EFFECTS OF FREEZE DRYING, REFRACTANCE WINDOW DRYING AND HOT-AIR DRYING ON THE QUALITY PARAMETERS OF AÇAI

BY

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THESIS

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Abstract

Açaí is a dark purple berry native to the Amazonian region in Brazil and widely consumed in South America. The fruit is a major component of the diet and significant to the local economy. Recently, more attention has been paid to açaí due to its high antioxidant properties. However, açaí is a highly perishable fruit and should be processed quickly after harvesting in order to preserve its nutritional and sensory properties as well as its bioactive compounds.

Drying is one of the processing techniques used to preserve the fruit. Dehydrated products present high stability and are easy to transport and store. Dried açaí is, currently, mainly produced by freeze drying. Even though this method results in high quality products, the high cost associated with capital investment and operation is its major disadvantage. Thus, the search for alternative and more economic drying methods is of interest. Refractance Window drying is a novel and promising drying technique, and it has been demonstrated to retain food quality. Hot-air convective drying is an ancient and inexpensive process. It is the most widely used drying method in the food industry, although care should be taken to ensure product quality. The objective of this research was to evaluate the impact of three drying methods - freeze drying, refractance window drying and hot-air drying - on the quality parameters of açaí after drying and over a 3 month storage period at 25°C. To examine the potential quality changes, the following analyses were performed: moisture content, water activity, moisture working isotherm, glass transition temperature, color, antioxidant capacity, anthocyanin quantification, and flavor analysis.

The moisture contents of the dried samples were all below the monolayer values. The water activity values of the açaí immediately after drying and during storage were also low, indicating relatively good product stability. The Brunauer-Emmett-Teller (BET) and Guggenheim-Anderson-de Boer (GAB) models showed a good fit to the isotherm data. Differential Scanning Calorimetry (DSC) thermograms suggested that there exists a subtle glass transition between 50-60°C. DSC analysis also revealed that the lipids present in açaí are liquid at room temperature. Drying affected both the color and flavor of açaí juice. Dried samples were featured by a lighter color and lower hue angle and chroma when compared to the juice. Storage was marked by a decrease in lightness, most likely because of the formation of brown pigments by Maillard reaction and polymerization of oxidized phenolic compounds. For flavor analysis, the compounds \((E,Z)\) 2,6-nonadienal, \(\alpha\)-ionone and 2-phenylethanol/\(\beta\)-ionone were the most important odorants identified in açaí samples. The dried açaí had a higher concentration of
Strecker aldehydes and compounds derived from lipid oxidation, which indicates the occurrence of those reactions during drying. During storage, lipid oxidation was the most important reaction that took place in the dried samples. Freeze drying proved to be superior to the other drying methods, as shown by a best retention of the anthocyanins and antioxidant capacity (ORAC) of the fruit. Refractance Window dried açaí also exhibited a good retention of anthocyanin content similar to that of freeze-dried samples and an ORAC value higher than that of the hot-air dried powders. Anthocyanin content and antioxidant capacity, within each treatment, did not change over the 3 months of study.

**Keywords:** açaí, refractance window drying, freeze drying, ORAC, anthocyanins, glass transition
With love to my parents, Nizar and Marina, and my brother Felipe for all their love and for being my motivation to succeed.

And to Marcelo for his unconditional love and support.

Com amor aos meus pais, Nizar e Marina, e ao meu irmão Felipe por todo o seu amor e por serem minha motivação para triunfar.

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Chapter 1: 
Introduction

It has been suggested that consumption of fruits and vegetables contributes to the prevention of many chronic diseases, such as cancer and coronary heart disease. The health benefits associated with consumption of those foods are mainly attributed to their phytochemicals, especially polyphenolic compounds (Dauchet et al. 2006; Franceschi et al. 1998; Joshipura et al. 2001). Trends towards healthier lifestyles have resulted in an increase in consumer’s demand for health-promoting foods and food products, such as fresh fruits and fruit juices. A report from the United States Department of Agriculture (USDA) showed that the consumption of fruits and vegetables in U.S. increased 25% from 1977-79 to 1997-99 (Pollack 2001). However, most fruits with potential health benefits, such as wild blueberries, are very perishable. To find appropriate food preservation methods that retain the bioactive compounds with relatively low cost is challenging.

Açaí, a fruit of Euterpe oleracea Mart palm tree, has recently received considerable attention, mainly due to its high antioxidant capacity and potential health benefits. The fruit, a dark purple berry native to the Amazonian region, has a high nutritional value and is rich in polyphenolic compounds (Lichtenthaler et al. 2005; Menezes et al. 2008b; Schauss et al. 2006). However, açaí is highly perishable, being degraded due to enzyme activity, high microbial load and elevated temperatures and relative humidity in the harvesting/production area (Menezes et al. 2008a). Therefore, the fruit must be pulped within 24 h after harvest. Fresh pulp or juice, which has a shelf life of 12 h, should be either frozen or dried in order to increase its shelf life and preserve its bioactive compounds (Tonon et al. 2009).

Drying is one of the most efficient ways to preserve foods. It reduces product’s water activity, which inhibits microbial growth and decreases degradative reactions, resulting in higher stability. Besides, drying results in substantial volume reduction, which facilitates transport and storage (Marques et al. 2009; Maskan 2001). Dehydrated açaí is currently produced primarily by freeze drying. Freeze dried products are known to have high quality, since the technique preserves bioactive compounds, color, texture and flavor. However, due to the use of vacuum and very low temperatures, freeze drying is the most expensive drying technology (Hammami et al. 1997; Khaliloufi et al. 2003). Therefore, the search for less expensive drying methods, which are able to result in high quality products, is of interest.

Refractance Window drying is a relatively new drying method introduced by MCD Technologies (Tacoma, Washington, USA). The technique involves applying the product, as a
thin layer, to the top surface of a transparent plastic conveyor belt. Under the plastic sheet, hot water circulates and it is used to carry thermal energy to the product. The method uses moderate temperatures and short drying times, which has been reported to result in high quality products. The technique is especially suitable for liquid and semi-liquid products, such as puree and juices with particulates (Nindo et al. 2007).

Hot-air drying is the most extensively used drying method. The process consists of blowing a stream of hot air on top of the product, which results in moisture evaporation. Although been very common, the method involves high temperatures and long processing times, which are known to damage nutritional and sensory properties of foods (Ratti 2001). For comparison purposes hot-air drying is frequently used in drying studies.

The objective of this project was to examine how freeze drying, refractance window drying and hot-air drying affect the quality of açai juice. It was also of interest to evaluate the effects of storage on the quality of the powders and, therefore, dried açai was stored for 3 months at room temperature, with samples being taken monthly for analysis. Antioxidant capacity and anthocyanin content were evaluated in order to further understand potential health benefits of the product. Moisture content, water activity, glass transition temperature and moisture sorption isotherms were analyzed with the aim of understanding and predicting product stability. Color and flavor analyses were performed as possible indicators of consumer's acceptability.

The hypothesis of this project was that the quality of the refractance window dried açai juice would be comparable to that of the freeze-dried product.

References


Chapter 2: Literature Review

Açai

General Aspects

_Euterpe oleracea_ Martius is a palm tree native to the Amazonian region, where it can be abundantly found in the Amazon River estuary (Muñiz-Miret et al. 1996). In Brazil, the state of Pará is the main producer of this palm, but it can be also found in other Brazilian states, including Amapá, Maranhão, Mato Grosso, and Tocantins, as well as in other Central and South American countries, such as Venezuela, Colombia, Ecuador, Suriname, and Panama (De Sousa 2000).

The tree is a slender, multi-stemmed, monoecious palm that can reach over 30 meters in height. It is mainly found on estuarine floodplains, slightly less so on perennially flooded areas and not very common on upland areas (Lewis 2008). It is often known as açai palm and it is famous for its hearts of palm and for its fruit, called açai. Each palm produces 3 or 4 bunches of acai per year (Figure 1), each one containing 3 to 6 kg of fruit (Del Pozo-Insfran et al. 2004). The palm is of great importance in the Amazonian region, since its products are major components of the diet and of great significance to the local economy (Brondizio et al. 1994).

Figure 1. Bunch of acai (www.liquidhealth.com.au)
The heart of palm is the inner core of the tree and it is treated as a delicacy, because of the intensive labor task required for its harvesting (Bovi et al. 1993). The product is often eaten in salads or as a filling. Nowadays, 95% of the hearts of palm produced in Brazil come from açaí palms, since the native trees were devastated without preservation (Tonon 2009).

Açaí is a round-shaped fruit with a diameter ranging from 1.1 to 1.5 cm (Figure 2). Most of the açaí varieties are green when young and turn into a dark purple color when ripe. However, some varieties remain green in their mature stage, being called “açaí branco” or white açaí (Bovi et al. 1993). The seed corresponds to 85% of the fruit total weight and is used for oil extraction, animal feed or as a fertilizer, among others. The seed is covered by fibrous fibers on top of which is the edible part (pulp), accounting for 15% of the fruit (Nogueira 2006).

Figure 2. Açaí berries (www.truestarhealth.com)

After being processed into juice, açaí is widely used in smoothies, ice cream, jelly and a variety of other products. It is estimated that approximately 120,000 liters per day of açaí juice are consumed only in the city of Belém, Pará state, where the product is part of the staple food of the population (Carneiro 2000). Until a couple years ago, production of the juice was almost exclusively intended for the local market. However, recently, the product is becoming more and more popular in other Brazilian states and internationally. The production of açaí is growing around 15% per year. In 2008, 540,000 tons of açaí juice were produced in Brazil (Sampaio 2009).

