is shown in Table 3.1.4.4 and the sample that contained 95% maltodextrin showed the least degradation and vice versa.

Table 3.1.4.5 Malvidin determination of blueberry samples containing 5, 10 and 30% blueberry solids before and after spray drying

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Blueberry Extract (Before Spray Drying)	µg antho-cyanidins / g Blueberry Powder (After Spray Drying)	µg anthocyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg anthocyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of anthocyanidin[a]
5:95 Malvidin	62.23±1.45	55.58±0.85	1244.63±29.01 **A**	1193.20±18.30 **A**	4.13%
10:90 Malvidin	122.19±0.39	69.99±2.47	1221.94±3.89 **A**	756.63±26.69 **B**	38.08%
30:70 Malvidin	368.33±3.31	112.38±10.16	1227.75±11.03 **A**	407.52±36.83 **C**	66.81%

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

Table 3.1.4.5 shows the values of malvidin obtained from the three different spray dried blueberry samples containing different ratios of blueberry solids. When analyzed in both extract form (before spray drying) and powder form (after spray drying), there was a significant difference in all three samples, with an increasing µg malvidin detected per mL or g of sample respectively. When converted to per gram blueberry solids basis, no significant difference was found in the extract prior to spray drying; however, there was a significant difference between the samples obtained after spray drying when expressed in per gram blueberry solids basis. The concentration of malvidin decreased with decreasing percent blueberry solids. The percentage degradation of the samples is shown in Table 3.1.4.5 and the sample that contained 95% maltodextrin showed the least degradation and vice versa.

3.1.5 Conclusion

A clear trend could be observed from the research results. There was a higher retention of antioxidants when there was an increased proportion of

maltodextrin in the spray dried sample. The samples with higher ratios of fruit solids had a higher antioxidant capacity. This suggests that maltodextrin has a protective effect during spray drying because the sole variable in this experimental setup was the ratio of blueberry solids to maltodextrin; all spray drying conditions were kept constant.

However, it is important to note that if the spray dried powder were to be used as an ingredient to increase antioxidant capacity of a food product, it would be more important to obtain a product with higher antioxidant power such as the blueberry powder containing 30:70 fruit solids to maltodextrin.

3.2 Study 2: Effects of Spray Dryer Outlet Temperatures on Nutraceutical Content of Blueberry By-Products

Table 3.2.1 Spray drying conditions and data for cull blueberry extract containing same ratios of blueberry solids to maltodextrin but varying outlet temperatures.

Blueberry solids to Maltodextrin	30:70 (a^1)[a,b]	30:70 (a^2)	30 : 70 (b^1)	30 : 70 (b^2)
Feed Temp (°C)	60	60	60	60
Air inlet Temp (°C)	150 ± 5	150 ± 5	150 ± 5	150 ± 5
Air outlet Temp (°C)	80	80	90	90
Wet Bulb Temp at outlet (°C)	40 ± 5	40 ± 5	40 ± 5	40 ± 5
Pump Pressure (psi)	1500	1750	1000	1000
Specific gravity	1.01	1.008	1.006	1.045
Feed weight (lbs)	28.66	27.98	26.90	28.84
Bowl Feed Rate (cm / min)	0.36	0.35	0.28	0.29
Powder weight (lbs)	1.54	1.36	1.78	1.64
Feed total solids (%)	6.48	6.02	6.63	6.16
Feed moisture (%)	93.52	93.98	93.37	93.84
Powder moisture (%)	4.11	5.78	5.13	4.11
Powder solids (%)	95.89	94.22	94.87	95.89
Calculated sample Solids (lbs)	1.86	1.68	1.78	1.78
Solids in powder (lbs)	1.48	1.28	1.69	1.57
Yield (%)	79.51	76.07	94.69	88.52
Estimated Particle Residence Time (s)	23.7	21.9	23.9	24.7

[a] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table 3.2.1 shows the spray drying conditions and additional data collected in this study. The levels of maltodextrin were kept constant in the run and samples were spray dried in duplicates with two varied outlet temperatures: ~80 and ~90°C.

The feed temperature was kept constant at ~60°C and the air inlet conditions were maintained as closely as possible at ~150°C. This allowed the study of the

impacts of spray drying outlet temperatures on the antioxidant capacity of cull blueberry extracts.

One difficulty encountered during the spray drying runs was maintaining a constant temperature range. Slight temperature fluctuations were experienced throughout the runs and hence might lead to data inaccuracy. This was due to the nature of the spray dryer itself, because it cannot be operated with tight temperature control.

Spray drying yields were satisfactory for all the runs performed, with at least >75% yield. After the spray drying runs, the dryer was checked visually for residual powder and there was only a slight coating of powder in the cyclone and in the spray dryer ducts.

The maximum particle residence time in the spray dryer was estimated to be from 22 – 25 seconds. Based on the results, at higher outlet temperatures, the residence time for the particle increased because of a lower pump pressure and hence lower throughput throughout the system.

3.2.1 Particle Size Analysis

Particle size analysis of the blueberry powder collected at different outlet temperatures showed no significant differences, with an estimated particle size ranging from 32 to 45 microns, corresponding 450 and 325 mesh size sieves, respectively. This suggests that outlet temperature has little or no impact on the particle size of powder.

3.2.2 Oxygen Radical Absorbance Capacity

Table 3.2.2.1 $ORAC_{FL}$ values of blueberry samples before and after spray drying at different outlet temperatures

Sample	µmol TE / mL Blueberry Extract (Before Spray Drying)	µmol TE / g Blueberry Powder (After Spray Drying)	µmol TE / g Blueberry Solids (Extract, Before Spray Drying)	µmol TE / g Blueberry Solids (Powder, After Spray Drying)	% reduction in $ORAC_{FL}$ value[a]
Blueberry Extract 30:70 (a^1)[b, c]	15.47±0.06	183.65±2.88	795.83±2.88	638.41±10.03 **A**	19.78
Blueberry Extract 30:70 (a^2)	14.41±0.04	171.96±2.40	797.70±2.42	608.35±8.49 **A**	23.74
Blueberry Extract 30:70 (b^1)	15.81±0.02	174.82±11.05	794.71±1.00	614.25±38.82 **A**	22.71
Blueberry Extract 30:70 (b^2)	14.71±0.02	188.41±1.37	795.83±1.05	654.96±4.76 **A**	16.65

[a] Calculated from µmol TE / g Blueberry Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

As observed in Table 3.2.2.1, there was no significant difference in $ORAC_{FL}$ value between the extract samples prior to spray drying both and when converted to per gram blueberry solids basis. Unlike study 1 where the trend was decreased $ORAC_{FL}$ value with decreased maltodextrin concentrations during spray drying; there was no significant difference among the powders samples obtained after spray drying. There was however close to 20% reduction in $ORAC_{FL}$ values for all the samples.

One possible explanation for the similar reduction in $ORAC_{FL}$ values is that the spray drying conditions were fairly similar with only slight outlet temperature differences between the runs. Another hypothesis would be that

after spray drying, the powder particles are porous(Elversson et al., 2003; Reineccius 2004); and since the particle size of the powders showed no significant difference, each particle might be surrounded by the same amount of oxygen and thus lead to similar effects of oxygen damage to the antioxidant properties.

3.2.3 Total Phenolics

Table 3.2.3.1 Total phenolic of blueberry samples before and after spray drying at different outlet temperatures, measured at 765nm

Sample	mg GAE / mL Blueberry Extract (Before Spray Drying)	mg GAE / g Blueberry Powder (After Spray Drying)	mg GAE / g Blueberry Solids (Extract, Before Spray Drying)	mg GAE / g Blueberry Solids (Powder, After Spray Drying)	% reduction in Total Phenolics value[a]
Blueberry Solids 30:70 (a^1)[b,c]	10.52±0.12	9.38±0.08	35.06±0.39	31.26±0.28 **A**	10.84
Blueberry Solids 30:70 (a^2)	11.01±0.27	9.08±0.26	36.70±0.90	30.27±0.88 **A**	17.51
Blueberry Solids 30:70 (b^1)	10.47±0.30	9.61±0.95	34.90±1.01	32.03±3.17 **A**	8.22
Blueberry Solids 30:70 (b^2)	10.88±0.21	9.71±0.16	36.27±0.69	32.38±0.55 **A**	10.72

[a] Calculated from mg GAE / g Blueberry Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

As observed in Table 3.2.3.1, there was no significant difference in total phenolic value between the extract samples prior to spray drying both and when converted to per gram blueberry solids basis. In this study, the data obtained for total phenolics also correlated well with that of $ORAC_{FL}$, where there were no

significant differences between the spray dried samples when expressed as mg GAE / g blueberry solids. The reduction in total phenolics value ranged from 8.22 – 17.51%.

3.2.4 High Performance Liquid Chromatography

Table 3.2.4.1 Delphinidin determination of blueberry samples containing 30:70 blueberry solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Blueberry Extract (Before Spray Drying)	µg antho-cyanidins / g Blueberry Powder (After Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Delphinidin	132.26± 2.61	38.54± 2.14	440.88± 8.69	133.96± 7.45 **A**	69.62	0.051
30:70 (a^2) Delphinidin	130.95± 0.53	40.07± 2.89	436.49± 1.76	141.76± 10.24 **A**	67.52	0.051
30:70 (b^1) Delphinidin	130.94± 2.84	41.89± 0.90	436.47± 9.47	147.19± 3.16 **A**	66.28	0.046
30:70 (b^2) Delphinidin	128.84± 5.51	39.71± 3.12	429.46± 18.35	138.02± 10.86 **A**	67.86	0.046

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

Literature shows for hot pressed blueberry juice, the delphinidin-glycosides detected was 5.9 mg / 100 g blueberries (Lee et al., 2002). When compared to the blueberry extract for spray drying, the values were converted into µmole anthocyanin / g blueberry solids. It was estimated that fresh blueberries contained 5% solids. Conversion showed that there were approximately 2.52 µmol delphinidin / g blueberry solids in the hot pressed blueberry juice and 1.30 µmol delphinidin / g blueberry solids for the blueberry extract used prior to spray drying. It was expected that the concentration of

delphinidin to be lower in the blueberry extract used in this study because cull blueberries were used opposed to high quality blueberries, which were used in the study conducted by Lee et al. (2002).

The anthocyanidin delphinidin was found to have 66.28 – 69.62% degradation after spray drying. Amongst the extract samples prior to spray drying, no significant difference in delphinidin concentration was detected and neither in the blueberry powder samples obtained after spray drying. The calculated overall rate constant for anthocyanidin degradation at wet bulb ~45°C was 0.046 – 0.051 s^{-1} (Table 3.2.4.1). It was assumed the anthocyanins degraded at the wet-bulb temperature during spray drying.

Table 3.2.4.2 Cyanidin determination of blueberry samples containing 30:70 blueberry solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Blueberry Extract (Before Spray Drying)	µg antho-cyanidins / g Blueberry Powder (After Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Cyanidin	34.15± 1.62	8.38± 0.69	113.82± 5.38	29.13±2.39 **A**	74.41	0.057
30:70 (a^2) Cyanidin	33.14± 2.33	10.21± 1.34	110.48± 7.77	36.12±4.74 **A, B**	67.31	0.051
30:70 (b^1) Cyanidin	30.46± 2.28	11.46± 0.12	101.52± 7.60	40.25±0.41 **B**	60.35	0.039
30:70 (b^2) Cyanidin	31.94± 1.80	11.53± 1.12	106.48± 6.02	40.07±3.88 **B**	62.37	0.041

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

Lee et al. (2002) showed 0.5 mg cyanidin-glycosides / 100 g blueberries for hot pressed blueberry juice. When converted to µmole anthocyanin / g

blueberry solids, there were approximately 0.31 µmol cyanidin / g blueberry solids in the hot pressed blueberry juice and 0.35 µmol cyanidin / g blueberry solids for the blueberry extract used prior to spray drying.

The anthocyanidin cyanidin was found to have 60.35 – 74.41% degradation post spray drying. Among the juice samples prior to spray drying, no significant difference in cyanidin concentration was detected. However, there was a significant difference detected between the first sample (a^1) spray dried and the remaining samples. The overall rate constant for cyanidin degradation at wet bulb ~45°C was found to be from 0.039 – 0.057 s^{-1} (Table 3.2.4.2).

Table 3.2.4.3 Petunidin determination of blueberry samples containing 30:70 blueberry solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Blueberry Extract (Before Spray Drying)	µg antho-cyanidins / g Blueberry Powder (After Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Petunidin	31.81± 0.84	12.43± 0.75	106.02± 2.80	43.20± 2.60 **A**	59.23	0.038
30:70 (a^2) Petunidin	32.93± 1.29	13.67± 1.43	109.76± 4.30	48.37± 5.06 **A**	55.93	0.037
30:70 (b^1) Petunidin	33.28± 0.75	14.57± 0.27	110.93± 2.50	51.19± 0.96 **A**	53.85	0.034
30:70 (b^2) Petunidin	32.95± 1.53	12.81± 1.37	109.84± 5.11	44.52± 4.75 **A**	59.47	0.028

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

Lee et al. (2002) showed 4.9 mg petunidin-glycosides / 100 g blueberries for hot pressed blueberry juice. When converted to µmole anthocyanin / g

blueberry solids, there were approximately 3.18 µmol petunidin / g blueberry solids in the hot pressed blueberry juice and 0.30 µmol petunidin / g blueberry solids for the blueberry extract used prior to spray drying. It was expected that the concentration of petunidin to be lower in the blueberry extract used in this study because cull blueberries were used opposed to high quality blueberries, which were used in the study conducted by Lee et al. (2002).

The anthocyanidin petunidin was found to have 53.85 – 59.47% degradation after spray drying. Amongst the extract samples prior to spray drying, no significant difference in petunidin concentration was detected and neither in the blueberry powder samples obtained after spray drying. The rate for petunidin degradation at wet bulb 45°C was found to be from 0.028 – 0.038 s^{-1} in this study (Table 3.2.4.3).

Table 3.2.4.4 Peonidin determination of blueberry samples containing 30:70 blueberry solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Blueberry Extract (Before Spray Drying)	µg antho-cyanidins / g Blueberry Powder (After Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Peonidin	6.00± 0.08	1.98± 0.01	20.01± 0.27	6.89± 0.04 **A**	65.57	0.045
30:70 (a^2) Peonidin	7.17± 0.59	3.16± 0.37	23.89± 1.97	11.17± 1.30 **A**	53.24	0.035
30:70 (b^1) Peonidin	6.44± 0.50	3.91± 0.44	21.48± 1.66	13.74± 1.53 **A**	36.03	0.019
30:70 (b^2) Peonidin	7.03± 0.48	2.99± 0.17	23.43± 1.61	10.39± 0.58 **A**	55.66	0.033

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

Lee et al. (2002) showed 0.2 mg peonidin-glycosides / 100 g blueberries for hot pressed blueberry juice. When converted to µmole anthocyanin / g blueberry solids, there were approximately 0.09 µmol peonidin / g blueberry solids in the hot pressed blueberry juice and 0.05 µmol peonidin / g blueberry solids for the blueberry extract used prior to spray drying.

The anthocyanidin peonidin was found to have 36.03 – 65.57% degradation after spray drying. Amongst the extract samples prior to spray drying, no significant difference in peonidin concentration was detected. There was also no significant difference in peonidin concentration in the blueberry powder samples obtained after spray drying. The same trend was also observed in this study for the analysis of delphinidin and petunidin. The overall rate constant for peonidin degradation at wet bulb ~45°C was between 0.019 and 0.045 in this study (Table 3.2.4.4).

Table 3.2.4.5 Malvidin determination of blueberry samples containing 30:70 blueberry solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Blueberry solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Blueberry Extract (Before Spray Drying)	µg antho-cyanidins / g Blueberry Powder (After Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Blueberry Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for anthocyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Malvidin	643.87± 54.62	242.80± 13.99	2146.23± 182.06	844± 48.62 **A**	60.65	0.039
30:70 (a^2) Malvidin	671.76± 41.23	278.88± 22.25	2239.20± 137.44	986.63± 78.71 **B**	55.94	0.037
30:70 (b^1) Malvidin	691.54± 9.08	306.75± 4.78	2305.15± 30.25	1077.81± 16.79 **B**	53.24	0.032
30:70 (b^2) Malvidin	655.21± 16.05	233.91± 29.78	2184.03± 53.51	813.11± 103.52 **A**	62.77	0.040

[a] Calculated from µg anthocyanidins / g Blueberry Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

Lee et al. (2002) showed 16.9 mg malvidin-glycosides / 100 g blueberries for hot pressed blueberry juice. When converted to µmole anthocyanin / g blueberry solids, there were approximately 10.7 µmol malvidin / g blueberry solids in the hot pressed blueberry juice and 5.9 µmol malvidin / g blueberry solids for the blueberry extract used prior to spray drying.