Açaí is considered a fruit of high nutritional value, representing a good source of proteins, fiber and minerals, mainly potassium and calcium. Interestingly, it also has a high lipid content, being able to provide approximately 65% of the recommended daily value (Tonon 2009). The oil extracted from açaí juice is rich in monounsaturated (60%) and polyunsaturated
(10%) fatty acids, mainly oleic and linoleic acids. Unsaturated fatty acids are said to be important for cardiovascular diseases prevention (Do Nascimento et al. 2008). Açai oil has also a high phenolic content, mainly phenolic acids and procyanidins (Pacheco-Palencia et al. 2008). Table 1 shows the nutrient analysis for açai pulp.

Table 1. Nutrient analysis of açai pulp

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Weight (%)</td>
<td>15.26</td>
</tr>
<tr>
<td>Proteins (g/100g DW)</td>
<td>10.05</td>
</tr>
<tr>
<td>Total Lipids (g/100g DW)</td>
<td>52.64</td>
</tr>
<tr>
<td>Total Sugars (g/100g DW)</td>
<td>2.96</td>
</tr>
<tr>
<td>Reducing Sugars (g/100g DW)</td>
<td>2.91</td>
</tr>
<tr>
<td>Sucrose (g/100g DW)</td>
<td>0.05</td>
</tr>
<tr>
<td>Fiber (g/100g DW)</td>
<td>25.22</td>
</tr>
<tr>
<td>Ash (g/100g DW)</td>
<td>3.09</td>
</tr>
</tbody>
</table>

Source: Tonon 2009

The fruit’s purple color is due to the presence of anthocyanins, natural pigments that belong to the flavonoid group. Anthocyanins are powerful antioxidants and may have other potential benefits for humans, like antiinflammatory and anticarcinogenic properties (Del Pozo-Insfran et al. 2004).

Açai fruits are produced throughout the year, with production peaks varying from state to state. However, fruits harvested during August to December (“dry months”) usually have shown higher yields and better organoleptic quality (Lichtenthaler et al. 2005) Harvesting is typically done manually and is an arduous task, since the bunches of fruits may reach 10 – 15 m in height. The harvester climbs the palm tree and cuts the bunches with a knife. After that, the bunches are placed on the floor and the fruits are picked and selected by hand. Rotten fruits or those attacked by insects are removed (De Vasconcelos et al. 2006).

Açai fruits are perishable and should be processed in 24 hours, maximum, after harvesting (Tonon et al. 2009b). Their degradation is due to high microbial load, enzymes (mainly peroxidase and polyphenol oxidase), and elevated temperatures and relative humidity in the harvesting/production area (Menezes et al. 2008).

A typical processing of açai fruits (Figure 3) involves, mainly, the following steps (Cohen et al. 2006):
- Reception of fruits: after harvesting, the fruits are placed in plastic boxes or baskets, which are then transported, usually in boats, to processing plants.
- Selection of fruits: during selection, unripe and damaged fruits are removed.
- Pre-washing, Softening, and Washing:
  - Pre-washing: fruits are immersed into water to remove dirt;
  - Softening: fruits are immersed into water with temperature ranging from room temperature to 60°C for 10 to 60 minutes. This step is used to soften the fruits, facilitating pulping, and
  - Washing: fruits are then washed with chlorinated water, followed by potable water.
- Blanching: an optional step used to inactivate enzymes, reduce microbial load and stabilize color. Blanching is done at 80°C for 10 seconds.
- Pulping: açaí pulp is removed. Water is added during pulping to facilitate the process.
- Homogenization: after pulping, pulp is sieved, to remove any dirt remaining, and homogenized.
- Pasteurization: the time/temperature used is 80-85°C / 10sec. After pasteurization, product can be frozen or dried.

Figure 3. Processing of açaí fruits
According to the Brazilian Regulation there are four types of processed açai (Ministerio da Agricultura, Pecuaria e Abastecimento 2000) and they are presented in Table 2:

<table>
<thead>
<tr>
<th>Type</th>
<th>Addition of water</th>
<th>% Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Açaí Pulp</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Thick or special (type A)</td>
<td>Yes</td>
<td>&gt;14</td>
</tr>
<tr>
<td>Medium or regular (type B)</td>
<td>Yes</td>
<td>11-14</td>
</tr>
<tr>
<td>Thin or popular (type C)</td>
<td>Yes</td>
<td>8-11</td>
</tr>
</tbody>
</table>

Functional Properties

Recently, much attention has being paid to açai due to potential health benefits associated with its high antioxidant capacity and phytochemical composition. The fruit is abundant in polyphenolic compounds, which are thought to prevent many chronic diseases, including cancer, hyperlipidemia, cardiovascular, and neurodegenerative diseases (Hogan et al. 2010). Some polyphenolics already identified in açai include anthocyanins, ferulic acid, gallic acid, ellagic acid, (-)-epicatechin, (+)-catechin, orientin and procyanidin polymers, among others (Del Pozo-Insfran et al. 2004; Pacheco-Palencia et al. 2009).

Schauss et al. (2006a) evaluated the antioxidant capacity and other bioactivities of freeze-dried açai and reported a high scavenging capacity for superoxide and peroxyl radical (the highest of any fruit or vegetable reported to date). Mild activity was detected against the peroxynitrite and hydroxyl radical. Freeze-dried açai also seemed to inhibit the formation of reactive oxygen species in freshly purified human neutrophils. The extract appeared to be effective at very low doses (5μg/mL). In addition, the product was found to be a potential cyclooxygenase (COX)-1 and COX-2 inhibitor, indicating anti-inflammatory and pain-relieving properties.

Oxidative damage of brain tissue leads to an increased susceptibility to neurodegenerative diseases, such as Parkinson’s and Alzheimer’s. The effects of frozen açai juice in reducing oxidative stress induced by H₂O₂ in cerebellum, cerebral cortex, and hippocampus from rats was studied by Spada et al. (2009). H₂O₂ caused an increase in lipid and protein damage in brain tissue from rats. However, when tissues were pretreated with açai a significant decrease in lipid and protein damage and in superoxide dismutase and catalase activities were observed. The reduction of lipid damage was around 48% in the cerebral cortex, 64% in the hippocampus, and 72% in the cerebellum. Protein damage reduction was 55% in the
cerebral cortex, 36% in the hippocampus, and 42% in the cerebellum. The results suggest possible use of açaí to help prevent the development of age-related neurodegenerative diseases.

Oliveira de Souza et al. (2009) studied the antioxidant and hypocholesterolemic effects of açaí pulp in control and in hypercholesterolemic fed rats. The addition of açaí pulp to control and hypercholesterolemic diets significantly improved antioxidant capacity by decreasing the level of carbonyl protein (marker of oxidative stress) and increasing the sulfhydryl groups (free radical scavengers) in the sera of animals fed those diets. Rats fed the hypercholesterolemic – açaí diet also showed significant reduction of SOD (antioxidant enzyme) activity, compared with the control rats. This suggested that açaí supplementation reduced oxidative stress, which diminished the need for protective responses. Also, addition of açaí juice in the hypercholesterolemic diet reduced cholesterol levels (total and non-HDL) of rats fed that diet.

**Dehydration Process**

As previously mentioned, açaí is a highly perishable fruit and processing is essential to preserve its quality and functional properties. Unless the fresh fruit is consumed quickly, it must be preserved by drying or freezing.

The dehydration process, as defined by Fellows (2000), constitutes “the application of heat under controlled conditions to remove the majority of the water normally present in a food”. Removal of water can be done by evaporation or sublimation (in case of freeze drying) (Fellows 2000).

The main goal of dehydrating food products is to extend their shelf life (Vega-Mercado et al. 2001). Extension of shelf life is achieved by reducing the product’s water activity, which inhibits or retards microbial growth as well as the occurrence of chemical reactions (Zhang et al. 2006; Mayor et al. 2004). Drying also decreases the weight and bulk of foods, which reduces packaging, shipping and storage costs (Chou et al. 2001).

An efficient drying process must consider the following (Hawlader et al. 2006):
- Avoid undesirable changes, preserving food quality,
- Operate at optimum conditions, lowering cost,
- Reduce environmental impact (low energy consumption and waste generation).
Currently, dried açaí is produced mainly by freeze drying. Freeze drying consists of a low temperature drying process, in which most of the water is removed by sublimation. The technique involves three main stages (Koroishi et al. 2009):
- Freezing: quickly lowers the product below its freezing temperature to maximize ice content;
- Primary drying: sublimation of ice, at a temperature below freezing and under reduced pressure (below triple point);
- Secondary drying: removal of unfrozen, bound water by evaporation at a temperature above 0°C.

The water vapor, removed from the product chamber by a vacuum pump, is directed to a condenser, where it is retained frozen. Figure 4 shows the basic configuration of a freeze dryer.

During the freeze drying process, heat is provided to the product in order to sublime the ice and remove the water. It is important to ensure that the product temperature is below its glass translation temperature to avoid collapse (Okos et al. 2007). Sublimation starts at the surface of the product and then moves toward the bottom. During the process, the dry layer acts as an insulation material and the drying rate slows as the layer thickens (Vega-Mercado et al. 2001).

It is well known that freeze-dried foods have high quality. When water is removed by sublimation a porous structure with minimal shrinkage remains. Also, the use of low
temperatures and vacuum prevents degradative reactions, such as lipid oxidation and nonenzymatic browning, and preserves nutrients and bioactive compounds. In addition, there is little or no flavor loss during the process (Marques et al. 2009).