The anthocyanidin malvidin was found to have 53.24 – 62.77% degradation after spray drying. Amongst the extract samples prior to spray drying, no significant difference in malvidin concentration. However, there was a significant difference detected in supposedly duplicate runs of 30:70 (a^1) and 30:70 (a^2); and runs of 30:70 (b^1) and 30:70 (b^2). The rate constant for malvidin degradation was between 0.032 – 0.040 s^{-1} in this study (Table 3.2.4.5).

3.2.5 Conclusions

Particle size, $ORAC_{FL}$, total phenolics and HPLC results show the same trend where there was little or no significant difference detected in the powders spray dried under different outlet conditions. From this the following conclusions could be drawn from the study:

1. The pilot-sized spray dryer could only be controlled to approximately ±10°C desired inlet and outlet temperature range.
2. There might not be a great enough difference between the chosen temperatures, which in turn causes the uniformity in the results obtained. However, it would be difficult to spray dry the blueberry extracts at too high or too low inlet and outlet temperatures. If the temperatures were too

high, it would lead to the stickiness problems in the spray dryer due to the low glass transition temperature of the sugars in the fruit extract. Lower drying temperatures might lead to insufficient drying. Both scenarios would be undesirable which not only leads to reduced yield, but also clogging problems in the spray dryer making cleaning difficult.

3.3 Study 3: Effects of Spray Dryer Outlet Temperatures on Nutraceutical Content of Grape By-Products

Table 3.3.1 Spray drying conditions and data for grape pomace extract containing same ratios of grape solids to maltodextrin but varying outlet temperatures

Grape solids to Maltodextrin	30:70 (a_1)[a,b]	30:70 (a_2)	30 : 70 (b_1)	30 : 70 (b_2)
Feed Temp (°C)	60	60	60	60
Air inlet Temp (°C)	150 ± 5	150 ± 5	150 ± 5	150 ± 5
Air outlet Temp (°C)	85 ± 5	85 ± 5	85 ± 5	85 ± 5
Wet Bulb Temp at outlet (°C)	40 ± 5	40 ± 5	40 ± 5	40 ± 5
Pump Pressure (psi)	1500	1750	1000	1000
Specific gravity	1.018	1.022	1.023	1.024
Feed weight (lbs)	29.00	28.44	28.76	26.08
Bowl Feed Rate (cm / min)	0.31	0.35	0.28	0.28
Powder weight (lbs)	2.06	1.96	2.32	2.00
Feed total solids (%)	8.49	8.22	9.04	8.64
Feed moisture (%)	91.51	91.78	90.96	91.36
Powder moisture (%)	4.71	4.87	4.10	4.19
Powder solids (%)	95.29	95.13	95.90	95.81
Calculated sample Solids (lbs)	2.46	2.34	2.60	2.25
Solids in powder (lbs)	1.96	1.86	2.22	1.92
Yield (%)	79.73	79.76	85.58	85.04
Estimated Particle Residence Time (s)	23.0	20.8	25.3	24.3

[a] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table 3.3.1 shows the spray drying conditions and additional data collected in this study. The levels of maltodextrin were kept constant in the run and samples were spray dried in duplicates with two varied outlet temperatures: ~80 and ~90°C.

The feed temperature was kept constant at approximately 60°C and the air inlet conditions were maintained as closely as possible at ~150°C. This allowed the study of the impacts of spray drying outlet temperatures on the antioxidant capacity of cull blueberry extracts.

One difficulty encountered during the spray drying runs was maintaining a tight temperature range. Slight temperature fluctuations were experienced throughout the runs and hence might lead to data inaccuracy. This was due to the nature of a commercial type spray dryer.

Spray drying yields were satisfactory for all the runs performed, with at least 80% recovery. The spray dryer was checked visually for residual powder post run and there was only a slight coat of powder in the cyclone and in the spray dryer ducts.

3.3.1 Particle Size Analysis

Particle size analysis of the grape powder collected at different outlet temperatures showed no significant differences, with an estimated particle size of 32 - 45 microns, corresponding 450 and 325 mesh size sieves, respectively.. This suggests that outlet temperature has little or no impact on the powder particle size. All the samples from studies 1, 2 and 3 that contained a 30:70 fruit solids to maltodextrin ratio showed no significant differences in particle sizes.

3.3.2 Oxygen Radical Absorbance Capacity

Table 3.3.2.1 $ORAC_{FL}$ values of grape samples before and after spray drying at different outlet temperatures

Sample	µmol TE / mL Grape Extract (Before Spray Drying)	µmol TE / g Grape Powder (After Spray Drying)	µmol TE / g Grape Solids (Extract, Before Spray Drying)	µmol TE / g Grape Solids (Powder, After Spray Drying)	% reduction in $ORAC_{FL}$ value[a]
Grape Solids 30:70 (a^1)[b,c]	25.72±0.31	271.59±1.83	1009.64±12.13	950.05±6.41 **A**	5.90
Grape Solids 30:70 (a^2)	24.14±0.41	245.47±0.47	989.81±16.46	860.13±2.58 **B**	13.10
Grape Solids 30:70 (b^1)	26.96±0.30	246.69±0.38	994.23±10.95	848.60±1.32 **B**	14.65
Grape Solids 30:70 (b^2)	25.57±0.12	243.13±2.66	986.57±4.57	845.92±9.27 **B**	14.26

[a] Calculated from µmol TE / g Grape Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

There was no significant difference in $ORAC_{FL}$ value between the grape extracts prior to spray drying and when converted to per gram grape solids basis. Literature showed an $ORAC_{FL}$ value for grape pomace from winemaking to range from 1380 – 2230 µmol TE / g of grape pomace (Monagas et al., 2006). The $ORAC_{FL}$ values for the extracts prior to spray drying (986 – 1009.64 µmol TE / g grape solids) obtained in this study was comparable to the values found in literature. Only a 6% reduction in $ORAC_{FL}$ value was observed in run (a^1), and its $ORAC_{FL}$ value when expressed in µmol TE / g grape solids, was significantly different than the other runs (Table 3.3.2.1).

When compared to study 2, which blueberry samples were spray dried under the same conditions, the grape samples had a lower reduction in $ORAC_{FL}$

value (5.9-14.65% reduction as compared to approximately 20% reduction for blueberry samples). The $ORAC_{FL}$ values obtained for the grape extract samples were slightly higher than that of the blueberry extract samples when expressed in μmol TE / g fruit solids.

3.3.3 Total Phenolics

Table 3.3.3.1 Total phenolic of grape samples before and after spray drying at different outlet temperatures

Sample	mg GAE / mL Grape Extract (Before Spray Drying)	mg GAE / g Grape Powder (After Spray Drying)	mg GAE / g Grape Solids (Extract, Before Spray Drying)	mg GAE / g Grape Solids (Powder, After Spray Drying)	% reduction in Total Phenolics value[a]
Grape Solids 30:70 (a^1)[b,c]	20.04±0.26	18.20±0.20	66.79±0.85 **A,B**	60.67±0.67 **A**	9.16
Grape Solids 30:70 (a^2)	20.15±0.18	18.48±0.22	67.17±0.61 **A**	61.60±0.75 **A**	8.29
Grape Solids 30:70 (b^1)	19.56±0.22	16.89±0.27	65.21±0.74 **B**	56.30±0.89 **B**	13.66
Grape Solids 30:70 (b^2)	19.86±0.13	16.04±0.12	66.21±0.42 **A,B**	53.47±0.40 **C**	19.24

[a] Calculated from mg GAE / g Grape Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

There were slight differences in total phenolic values between the grape extracts prior to spray drying. Literature showed the total phenolics value for grape pomace from winemaking to range from 50.3 – 59.9 mg GAE / g of grape pomace (Monagas et al. 2006). The total phenolics values for the extracts prior to spray drying (65.21 – 67.17 μmol TE / g grape solids) obtained in this study was slightly higher than the values found in literature. When converted into per gram grape solids basis, runs (a^1) and (a^2) showed no significant differences and

had the highest mg GAE / g grape solids. Runs (b^1) and (b^2) were also significantly different from each other (Table 3.3.3.1)

The percent reduction in total phenolics value was comparable to those obtained from study 2. After spray drying, the blueberry samples in study 2 showed a 8.22 – 17.51% reduction in mg GAE / g blueberry solids, whereas in this study, there was 8.29 – 19.24% reduction in mg GAE / g grape solids.

When comparing the values of total phenolics obtained from study 2, the blueberry extract had around 35 mg GAE / g blueberry solids, whereas the grape extract has almost double the amount.

3.3.4 High Performance Liquid Chromatography

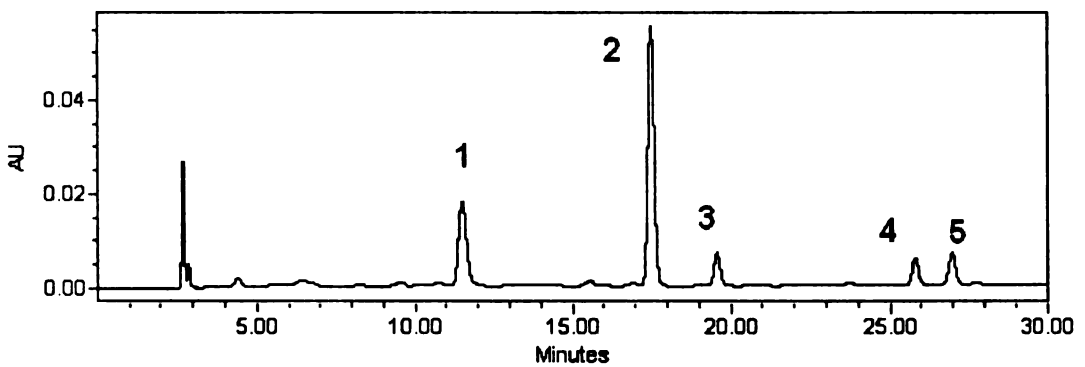


Figure 3.3.4.1 Typical chromatogram of anthocyanidins detected in grape samples. Corresponding anthocyanidin peak assignments: 1= delphinidin, 2 = cyanidin, 3 = petunidin, 4 = peonidin, 5 = malvidin

Figure 3.3.4.1 shows the chromatogram the anthocyanidins found in grape samples treated by acid hydrolysis. When compared to the chromatogram for

blueberries, both have similar profiles containing all five anthocyanidins but the amount of anthocyanidin present in each sample varied.

Table 3.3.4.1 Delphinidin determination of grape samples containing 30:70 grape solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Grape solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Grape Extract (Before Spray Drying)	µg antho-cyanidins / g Grape Powder (After Spray Drying)	µg antho-cyanidins / g Grape Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Grape Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Delphinidin	93.91± 2.20	42.19± 0.75	313.02± 7.33	147.73± 2.64 **A,B**	52.80	0.033
30:70 (a^2) Delphinidin	99.41± 4.43	44.36± 0.64	331.38± 14.77	155.45± 2.24 **A**	53.09	0.036
30:70 (b^1) Delphinidin	94.22± 1.61	41.39± 0.89	314.08± 5.46	143.87± 3.10 **B**	54.19	0.031
30:70 (b^2) Delphinidin	93.99± 3.57	41.50± 1.06	313.30± 11.90	144.37± 3.67 **B**	53.92	0.032

[a] Calculated from µg anthocyanidin / g Grape Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

The anthocyanidin delphinidin was found to have 52.80 – 54.19% degradation after spray drying. Amongst the extracts prior to spray drying, no significant difference in delphinidin concentration was detected. When compared to the extracts in study 2, the extracts contained similar amounts of delphinidin per gram of fruit solids. This can be confirmed visually by the chromatograms of both samples; and it can also be confirmed by the area obtained under the delphinidin peak. Since the volume of blueberry and grape extracts used in the analysis were equal and the fruit solids concentration were also the same, it would give a somewhat accurate estimate. The rate for delphinidin degradation

at wet bulb ~45°C was estimated to be 0.031 – 0.036 s^{-1} for this study (Table 3.3.4.1).

Table 3.3.4.2 Cyanidin determination of grape samples containing 30:70 grape solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Grape solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Grape Extract (Before Spray Drying)	µg antho-cyanidins / g Grape Powder (After Spray Drying)	µg antho-cyanidins / g Grape Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Grape Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Cyanidin	87.01± 6.43	40.25± 1.05	290.04± 21.43	140.94± 3.68 **A**	51.41	0.031
30:70 (a^2) Cyanidin	87.98± 0.99	40.62± 1.67	293.26± 3.29	142.35± 5.87 **A**	51.46	0.035
30:70 (b^1) Cyanidin	83.87± 0.92	34.92± 0.65	279.55± 3.08	121.37± 2.26 **B**	56.58	0.033
30:70 (b^2) Cyanidin	86.89± 2.61	36.87± 1.02	289.63± 8.71	128.28± 3.55 **B**	55.71	0.034

[a] Calculated from µg anthocyanidin / g Grape Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

The anthocyanidin cyanidin was found to have roughly 50 – 60% degradation post spray drying. Amongst the extracts samples prior to spray drying, no significant difference in cyanidin concentration was detected. There was no significant differences detected between powder samples obtained from the duplicate runs of the same outlet temperature, but a significant difference was detected among the samples spray dried at different outlet temperatures.

Cyanidin degradation from this study was also comparable to that of study 2, which spray dried blueberry samples. It showed around 60 – 70% degradation for the blueberry samples. The cyanidin occurrence in the grape sample seemed much higher than that in the blueberry sample and the results could again be

confirmed by observation from the respective chromatograms. The rate constant for cyanidin degradation at wet bulb ~45°C was calculated to be from 0.031 – 0.035 s^{-1}(Table 3.3.4.2).

Table 3.3.4.3 Petunidin determination of grape samples containing 30:70 grape solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Grape solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Grape Extract (Before Spray Drying)	µg antho-cyanidins / g Grape Powder (After Spray Drying)	µg antho-cyanidins / g Grape Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Grape Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Petunidin	11.90± 0.39	7.53± 0.50	39.67± 1.31	26.38± 1.75 **A**	33.50	0.018
30:70 (a^2) Petunidin	12.51± 0.70	7.72± 0.16	41.70± 2.35	27.05± 0.56 **A**	33.13	0.019
30:70 (b^1) Petunidin	11.50± 0.19	6.63± 0.12	38.35± 0.63	23.04± 0.43 **B**	39.92	0.020
30:70 (b^2) Petunidin	12.13± 0.78	7.39± 0.11	40.44± 2.60	25.72± 0.39 **A**	36.40	0.019

[a] Calculated from µg anthocyanidin / g Grape Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

The anthocyanidin petunidin was found to have 33.13 – 39.92% degradation after spray drying. Amongst the extracts prior to spray drying, no significant difference in petunidin concentration was detected. There was no significant difference between the spray dried samples except for run (b^1).

When compared to the percent reduction obtained from the spray drying of blueberry extract in study 2 (53.85 – 59.47%), the spray drying of grape extract had a less degradation of petunidin. The blueberry extract also had a higher concentration in petunidin than grape extract and this can be observed also in the chromatogram. In this study, the rate constant for petunidin degradation at

wet bulb ~45°C in grapes was estimated to be from 0.018 – 0.020 s^{-1} (Table 3.3.4.3).

Table 3.3.4.4 Peonidin determination of grape samples containing 30:70 grape solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Grape solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Grape Extract (Before Spray Drying)	µg antho-cyanidins / g Grape Powder (After Spray Drying)	µg antho-cyanidins / g Grape Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Grape Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Peonidin	11.76± 1.06	8.07± 0.25	39.21± 3.54	28.26± 0.88 **A**	27.93	0.014
30:70 (a^2) Peonidin	11.96± 1.28	8.26± 0.53	39.87± 4.25	28.95± 1.86 **A**	27.39	0.015
30:70 (b^1) Peonidin	10.37± 0.64	7.25± 0.13	34.55± 2.13	25.19± 0.46 **A,B**	27.09	0.012
30:70 (b^2) Peonidin	11.69± 0.88	8.03± 0.08	38.67± 2.92	27.95± 0.28 **B**	27.72	0.013

[a] Calculated from µg anthocyanidin / g Grape Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

The anthocyanidin peonidin was found to have around 27% degradation after spray drying. Amongst the extracts prior to spray drying, no significant difference in peonidin concentration was detected. There were only slight differences in the µg peonidin / g grape solids detected in the powder samples. The rate constant for peonidin degradation at wet bulb ~45°C was found to be 0.012 – 0.015 s^{-1} for this study (Table 3.3.4.4). When compared to the values obtained from study 2, there was a much less reduction (almost 30% less) in peonidin post spray drying.