There are a large number of published data showing the superior quality of freeze-dried products. Yurdugül (2008) compared the quality characteristics of fresh and freeze-dried alpine strawberries and found no difference between the two products. The researcher evaluated sugar content, pH, color, vitamin C and anthocyanins, among others, and all the results were very similar between the fresh and dried samples, indicating that the freeze drying process preserved the quality of the fruit.

The effect of different drying methods - freeze drying, hot-air drying, vacuum microwave drying, and combination drying - on phytochemical content and antioxidant activity of Saskatoon berries was studied by Kwok et al. (2004). Freeze-dried berries showed the greatest retention of phenolics, anthocyanins and reducing power and the highest antioxidant activity compared to berries processed by other methods. Results were attributed to the reduced exposure of berries to heat and oxygen during freeze drying.

Krokida et al. (2006) evaluated the retention of aroma during air and freeze drying of apples. Three representative compounds of apple flavor were evaluated before, during and after the drying processes. The researchers found a higher retention of flavor in freeze-dried samples, attributed to the lower temperatures used in the process.

On the other hand, because of the use of vacuum, sub-zero temperatures, and thermal energy for sublimation and evaporation (phase change), freeze drying is the most expensive drying method. Low temperature drying results in slow drying rates and long drying times. In addition, the low pressure required for sublimation and therefore the use of a vacuum pump, as well as the refrigeration system for maintaining a low temperature to collect moisture in the form of ice on the condenser all add cost to the process. As a result, both the capital investment for purchasing a freeze drying system and the production cost, mainly the high energy consumption, are high compared to other drying technologies. The process is therefore mainly employed for very sensitive foods or high value products (Sablani et al. 2007b).

Consequently, the search for an alternative drying method, which would result in a product with quality parameters comparable to those of freeze-dried material, is of great interest. Refractance Window® (RW) drying is a novel drying process developed by MCD Technologies (Tacoma, Washington, USA). In this method hot water is used to carry thermal energy to the product to be dehydrated (Nindo et al. 2003a).
The temperature of the water is usually a few degrees below boiling point (96-98°C) and is kept at that range to avoid formation of bubbles, which would reduce heat transfer. During the process the temperature of the food is usually around 71°C, far below the circulating water temperature. Also, the residence time of the food on the equipment is around 3 to 5 min (Nindo et al. 2004). This relatively low temperature and short residence time reduce product degradation (Vega-Mercado et al. 2001).

Figure 5 shows the layout of a Refractance Window® dryer. The product is spread as a thin film on top of a transparent plastic conveyor belt, under which hot water circulates. The food flows co-currently with the hot water. Heat is transferred through the plastic sheet directly into the product for drying. At the end of drying the product is cooled down, by moving over cold water, and separated from the belt by a scraper device (Nindo et al. 2007).

![Figure 5. Refractance Window dryer (Abonyi et al. 2002)](image)

Refractance Window drying has shown to be a promising technique. Abonyi et al. (2002) studied the effect of Refractance Window drying on quality retention of strawberry and carrot purees. The retention of vitamin C in strawberry purees dried with RW drying was 94% and was comparable to 93.6% in freeze-dried samples. Also, the color of RW dried strawberry purees was similar to freeze-dried products. The overall flavor of strawberry purees was altered by RW drying, with a decrease in fruity and green notes. For carrot purees, the color of RW dried product was similar to fresh puree. The carotene losses for RW dried puree were 8.7% (total carotene), 7.4% (α-carotene) and 9.9% (β-carotene) and were similar to losses for the freeze-dried product.
Nindo et al. (2003b) analyzed the effects of different drying methods on the retention of physical quality and antioxidants in asparagus. RW-dried pureed asparagus was closest in greenness to freeze-dried product. RW and freeze drying enhanced the total antioxidant activity of asparagus. RW drying retained the highest amount of ascorbic acid compared to other drying methods.

The effect of different drying methods and storage on color characteristics of paprika was studied by Topuz et al. (2009). The processes used were RW drying, freeze drying, hot-air oven drying and natural convective drying. For reflected color, RW and freeze drying resulted in products with better characteristics. The less color alterations were attributed to the mild drying conditions of those methods. RW and freeze drying also resulted in samples with the lowest browning index, indicating the occurrence of less non-enzymatic browning reaction during those processes. During storage, a gradual discoloration in all paprika samples was noted.

Based on the results reported by other researchers, it is of interest to analyze how RW drying would affect the quality of açai juice and, therefore, this technique was selected for this research.

Hot-air convective drying is the most widely used process for production of dehydrated foods (Krokida et al. 2003). This technique consists of exposing the food product to a continuously circulating stream of hot air, which supplies the thermal energy for vaporization and also carries away moisture (Ratti 2001). The cabinet dryer consists of a closed cabinet fitted with metal trays, which can be perforated or not. The product is placed on the trays as a thin layer, usually 2 – 6 cm deep. Air is first heated and then blown over and/or through each tray at 0.5 – 5 ms⁻¹ (Fellows 2009). Figure 6 shows the basic layout of a convective cabinet dryer.

Figure 6. Hot air dryer (Heldman et al. 1997)
Despite being very popular, hot-air convective drying uses high temperatures and long drying times, which can cause serious damage to food color, flavor, nutrients, and texture, negatively affecting the quality of the final product (Marfil et al. 2008). Nevertheless, for being an ancient process and extensively used in the food industry, hot air drying is often used in drying studies for comparison purposes. It was therefore selected for the present research.

**Water Activity, Moisture Sorption Isotherms, and Glass Transition Temperature**

**Water Activity**

It is well known that a relationship exists between the water content of foods and their perishability (Franks 1991). However, different foods with the same moisture content may show different perishability, implying that the water content, alone, is not a reliable indicator of product deterioration. This is, partially, due to differences in intensity of association of water molecules with nonaqueous constituents. In order to reflect the intensity of water association with other compounds, the “water activity” \( a_w \) concept was developed (Reid et al. 2008).

Water activity can be described as:

\[
aw = \frac{p}{p^0} = \frac{ERH}{100}
\]  

(1)

where \( p \) is the partial vapor pressure of water above the food, \( p^0 \) is the vapor pressure of pure water at the same temperature, and ERH is the equilibrium relative humidity (%) (Labuza et al. 1998).

The water activity concept can be used to assess moisture sorption isotherms, develop new products, and aid in process design and control, among others (Schmidt 2004). However, probably, the most important use of the water activity concept is to determine product stability and shelf life. It has been extensively reported that water activity influences the rate of chemical reactions, physical changes, and microbial growth/resistance in food products. The “stability map” (Figure 7), introduced by Labuza et al. (1970), shows the general relationship between water activity and several food stability phenomena (Nelson et al. 1994).
The map illustrates that lipid oxidation occurs rapidly at low water activities, which means dehydrated foods are susceptible to this reaction. The rate of non-enzymatic browning is very low at low water activities (Labuza et al. 1970). There is also a critical $a_w$ below which no microorganisms can grow. For most foods, this value is around 0.6 – 0.7 $a_w$ (Vos et al. 1974).

Domínguez et al. (2007) studied the effect of water activity on the stability of macadamia nuts. For lipid oxidation evaluation, the $a_w$ values used were 0.215, 0.436 and 0.628. A higher peroxide value was observed for samples stored at the lowest and highest $a_w$. The total oxidation index (TOTOX) was also higher for nuts stored at 0.215 and 0.628 $a_w$. This is in agreement with the stability map, which shows that lipid oxidation occurs faster at low and high water activities.

Acevedo et al. (2008) analyzed the kinetics of non-enzymatic browning in dried potatoes through water-solids interactions and water mobility. The non-enzymatic browning rate, measured at 70°C, showed a maximum value at $a_w$ equal to 0.84 and decreased markedly above this value. At low water activities, an increase in $a_w$ accelerated the browning reaction, probably due to increased molecular mobility. At high water activities water inhibited the reaction and/or diluted the reactants, causing a decrease in non-enzymatic browning.

The effects of water activity and temperature on growth of Aspergillus niger, A. awamori and A. carbonarius isolated from different substrates were investigated by Astoreca et al. (2007). Mycelial growth and lag phase prior to growth were significantly influenced by $a_w$, temperature and their interactions. For most of the isolates the optimum $a_w$ for growth was 0.97, with optimum temperature of 30°C. Overall growth was reduced up to 50% at 0.93 $a_w$. Minimal
$a_w$ for growth was 0.85 at 30°C. Lag times at the optimal temperature varied a lot depending on the water activity. Lag time for *A. niger*, for example, varied from 2 h at 0.97 $a_w$ to 260 h at 0.85 $a_w$.

Sauvageot *et al.* (1991) studied the effect of water activity on crispness of different breakfast cereals. Samples were equilibrated over saturated salt slurries with $a_w$ varying from 0 to 0.843. Sensory tests and mechanical analysis were used to investigate crispness. All the products analyzed showed very similar results. In the sensory evaluation, a high crispness intensity was observed until 0.53 $a_w$. From 0.53 to 0.71 $a_w$, however, there was a rapid decrease in crispness intensity, followed by a slight decrease of that sensation as $a_w$ increased above 0.71. The results of the mechanical analysis were in agreement with the sensory test.

*Moisture Sorption Isotherms*

Moisture sorption isotherms describe the equilibrium relationship between moisture content of a food and water activity, at constant temperature (Moreira *et al.* 2008). Isotherms provide valuable information for food processing operations, such as drying and packaging. They are also important for predicting final quality and product stability during storage (Moraga *et al.* 2004).