Table 3.3.4.5 Malvidin determination of grape samples containing 30:70 grape solids to maltodextrin ratios before and after spray drying at different outlet temperatures

Ratio of Grape solids to Maltodextrin and Anthocyanidin Analyzed	µg antho-cyanidins / mL Grape Extract (Before Spray Drying)	µg antho-cyanidins / g Grape Powder (After Spray Drying)	µg antho-cyanidins / g Grape Solids (Extract, Before Spray Drying)	µg antho-cyanidins / g Grape Solids (Powder, After Spray Drying)	% Degradation of antho-cyanidin[a]	Rate constant estimation for antho-cyanidin degradation (s^{-1})
30:70 (a^1)[b,c] Malvidin	113.42± 2.84	74.18± 2.92	378.07± 9.48	259.77± 10.24 **A**	31.29	0.016
30:70 (a^2) Malvidin	114.28± 2.17	75.36± 1.44	380.92± 7.22	264.06± 5.05 **A**	30.68	0.018
30:70 (b^1) Malvidin	110.72± 1.77	65.63± 2.16	369.06± 5.89	228.12± 7.51 **B**	38.19	0.019
30:70 (b^2) Malvidin	109.26± 5.19	67.09± 1.74	364.18± 17.29	233.43± 6.06 **B**	35.90	0.018

[a] Calculated from µg anthocyanidin / g Grape Solids before and after spray drying
[b] Same letters denote runs of the same conditions: a = outlet temperature = 80°C; b = outlet temperature = 90°C
[c] Superscript numbers denote the number of replicates per run
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

The anthocyanidin malvidin was found to have 30.68 – 38.19% degradation after spray drying. Amongst the extracts prior to spray drying, there was no significant difference in malvidin concentration. There was, however, no significant differences detected between the duplicate runs, but there significant differences were detected between the runs with different outlet temperatures. The rate constant for malvidin degradation at wet bulb ~45°C was calculated to be 0.016 – 0.019 s^{-1} in this study (Table 3.3.4.5).

Comparison to malvidin levels from study 2 shows that the grape extract used had much lower levels of malvidin. However, malvidin degradation was around 20% less severe in this study using grapes.

3.3.5 Conclusion

The findings in this study 3 confirmed some of those of study 2. Both sets of data suggest that it would be difficult to control the temperatures and conditions precisely and it would be prone to temperature fluctuations. However, the pilot plant scale spray dryer would be a closer prediction to the problems that would be faced commercially. It would also be a closer prediction for percentage reduction of both antioxidant capacity and anthocyanin degradation.

In this study, the % reduction in both $ORAC_{FL}$ value and total phenolics after spray drying were similar. Anthocyanidin analysis by HPLC does show a clear trend of little or no significant differences between the powder samples when expressed as µg anthocyanin / g fruit solids. Since anthocyanins are heat sensitive, the differences in experimental outlet temperatures might not be great enough to produce a detectable difference. Also, if the spray drier were to be attached with the fluidized bed cooling system, the anthocyanins in the fruit powders would undergo less degradation due to heat after exiting the spray dryer.

When compared to study 2 which used cull blueberries, the spray dried grape powders obtained in this study showed smaller reduction in $ORAC_{FL}$ value after spray drying. The reduction for total phenolics, however, was similar for both studies with a reduction of 8.29 – 19.24%. The spray dried grape powder showed a smaller percentage degradation for each anthocyanidin analyzed.

3.4 Study 4: Comparison to Commercial Blueberry Products

Five commercial blueberry powder samples were obtained and compared with the spray dried blueberry and grape powder which contains 30:70 fruit solids to maltodextrin ratio for antioxidant power. 30:70 fruit solids to maltodextrin spray-dried powders were chosen because they contained higher antioxidant capacity per gram of fruit powder than the 5:95 and 10:90 samples. They would be a more probable ingredient used when incorporating into a food system to increase the antioxidant capacity of a product. Since the blueberry and grape powders obtained from the spray drying runs had similar antioxidant properties, one of each sample was randomly selected for comparison: Blueberry Powder 30:70 (b^2) and Grape Powder 30:70 (a^1). A blueberry concentrate / puree powder was obtained from FruitSmart®. It is a spray dried blueberry puree powder, with maltodextrin used as a spray drying agent. The raw material used to produce the FruitSmart® spray dried blueberry concentrate / puree powder was strictly selected blueberry concentrate or pure (*Vaccinium spp.*). A blueberry fiber powder was also obtained from FruitSmart®. It was produced by drying wholesome blueberry pomace. Additional blueberry powders obtained from Van Drunen Farms include: spray dried blueberry powder, drum dried blueberry powder (from *Vaccinium angustifolium*), and freeze dried blueberry powder (from *Vaccinium corymbosum*).

3.4.1 Oxygen Radical Absorbance Capacity for Commercial Blueberry Powders and Those Produced in This Study

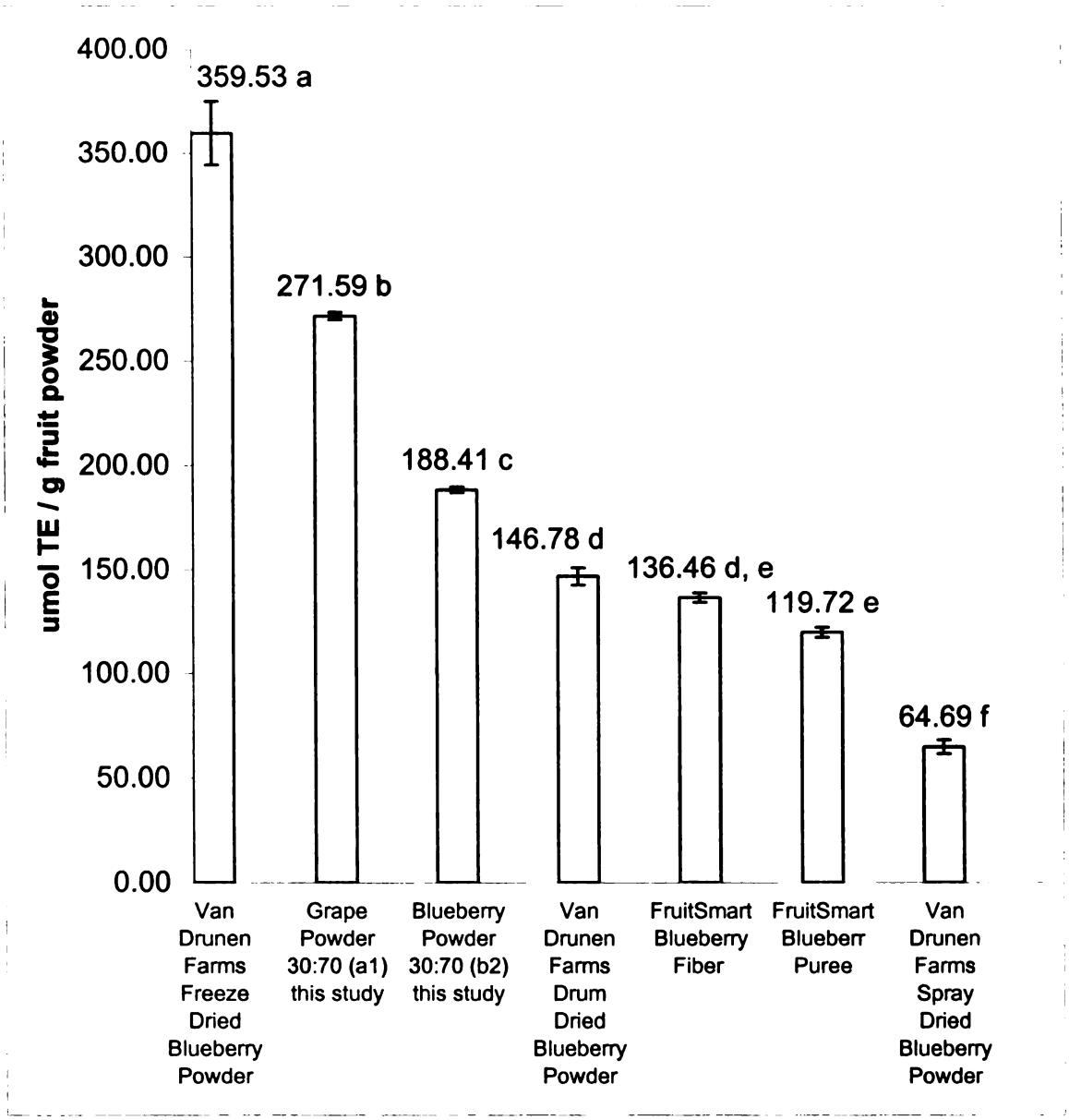


Figure 3.4.1.1 $ORAC_{FL}$ value comparison of commercial blueberry powders
*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)
**Results are expressed as micromoles of Trolox Equivalents per gram of fruit powder (µmol TE / g fruit powder)

From figure 3.4.1.1, it can be seen that the freeze dried sample contained the highest $ORAC_{FL}$ value. All other powders were produced using significant heating. Since oxygen and heat have the most pronounced effect on antioxidant capacity, the heated samples would be expected to have a lower $ORAC_{FL}$ value.

3.4.2 Total Phenolics for Commercial Blueberry Powders and Those Produced in This Study

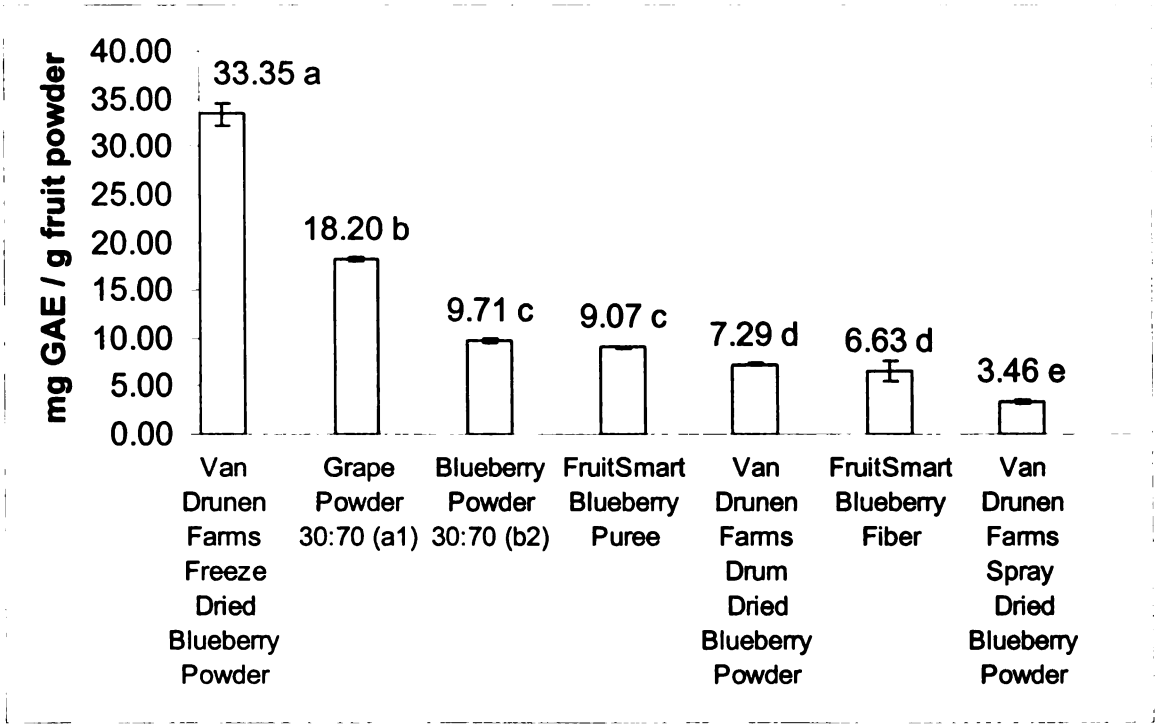


Figure 3.4.2.1 Total Phenolic value comparison of commercial blueberry powders, measured at 765 nm

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

**Results are expressed as milligrams of Gallic Acid Equivalents per gram of fruit powder (mg GAE / g fruit powder)

Again, as expected, the freeze dried sample scored the highest in total phenolic value. The remaining samples followed a close trend to the $ORAC_{FL}$ analysis; with the Van Drunen Farms spray dried blueberry powder having the lowest total phenolic content (figure 3.4.2.1).

3.4.3 High Performance Liquid Chromatography for Commercial Blueberry Powders and Those Produced in This Study

Different cultivars of blueberries were used for the production of the various commercial powders. Therefore, the HPLC profile for each sample would differ from each other.

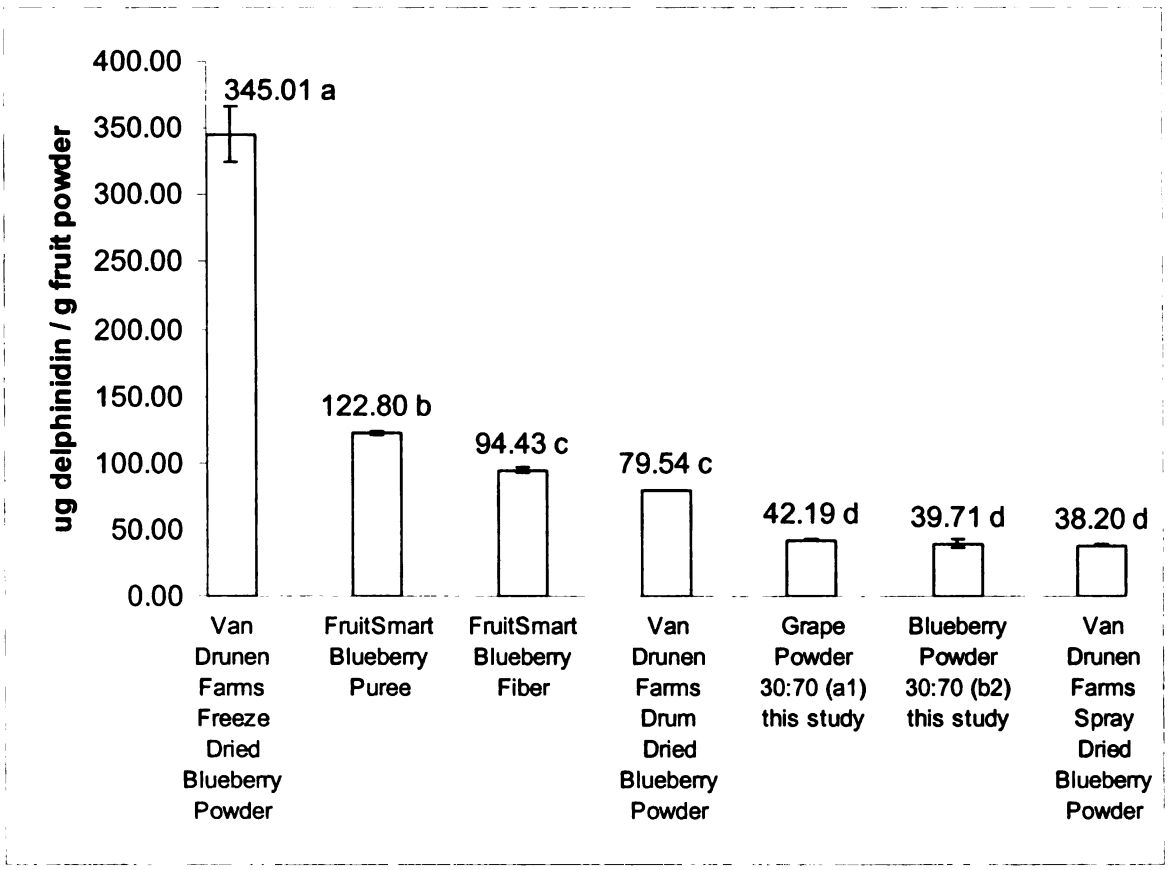


Figure 3.4.3.1 Delphinidin determination of various commercial blueberry powder samples.

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

**Results are expressed as micrograms of delphinidin per gram of fruit powder (µg delphinidin / g fruit powder)

The results for delphinidin analysis were consistent with that of $ORAC_{FL}$ and total phenolics, with the freeze dried sample having the highest levels of

delphinidin. The experimental spray dried blueberry powder and Van Drunen Farms spray dried blueberry powder showed no significant differences and both scored the lowest for delphinidin analysis of only 38.20 µg delphinidin / g fruit powder when compared to the freeze dried blueberry powder, which contained almost ten times delphinidin per gram of powder (Figure 3.4.3.1).

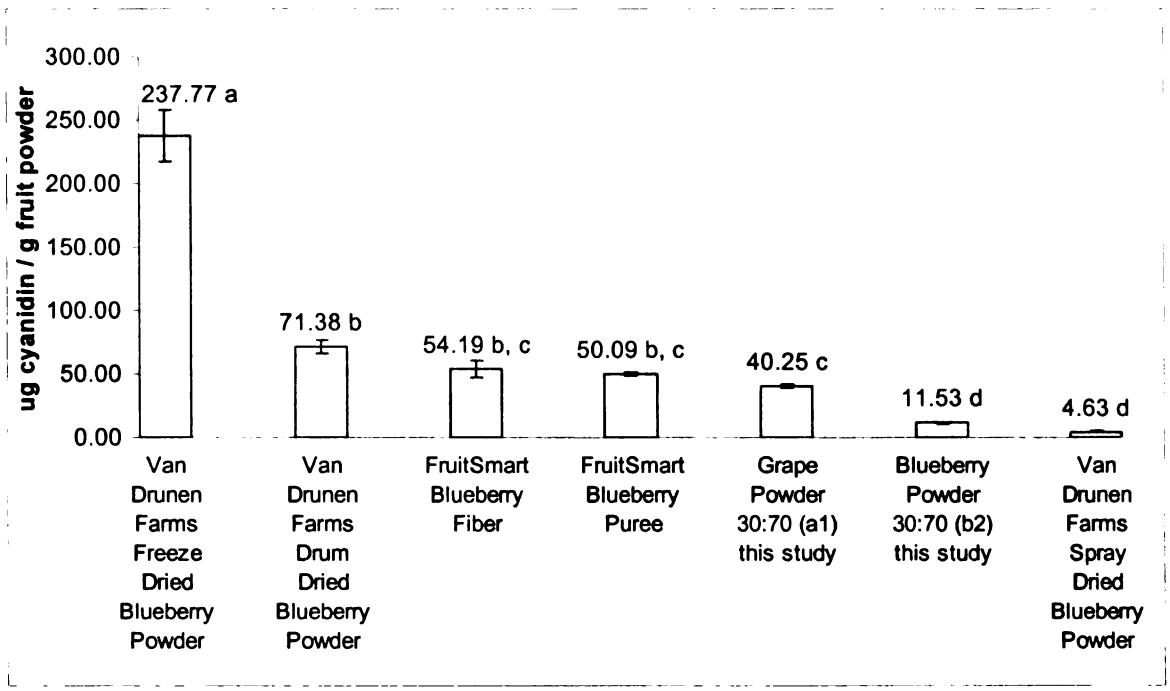


Figure 3.4.3.2 Cyanidin determination of various commercial blueberry powder samples.

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

**Results are expressed as micrograms of cyanidin per gram of fruit powder (µg cyanidin / g fruit powder)

The freeze dried blueberry powder had the highest value in cyanidin analysis. Both spray dried blueberry and grape powders scored lower than all powders except the Van Drunen Farms spray dried blueberry powder. The cyanidin concentration in the Van Drunen Farms spray dried sample was very low of only 4.63 µg cyanidin / g fruit powder (Figure 3.4.3.2).

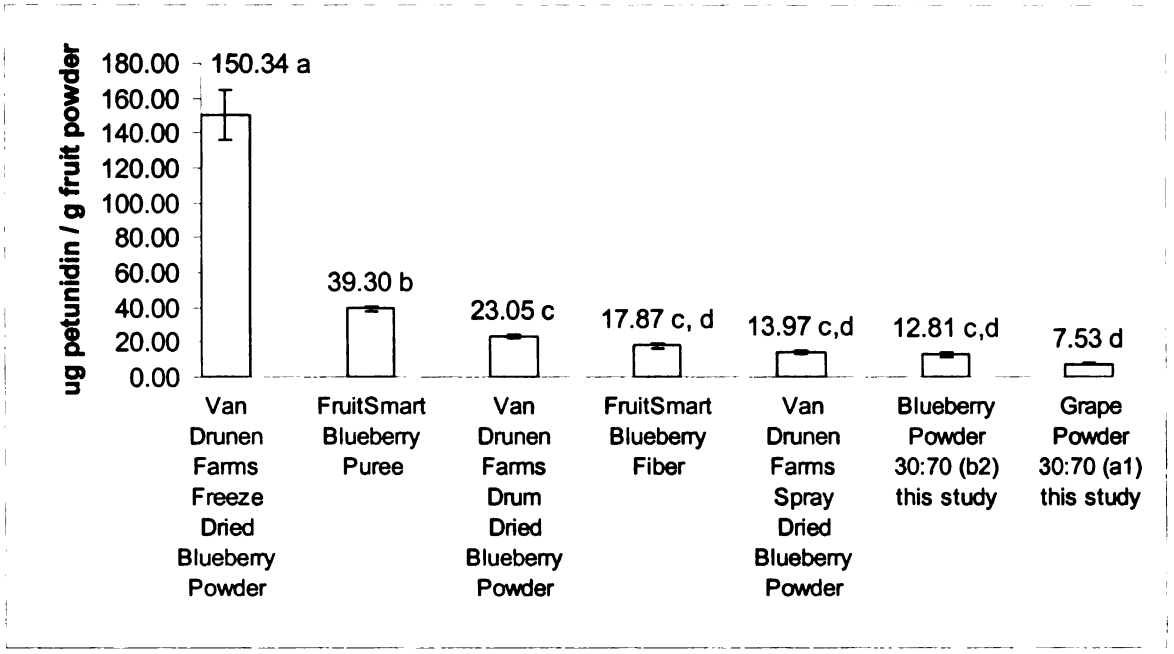


Figure 3.4.3.3 Petunidin determination of various commercial blueberry powder samples.

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

**Results are expressed as micrograms of petunidin per gram of fruit powder (µg petunidin / g fruit powder)

The highest level of petunidin was found in the freeze dried blueberry powder. However, the spray dried grape powder contained the lowest concentration of petunidin per gram powder. This could be explained by observing the chromatograms of both blueberry and grape (Figures 3.3.4.1 and 3.3.4.3). The peak area of grape sample was significantly smaller than that of blueberry and thus contributing to grape being the lowest petunidin containing powder.

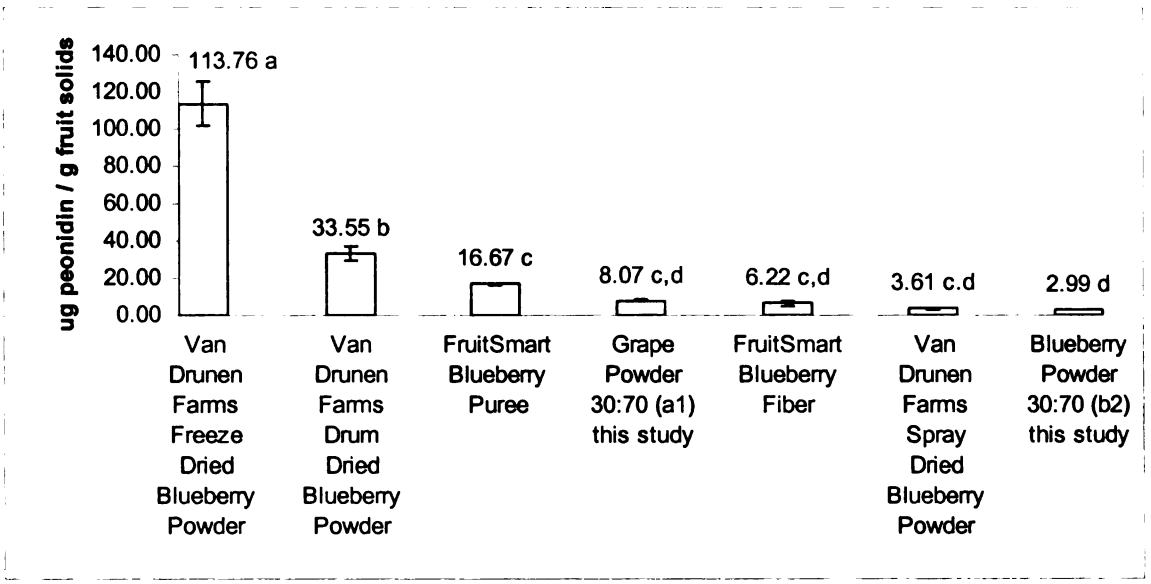


Figure 3.4.3.4 Peonidin determination of various commercial blueberry powder samples.

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, *P<0.001*, n = 3)

**Results are expressed as micrograms of peonidin per gram of fruit powder (µg peonidin / g fruit powder)

Both spray dried blueberry powders, showing no significant difference, contained the least amount of peonidin per gram powder. The freeze dried blueberry sample obtained from Van Drunen Farms continues to show superiority over other samples, with three times higher in peonidin than its immediate follower, the drum dried blueberry powder, and around 30 times higher than the spray dried blueberry samples (Figure 3.4.3.4).

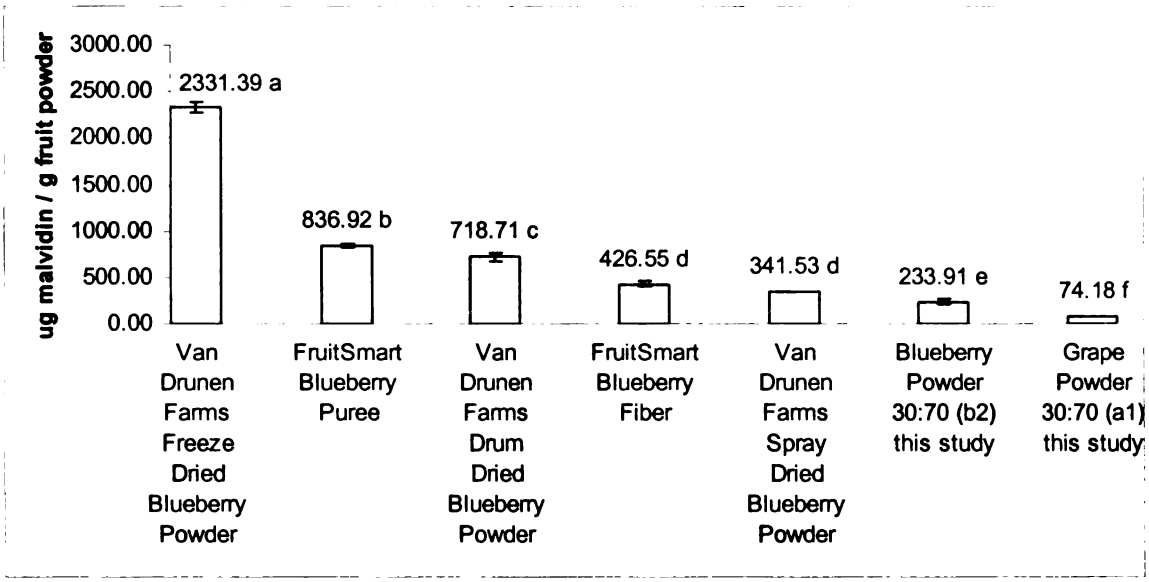


Figure 3.4.3.5 Malvidin determination of various commercial blueberry powder samples.

*Means sharing the same letter are not significantly different from each other (Tukey's HSD test, $P<0.001$, n = 3)

**Results are expressed as micrograms of malvidin per gram of fruit powder (µg malvidin / g fruit powder)

For the malvidin determination, the grape powder had the lowest concentration due to the difference in make up of malvidin in nature. The freeze dried sample continued to show high concentration of anthocyanidins throughout the analyses (Figure 3.4.3.5).

3.4.4 Conclusions

Amongst the commercial samples and the experimental blueberry and grape samples, the freeze dried sample showed superior quality in the aspects of $ORAC_{FL}$, total phenolics and anthocyanidin analysis. This confirmed that freeze dried fruit products have the highest quality of all and comparable to their fresh counterpart because it was treated under refrigerated vacuum.

Van Drunen spray dried blueberry powder consistently tested as the worst in antioxidant activity, even when compared to the experimental spray dried blueberry and grape powders which were obtained from low quality blueberries and grape pomace. With that in mind, it should be recognized that instead of discarding these unwanted materials, the cull blueberries and grape pomace could be utilized as a valuable source of anthocyanins, for the production of lower cost value-added nutraceutical products. The use of by-products becomes apparent especially in this study where most of the ingredients used to manufacture the commercial blueberry powders obtained are of high quality and would add to the production cost of these powders. Utilizing fruit by-products is a way to lower production cost with only slight compromise in its antioxidant capacity.

4. Future Recommendations

The following topics are recommended for future research:

1. To study the protective mechanism of maltodextrin during spray drying.
2. To study the shelf-life of spray dried powder in terms of color and anthocyanin retention.
3. To incorporate the spray dried powder in a food system to determine the maximum amount that could be added; and then determine the health benefits associated with the addition of the powders.
4. To obtain a powder containing high ratios of fruit solids to maltodextrin for spray drying with the correlation of glass transition temperature of the feed to avoid sticky issues in the spray dryer.
5. To investigate the effect of residence time by controlling the air flow in the spray dryer to antioxidant capacity degradation.
6. To study whether microcystalline cellulose would be a better replacement for maltodextrin during spray drying.
7. To study whether immature blueberries affect antioxidant capacity.

Appendices

Appendix 1 Raw data for Spray Drying of cull blueberries with varying levels of maltodextrin

Table A.1.1 Raw data for Oxygen Radical Absorbance Capacity ($ORAC_{FL}$) analysis for blueberry extract used prior to spray drying, n=3

Sample	µmol TE / mL Extract	Average	Standard Deviation	umol TE / g fruit solids	Average	Standard Deviation
5:95 Blueberry Extract	13.69			936.45		
5:95 Blueberry Extract	13.52	13.51	0.18	924.74	924.23	12.48
5:95 Blueberry Extract	13.33			911.51		
10:90 Blueberry Extract	16.40			911.89		
10:90 Blueberry Extract	16.53	16.43	0.10	919.03	913.17	5.33
10:90 Blueberry Extract	16.35			908.60		
30:70 Blueberry Extract	19.14			913.90		
30:70 Blueberry Extract	18.93	18.97	0.14	903.84	906.13	6.92
30:70 Blueberry Extract	18.86			900.65		

Table A.1.2 Raw data for Oxygen Radical Absorbance Capacity ($ORAC_{FL}$) analysis for blueberry powder obtained after spray drying, n=3

Sample	µmol TE / mL Extract	Average	Standard Deviation	umol TE / g fruit solids	Average	Standard Deviation
5:95 Blueberry Powder	33.75			725.96		
5:95 Blueberry Powder	33.66	33.99	0.49	723.94	731.02	10.57
5:95 Blueberry Powder	34.55			743.17		
10:90 Blueberry Powder	61.77			665.86		
10:90 Blueberry Powder	59.22	60.87	1.43	638.38	656.15	15.41
10:90 Blueberry Powder	61.62			664.22		
30:70 Blueberry Powder	122.67			448.15		
30:70 Blueberry Powder	119.27	121.27	1.78	435.75	443.06	6.49
30:70 Blueberry Powder	121.88			445.28		

Table A.1.3 Raw data for total phenolics analysis for blueberry extract prior spray drying, measured at 750 nm, n=3

Sample	mg GAE / mL extract @ 750nm	Average	Standard Deviation	mg GAE / g solids @ 750nm	Average	Standard Deviation
5:95 Extract	1.74			34.88		
5:95 Extract	1.92	1.89	0.13	38.42	37.74	2.59
5:95 Extract	2.00			39.91		
10:90 Extract	3.34			33.44		
10:90 Extract	3.97	3.65	0.31	39.70	36.48	3.14
10:90 Extract	3.63			36.29		
30:70 Extract	9.56			31.87		
30:70 Extract	10.20	9.97	0.36	34.00	33.23	1.18
30:70 Extract	10.15			33.83		

Table A.1.4 Raw data for total phenolics analysis for blueberry extract prior to spray drying, measured at 765 nm, n=3