Sorption isotherms can be obtained by rehydrating a dried sample (adsorption isotherm), drying a wetted sample (desorption isotherm) or by the combination of the two methods (working isotherm). Brunauer *et al.* (1940) classified adsorption isotherms into five types, as showed in Figure 8. Most foods show a sigmoidal shape (type II) isotherm, while foods containing soluble crystalline molecules, such as crystalline sugars, show a J-shape isotherm (type III) (Al-Muhtaseb *et al.* 2002). Several factors influence the position and shape of an isotherm, for example, sample composition, crystalline or amorphous sample structure, sample preparation, temperature, and method of determination.
Figure 8. Classification of van der Waals adsorption isotherms (Brunauer et al. 1940)

Figure 9. Sorption isotherm (Okos et al. 2007)

According to Figure 9, type II sorption isotherms may be divided into three main regions (Al-Muhtaseb et al. 2002):
- Region A: strongly bound and least mobile water (unfreezable at -40°C, not available for chemical reactions, no plasticizing effect);
- Region B: less tightly bound water (also unfreezable at -40°C);
- Region C: exhibits properties of bulk water (available as solvent for reactions, supports the growth of microorganisms).
The boundary of zones A and B represents the monolayer moisture content, which can be thought as single layer of water molecules bound only to highly polar groups of the solid matrix. Most dried foods show moisture content comparable to the monolayer value. At that moisture content dry products exhibit their highest stability (Sablani et al. 2007a).

Mathematical models are usually used to describe sorption isotherms. The most commonly ones are Brunauer-Emmett-Teller (BET) and Guggenhein-Anderson-de Boer (GAB) models. BET is only linear at lower \( a_w \) and fails above 0.5. The BET is a two-parameter equation and is expressed as:

\[
\frac{M}{M_0} = \frac{C a_w}{(1 - a_w)[1 + (C - 1)a_w]} \tag{2}
\]

where \( M \) is the equilibrium moisture content (dry basis, db), \( M_0 \) is the monolayer moisture content (db), and \( C \) is a constant related to the heat of sorption of monolayer.

The GAB model is an extension of the Langmuir and BET theory, having three parameters. The model is successful up to high water activities, but underestimates moisture content values at \( a_w \) > 0.93. The GAB equation is expressed as:

\[
\frac{M}{M_0} = \frac{C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \tag{3}
\]

where \( M \) is the equilibrium moisture content (db), \( M_0 \) is the monolayer moisture content (db), \( C \) is a constant related to the heat of sorption of monolayer, and \( K \) is a constant related to the heat of sorption of multilayer region (Basu et al. 2006; Brunauer et al. 1938).

Several methods are available for determining sorption isotherms. These methods can be classified into the following categories: gravimetric (involves the measurement of weight changes); manometric (measures the vapor pressure of water in the vapor space surrounding the food); and hygrometric (measures the equilibrium relative humidity of air in contact with a food product, at a specific moisture content) (Gal 1981).

Research about sorption isotherms of fruit powders is vast. Syamaladevi et al. (2009) studied the water adsorption isotherm of freeze-dried raspberry at room temperature. The isotherm exhibited a sigmoidal shape and was modeled using BET and GAB models. The
monolayer water content was 0.059 kg water/kg solids for the BET model and 0.074 kg water/kg solids for the GAB model.

Sorption isotherms of vacuum dried mulberry at different temperatures (10, 20 and 30°C) were analyzed by Maskan et al. (1998). The isotherms obtained for the three temperatures were very similar and showed a sigmoidal shape. Although isotherms followed a typical type II behavior, a sharp increase in moisture content at high water activities was observed, probably due to the elevated sugar content of the product.

A J-shape isotherm was characteristic of freeze-dried acerola, a high sugar fruit. The samples sorbed relatively small amounts of water at low $a_w$, but an increase of sorption capacity was observed at high water activities. Sorption isotherms were practically not affected by the different freezing techniques analyzed (cryogenic freezing with liquid nitrogen, with vapor of nitrogen, and by putting the samples in a freezer) (Marques et al. 2007).

Information about moisture sorption characteristics of dried açaí is important for selection of appropriate packaging materials and prediction of its stability during storage. Previous work of Tonon et al. (2009a) with spray dried açaí at 25°C showed that the product presented a type III isotherm, which is probably due to the presence of carrier agents (crystalline molecules). Da Silva et al. (2008) also studied the water sorption of spray dried açaí and reported a type III isotherm for the product, at all temperatures used (15, 25 and 35°C).

Up to now, there is no information about the water sorption characteristics of freeze dried, RW-dried or hot-air dried açaí.

Glass Transition Temperature

The moisture sorption isotherm of a food product is influenced, among others, by the structure of the solid. Solids can exist as a crystal (ordered molecular arrangement) or as an amorphous product (random molecular arrangement) (Bell et al. 2000).

The amorphous state can be further divided into glassy and rubbery states. Products in the glassy state show low internal mobility and high internal viscosity, and are described as solids. Rubbery materials show viscoelastic behavior and are described as supercooled liquids (Le Meste et al. 2002).

The conversion between the glassy and the rubbery states is known as glass transition and it occurs over a temperature range, which is frequently referred to as single temperature, called glass transition temperature ($T_g$). Glass transition is a second-order transition and it is characterized by a change in physical properties of the material, mainly heat capacity, free
volume, thermal expansion coefficient, and viscoelastic properties. The main factors affecting glass transition are moisture content and temperature (Slade et al. 1995b; Roudaut et al. 2004; Kasapis 2008).

The concept of glass transition has been used to predict food stability, especially of low moisture products. Changes from the glassy to the rubbery state have shown to affect food structure and have been suggested to influence molecular mobility and, consequently, the rates of chemical reactions. Products in the glassy state (lower molecular mobility) have a higher stability compared to products in the rubbery state (Roos 2003). At temperatures above glass transition, the solid state is converted to a rubbery material and undesirable changes will occur, like caking, stickiness, crystallization, collapse and loss of crispiness. As a result, the final product might be unattractive and unfit for consumption (Schmidt 2004).

According to studies in the field of polymer science, the glass transition temperature of a mixture is a non-linear function of the glass transition temperature of the individual components. Due to the complexity of food systems and the occurrence of several thermal changes and chemical reactions in the same temperature range, it is usually difficult to determine \( T_g \) of food products (Bhandari et al. 2000).

Glass transition temperature is highly dependent on the molecular weight of the material. In foods, \( T_g \) decreases with increase in low molecular weight compounds, mainly water. It is well known that water acts as a plasticizer, increasing mobility due to increased free volume and decreased local viscosity (Slade et al. 1995a; Slade et al. 1991). Also, due to the non-equilibrium nature of the amorphous phase, glass transition is time-dependent. Therefore, different glass transition temperatures may be found for the same product depending on the time scale of the method used (Roos 2003). In addition, sample preparation, sample history and the analytical procedure used will also influence glass transition temperature.

Many experimental methods can be used to measure glass transition temperature. Among them, differential scanning calorimetry (DSC) is one of the most commonly used. DSC measures changes in heat flow during heating or cooling of the test material. The glass transition is manifested as a step change in the heat flow, due to different heat capacities of the glassy (lower specific heat capacity) and rubbery states (higher specific heat capacity) (Schmidt 2004; Liu et al. 2006).

Methods used to produce materials in the amorphous state involve mainly two events: rapid decrease in water content or rapid cooling (avoiding the formation of the crystalline state due to lack of time). Dehydration processes result in foods in the amorphous state. For higher stability, it is important to assure that dried products are in the glassy state. Any change in that
state may result in alteration of physico-sensorial attributes, structural damage and increase in the rate of biochemical reactions, affecting the quality of the product (Bhandari et al. 1999).

Knowledge about glass transition temperature of açai is still lacking. Tonon et al. (2009a) analyzed the glass transition temperature of spray-dried açai juice produced with different carrier agents (maltodextrin with 10DE, maltodextrin with 20DE, gum Arabic and tapioca starch). Temperatures varying from, approximately, -62 to 74°C were reported, depending on the water activity at which the product was stored and the carrier agent used. The researchers stated that spray dried pure açai juice might have a much lower glass transition temperature than the values obtained for the materials produced with additives. No information about glass transition temperature of freeze dried, RW-dried or hot-air dried açai is currently available.

**Anthocyanins**

Anthocyanins are pigments that belong to the flavonoid group. They are responsible for a wide variety of colors in plants, including purple, blue, red and orange. Anthocyanins are water-soluble and have been widely used as food colorants (Castañeda-Ovando et al. 2009).

Anthocyanidins are the basic structure of anthocyanins. When anthocyanidins are bonded to a sugar moiety (glycoside form), they are known as anthocyanins (Mazza et al. 1987). Figure 10 shows the general structure, also called flavilium cation, of anthocyanins.

![Figure 10. General anthocyanin structure (the flavilium cation) (Mazza et al. 1987)
R₁ and R₂ are H, OH or OCH₃, R₃ is a glycosyl or H and R₄ is OH or a glycosyl](image)

Differences in anthocyanins are due to: 1) number of hydroxyl/methoxyl groups present; 2) nature, number and sites of sugar attachment; and 3) types and number of aliphatic or aromatic acids attached to the sugars. The most commonly encountered sugars are glucose, galactose, rhamnose and arabinose. Caffeic, p-coumaric, ferulic and sinapic acids are the most
common aromatic acids, while acetic, malonic, malic, oxalic and succinic acids are examples of aliphatic acids involved in acylation of sugars (Clifford 2000).

Kong et al. (2003) estimated that more than 400 different anthocyanins exist in nature. The researchers also report the existence of 17 anthocyanidins, with pelargonidin, peonidin, cyanidin, malvidin, petunidin and delphinidin being the most common in plants.

Anthocyanins are soluble in polar solvents and are generally extracted by using acidified methanol. Identification and quantification of anthocyanins are done, primarily, by HPLC and HPLC-MS. Several studies about anthocyanins in açaí juice have been published, but with contradictory results. Lichtenthaler et al. (2005), Gallori et al. (2004) and Vera de Rosso et al. (2008) detected cyaniding-3-rutinoside and cyaniding-3-glucoside as the main anthocyanins in açaí whereas Del Pozo-Insfran et al. (2004) reported cyaniding-3-glucoside and pelargonidin-3-glucoside as the main compounds. Schauss et al. (2006b) analyzed anthocyanins in freeze-dried açaí and concluded that the cyaniding-3-rutinoside and cyaniding-3-glucoside were the most abundant ones.

One of the most significant properties of anthocyanins is their antioxidant capacity. By donating phenolic hydrogen atoms, these compounds are able to capture free radicals and prevent oxidative damage. It is being suggested that anthocyanins contribute to the protective effect of fruits and vegetables against degenerative and chronic diseases. These compounds also exhibit therapeutic benefits, including cardioprotective, antiinflammatory and anticarcinogenic properties (Heinonen et al. 1998; Stoner et al. 2007; Zafra-Stone et al. 2007).

Many assays have been used to measure the antioxidant capacity of anthocyanins and other phenolic compounds. Among them, Oxygen Radical Absorbance Capacity (ORAC) has been extensively used. ORAC provides a measure of antioxidant capacity against peroxyl radicals. The test uses the following components: (a) an azo radical initiator, usually 2,2’-azobis(2-methylpropionamidine) dihydrochloride (AAPH); (b) a molecular probe, normally fluorescein (FL), to monitor the reaction progress; (c) the antioxidant compound of interest; and (d) reaction kinetic parameter to quantify the antioxidant capacity. The method, basically, involves the mixture of samples, controls (phosphate buffer) or standard (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid - Trolox) with fluorescein and incubation at 37°C, followed by addition of AAPH to initiate the reaction. The fluorescence intensity is measured periodically and, as the reaction progresses, fluorescein is consumed and its intensity decreases. Fluorescein decay is inhibited / limited in the presence of antioxidants (Huang et al. 2005).

Anthocyanins are fairly unstable and quite susceptible to degradation. Their greatest stability occurs under acidic conditions. The main factors affecting anthocyanins stability are pH,
chemical structure, temperature, and oxygen concentration. Secondary factors include light, metal ions, and presence of degradative enzymes (Markakis 1982).

In an aqueous medium, depending on the pH of the solution, anthocyanins can exist in different chemical forms (Figure 11): red flavylium cation (AH⁺), blue quinonoidal base (A), colorless carbinol pseudobase (B), and colorless chalcone (C). Usually, as the pH increases anthocyanins are converted into colorless forms (Brouillard 1982).

![Figure 11. Anthocyanin structures in aqueous solutions (Brouillard 1982)](image)

Anthocyanins are susceptible to molecular oxygen due to their unsaturated nature and reaction with oxygen causes degradation of their color. Anthocyanins are also readily destroyed by heat during processing and storage of foods (Delgado-Vargas et al. 2000).

Mejia-Meza et al. (2010) studied the effect of drying on the anthocyanin content and antioxidant capacity of raspberries. Dehydration resulted in a significant decrease in anthocyanin content. Losses ranged from, approximately, 30-80% for glycosides and 75-95% for aglycones, depending on the drying method used. Considerable loss of antioxidant capacity was also observed.

The effect of different drying methods – convective drying, vacuum-microwave drying, vacuum drying and freeze drying - on bioactive compounds of strawberry fruits was studied by Wojdylo et al. (2009). The researchers found that drying destroyed anthocyanins and flavanols. Also, all dried products showed a significantly lower antioxidant capacity.
Lohachoompol *et al.* (2004), by analyzing anthocyanin degradation during drying of blueberries, reported losses of 41% for samples dried in a cabinet drier and 49% for fruits dried using osmotic pretreatment followed by cabinet drying.

Meschter (1953) examined the effect of temperature on the stability of anthocyanins in strawberry preserves. At a storage temperature of 20°C, the half-life of the pigment was 54 days whereas at 38°C the half-life was 10 days. Processing strawberry preserve at 100°C would result in a half-life of 1 hour.

**Flavor Analysis**

Flavor is a sensory impression of a food and is established by the chemical senses of taste, smell and “trigeminal” (d’Acampora Zellner *et al.* 2008). Among those senses, smell is, probably, the most important flavor determinant. Smell can be divided into aroma - smell of a food before it is put in the mouth - and odor - retronasal smell of a food in the mouth (Acree 1993).

The study of flavor is of great importance for food, since, together with color, texture and other parameters, it determines food quality (Acree 1993). Flavor is also used to define characteristics and identity of products, such as in wines (Flamini 2005).

The knowledge and identification of odor active compounds, also called flavor compounds, has improved with the advent of gas chromatography (GC) and mass spectrometry (MS) (d’Acampora Zellner *et al.* 2008). Gas chromatography is a separation technique, not an identification technique. However, when coupled with a mass spectrometer the instruments provide a great identification method (Mussinan 1993). Currently, approximately 7000 flavor compounds have been identified (Rowe 2005).

It has been reported that just a small portion of the large number of volatiles occurring in foods contributes to their perceived odor (Grosch 1994). Also, human perception of volatile compounds depends on the extent of release from the matrix and their odor properties (Van Ruth 2001). Further, the contribution of those molecules to the flavor profile of a product is not equal and the peak area generated by a “chemical” detector is not directly translated into intensity (d’Acampora Zellner *et al.* 2008).

Therefore, the grouping of olfactometry and GC (GC-O) results in another useful tool for discrimination of odor active compounds. As the human nose is more sensitive than “chemical” detectors for many flavor compounds, GC-O uses the human olfactory system as one of the
detectors. In this method, the human subject sniffs the gas chromatographic effluent of a food extract, determining which volatiles are odor active and providing descriptors. With the use of GC-O it is possible to list and order the odorants present in a food (Van Ruth 2001).

The detection of flavor compounds by GC-O depends on several factors, such as odor threshold (main factor), amount of food sampled, dilution of the volatile fraction, and sample size analyzed. Therefore, a screening method is necessary to identify the most important odorants (Grosch 1993). Aroma extract dilution analysis (AEDA) is probably the most frequently used method for that purpose. In this technique, the flavor extract is serially diluted (usually 1:2, 1:3, 1:5 or 1:10) and each dilution is analyzed by GC-O. The result is expressed as a flavor dilution (FD) factor, which corresponds to the highest dilution at which the odorant can be perceived (Ferreira et al. 2002).

The flavor profile of a food product is closely related to the extraction procedure used, which should yield an extract representative of the sample. For that reason, the choice of an adequate isolation procedure is also very important. Two very popular techniques used for sample preparation are solvent-assisted flavor evaporation (SAFE) and solid-phase microextraction (SPME) (d’Acampora Zellner et al. 2008).

SAFE is a technique that extracts volatiles under high vacuum and low temperature conditions. The method involves adding, into the apparatus, small droplets of samples, which will be immediately transformed into a vapor spray. As a result, volatiles and solvent are transferred into a flask, which is cryogenically cooled with liquid nitrogen. The method is suitable for a solvent extract or a food matrix (aqueous foods or matrices with high oil content) (Engel et al. 1999).

SPME uses a fused silica fiber coated with a specific stationary phase to adsorb the flavor compounds. The fiber is first submerged in a liquid phase or exposed to a gaseous phase, allowing the analytes to be directly extracted. Next, absorbed analytes are thermally desorbed in the GC injection port. The method involves short preparation time and saves solvent and disposal costs (Kataoka et al. 2000; Deibler et al. 1999).

Many factors can affect the flavor of a food product and processing is, probably, one of the most important. Thermal processing of foods usually results in loss of volatile compounds, or reduction of their concentration, and development of new odors due to a series of chemical reactions, such as Maillard and lipid oxidation. These factors will change the flavor profile of the product, which can affect its acceptability (Ruiz Perez-Cacho et al. 2008).

The characterization of the flavor compounds of açaí juice is of great interest to food companies, since a large number of new products containing the fruit are being launched. It is
also important to evaluate how drying affects the flavor of açaí. However, up to date, information about the flavor profile of açaí juice or dried açaí is still not available.

The effect of heat treatment on the flavor profile of fruits has been widely studied. Feng et al. (1999) analyzed the effect of different drying methods on flavor retention of blueberries. Heating caused some odor compounds to disappear while new volatiles were created or had their concentration increased, which changed the flavor profile of the fruit.

Changes in volatile compounds during dehydration of d’Agen prunes was evaluated by Sabarez et al. (2000). Four major components were identified in fresh plums. After drying, three of the four main compounds completely disappeared and three new volatiles were generated. Among the new ones, the researchers highlighted the presence of a furan derivative, which was probably derived from caramelization or Maillard reactions.

Wang et al. (2007) compared the volatiles of banana powder dehydrated by air drying (AD), vacuum belt drying (VBD), and freeze drying (FD). The researchers found that the characteristic aroma of fresh banana was present in the dried samples, but the level of flavor in those products was different depending on which drying technique had been used. As the drying temperatures used in AD and VBD were higher than that of FD, some of the original esters disappeared in the AD and VBD samples while some new compounds were formed.