Sample	mg GAE / mL extract @ 765 nm	Average	Standard Deviation	mg GAE / g solids @ 765nm	Average	Standard Deviation
5:95 Extract	1.74			34.72		
5:95 Extract	1.92	1.88	0.13	38.39	37.58	2.55
5:95 Extract	1.98			39.63		
10:90 Extract	3.36			33.61		
10:90 Extract	3.98	3.64	0.31	39.81	36.43	3.14
10:90 Extract	3.59			35.88		
30:70 Extract	9.65			32.15		
30:70 Extract	9.63	9.71	0.12	32.10	32.37	0.42
30:70 Extract	9.85			32.85		

Table A.1.5 Raw data for total phenolics analysis for blueberry powder after spray drying, measured at 750 nm, n=3

Sample	mg GAE / g powder @ 750nm	Average	Standard Deviation	mg GAE / g solids @ 750nm	Average	Standard Deviation
5:95 Powder	1.63			32.67		
5:95 Powder	1.71	1.65	0.05	34.16	32.96	1.08
5:95 Powder	1.60			32.05		
10:90 Powder	3.06			30.60		
10:90 Powder	2.98	3.00	0.05	29.80	30.04	0.49
10:90 Powder	2.97			29.72		
30:70 Powder	7.44			24.81		
30:70 Powder	7.31	7.40	0.08	24.36	24.66	0.26
30:70 Powder	7.44			24.81		

Table A.1.6 Raw data for total phenolics analysis for blueberry powder after spray drying, measured at 765 nm, n=3

Sample	mg GAE / g powder @ 765nm	Average	Standard Deviation	mg GAE / g solids @ 765nm	Average	Standard Deviation
5:95 Powder	1.71			34.11		
5:95 Powder	1.72	1.68	0.06	34.43	33.53	1.29
5:95 Powder	1.60			32.06		
10:90 Powder	3.16			31.64		
10:90 Powder	2.95	3.02	0.13	29.51	30.15	1.29
10:90 Powder	2.93			29.31		
30:70 Powder	7.42			24.75		
30:70 Powder	7.27	7.38	0.10	24.23	24.61	0.32
30:70 Powder	7.45			24.83		

Table A.1.7 Raw data for HPLC analysis for individual anthocyanins in blueberry extract prior to spray drying, n=3

Anthocyanin: Delphinidin	ug/g Blueberry Solids	Average	Standard Deviation	ug/ ml Blueberry Extract	Average	Standard Deviation
5:95 Blueberry Extract	460.56			23.03		
5:95 Blueberry Extract	466.69	461.92	4.25	23.33	23.10	0.21
5:95 Blueberry Extract	458.52			22.93		
10:90 Blueberry Extract	463.23			46.32		
10:90 Blueberry Extract	459.08	458.10	5.68	45.91	45.81	0.57
10:90 Blueberry Extract	452.00			45.20		
30:70 Blueberry Extract	463.70			139.11		
30:70 Blueberry Extract	458.80	461.52	2.49	137.64	138.46	0.75
30:70 Blueberry Extract	462.05			138.62		
Anthocyanin: Cyanidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ ml Blueberry Extract**	**Average**	**Standard Deviation**
5:95 Blueberry Extract	73.53			3.68		
5:95 Blueberry Extract	63.12	70.64	6.57	3.16	3.53	0.33
5:95 Blueberry Extract	75.27			3.76		
10:90 Blueberry Extract	68.99			6.90		
10:90 Blueberry Extract	60.57	69.42	9.07	6.06	6.94	0.91
10:90 Blueberry Extract	78.69			7.87		
30:70 Blueberry Extract	85.58			25.67		
30:70 Blueberry Extract	80.43	86.05	5.87	24.13	25.81	1.76
30:70 Blueberry Extract	92.13			27.64		
Anthocyanin: Petunidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ ml Blueberry Extract**	**Average**	**Standard Deviation**
5:95 Blueberry Extract	66.73			3.34		
5:95 Blueberry Extract	68.05	68.73	2.40	3.40	3.44	0.12
5:95 Blueberry Extract	71.39			3.57		
10:90 Blueberry Extract	67.70			6.77		
10:90 Blueberry Extract	61.51	65.07	3.20	6.15	6.51	0.32
10:90 Blueberry Extract	65.99			6.60		
30:70 Blueberry Extract	62.54			18.76		
30:70 Blueberry Extract	63.28	64.20	2.26	18.98	19.26	0.68
30:70 Blueberry Extract	66.77			20.03		
Anthocyanin: Peonidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ ml Blueberry Extract**	**Average**	**Standard Deviation**
5:95 Blueberry Extract	14.92			0.75		
5:95 Blueberry Extract	15.22	16.07	1.73	0.76	0.80	0.09
5:95 Blueberry Extract	18.05			0.90		
10:90 Blueberry Extract	13.31			1.33		
10:90 Blueberry Extract	12.83	12.82	0.49	1.28	1.28	0.05
10:90 Blueberry Extract	12.33			1.23		
30:70 Blueberry Extract	11.66			3.50		
30:70 Blueberry Extract	13.26	13.12	1.40	3.98	3.94	0.42
30:70 Blueberry Extract	14.46			4.34		

Table A.1.7 Continued

Anthocyanin: Malvidin	ug/g Blueberry Solids	Average	Standard Deviation	ug/ ml Blueberry Extract	Average	Standard Deviation
5:95 Blueberry Extract	1267.09			63.35		
5:95 Blueberry Extract	1211.89	1244.63	29.01	60.59	62.23	1.45
5:95 Blueberry Extract	1254.92			62.75		
10:90 Blueberry Extract	1222.66			122.27		
10:90 Blueberry Extract	1217.74	1221.94	3.89	121.77	122.19	0.39
10:90 Blueberry Extract	1225.42			122.54		
30:70 Blueberry Extract	1215.99			364.80		
30:70 Blueberry Extract	1237.86	1227.75	11.03	371.36	368.33	3.31
30:70 Blueberry Extract	1229.42			368.83		

Table A.1.8 Raw data for HPLC analysis for individual anthocyanins in blueberry powder after spray drying, n=3

Anthocyanin: Delphinidin	ug/g Blueberry Solids	Average	Standard Deviation	ug/ g Blueberry Powder	Average	Standard Deviation
5:95 Blueberry Powder	457.29			21.30		
5:95 Blueberry Powder	454.61	458.02	3.83	21.18	21.33	0.18
5:95 Blueberry Powder	462.17			21.53		
10:90 Blueberry Powder	220.64			20.41		
10:90 Blueberry Powder	279.42	258.57	32.90	25.85	23.92	3.04
10:90 Blueberry Powder	275.65			25.50		
30:70 Blueberry Powder	113.31			31.25		
30:70 Blueberry Powder	101.85	107.89	5.75	28.09	29.75	1.59
30:70 Blueberry Powder	108.52			29.93		
Anthocyanin: Cyanidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ g Blueberry Powder**	**Average**	**Standard Deviation**
5:95 Blueberry Powder	34.15			1.59		
5:95 Blueberry Powder	37.72	36.47	2.01	1.76	1.70	0.09
5:95 Blueberry Powder	37.55			1.75		
10:90 Blueberry Powder	33.80			3.13		
10:90 Blueberry Powder	36.44	35.46	1.45	3.37	3.28	0.13
10:90 Blueberry Powder	36.15			3.34		
30:70 Blueberry Powder	19.71			5.44		
30:70 Blueberry Powder	17.40	17.95	1.57	4.80	4.95	0.43
30:70 Blueberry Powder	16.72			4.61		

Table A.1.8 Continued

Anthocyanin: Petunidin	ug/g Blueberry Solids	Average	Standard Deviation	ug/ g Blueberry Powder	Average	Standard Deviation
5:95 Blueberry Powder	59.09			2.75		
5:95 Blueberry Powder	61.82	61.51	2.28	2.88	2.87	0.11
5:95 Blueberry Powder	63.62			2.96		
10:90 Blueberry Powder	50.21			4.64		
10:90 Blueberry Powder	50.10	49.58	1.00	4.63	4.59	0.09
10:90 Blueberry Powder	48.43			4.48		
30:70 Blueberry Powder	28.91			7.97		
30:70 Blueberry Powder	23.09	25.95	2.91	6.37	7.16	0.80
30:70 Blueberry Powder	25.86			7.13		
Anthocyanin: Peonidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ g Blueberry Powder**	**Average**	**Standard Deviation**
5:95 Blueberry Powder	7.27			0.34		
5:95 Blueberry Powder	7.48	7.30	0.17	0.35	0.34	0.01
5:95 Blueberry Powder	7.15			0.33		
10:90 Blueberry Powder	4.03			0.37		
10:90 Blueberry Powder	4.90	4.29	0.53	0.45	0.40	0.05
10:90 Blueberry Powder	3.94			0.36		
30:70 Blueberry Powder	2.56			0.71		
30:70 Blueberry Powder	2.76	2.82	0.29	0.76	0.78	0.08
30:70 Blueberry Powder	3.13			0.86		
Anthocyanin: Malvidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ g Blueberry Powder**	**Average**	**Standard Deviation**
5:95 Blueberry Powder	1186.90			55.29		
5:95 Blueberry Powder	1213.82	1193.20	18.30	56.54	55.58	0.85
5:95 Blueberry Powder	1178.88			54.91		
10:90 Blueberry Powder	727.67			67.31		
10:90 Blueberry Powder	780.23	756.63	26.69	72.17	69.99	2.47
10:90 Blueberry Powder	762.01			70.49		
30:70 Blueberry Powder	439.15			121.10		
30:70 Blueberry Powder	367.08	407.52	36.83	101.23	112.38	10.16
30:70 Blueberry Powder	416.32			114.81		

Appendix 2 Raw data for Different Spray Drying Outlet Temperatures on Nutraceutical Content of Blueberry By-Products

Table A.2.1 Raw data for Oxygen Radical Absorbance Capacity ($ORAC_{FL}$) analysis for blueberry extract used prior to spray drying, n=3

Sample	µmol TE / mL Etract	Average	Standard Deviation	umol TE / g fruit solids	Average	Standard Deviation
Blueberry Extract 30:70 (a^1)[a,b]	15.41			792.89		
Blueberry Extract 30:70 (a^1)	15.47	15.47	0.06	795.94	795.83	2.88
Blueberry Extract 30:70 (a^1)	15.53			798.65		
Blueberry Extract 30:70 (a^2)	14.41			798.14		
Blueberry Extract 30:70 (a^2)	14.36	14.41	0.04	795.09	797.70	2.42
Blueberry Extract 30:70 (a^2)	14.45			799.88		
Blueberry Extract 30:70 (b^1)	15.79			793.78		
Blueberry Extract 30:70 (b^1)	15.83	15.81	0.02	795.77	794.71	1.00
Blueberry Extract 30:70 (b^1)	15.80			794.57		
Blueberry Extract 30:70 (b^2)	14.71			795.73		
Blueberry Extract 30:70 (b^2)	14.69	14.71	0.02	794.84	795.83	1.05
Blueberry Extract 30:70 (b^2)	14.73			796.93		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.2.2 Raw data for Oxygen Radical Absorbance Capacity ($ORAC_{FL}$) analysis for blueberry powder obtained after spray drying, n=3

Sample	µmol TE / mL Extract	Average	Standard Deviation	umol TE / g fruit solids	Average	Standard Deviation
Blueberry Powder 30:70 (a^1)[a,b]	180.33			626.88		
Blueberry Powder 30:70 (a^1)	185.08	183.65	2.88	643.37	638.41	10.03
Blueberry Powder 30:70 (a^1)	185.55			645.00		
Blueberry Powder 30:70 (a^2)	174.57			617.60		
Blueberry Powder 30:70 (a^2)	169.85	171.96	2.40	600.91	608.35	8.49
Blueberry Powder 30:70 (a^2)	171.44			606.53		
Blueberry Powder 30:70 (b^1)	168.50			592.05		
Blueberry Powder 30:70 (b^1)	168.38	174.82	11.05	591.62	614.25	38.82
Blueberry Powder 30:70 (b^1)	187.58			659.07		
Blueberry Powder 30:70 (b^2)	187.19			650.70		
Blueberry Powder 30:70 (b^2)	188.16	188.41	1.37	654.08	654.96	4.76
Blueberry Powder 30:70 (b^2)	189.89			660.11		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.2.3 Raw data for total phenolics analysis for blueberry extract prior to spray drying, measured at 750 nm, n=3

Sample	mg GAE / mL blueberry extract @750nm	Average	Standard Deviation	mg GAE / g blueberry solids @750nm	Average	Standard Deviation
Blueberry Extract 30:70 (a^1)[a,b]	10.30			34.33		
Blueberry Extract 30:70 (a^1)	10.71	10.59	0.25	35.69	35.29	0.83
Blueberry Extract 30:70 (a^1)	10.75			35.84		
Blueberry Extract 30:70 (a^2)	10.50			35.00		
Blueberry Extract 30:70 (a^2)	11.07	10.92	0.37	36.90	36.40	1.23
Blueberry Extract 30:70 (a^2)	11.19			37.30		
Blueberry Extract 30:70 (b^1)	10.70			35.68		
Blueberry Extract 30:70 (b^1)	10.74	10.59	0.22	35.80	35.31	0.75
Blueberry Extract 30:70 (b^1)	10.34			34.45		
Blueberry Extract 30:70 (b^2)	10.91			36.37		
Blueberry Extract 30:70 (b^2)	11.00	11.05	0.17	36.68	36.84	0.56
Blueberry Extract 30:70 (b^2)	11.24			37.46		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.2.4 Raw data for total phenolics analysis for blueberry extract prior to spray drying, measured at 765 nm, n=3

Sample	mg GAE / mL blueberry extract @765nm	Average	Standard Deviation	mg GAE / g blueberry solids @765nm	Average	Standard Deviation
Blueberry Extract 30:70 (a^1)[a,b]	10.39			34.63		
Blueberry Extract 30:70 (a^1)	10.55	10.52	0.12	35.17	35.06	0.39
Blueberry Extract 30:70 (a^1)	10.61			35.38		
Blueberry Extract 30:70 (a^2)	10.87			36.23		
Blueberry Extract 30:70 (a^2)	11.32	11.01	0.27	37.73	36.70	0.90
Blueberry Extract 30:70 (a^2)	10.84			36.13		
Blueberry Extract 30:70 (b^1)	10.69			35.63		
Blueberry Extract 30:70 (b^1)	10.59	10.47	0.30	35.31	34.90	1.01
Blueberry Extract 30:70 (b^1)	10.13			33.75		
Blueberry Extract 30:70 (b^2)	10.85			36.18		
Blueberry Extract 30:70 (b^2)	10.69	10.88	0.21	35.63	36.27	0.69
Blueberry Extract 30:70 (b^2)	11.10			37.00		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.2.5 Raw data for total phenolics analysis for blueberry powder after spray drying, measured at 750 nm, n=3

Sample	mg GAE / g powder	Average	Standard Deviation	mg GAE / g solids 750nm	Average	Standard Deviation
Blueberry Powder 30:70 (a^1)[a,b]	9.58			31.92		
Blueberry Powder 30:70 (a^1)	9.48	9.50	0.07	31.61	31.68	0.22
Blueberry Powder 30:70 (a^1)	9.45			31.49		
Blueberry Powder 30:70 (a^2)	9.14			30.46		
Blueberry Powder 30:70 (a^2)	9.56	9.19	0.35	31.86	30.63	1.16
Blueberry Powder 30:70 (a^2)	8.87			29.56		
Blueberry Powder 30:70 (b^1)	9.39			31.30		
Blueberry Powder 30:70 (b^1)	10.26	9.45	0.79	34.19	31.49	2.62
Blueberry Powder 30:70 (b^1)	8.69			28.97		
Blueberry Powder 30:70 (b^2)	9.74			32.48		
Blueberry Powder 30:70 (b^2)	10.05	9.80	0.22	33.50	32.67	0.75
Blueberry Powder 30:70 (b^2)	9.61			32.04		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.2.6 Raw data for total phenolics analysis for blueberry powder after spray drying, measured at 765 nm, n=3

Sample	mg GAE / g powder	Average	Standard Deviation	mg GAE / g solids 750nm	Average	Standard Deviation
Blueberry Powder 30:70 (a^1)[a,b]	9.47			31.58		
Blueberry Powder 30:70 (a^1)	9.34	9.38	0.08	31.13	31.26	0.28
Blueberry Powder 30:70 (a^1)	9.32			31.08		
Blueberry Powder 30:70 (a^2)	8.94			29.81		
Blueberry Powder 30:70 (a^2)	9.39	9.08	0.26	31.29	30.27	0.88
Blueberry Powder 30:70 (a^2)	8.92			29.72		
Blueberry Powder 30:70 (b^1)	10.25			34.18		
Blueberry Powder 30:70 (b^1)	10.06	9.61	0.95	33.53	32.03	3.17
Blueberry Powder 30:70 (b^1)	8.52			28.39		
Blueberry Powder 30:70 (b^2)	9.67			32.25		
Blueberry Powder 30:70 (b^2)	9.90	9.71	0.16	32.99	32.38	0.55
Blueberry Powder 30:70 (b^2)	9.57			31.91		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.2.7 Raw data for HPLC analysis for individual anthocyanins in blueberry extract prior to spray drying, n=3

Anthocyanin: Delphinidin	ug/g Blueberry Solids	Average	Standard Deviation	ug/ ml Blueberry Extract	Average	Standard Deviation
Blueberry Extract 30:70 (a^1)[a,b]	436.39	440.88	8.69	130.92	132.26	2.61
Blueberry Extract 30:70 (a^1)	450.89			135.27		
Blueberry Extract 30:70 (a^1)	435.35			130.60		
Blueberry Extract 30:70 (a^2)	437.13	436.49	1.76	131.14	130.95	0.53
Blueberry Extract 30:70 (a^2)	437.84			131.35		
Blueberry Extract 30:70 (a^2)	434.51			130.35		
Blueberry Extract 30:70 (b^1)	447.26	436.47	9.47	134.18	130.94	2.84
Blueberry Extract 30:70 (b^1)	429.55			128.86		
Blueberry Extract 30:70 (b^1)	432.59			129.78		
Blueberry Extract 30:70 (b^2)	410.51	429.46	18.35	123.15	128.84	5.51
Blueberry Extract 30:70 (b^2)	447.15			134.14		
Blueberry Extract 30:70 (b^2)	430.73			129.22		
Anthocyanin: Cyanidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ ml Blueberry Extract**	**Average**	**Standard Deviation**
Blueberry Extract 30:70 (a^1)	111.70	113.82	5.38	33.51	34.15	1.62
Blueberry Extract 30:70 (a^1)	119.94			35.98		
Blueberry Extract 30:70 (a^1)	109.82			32.95		
Blueberry Extract 30:70 (a^2)	111.63	110.48	7.77	33.49	33.14	2.33
Blueberry Extract 30:70 (a^2)	117.60			35.28		
Blueberry Extract 30:70 (a^2)	102.19			30.66		
Blueberry Extract 30:70 (b^1)	96.22	101.52	7.60	28.87	30.46	2.28
Blueberry Extract 30:70 (b^1)	110.23			33.07		
Blueberry Extract 30:70 (b^1)	98.12			29.43		
Blueberry Extract 30:70 (b^2)	109.55	106.48	6.02	32.87	31.94	1.80
Blueberry Extract 30:70 (b^2)	110.33			33.10		
Blueberry Extract 30:70 (b^2)	99.54			29.86		
Anthocyanin: Petunidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ ml Blueberry Extract**	**Average**	**Standard Deviation**
Blueberry Extract 30:70 (a^1)	105.88	106.02	2.80	31.76	31.81	0.84
Blueberry Extract 30:70 (a^1)	108.88			32.66		
Blueberry Extract 30:70 (a^1)	103.29			30.99		
Blueberry Extract 30:70 (a^2)	114.62	109.76	4.30	34.39	32.93	1.29
Blueberry Extract 30:70 (a^2)	108.26			32.48		
Blueberry Extract 30:70 (a^2)	106.41			31.92		
Blueberry Extract 30:70 (b^1)	113.76	110.93	2.50	34.13	33.28	0.75
Blueberry Extract 30:70 (b^1)	109.99			33.00		
Blueberry Extract 30:70 (b^1)	109.04			32.71		
Blueberry Extract 30:70 (b^2)	105.43	109.84	5.11	31.63	32.95	1.53
Blueberry Extract 30:70 (b^2)	108.64			32.59		
Blueberry Extract 30:70 (b^2)	115.45			34.63		

Table A.2.7 Continued

Anthocyanin: Peonidin	ug/g Blueberry Solids	Average	Standard Deviation	ug/ ml Blueberry Extract	Average	Standard Deviation
Blueberry Extract 30:70 (a^1)	20.27			6.08		
Blueberry Extract 30:70 (a^1)	19.73	20.01	0.27	5.92	6.00	0.08
Blueberry Extract 30:70 (a^1)	20.03			6.01		
Blueberry Extract 30:70 (a^2)	21.64			6.49		
Blueberry Extract 30:70 (a^2)	25.28	23.89	1.97	7.58	7.17	0.59
Blueberry Extract 30:70 (a^2)	24.76			7.43		
Blueberry Extract 30:70 (b^1)	23.19			6.96		
Blueberry Extract 30:70 (b^1)	19.89	21.48	1.66	5.97	6.44	0.50
Blueberry Extract 30:70 (b^1)	21.35			6.40		
Blueberry Extract 30:70 (b^2)	24.08			7.22		
Blueberry Extract 30:70 (b^2)	21.60	23.43	1.61	6.48	7.03	0.48
Blueberry Extract 30:70 (b^2)	24.60			7.38		
Anthocyanin: Malvidin	**ug/g Blueberry Solids**	**Average**	**Standard Deviation**	**ug/ ml Blueberry Extract**	**Average**	**Standard Deviation**
Blueberry Extract 30:70 (a^1)	1968.48			590.54		
Blueberry Extract 30:70 (a^1)	2332.31	2146.23	182.06	699.69	643.87	54.62
Blueberry Extract 30:70 (a^1)	2137.89			641.37		
Blueberry Extract 30:70 (a^2)	2395.96			718.79		
Blueberry Extract 30:70 (a^2)	2139.39	2239.20	137.44	641.82	671.76	41.23
Blueberry Extract 30:70 (a^2)	2182.26			654.68		
Blueberry Extract 30:70 (b^1)	2279.74			683.92		
Blueberry Extract 30:70 (b^1)	2338.61	2305.15	30.25	701.58	691.54	9.08
Blueberry Extract 30:70 (b^1)	2297.08			689.13		
Blueberry Extract 30:70 (b^2)	2245.81			673.74		
Blueberry Extract 30:70 (b^2)	2152.04	2184.03	53.51	645.61	655.21	16.05
Blueberry Extract 30:70 (b^2)	2154.24			646.27		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.2.8 Raw data for HPLC analysis for individual anthocyanins in blueberry powder after spray drying, n=3

Anthocyanin: Delphinidin	ug/g Blueberry solids	Average	Standard Deviation	ug / g Blueberry powder	Average	Standard Deviation
Blueberry Powder 30:70 (a^1)[a,b]	125.39	133.96	7.45	36.07	38.54	2.14
Blueberry Powder 30:70 (a^1)	138.79			39.93		
Blueberry Powder 30:70 (a^1)	137.72			39.62		
Blueberry Powder 30:70 (a^2)	130.31	141.76	10.24	36.83	40.07	2.89
Blueberry Powder 30:70 (a^2)	150.01			42.40		
Blueberry Powder 30:70 (a^2)	144.97			40.98		
Blueberry Powder 30:70 (b^1)	145.24	147.19	3.16	41.34	41.89	0.90
Blueberry Powder 30:70 (b^1)	150.83			42.93		
Blueberry Powder 30:70 (b^1)	145.50			41.41		
Blueberry Powder 30:70 (b^2)	150.49	138.02	10.86	43.29	39.71	3.12
Blueberry Powder 30:70 (b^2)	130.57			37.56		
Blueberry Powder 30:70 (b^2)	133.02			38.27		
Anthocyanin: Cyanidin	**ug/g Blueberry solids**	**Average**	**Standard Deviation**	**ug / g Blueberry powder**	**Average**	**Standard Deviation**
Blueberry Powder 30:70 (a^1)	26.45	29.13	2.39	7.61	8.38	0.69
Blueberry Powder 30:70 (a^1)	29.91			8.60		
Blueberry Powder 30:70 (a^1)	31.03			8.93		
Blueberry Powder 30:70 (a^2)	31.16	36.12	4.74	8.81	10.21	1.34
Blueberry Powder 30:70 (a^2)	40.61			11.48		
Blueberry Powder 30:70 (a^2)	36.61			10.35		
Blueberry Powder 30:70 (b^1)	40.10	40.25	0.41	11.41	11.46	0.12
Blueberry Powder 30:70 (b^1)	40.71			11.59		
Blueberry Powder 30:70 (b^1)	39.94			11.37		
Blueberry Powder 30:70 (b^2)	44.50	40.07	3.88	12.80	11.53	1.12
Blueberry Powder 30:70 (b^2)	37.32			10.74		
Blueberry Powder 30:70 (b^2)	38.39			11.04		
Anthocyanin: Petunidin	**ug/g Blueberry solids**	**Average**	**Standard Deviation**	**ug / g Blueberry powder**	**Average**	**Standard Deviation**
Blueberry Powder 30:70 (a^1)	40.44	43.20	2.60	11.63	12.43	0.75
Blueberry Powder 30:70 (a^1)	43.55			12.53		
Blueberry Powder 30:70 (a^1)	45.61			13.12		
Blueberry Powder 30:70 (a^2)	42.60	48.37	5.06	12.04	13.67	1.43
Blueberry Powder 30:70 (a^2)	52.05			14.71		
Blueberry Powder 30:70 (a^2)	50.45			14.26		
Blueberry Powder 30:70 (b^1)	51.99	51.19	0.96	14.80	14.57	0.27
Blueberry Powder 30:70 (b^1)	51.45			14.64		
Blueberry Powder 30:70 (b^1)	50.12			14.26		
Blueberry Powder 30:70 (b^2)	49.95	44.52	4.75	14.37	12.81	1.37
Blueberry Powder 30:70 (b^2)	41.21			11.85		
Blueberry Powder 30:70 (b^2)	42.38			12.19		

Table A.2.8 Continued

Anthocyanin: Peonidin	ug/g Blueberry solids	Average	Standard Deviation	ug / g Blueberry powder	Average	Standard Deviation
Blueberry Powder 30:70 (a^1)	6.92	6.89	0.04	1.99	1.98	0.01
Blueberry Powder 30:70 (a^1)	6.84			1.97		
Blueberry Powder 30:70 (a^1)	6.91			1.99		
Blueberry Powder 30:70 (a^2)	9.69	11.17	1.30	2.74	3.16	0.37
Blueberry Powder 30:70 (a^2)	12.14			3.43		
Blueberry Powder 30:70 (a^2)	11.67			3.30		
Blueberry Powder 30:70 (b^1)	12.27	13.74	1.53	3.49	3.91	0.44
Blueberry Powder 30:70 (b^1)	13.61			3.87		
Blueberry Powder 30:70 (b^1)	15.33			4.36		
Blueberry Powder 30:70 (b^2)	10.13	10.39	0.58	2.91	2.99	0.17
Blueberry Powder 30:70 (b^2)	9.98			2.87		
Blueberry Powder 30:70 (b^2)	11.05			3.18		
Anthocyanin: Malvidin	**ug/g Blueberry solids**	**Average**	**Standard Deviation**	**ug / g Blueberry powder**	**Average**	**Standard Deviation**
Blueberry Powder 30:70 (a^1)	788.63	844.04	48.62	226.87	242.80	13.99
Blueberry Powder 30:70 (a^1)	879.61			253.04		
Blueberry Powder 30:70 (a^1)	863.88			248.51		
Blueberry Powder 30:70 (a^2)	920.87	986.63	78.71	260.29	278.88	22.25
Blueberry Powder 30:70 (a^2)	1073.84			303.53		
Blueberry Powder 30:70 (a^2)	965.18			272.82		
Blueberry Powder 30:70 (b^1)	1085.19	1077.81	16.79	308.85	306.75	4.78
Blueberry Powder 30:70 (b^1)	1089.64			310.12		
Blueberry Powder 30:70 (b^1)	1058.59			301.28		
Blueberry Powder 30:70 (b^2)	921.71	813.11	103.52	265.15	233.91	29.78
Blueberry Powder 30:70 (b^2)	802.05			230.73		
Blueberry Powder 30:70 (b^2)	715.56			205.84		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Appendix 3 Raw data for different spray drying outlet temperatures on the nutraceutical content of grape by-products

Table A.3.1 Raw data for Oxygen Radical Absorbance Capacity ($ORAC_{FL}$) analysis for grape extract used prior to spray drying, n=3

Sample	µmol TE / mL Extract	Average	Standard Deviation	umol TE / g fruit solids	Average	Standard Deviation
Grape Extract 30:70 (a^1)[a,b]	25.86			1015.29		
Grape Extract 30:70 (a^1)	25.93	25.72	0.31	1017.91	1009.64	12.13
Grape Extract 30:70 (a^1)	25.36			995.71		
Grape Extract 30:70 (a^2)	24.47			992.46		
Grape Extract 30:70 (a^2)	24.78	24.41	0.41	1004.78	989.81	16.46
Grape Extract 30:70 (a^2)	23.97			972.18		
Grape Extract 30:70 (b^1)	26.63			982.02		
Grape Extract 30:70 (b^1)	27.05	26.96	0.30	997.46	994.23	10.95
Grape Extract 30:70 (b^1)	27.21			1003.19		
Grape Extract 30:70 (b^2)	25.71			991.76		
Grape Extract 30:70 (b^2)	25.48	25.57	0.12	983.18	986.57	4.57
Grape Extract 30:70 (b^2)	25.52			984.76		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.3.2 Raw data for Oxygen Radical Absorbance Capacity ($ORAC_{FL}$) analysis for grape powder obtained after spray drying, n=3

Sample	µmol TE / g powder	Average	Standard Deviation	umol TE / g fruit solids	Average	Standard Deviation
Grape Powder 30:70 (a^1)[a,b]	272.28			952.46		
Grape Powder 30:70 (a^1)	269.51	271.59	1.83	942.78	950.05	6.41
Grape Powder 30:70 (a^1)	272.98			954.91		
Grape Powder 30:70 (a^2)	246.29			863.01		
Grape Powder 30:70 (a^2)	244.87	245.47	0.74	858.02	860.13	2.58
Grape Powder 30:70 (a^2)	245.26			859.37		
Grape Powder 30:70 (b^1)	246.31			847.29		
Grape Powder 30:70 (b^1)	247.08	246.69	0.38	849.93	848.60	1.32
Grape Powder 30:70 (b^1)	246.68			848.57		
Grape Powder 30:70 (b^2)	246.01			855.90		
Grape Powder 30:70 (b^2)	242.67	243.14	2.66	844.26	845.92	9.27
Grape Powder 30:70 (b^2)	240.75			837.59		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.3.3 Raw data for total phenolics analysis for grape extract prior to spray drying, measured at 750 nm, n=3

Sample	mg GAE / mL extract @ 750 nm	Average	Standard Deviation	mg GAE / g solids @ 750nm	Average	Standard Deviation
Grape Extract 30:70 (a^1)[a,b]	20.26			67.53		
Grape Extract 30:70 (a^1)	19.83	20.08	0.22	66.11	66.92	0.73
Grape Extract 30:70 (a^1)	20.14			67.12		
Grape Extract 30:70 (a^2)	20.50			68.34		
Grape Extract 30:70 (a^2)	20.11	20.27	0.21	67.02	67.56	0.69
Grape Extract 30:70 (a^2)	20.20			67.32		
Grape Extract 30:70 (b^1)	19.51			65.02		
Grape Extract 30:70 (b^1)	19.80	19.74	0.21	65.99	65.79	0.68
Grape Extract 30:70 (b^1)	19.90			66.34		
Grape Extract 30:70 (b^2)	19.51			65.02		
Grape Extract 30:70 (b^2)	20.10	19.78	0.30	67.00	65.93	1.00
Grape Extract 30:70 (b^2)	19.73			65.78		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.3.4 Raw data for total phenolics analysis for grape extract prior to spray drying, measured at 765 nm, n=3