Luning et al. (1995) evaluated the effect of hot air drying on flavor compounds of bell peppers and found that many “fresh” odor notes decreased or disappeared after drying, whereas several compounds derived from lipid oxidation were formed or had their concentrations increased during the drying process.

References


Grosch, W. 1994. Determination of potent odourants in foods by aroma extract dilution analysis (AEDA) and calculation of odour activity values. Flavour Frag. J. 9, 147-158.


Chapter 3:
Effects of freeze drying, Refractance Window drying, and hot-air drying on the quality parameters of açaí

Materials and Methods

Chemicals
- Moisture Working Isotherm: NaCl, KI, Mg(NO₃)₂·6H₂O, K₂CO₃, MgCl₂, and LiCl salts were obtained from Fisher (Fair Lawn, NJ), and KC₂H₃O₂ was obtained from Sigma-Aldrich (St. Louis, MO).
- HPLC: Cyanidin-3-glucoside and cyaniding-3-rutinoside were purchased from Polyphenols Laboratories (Sandnes, Norway).
- ORAC assay: 2,2’-Azobis-(2-methylpropionamidine) dihydrochloride (AAPH) and 6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were obtained from Sigma-Aldrich (St. Louis, MO). Fluorescein was purchased from Fisher (Hanover, IL). Potassium phosphate monobasic and potassium phosphate dibasic were purchased from Fisher (Fair Lawn, NJ).
- Flavor Standards: All standard compounds were purchased from Sigma-Aldrich (St. Louis, MO), except for (Z) 3-hexen-1-ol and α-ionone, which were obtained from Bedoukian Research (Danbury, CT); isoeugenol and 1-octen-3-one were purchased from Alfa-Aesar (Ward Hill, MA); (E,E,Z) 2,4,6 nonatrienal was synthesized following the method described by Schuh et al. (2005); (Z) 2-nonenal was synthesized from (Z) 2-nonen-1-ol (Bedoukian Research, Danbury, CT) by oxidation with Dess-Martin periodinane (0.3M in dichloromethane) based on the procedure described by Meyer et al. (1994); β-damascenone was provided by Firmenich (Princeton, NJ), and (Z) 1,5-octadien-3-one was synthesized as previously described by Ullrich et al. (1988a).

Açaí Juice
Açaí juice (36lb) was purchased from Earthfruits (South Jordan, UT) and shipped frozen overnight to the Department of Food Science and Human Nutrition at University of Illinois at Urbana-Champaign. The juice was produced with fruits of Euterpe oleracea Martius species and contained 11-13% total solids, 2 - 5 °Brix, pH < 4.6 and 0.4 – 0.45% acidity (data from specification sheet). Juice production involved a pasteurization step.
Upon arrival, the juice was thawed overnight and then divided into 3 buckets containing 14 lb (to be used for hot-air drying), 14 lb (to be used for Refractance Window drying), and 8 lb (to be used for analysis of the fresh juice).

**Drying Methods**

**Freeze drying**

Freeze-dried açaí was kindly donated by Liotécnica (Embu, São Paulo, Brazil). The product was vacuum packed and was kept in the original package at -20°C until beginning of storage test. The fruits used to produce the freeze-dried product were from the same species and were harvested at the same location as the fruits used to produce the açaí juice from Earthfruits.

Although freeze-dried açaí was from a different lot of fruit, this product was used for comparison with RW-dried and hot-air dried samples in order to evaluate the effect of each drying method.

**Hot-air drying**

For hot-air drying, açaí juice was thawed overnight and then placed in metal trays, 1-2 cm deep. Product was dried at 65°C for approximately 20 hours. Drying was performed on a convection cabinet dryer V-33 (Despatch Oven Co, Minneapolis, MN). The procedure was based on the work of Krokida *et al.* (2003).

**Refractance Window drying**

Frozen açaí juice was shipped overnight to Tacoma, WA. MCD Technologies performed the RW drying of the product. The dwell time of the juice on the dryer’s heated surface varied between 1min 15 sec to 1min 29 sec. The circulating water temperature was approximately 94°C and the product temperature was around 62 to 71°C.

**Storage Test**

After drying, products were placed in amber glass bottles, flushed with nitrogen for 4 min and stored at room temperature (25°C) for up to 3 months. Samples of dried açaí were taken from storage every month and placed at -20°C until analysis (Piga *et al.* 2003). Açaí juice was analyzed only on day zero and the results were used as a reference for comparison with dried samples.
Moisture Content and Water Activity

The moisture content of the açaí powders (2 g) was determined using a vacuum oven (Equatherm, Curtin Matheson Scientific, Inc., Houston, TX) at 60°C and 30 inches Hg for 24 hours (Yu et al. 2008). The moisture content of the açaí juice was determined in two steps: first, 16 g of juice were dried in a convection oven (Precision Scientific, Inc.) at 80°C for 2.5 hours; then, samples were dried in a vacuum oven (Equatherm, Curtin Matheson Scientific, Inc., Houston, TX) at 60°C and 30 inches Hg for 24 hours.

The water activity of açaí powders was measured using the AquaLab® aw meter (Decagon Devices, Inc., Pullman, WA) at 25°C.

Color

Instrumental color was determined using a HunterLab spectrocolorimeter (LabScan II, Hunter Associates Laboratory Inc., Reston, VA), calibrated with white and black standards. The spectral curve was determined over the 400 to 700 nm range. Color values were expressed as L (whiteness/darkness), a (redness/greenness) and b (yellowness/blueness). Also the hue angle (Eq. (4)) and chroma (Eq. (5)) were used to characterize the products.

\[
h^0 = \arctan \left( \frac{b}{a} \right) \quad (4)
\]

\[
C = \left( a^2 + b^2 \right)^{1/2} \quad (5)
\]

Moisture Sorption Working Isotherm

To obtain the sorption isotherms, duplicate samples from each drying method (1.5 g) were placed in previously weighed plastic cups. Samples were then placed in “Lock & Lock” (Heritage Mint, Ltd., Scottsdale, AZ) containers and equilibrated to seven saturated salt slurries at 25°C. The relative humidity values of NaCl (75%), KI (69%), K₂CO₃ (43%), MgCl₂ (33%), KC₂H₃O₂ (23%), and LiCl (11%) were obtained from Greenspan (1977), and Mg(NO₃)₂·6H₂O (55%) was obtained from Hirose et al. (2006).

During the equilibration period, samples were weighed every week until the observed weight change was within criteria (2 mg/g). After that, equilibrium moisture content (db) of the dried açaí was calculated based on the weight change and initial moisture content. The water activity of samples and salt slurries were also determined using the AquaLab®. The moisture content of the samples and the relative humidity values from the references were used to
generate the working isotherms, which were then fit to GAB and BET models. BET model was applied to water activity values lower than 0.5.

The root mean square error (RMSE) was calculated and used to represent the fitting ability of the models in relation to the number of data points.

Glass Transition Temperature

Glass transition temperature was determined by differential scanning calorimetry in a DSC Q2000 (TA Instruments, Newcastle, DE) using Tzero hermetically sealed aluminum pans and lids. DSC was equipped with a refrigerated cooling system.

Açai powders (~10 mg) were placed into the DSC pans and analyzed. Samples were first cooled to -65°C, at 50°C/min, then equilibrated to -65°C, and finally heated to 250°C, at 10°C/min. An empty pan was used as a reference. Dry nitrogen, 50 mL/min, was used as a purge gas. Analysis of data was done using the software Universal Analysis 2000.

Preliminary studies suggested that the high fat content of açai was interfering with the DSC results. Therefore, it was decided to also perform an oil extraction and run DSC with both the oil and solid phases in order to try to identify the glass transition temperature of the product and to estimate the influence of the fat on the thermogram. For oil extraction 1g of dried sample plus 5 mL of pentane:ether (50:50, v/v) were placed in test tubes. Tubes were shaken 30 min and centrifuged. Supernatant containing the oil phase was collected and the above extraction procedure was repeated 2 more times. Solvent was removed under a stream of nitrogen in order to recover the oil and solids.

Anthocyanin Analysis

Extraction Procedure

Extraction of anthocyanins was based on the method of Wu et al. (2004b) with modifications. For açai juice, 5 g of samples were placed in 125 mL screw cap erlenmeyers. Next, 25 mL of methanol and 150 μL of acetic acid (resulting in 85:15:0.5 methanol/water/acetic acid; v/v) were added and samples were extracted on an orbital shaker (250 rpm) at room temperature for 2 h. Product was then centrifuged at 4550 g for 10 min, at 4°C. The supernatant was filtered using a 0.2 μm Teflon syringe filter prior to HPLC analysis.

For açai powders, 1 g of freeze-dried, 1g of RW-dried or 3 g of hot-air dried samples were placed in 125 mL screw cap erlenmeyers. After that, 25 mL of methanol/water/acetic acid (85:15:0.5; v/v) were added and samples were extracted on an orbital shaker (250 rpm) at room
temperature for 2 h. Product was then centrifuged at 4550 g for 10 min, at 4°C. The supernatant was filtered using a 0.2 μm Teflon syringe filter prior to HPLC analysis.

**Analysis by HPLC and HPLC-MS**

Anthocyanin separation was based on the method of Grace *et al.* (2009) with modifications.

Analysis was performed on a Waters Alliance 2695 HPLC (Waters, Milford, MA) equipped with a photodiode array detector (HP Series 1050). Separation was carried out on a reversed phase Phenomenex Prodigy 5u ODS (3) 100A column, 250 x 4.6mm x 5 micron, with a Phenomenex Prodigy 5u ODS (3) 100A guard column, 30 x 4.6mm x 5 micron. Mobile phases consisted of 5% formic acid aqueous solution (A) and 100% methanol (B). The flow rate was 1ml/min and detection was at 520 nm. The gradient system used was 10%, 15%, 20%, 25%, 30%, 45%, 10%, and 10% of solvent B at 0, 5, 15, 20, 25, 35, 37, and 50 min, respectively. The volume of samples injected was 15 μL.

The HPLC-MS analysis was made with an LCQ Deca XP mass spectrometer (Thermo Finnigan Corp., San Jose, CA), electrospray ionization (ESI) in the positive ion mode (m/z 200-2000) and a photodiode array (PDA) detector (200-600 nm). Separation was carried out on a 150 x 2.1mm x 5 micron C18 reversed-phase column (Vydac, Western Analytical, Murrieta, CA). Mobile phases consisted of 0.1% formic acid in water (A) and 100% methanol (B). A step gradient of 10%, 15%, 20%, 25%, 30%, 60%, 10%, and 10% of solvent B at 0, 5, 15, 20, 25, 45, 47, and 60 min, respectively, a flow rate of 200 μL/min, and an injection volume of 15 μL were employed.

For quantification and identification purposes cyaniding-3-glucoside (C-3-G) and cyaniding-3-rutinoside (C-3-R) were used as external standards. Results were expressed as mg anthocyanin (C-3-G + C-3-R) / g dry weight (DW).

**Oxygen Radical Absorbance Capacity (ORAC)**

**Extraction Procedure**

Extracts were prepared according to the method of Ou *et al.* (2001) with modifications.

For açaí juice, 4.17 g of sample were placed in 125 mL screw cap erlenmeyers. Then, 6.3 mL of water and 10 mL of acetone (resulting in 50:50 acetone/water; v/v) were added and samples were extracted on an orbital shaker (250 rpm) at room temperature for 2 h. Product
was centrifuged at 16300 g for 15 min, at 4°C. Supernatant was diluted (1:200) with phosphate buffer before analysis.

For dried açaí, 0.5 g of powders were placed in 125 mL screw cap erlenmeyers. Samples were extracted with 20 mL of acetone/water (50:50; v/v) on an orbital shaker (250 rpm) at room temperature for 2 h. Product was then centrifuged at 16300 g for 15 min, at 4°C. Supernatant was diluted (1:200) with phosphate buffer before analysis.

**Solutions**
- Phosphate buffer: 0.075 M phosphate buffer, pH = 7.4, was used for all dilutions and as a blank in the assay.
- Fluorescein (FL): A stock fluorescein solution (Stock #1) was prepared by dissolving 0.0188 g FL in 50 mL of phosphate buffer. A second stock solution (Stock #2) was prepared by diluting 516 μL of Stock #1 in 25 mL of phosphate buffer. Then, 141 μL of Stock #2 were diluted in 25 mL of phosphate buffer and 120 μL of this solution was added to each well.
- AAPH: The AAPH solution was prepared by dissolving 0.1085 g AAPH in 10 mL of phosphate buffer. Sixty microliters of that solution were added to each well.
- Trolox standards: A Trolox stock solution (1 mM) was prepared by adding 0.0129 g of Trolox in 50 mL of phosphate buffer. The stock solution was further diluted with phosphate buffer to give the following concentrations: 150, 100, 80, 60, 40 and 20 μM. The Trolox solutions were used as standards to generate the calibration curve.

**Microplate Assay**

For ORAC assay, the method of Dávalos et al. (2004) was used. The assay was carried out in black-walled 96-well plates (Fisher Scientific, Hanover Park, IL). Aliquots of 20 μL of phosphate buffer (blank); either 20 μL of Trolox standards or 20 μL of samples; were added into appropriate wells. Then, 120 μL of fluorescein was added to each well and the plate was incubated at 37°C for 15 min. After incubation, 60 μL of AAPH were added. The plate was read in a fluorescent plate reader, FLx800tbi (Bio-Tek, Winooski, VT) at 37°C, sensitivity 60, excitation 485 nm and emission 582 nm. Readings were done every 2 min for 120 min.

The final ORAC values were calculated by using a regression equation between the Trolox concentrations and the net area under the FL decay curve. Data are expressed as micromoles of Trolox equivalents (TE) per gram dry weight (μmol TE/g DW).
**Flavor Analysis**

Açaí juice

**Internal Standards**
An internal standard solution, containing 2-methyl-3-heptanone and 2-ethylbutyric acid, was prepared at concentration of 1 mg/mL each.

**Sample Preparation**
Açaí juice, 500 g, was first thawed and then placed in a beaker. Under stirring, 5 μL of internal standard solution was added to the product. Juice was then mixed for 2 min and sieved prior to extraction of volatiles.

**Isolation of Volatiles**
Solvent-assisted flavor evaporation (SAFE) was used to isolate the volatile compounds and was based on the procedure of Lozano et al. (2007b), with slight modifications. Over a period of 1h the sample was fed in dropping aliquots into the SAFE system (distillation head at 40°C, sample flask at 40°C and vacuum at less than 1 x 10^-4 Torr). SAFE unit was then kept at 10^-5 Torr for 2 h prior to removal of the product from the system. Product was kept outside for 30 min and then 50 mL of ether was added. Mixture was thawed overnight before extraction.

Extraction was done according to the procedure of Lozano et al. (2007a), with some modifications. First, 2 M NaOH was added to the SAFE extract until pH=9 (approximately 0.5 mL). Product was then transferred to a separatory funnel and 40 g of NaCl were added. The mixture was shaken for 3 min and let stand for 3 min. The ether layer was placed in a 500 mL round-bottom flask and the aqueous layer was extracted two more times with 30 mL of ether, following the same procedure. After that, the aqueous layer was acidified with 4N HCl to a pH=2 (around 0.7 mL). Aqueous layer was extracted three times with 30 mL of ether.

The combined ether layers (in 500 mL round-bottom flask) were concentrated to 30 mL by distillation at 42°C using a Vigreaux column. The concentrate was fractionated into neutral/basic (NB) and acidic (AC) fractions, according to the procedure of Karagül-Yüceer et al. (2003) with modifications. Extract was first washed with sodium carbonate (3 x 20 mL), followed by separation of the ether (NB fraction) and aqueous (AC fraction) layers. The ether layer was washed twice with 10 mL of saturated NaCl and the upper ether phase was collected and concentrated to 10 mL by distillation at 42°C using a Vigreaux column. It was next dried over
anhydrous Na$_2$SO$_4$ and concentrated to 1 mL, again by distillation. Extract containing NB volatiles was transferred to 2 mL vial and concentrated to 200 μL under N$_2$. The aqueous layer was washed twice with 15 mL of ether (which was discarded) and then acidified with 4N HCl saturated with NaCl to pH ~2. Acidic volatiles were extracted with ether (3 x 20 mL). Ether layer was concentrated to 10 mL by distillation at 42°C using a Vigreux column, dried over anhydrous Na$_2$SO$_4$ and concentrated to 1 mL again by distillation. AC extract was transferred to 2 mL vial and concentrated to 200 μL under N$_2$. Both fractions were kept at -70°C until analyses. In order to determine the predominant odorants in açai juice, each of the fractions was diluted sequentially with diethyl ether in a ratio of 1:3 according to the aroma extract dilution analysis technique. Each dilution (1 μL) was later injected in GC-O.

Identification of volatiles

GC-MS and GC-O were used to identify the main volatile compounds of açai juice. GC-MS was performed on an Agilent 6890N GC/5973N mass selective detector (MSD) system. Each extract (1 μL) was injected in the cold on-column injection mode. Two columns with the same dimensions (30 m length x 0.25 mm i.d x 0.25 μm film thickness) but different polarities (Stabilwax and SAC-5) (Restek, Bellefont, PA and Supelco, Bellefont, PA, respectively) were used. The oven was programmed from 35 to 225°C at a rate of 4°C/min with initial and final hold times of 5 and 25 min, respectively. Helium was used as carrier gas at a constant rate of 1.0 mL/min. MSD conditions were as follows: MS transfer line heater, 280 °C; ionization energy, 70 eV; mass range, 33–350 amu; and scan rate, 5 scans/s. For better sensitivity the electron multiplier voltage was 200 V above the autotune setting.

GC-O was conducted on an Agilent 6890 GC (Palo Alto, CA) equipped with an FID and a sniffing port (DATU, Geneva, NY). Two different polarity columns (Stabilwax and RTX-5SILMS) (Restek, Bellefont, PA) with the same dimensions (15 m length x 0.32 mm i.d x 0.5 μm film thickness) were used to obtain odor description and retention indices. Each extract (1 μL) was injected in the cold on-column injection mode. The oven was programmed from 35 to 225°C at a rate of 10°C/min for NB fraction and 6°C/min for AC fraction in Stabilwax column and 6°C/min for both fractions in RTX-5SILMS column. Initial and final hold times were 5 and 25 min, respectively. Helium was used as carrier gas at a constant rate of 1.0 mL/min. Temperature of FID and transfer line were held at 250°C. The end of the capillary column was split 1:5 between the FID and sniffing port.

Compounds were, first, tentatively identified based on comparison with published retention indices and odor quality (Rychlik et al. 1998; Acree et al. 2004). Positive identification
of odorants was based on matching retention indices, odor description (both on two different polarity columns), and mass spectra of unknown compounds with those of authentic standards. An n-alkane series was used for the determination of retention indices.