Sample	mg GAE / mL extract @ 765 nm	Average	Standard Deviation	mg GAE / g solids @ 765nm	Average	Standard Deviation
Grape Extract 30:70 (a^1)[a,b]	20.26			67.54		
Grape Extract 30:70 (a^1)	19.76	20.04	0.26	65.87	66.79	0.85
Grape Extract 30:70 (a^1)	20.09			66.96		
Grape Extract 30:70 (a^2)	20.34			67.79		
Grape Extract 30:70 (a^2)	19.97	20.15	0.18	66.57	67.17	0.61
Grape Extract 30:70 (a^2)	20.14			67.14		
Grape Extract 30:70 (b^1)	19.32			64.41		
Grape Extract 30:70 (b^1)	19.60	19.56	0.22	65.34	65.21	0.74
Grape Extract 30:70 (b^1)	19.76			65.88		
Grape Extract 30:70 (b^2)	19.86			66.20		
Grape Extract 30:70 (b^2)	19.99	19.86	0.13	66.63	66.21	0.42
Grape Extract 30:70 (b^2)	19.74			65.80		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.3.5 Raw data for total phenolics analysis for grape powder after spray drying, measured at 750 nm, n=3

Sample	mg GAE / g powder @ 750nm	Average	Standard Deviation	mg GAE / g solids 750nm	Average	Standard Deviation
Grape Powder 30:70 (a^1)[a,b]	18.64			62.13		
Grape Powder 30:70 (a^1)	18.52	18.42	0.28	61.73	61.41	0.92
Grape Powder 30:70 (a^1)	18.11			60.37		
Grape Powder 30:70 (a^2)	18.57			61.89		
Grape Powder 30:70 (a^2)	19.01	18.71	0.26	63.37	62.37	0.87
Grape Powder 30:70 (a^2)	18.55			61.85		
Grape Powder 30:70 (b^1)	16.75			55.83		
Grape Powder 30:70 (b^1)	17.91	17.19	0.63	59.71	57.31	2.10
Grape Powder 30:70 (b^1)	16.92			56.40		
Grape Powder 30:70 (b^2)	16.27			54.24		
Grape Powder 30:70 (b^2)	15.72	15.96	0.29	52.40	53.19	0.95
Grape Powder 30:70 (b^2)	15.88			52.93		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.3.6 Raw data for total phenolics analysis for grape powder after spray drying, measured at 765 nm, n=3

Sample	mg GAE / g powder @ 765nm	Average	Standard Deviation	mg GAE / g solids 765nm	Average	Standard Deviation
Grape Powder 30:70 (a^1)[a,b]	18.39			61.30		
Grape Powder 30:70 (a^1)	18.22	18.20	0.20	60.74	60.67	0.67
Grape Powder 30:70 (a^1)	17.99			59.97		
Grape Powder 30:70 (a^2)	18.28			60.93		
Grape Powder 30:70 (a^2)	18.72	18.48	0.22	62.41	61.60	0.75
Grape Powder 30:70 (a^2)	18.44			61.47		
Grape Powder 30:70 (b^1)	16.59			55.31		
Grape Powder 30:70 (b^1)	17.11	16.89	0.27	57.05	56.30	0.89
Grape Powder 30:70 (b^1)	16.96			56.53		
Grape Powder 30:70 (b^2)	16.18			53.94		
Grape Powder 30:70 (b^2)	15.97	16.04	0.12	53.22	53.47	0.40
Grape Powder 30:70 (b^2)	15.98			53.27		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.3.7 Raw data for HPLC analysis for individual anthocyanins in grape extract prior to spray drying, n=3

Anthocyanin: Delphinidin	ug/g grape solids	Average	Standard Deviation	ug/ ml grape extract	Average	Standard Deviation
Grape Extract 30:70 (a^1)[a,b]	304.75			91.43		
Grape Extract 30:70 (a^1)	318.72	313.02	7.33	95.62	93.91	2.20
Grape Extract 30:70 (a^1)	315.59			94.68		
Grape Extract 30:70 (a^2)	341.07			102.32		
Grape Extract 30:70 (a^2)	314.38	331.38	14.77	94.31	99.41	4.43
Grape Extract 30:70 (a^2)	338.69			101.61		
Grape Extract 30:70 (b^1)	309.69			92.91		
Grape Extract 30:70 (b^1)	320.19	314.08	5.46	96.06	94.22	1.64
Grape Extract 30:70 (b^1)	312.36			93.71		
Grape Extract 30:70 (b^2)	306.21			91.86		
Grape Extract 30:70 (b^2)	306.66	313.30	11.90	92.00	93.99	3.57
Grape Extract 30:70 (b^2)	327.04			98.11		
Anthocyanin: Cyanidin	**ug/g grape solids**	**Average**	**Standard Deviation**	**ug/ ml grape extract**	**Average**	**Standard Deviation**
Grape Extract 30:70 (a^1)	293.24			87.97		
Grape Extract 30:70 (a^1)	309.69	290.04	21.43	92.91	87.01	6.43
Grape Extract 30:70 (a^1)	267.18			80.16		
Grape Extract 30:70 (a^2)	294.74			88.42		
Grape Extract 30:70 (a^2)	295.55	293.26	3.29	88.66	87.98	0.99
Grape Extract 30:70 (a^2)	289.49			86.85		
Grape Extract 30:70 (b^1)	276.67			83.00		
Grape Extract 30:70 (b^1)	282.79	279.55	3.08	84.84	83.87	0.92
Grape Extract 30:70 (b^1)	279.19			83.76		
Grape Extract 30:70 (b^2)	280.07			84.02		
Grape Extract 30:70 (b^2)	291.68	289.63	8.71	87.50	86.89	2.61
Grape Extract 30:70 (b^2)	297.13			89.14		
Anthocyanin: Petunidin	**ug/g grape solids**	**Average**	**Standard Deviation**	**ug/ ml grape extract**	**Average**	**Standard Deviation**
Grape Extract 30:70 (a^1)	39.10			11.73		
Grape Extract 30:70 (a^1)	41.17	39.67	1.31	12.35	11.90	0.39
Grape Extract 30:70 (a^1)	38.75			11.63		
Grape Extract 30:70 (a^2)	40.97			12.29		
Grape Extract 30:70 (a^2)	39.81	41.70	2.35	11.94	12.51	0.70
Grape Extract 30:70 (a^2)	44.33			13.30		
Grape Extract 30:70 (b^1)	38.66			11.60		
Grape Extract 30:70 (b^1)	38.76	38.35	0.63	11.63	11.50	0.19
Grape Extract 30:70 (b^1)	37.62			11.29		
Grape Extract 30:70 (b^2)	38.62			11.58		
Grape Extract 30:70 (b^2)	39.28	40.44	2.60	11.79	12.13	0.78
Grape Extract 30:70 (b^2)	43.42			13.03		
Anthocyanin: Peonidin	**ug/g grape solids**	**Average**	**Standard Deviation**	**ug/ ml grape extract**	**Average**	**Standard Deviation**
Grape Extract 30:70 (a^1)	40.67			12.20		
Grape Extract 30:70 (a^1)	41.78	39.21	3.54	12.53	11.76	1.06
Grape Extract 30:70 (a^1)	35.17			10.55		
Grape Extract 30:70 (a^2)	35.57			10.67		
Grape Extract 30:70 (a^2)	39.97	39.87	4.25	11.99	11.96	1.28
Grape Extract 30:70 (a^2)	44.07			13.22		
Grape Extract 30:70 (b^1)	36.87			11.06		
Grape Extract 30:70 (b^1)	34.09	34.55	2.13	10.23	10.37	0.64
Grape Extract 30:70 (b^1)	32.69			9.81		
Grape Extract 30:70 (b^2)	36.32			10.89		
Grape Extract 30:70 (b^2)	37.75	38.67	2.92	11.33	11.60	0.88
Grape Extract 30:70 (b^2)	41.94			12.58		

Table A.3.7 Continued

Anthocyanin: Malvidin	ug/g grape solids	Average	Standard Deviation	ug/ ml grape extract	Average	Standard Deviation
Grape Extract 30:70 (a^1)	387.45	378.07	9.48	116.24	113.42	2.84
Grape Extract 30:70 (a^1)	378.25			113.48		
Grape Extract 30:70 (a^1)	368.50			110.55		
Grape Extract 30:70 (a^2)	374.51	380.92	7.22	112.35	114.28	2.17
Grape Extract 30:70 (a^2)	388.75			116.62		
Grape Extract 30:70 (a^2)	379.51			113.85		
Grape Extract 30:70 (b^1)	375.77	369.06	5.89	112.73	110.72	1.77
Grape Extract 30:70 (b^1)	364.76			109.43		
Grape Extract 30:70 (b^1)	366.66			110.00		
Grape Extract 30:70 (b^2)	365.34	364.18	17.29	109.60	109.26	5.19
Grape Extract 30:70 (b^2)	346.35			103.90		
Grape Extract 30:70 (b^2)	380.87			114.26		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Table A.3.8 Raw data for HPLC analysis for individual anthocyanins in grape powder after spray drying, n=3

Anthocyanin: Delphinidin	ug/g grape solids	Average	Standard Deviation	ug / g grape powder	Average	Standard Deviation
Grape Powder 30:70 (a^1)[a,b]	149.97	147.73	2.64	42.83	42.19	0.75
Grape Powder 30:70 (a^1)	148.39			42.38		
Grape Powder 30:70 (a^1)	144.82			41.36		
Grape Powder 30:70 (a^2)	154.59	155.45	2.24	44.12	44.36	0.64
Grape Powder 30:70 (a^2)	157.99			45.09		
Grape Powder 30:70 (a^2)	153.77			43.89		
Grape Powder 30:70 (b^1)	147.04	143.87	3.10	42.30	41.39	0.89
Grape Powder 30:70 (b^1)	143.71			41.35		
Grape Powder 30:70 (b^1)	140.85			40.52		
Grape Powder 30:70 (b^2)	143.50	144.37	3.67	41.25	41.50	1.06
Grape Powder 30:70 (b^2)	148.40			42.65		
Grape Powder 30:70 (b^2)	141.21			40.59		
Anthocyanin: Cyanidin	**ug/g grape solids**	**Average**	**Standard Deviation**	**ug / g grape powder**	**Average**	**Standard Deviation**
Grape Powder 30:70 (a^1)	145.13	140.94	3.68	41.44	40.25	1.05
Grape Powder 30:70 (a^1)	139.49			39.83		
Grape Powder 30:70 (a^1)	138.20			39.47		
Grape Powder 30:70 (a^2)	135.97	142.35	5.87	38.80	40.62	1.67
Grape Powder 30:70 (a^2)	147.51			42.10		
Grape Powder 30:70 (a^2)	143.57			40.97		
Anthocyanin: Cyanidin	**ug/g grape solids**	**Average**	**Standard Deviation**	**ug / g grape powder**	**Average**	**Standard Deviation**
Grape Powder 30:70 (b^1)	122.10	121.37	2.26	35.13	34.92	0.65
Grape Powder 30:70 (b^1)	123.17			35.44		
Grape Powder 30:70 (b^1)	118.83			34.19		
Grape Powder 30:70 (b^2)	125.55	128.28	3.55	36.09	36.87	1.02
Grape Powder 30:70 (b^2)	132.29			38.02		
Grape Powder 30:70 (b^2)	127.01			36.51		
Anthocyanin: Petunidin	**ug/g grape solids**	**Average**	**Standard Deviation**	**ug / g BB grape powder**	**Average**	**Standard Deviation**
Grape Powder 30:70 (a^1)	24.50	26.38	1.75	7.00	7.53	0.50
Grape Powder 30:70 (a^1)	27.94			7.98		
Grape Powder 30:70 (a^1)	26.71			7.63		

Table 3.8 Continued

Anthocyanin: Petunidin	ug/g grape solids	Average	Standard Deviation	ug / g BB grape powder	Average	Standard Deviation
Grape Powder 30:70 (a^2)	27.07			7.73		
Grape Powder 30:70 (a^2)	27.60	27.05	0.56	7.88	7.72	0.16
Grape Powder 30:70 (a^2)	26.48			7.56		
Grape Powder 30:70 (b^1)	23.18			6.67		
Grape Powder 30:70 (b^1)	23.38	23.04	0.43	6.73	6.63	0.12
Grape Powder 30:70 (b^1)	22.55			6.49		
Grape Powder 30:70 (b^2)	25.74			7.40		
Grape Powder 30:70 (b^2)	26.10	25.72	0.39	7.50	7.39	0.11
Grape Powder 30:70 (b^2)	25.32			7.28		
Anthocyanin: Peonidin	**ug/g grape solids**	**Average**	**Standard Deviation**	**ug / g grape powder**	**Average**	**Standard Deviation**
Grape Powder 30:70 (a^1)	27.39			7.82		
Grape Powder 30:70 (a^1)	29.15	28.26	0.88	8.32	8.07	0.25
Grape Powder 30:70 (a^1)	28.23			8.06		
Grape Powder 30:70 (a^2)	30.64			8.74		
Grape Powder 30:70 (a^2)	29.26	28.95	1.86	8.35	8.26	0.53
Grape Powder 30:70 (a^2)	26.96			7.69		
Grape Powder 30:70 (b^1)	25.71			7.40		
Grape Powder 30:70 (b^1)	24.81	25.19	0.46	7.14	7.25	0.13
Grape Powder 30:70 (b^1)	25.06			7.21		
Grape Powder 30:70 (b^2)	28.04			8.06		
Grape Powder 30:70 (b^2)	28.17	27.95	0.28	8.10	8.03	0.08
Grape Powder 30:70 (b^2)	27.63			7.94		
Anthocyanin: Malvidin	**ug/g grape solids**	**Average**	**Standard Deviation**	**ug / g grape powder**	**Average**	**Standard Deviation**
Grape Powder 30:70 (a^1)	264.62			75.57		
Grape Powder 30:70 (a^1)	266.68	259.77	10.24	76.16	74.18	2.92
Grape Powder 30:70 (a^1)	248.01			70.83		
Grape Powder 30:70 (a^2)	259.56			74.08		
Grape Powder 30:70 (a^2)	263.09	264.06	5.05	75.08	75.36	1.44
Grape Powder 30:70 (a^2)	269.52			76.92		
Grape Powder 30:70 (b^1)	230.82			66.41		
Grape Powder 30:70 (b^1)	233.91	228.12	7.51	67.29	65.63	2.16
Grape Powder 30:70 (b^1)	219.63			63.19		
Grape Powder 30:70 (b^2)	237.22			68.19		
Grape Powder 30:70 (b^2)	236.62	233.43	6.06	68.01	67.09	1.74
Grape Powder 30:70 (b^2)	226.43			65.08		

[a] Same letters denote runs of the same conditions: a = outlet temperature =80°C, b = outlet temperature = 90°C

[b] Superscript numbers denote the number of replicates per run

Appendix 4 Raw Data for Commercial Blueberry Products

Table A.4.1 Raw data for Oxygen Radical Absorbance Capacity ($ORAC_{FL}$) analysis for different commercial blueberry powder samples, n=3

Sample	µmol TE / g powder	Average
Van Drunen Spray Farms dried Blueberry Powder	67.16	
Van Drunen Spray Farms dried Blueberry Powder	61.05	64.69
Van Drunen Spray Farms dried Blueberry Powder	65.87	
Van Drunen Farms Drum Dried Blueberry Powder	142.41	
Van Drunen Farms Drum Dried Blueberry Powder	150.42	146.78
Van Drunen Farms Drum Dried Blueberry Powder	147.49	
Van Drunen Farms Freeze Dried Blueberry Powder	341.84	
Van Drunen Farms Freeze Dried Blueberry Powder	368.88	359.53
Van Drunen Farms Freeze Dried Blueberry Powder	367.88	
FruitSmart Blueberry Fiber	133.86	
FruitSmart Blueberry Fiber	137.35	136.46
FruitSmart Blueberry Fiber	138.18	
FruitSmart Blueberry Puree	118.29	
FruitSmart Blueberry Puree	122.57	119.72
FruitSmart Blueberry Puree	118.28	

Table A.4.2 Raw data for total phenolics analysis for different commercial blueberry powder samples, measured at 750 nm, n=3

Sample	mg GAE / g fruit powder @ 750 nm	Average	Standard Deviation
Van Drunen Farms Freeze Dried Blueberry Powder	34.28		
Van Drunen Farms Freeze Dried Blueberry Powder	33.65	33.35	1.12
Van Drunen Farms Freeze Dried Blueberry Powder	32.11		
FruitSmart Blueberry Puree	9.16		
FruitSmart Blueberry Puree	9.09	9.07	0.10
FruitSmart Blueberry Puree	8.96		
Van Drunen Farms Drum Dried Blueberry Powder	7.32		
Van Drunen Farms Drum Dried Blueberry Powder	7.18	7.29	0.10
Van Drunen Farms Drum Dried Blueberry Powder	7.37		
FruitSmart Blueberry Fiber	7.84		
FruitSmart Blueberry Fiber	5.93	6.63	1.05
FruitSmart Blueberry Fiber	6.13		
Van Drunen Spray Farms dried Blueberry Powder	3.26		
Van Drunen Spray Farms dried Blueberry Powder	3.51	3.46	0.18
Van Drunen Spray Farms dried Blueberry Powder	3.60		

Table A.4.3 Raw data for total phenolics analysis for different commercial blueberry powder samples, measured at 765 nm, n=3

Sample	mg GAE / g fruit powder @ 765 nm	Average	Standard Deviation
Van Drunen Farms Freeze Dried Blueberry Powder	34.28	33.35	1.12
Van Drunen Farms Freeze Dried Blueberry Powder	33.65		
Van Drunen Farms Freeze Dried Blueberry Powder	32.11		
FruitSmart Blueberry Puree	9.16	9.07	0.10
FruitSmart Blueberry Puree	9.09		
FruitSmart Blueberry Puree	8.96		
Van Drunen Farms Drum Dried Blueberry Powder	7.32	7.29	0.10
Van Drunen Farms Drum Dried Blueberry Powder	7.18		
Van Drunen Farms Drum Dried Blueberry Powder	7.37		
FruitSmart Blueberry Fiber	7.84	6.63	1.05
FruitSmart Blueberry Fiber	5.93		
FruitSmart Blueberry Fiber	6.13		
Van Drunen Spray Farms dried Blueberry Powder	3.26	3.46	0.18
Van Drunen Spray Farms dried Blueberry Powder	3.51		
Van Drunen Spray Farms dried Blueberry Powder	3.60		

Table A.4.4 Raw data for HPLC analysis for individual anthocyanins in different commercial powder samples, n=3

Anthocyanin: Delphinidin	Ug / g fruit powder	Average	Standard Deviation
FruitSmart Blueberry Fiber	94.74	94.43	2.01
	92.29		
	96.27		
FruitSmart Blueberry Puree	122.01	122.80	1.61
	124.65		
	121.74		
Van Drunen Farms Drum Dried Blueberry Powder	79.04	79.54	0.57
	80.17		
	79.42		
Van Drunen Farms Freeze Dried Blueberry Powder	363.83	345.01	20.79
	348.51		
	322.69		
Van Drunen Farms Spray Dried Blueberry Powder	36.94	38.20	1.13
	38.53		
	39.13		
Anthocyanin: Cyanidin	**Ug / g fruit powder**	**Average**	**Standard Deviation**
FruitSmart Blueberry Fiber	57.61	54.19	6.44
	46.75		
	58.20		
FruitSmart Blueberry Puree	51.66	50.09	1.73
	48.24		
	50.37		
Van Drunen Farms Drum Dried Blueberry Powder	64.83	71.38	5.82
	75.95		
	73.35		
Van Drunen Farms Freeze Dried Blueberry Powder	250.70	237.77	20.22
	248.14		
	214.48		
Van Drunen Farms Spray Dried Blueberry Powder	4.23	4.63	0.34
	4.79		
	4.86		

Table A.4.4 Continued

Anthocyanin: Petunidin	ug / g fruit powder	Average	Standard Deviation
FruitSmart Blueberry Fiber	18.49 16.57 18.54	17.87	1.12
FruitSmart Blueberry Puree	40.07 37.70 40.13	39.30	1.39
Van Drunen Farms Drum Dried Blueberry Powder	21.85 23.51 23.78	23.05	1.05
Van Drunen Farms Freeze Dried Blueberry Powder	158.95 158.21 133.87	150.34	14.27
Van Drunen Farms Spray Dried Blueberry Powder	12.88 14.28 14.76	13.97	0.98
Anthocyanin: Peonidin	**ug / g fruit powder**	**Average**	**Standard Deviation**
FruitSmart Blueberry Fiber	5.70 5.35 7.61	6.22	1.22
FruitSmart Blueberry Puree	16.32 17.34 16.34	16.67	0.58
Van Drunen Farms Drum Dried Blueberry Powder	29.56 36.76 34.32	33.55	3.66
Van Drunen Farms Freeze Dried Blueberry Powder	121.97 119.22 100.08	113.76	11.92
Van Drunen Farms Spray Dried Blueberry Powder	3.18 3.83 3.81	3.61	0.37
Anthocyanin: Malvidin	**ug / g fruit powder**	**Average**	**Standard Deviation**
FruitSmart Blueberry Fiber	452.96 411.67 415.03	426.55	22.93
FruitSmart Blueberry Puree	844.98 816.32 849.44	836.92	17.97
Van Drunen Farms Drum Dried Blueberry Powder	690.93 770.19 695.00	718.71	44.63
Van Drunen Farms Freeze Dried Blueberry Powder	2323.44 2399.71 2271.02	2331.39	64.71
Van Drunen Farms Spray Dried Blueberry Powder	345.22 343.87 335.52	341.53	5.25

REFERENCES

Adams, J. (1973). "Thermal Degradation of Anthocyanins with Particular Reference to the 3-Glycosides of Cyanidin." Journal of Sci Food Agric **24**: 747-762.

Aguilar, C. A. and G. R. Ziegler (1994). "Physical and Microscopic Characterization of Dry Whole Milk with Altered Lactose Content. 1. Effect of Lactose Concentration " Journal of Dairy Science **77**: 1198-1204.

Ahmed, J., U. Shivhare and G. Raghavan (2004). "Thermal Degradation Kinetics of Anthocyanin and Visual Colour of Plum Puree." European Food Research and Technology **218**: 525-528.

Andrimbeloson, E., C. Magnier, G. Haan-Archipoff, A. Lobstein, R. Anton, A. Beretzz, J. Stoclet and R. Andriantsitohaina (1998). "Natural Dietary Polyphenolic Compounds Cause Endothelium-Dependent Vasorelazation in Rat Thoracic Aorta." Journal of Nutrition **128**(12): 2324-2333.

Brouillard, R. (1982). Chemical Structure of Anthocyanins. Anthocyanins as Food Colors. Markakis, P. New York, Academic Press Inc. **:** 1-38.

Cai, Y. Z. and H. Corke (2000). "Production and Properties of Spray-Dried *Amaranthus* Betacyanin Pigments." Journal of Food Science **65**(6): 1248-1252.

Cao, G. H. and R. L. Prior (1999). "Measurement of Oxygen Radical Absorbance Capacity in Biological Samples. Oxidants and Antioxidants." Methods Enzymol. **299**: 50-62.

Clydesdale, F. M., J. H. Main, F. J. Francis and R. A. D. Jr (1978). "Concord Grape Pigments as Colorants for Beverages and Gelatin Desserts." Journal of Food Science **43**: 1687-1692.

Daravingas, G. and R. Cain (1968). "Thermal Degradation of Black Raspberry Anthocyanin Pigments in Model Systems." Journal of Food Science **33**: 138-142.

Eck, P. (1988). Blueberry Science. Brunswick, N.J., Rutgers Press.

Elversson, J., A. Millqvist-Fureby, G. Alderborn and U. Elofsson (2003). "Droplet and Particle Size Relationship and Shell Thickness of Inhalable Lactose Particles During Spray Drying." Journal of Pharmaceutical Sciences **92**(4): 900-910.

Filkova, I. and A. S. Mujumdar (1995). Industrial Spray Drying Systems. Handbook of Industrial Drying. Mujumdar, A. S. New Yotk, Marcel Dekker, Inc. **1:** 263-308.

Francis, F. (1989). "Food Colorants: Anthocyanins." Critical Reviews in Food Science and Nutrition **28**: 273-314.

Halliwell, B. (1994). "Free Radicals and Antioxidants: A Personal View." Nutrition reviews **52**: 253-265.

Hovmand, S. (1995). Fluidized Bed Drying. Handbook of Industrial Drying. Mujumdar, A. S. New Yotk, Marcel Dekker, Inc. **1:** 195-248.

Howell, A., A. D. Marderosian and L. Foo (1998). "Inhibition of the Adherence of P-Fombriated *Escherichia Coli* to Uroepithelia-Cell Surgaces by Proanthocyanidin Extracts from Cranberries." New England Journal of Medicine **339**(15): 1085-1086.

Huang, D., B. Ou and R. L. Prior (2005). "The Chemistry Behind Antioxidant Capacity Assays." Journal of Agricultural and Food Chemistry **53**: 1841-1856.

Imre, L. (1995). Solar Drying. Handbook of Industrial Drying. Mujumdar, A. S. New Yotk, Marcel Dekker, Inc. **1:** 373-451.

Jackman, R., R. Yada, M. Tung and R. Speers (1987). "Anthocyanins and Food Colorants - a Review." Journal of Food Biochemistry **11**: 201-247.

Jaya, S. and H. Das (2002). Sticky Issues on Spray Drying of Fruit Juices. ASAE/CSAE North-Central Intersectional Meeting, Saskatoon, Saskatchewan, Canada.

(2005). "Accelerated Storage, Shelf Life and Color of Mango Powder." Journal of Food Processing and Preservation **29**(1): 45-62.

Jayaraman, K. S. and D. K. D. Gupta (1995). Drying of Fruits and Vegetables. Handbook of Industrial Drying. Mujumdar, A. S. New Yotk, Marcel Dekker, Inc. **1:** 643-690.

Kähkönen, M. P., A. I. Hopia and M. Heinonen (2001). "Berry Phenolics and Their Antioxidant Activity " Journal of Agricultural and Food Chemistry **49**(8): 4076-4082.

Kalt, W., J. E. McDonald, R. D. Ricker and X. Lu (1999). "Anthocyanin Content and Profile within and among Blueberry Species." Canadian Journal of Plant Science **79**(4): 617-624.

Kamei, H., T. Kojima, M. Hasegawa, T. Koide, T. Umeda, T. Yukawa and T. Terabe (1995). "Suppression of Tumor Cell Growth by Anthocyanins." Cancer Invest **13**: 590-594.

Kong, J.-M., L.-S. Chia, N.-K. Goh, T.-F. Chia and R. Brouillard (2003). "Analysis and Biological Activities of Anthocyanins " Phytochemistry **64**(5): 923-933.

Laplaud, P., A. Lelubre and M. Chapman (1997). "Antioxidant Action of Vaccinium Myrtillus Extract on Human Low Density Lipoproteins in Vitro: Initial Observations." Fundamental Clinical Pharmacology **11**(1): 35-40.

Lee, J., R. W. Durst and R. E. Wrolstad (2002). "Impact of Juice Processing on Blueberry Anthocyanins and Polyphenolics: Comparison of Two Pretreatments." Journal of Food Science **67**(5): 1660-1667.

Liapis, A. I. and R. Bruttini (1995). Freeze Drying. Handbook of Industrial Drying. Mujumdar, A. S. New Yotk, Marcel Dekker, Inc. **1:** 309-344.

Main, J. H., F. M. Clydesdale and F. J. Francis (1978). "Spray Drying Anthocyanin Concentrates for Use as Food Colorants." Journal of Food Science **43**: 1693-1695.

Markakis, P., G. Livingston and C. Fellers (1957). "Quantitive Aspects of Strawberry-Pigment Degradation." Food Research **22**: 117-130.

Markowski, A. S. and A. S. Mujumdar (1995). Safety Aspects of Industrial Dryers. Handbook of Industrial Drying. Mujumdar, A. S. New Yotk, Marcel Dekker, Inc. **2:** 1277-1312.

Mazza, G. (1995). "Anthocyanins in Grape and Grape Products." Critical Reviews in Food Science and Nutrition **35**(4): 341-371.

Mazza, G. and E. Miniati (1993). Anthocyanins in Fruits, Vegetables, and Grains. Press, C., Boca Ratan, FL: 85-130.

McGhie, T. K., G. D. Ainge, L. E. Barnett, J. M. Cooney and D. J. Jensen (2003). "Anthocyanin Glycosides from Berry Fruit Are Absorbed and Excreted Unmetabolized by Both Humans and Rats." Journal of Agricultural and Food Chemistry **51**(16): 4539-4548.

Meiers, S., M. Kemeny, U. Weyand, R. Gastpar, E. v. Angerer and D. Marko (2001). "The Anthocyanindins Cyanidin and Delphinidin Are Potent Inhibitors of the Epidermal Growth-Factor Receptor." Journal of Agricultural and Food Chemistry **49**: 958-962.

Monagas, M., B. Hernández-Ledesma, C. Gómez-Cordovés and B. Bartolomé (2006). "Commercial Dietary Ingredients from Vitis Vinifera L. Leaves and Grape Skins: Antioxidant and Chemical Characterization " Journal of Agricultural and Food Chemistry **54**: 319-327.

Moore, J. G. (1995). Drum Dryers. Handbook of Industrial Drying. Mujumdar, A. S. New Yotk, Marcel Dekker, Inc. **1:** 249-262.

Moore, J. N. (1994). "The Blueberry Industry of North America." Acta Horticulturae **346**: 15-26.

Nebesky, E., W. J. Esselen, J. McConnell and C. Fellers (1949). "Stability of Color in Fruit Juices." Food Research **14**: 261-274.

Ou, B., M. Hampsch-Woodill and R. L. Prior (2001). "Development and Validation of an Improved Oxygen Radical Absorbance Capacity Assay Using Fluorescein as the Fluorescent Probe." Journal of Agricultural and Food Chemistry **49**: 4619-4626.

Palamidis, N. and P. Markakis (1978). "Stability of Grape Anthocyanin in Carbonated Beverages." Semana Vitivinicola **33**: 2637-2639.

Prior, R. L., G. Cao, A. Martin, E. Sofic, J. McEwen, C. O'Brien, N. Lischner, M. Ehlenfeldt, W. Kalt, G. Krewer and C. M. Mainland (1998). "Antioxidant Capacity as Influenced by Total Phenolic and Anthocyanin Content, Maturity, and Variety of *Vaccinium* Species." Journal of Agricultural and Food Chemistry **46**(7): 2686-2693.

Prior, R. L., X. Wu and K. Schaich (2005). "Standardized Methods for the Determination of Antioxidant Capacity and Phenolics in Foods and Dietary Supplements." Journal of Agricultural and Food Chemistry **53**(10): 4290-4302.

Reineccius, G. A. (2004). "The Spray Drying of Food Flavors." Drying Technology **22**(6): 1289-1324.

Rossetto, M., P. Vanzani, L. Zannaro, F. Mattivi, U. Vrhovsek, M. Scarpa and A. Rigo (2004). "Stable Free Radicals and Peroxyl Radical Trapping Capacity in Red Wines." Journal of Agricultural and Food Chemistry **52**: 6151-6155.

Sastry, L. and R. Tischer (1952). "Behavior of the Anthocyanin Pigments in Concord Grapes During Heat Processing and Storage." Food Technology: 82-86.

Satue-Garcia, M., M. Heinonen and E. Frankel (1997). "Anthocyanins as Antioxidants on Human Low-Density Lipoprotin and Lecithin-Liposome Systems." Journal of Agricultural and Food Chemistry **45**(9): 3362-3367.

Singleton, V. and J. Rossi (1965). "Colormetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents." American Journal of Enology and Viticulture **16**: 144-158.

Threlfall, R. T., J. R. Morris, L. R. Howard, C. R. Brownmiller and T. L. Walker (2005). "Pressing Effects on Yield, Quality, and Nutraceutical Content of Juice, Seeds, and Skins from Black Beauty and Sunbelt Grapes." Journal of Food Science **70**(3): S167-S171.

Timberlake, C. F. and P. Bridle (1982). Anthocyanins as Food Colors. Distribution of Anthocyanins in Food Plants. Markakis. New York, Academic Press: 126-157.

Wang, H., G. Cao and R. L. Prior (1997). "Oxygen Radical Absorbing Capacity of Anthocyanins." Journal of Agricultural and Food Chemistry **45**(2): 304-309.

Wrolstad, R. E. (2000). Colorants. Food Chemistry: Principles and Applications. Christen, G. L. and Smith, J. S. West Sacamento, Science Technology System: 215-239.

Yu, B. P. (1994). "Celluar Defenses against Damage from Reactive Oxygen Species." Physiological Reviews **76**: 139-162.

Zhang, Z., X. Kou, K. Fugal and J. McLaughlin (2004). "Comparison of Hplc Methods for Determination of Anthocyanins and Anthocyanidins in Bilberry Extracts " Journal of Agricultural and Food Chemistry **52**(4): 688-691.