**Dried Açaí**

Headspace volatiles were extracted and concentrated using SPME headspace sampling. Açaí juice (used as control) and dried samples from day 0 and after 3 months of storage were used for the analysis.

**Sample Preparation**

For açaí juice, 5 mL of samples, 1 g of NaCl and a micro stirring bar were placed into 20 mL screw cap glass vials with PTFE/Silicone-coated septa (SPME vials). For açaí powders, samples were first rehydrated with deodorized water to a final moisture content of 87.86% (same moisture content of juice). Then, 5 mL of samples were added to SPME vials as previously described. An internal standard (IS) solution containing 2-methyl-3-heptanone, was prepared at concentration of 0.0232 mg/mL and 2 μL of IS were added to each vial.

**Headspace sampling**

Headspace sampling was based on the procedure of Mahattanatawee et al. (2007), with modifications. SPME vials were, first, incubated for 15 min at 40°C in a single magnetic mixer, with agitation set to 250 rpm. After that, a SPME fiber (50/30μm DVB/Carboxen/PDMS on a 1cm StableFlex fiber, Supelco, Bellefont, PA) was inserted into the headspace of the sample vial and exposed for 45 min at 40°C. Fiber was, then, thermally desorbed in the GC-MS injector port for 14 min at 260°C (vent after 4 min). The fiber was preconditioned prior to analysis at 270°C for 1 h.

**CG-MS**

GC-MS was performed on an Agilent 6890N GC/5973N mass selective detector (MSD) system equipped with an RTX-Wax (30 m length x 0.25 mm i.d x 0.25 μm film thickness) column (Restek, Bellefont, PA). The oven was programmed from 35 to 225°C at a rate of 4°C/min with initial and final hold times of 5 and 15 min, respectively. Helium was used as carrier gas at a constant flow rate of 1.0 mL/min. MSD conditions were as follows: MS transfer line heater, 280
°C; ionization energy, 70 eV; mass range, 33–350 amu; and scan rate, 5 scans/s. For better sensitivity the electron multiplier voltage was 200 V above the autotune setting.

Compound Quantification

For quantification purposes, standard curves of selected flavor compounds were used. Known amounts of authentic standards plus internal standard were added into a deodorized açai juice matrix and SPME was performed in the same way as described above. The ratios of authentic standards and IS concentrations were: 1:1, 1:10, 1:50 and 1:100. Deodorized juice matrix was achieved by running the product through SAFE twice and collecting the solids left after water evaporation.

Statistical Analysis

Significant differences between treatments were determined using the one-way ANOVA followed by Tukey’s test at \( \alpha = 0.05 \).

Results and Discussion

Moisture Content

The moisture content of the juice was 87.86 ± 0.04%, confirming that the product used was a Type B acai (11-14% solids) (Table 2). The moisture content of the dried products over time is presented in Figure 12. The RW-dried samples presented the highest moisture content (2.19% wb), followed by freeze-dried (1.55% wb) and hot-air dried samples (1.36% wb) (reported moisture content values on day 0). Similar results were obtained during the entire study.

Drying time and air relative humidity are very important in drying operations since they affect the final moisture content of the product (Kaya et al. 2008; Krokida et al. 1998). During RW drying, ambient air is in contact with the product and, therefore, air relative humidity is not
controlled. The higher moisture content of RW-dried açaí may have been caused by insufficient drying time or air with high relative humidity.

Figure 13 shows the effect of storage on the moisture content of açaí powders. The moisture content of all dried products on day 0 was significantly lower than the values obtained for samples after one month of storage. Changes in moisture might have been caused by changes in the material, resulting in more volatiles being produced during vacuum oven measurement. It could also be due to a measurement error on day 0. Water could also have been produced during the first month of storage, resulting in higher moisture content, although this fact is not compatible with the water activity results. Further research is necessary in order to explain why moisture content was significantly lower on day 0.

Figure 12. Effect of different drying methods on moisture content
* Within each segment, bars with different letters are significantly different
Figure 13. Effect of storage on moisture content
* Within each segment, bars with different letters are significantly different

Water Activity

All dried samples exhibited low water activity values, suggesting good product stability. When comparing different treatments (Figure 14) at day 0, the RW-dried açaí showed a significantly higher water activity (~0.240), followed by the freeze-dried (~0.196) and hot-air dried samples (~0.119), respectively. For samples having a relatively high moisture content, the water activity was also higher. The water activity for samples from the three drying methods is thus in the sequence of RW > FD > HAD.

The effect of storage time on water activity is presented in Figure 15. Water activity values, within each individual treatment, did not change over the studied period of time, suggesting that glass is a good packaging material to avoid moisture uptake from the surroundings during storage. Similar results were reported by Mahayothee et al. (2009), working with dried lychees stored in polyethylene film bags, and Yongsawatdigul et al. (1996), working with dehydrated cranberries (packaging material was not described).
Figure 14. Effect of different drying methods on water activity
* Within each segment, bars with different letters are significantly different

Figure 15. Effect of storage on water activity
* Within each segment, bars with different letters are significantly different

Color

For evaluation of color, L, a and b values were measured using a Hunter colorimeter. The values of a and b were used to calculate hue angle and chroma, measurements that are most significantly related to visual color scores than the individual a and b values (Shishehgarha et al. 2002). A comparison of the color readings of açaí juice with those in samples dried by
different methods at day 0 is given in Table 3. The L values increased significantly in all dried samples compared with the juice, with the L for the RW-dried being significantly higher or "lighter" than the hot-air and freeze-dried. The changes in a and b values after drying seemed to follow similar trend. A significant decrease in a and b values can be observed in all the samples. Obviously, the dried açaí had a color totally different from that of the juice.

In the analysis of color, plotting a and b values results in a color wheel, which subtends 360°, with red-purple placed at an angle 0°, yellow at 90°, bluish-green at 180° and blue at 270°, counterclockwise. The hue angle determines in which quadrant the sample will be placed and gives information about the actual hue of the product (McGuire 1992). Drying caused a significant decrease in hue angles for all dried samples (Table 3). However, all the samples were still in the same quadrant (Figure 16) and the changes in the hue angle, and consequently the hue, although significant, were relatively small. The higher hue angle of the juice represents a less redish and, consequently, higher yellowish color, which is probably due to its oily appearance. On the other hand, the lower hue angles of the dried samples stand for a more redish color. A red color reinforcement in dried samples has been attributed to pigment concentration due to water reduction (Hammami et al. 1997). In dried samples, the chroma values, which indicate color saturation or intensity, decreased compared to the açaí juice. A less vivid and less intense color may be expected in the dried products. Overall changes in color due to drying were most likely caused by anthocyanin degradation and formation of brown pigments by enzymatic browning and Maillard reaction.

<table>
<thead>
<tr>
<th></th>
<th>L</th>
<th>a</th>
<th>b</th>
<th>Hue angle</th>
<th>Chroma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juice</td>
<td>12.42c</td>
<td>16.61a</td>
<td>4.94a</td>
<td>0.29a</td>
<td>17.33a</td>
</tr>
<tr>
<td>Freeze-dried</td>
<td>14.56b</td>
<td>4.94c</td>
<td>0.35b</td>
<td>0.075b</td>
<td>4.97c</td>
</tr>
<tr>
<td>Hot-air dried</td>
<td>15.26b</td>
<td>3.66d</td>
<td>0.48b</td>
<td>0.13ab</td>
<td>3.69d</td>
</tr>
<tr>
<td>RW-dried</td>
<td>19.05a</td>
<td>6.44b</td>
<td>0.59b</td>
<td>0.092b</td>
<td>6.47b</td>
</tr>
</tbody>
</table>

* Within each column, bars with different letters are significantly different.
The color changes as affected by different drying methods are presented in Figures 17-19, using lightness, hue angle and chroma. Figure 17 shows the effect of the three drying methods on lightness. No significant difference was observed between freeze and hot-air dried samples. However, the RW-dried samples presented consistently higher L values compared to the other dried products. This higher lightness might have been caused by the açaí oil, which may have coated the surface of the thin layer of product used in this technology, giving it a shiny appearance and the impression of a lighter color. Figure 18 presents the effects of the drying techniques on hue angle. No significant difference in this parameter among the treatments was observed for up to two months of storage. However, on the third month, the hot-air dried samples showed a significantly higher hue angle, which represents a decrease in its red color. When considering chroma (Figure 19), the RW-dried açaí showed the highest chroma value, followed by the freeze and hot-air dried samples. A more saturated color in RW-dried samples might have been influenced by the oil coating, which gives it a more vivid appearance.
Figure 17. Effect of different drying methods on Lightness
* Within each segment, bars with different letters are significantly different

Figure 18. Effect of different drying methods on hue angle
* Within each segment, bars with different letters are significantly different
When considering the color differences within each drying method as a function of storage time, values of the lightness, hue angle, and chroma are plotted against each drying method and are shown in Figures 20-22. For all the drying technologies, lightness decreased during storage, which means that the products were turning darker. This was most likely due to the formation of brown pigments as a result of Maillard reaction and/or polymerization of oxidized phenolic compounds (Perera 2005). At the water activity values of the dried samples, occurrence of chemical reactions was not expected. However, it has been reported that even at low water activities and below glass transition temperature, Maillard reaction can occur (Karmas 1992; Telis et al. 2009). All dried samples presented an increase in hue angle over storage. A significant increase in hue angle indicates a reduction in red color. Storage also caused a significant increase in chroma for all dried samples. The occurrence of non-enzymatic browning reactions may account for part of the changes observed in hue angle and chroma during storage.
Figure 20. Effect of storage on Lightness
* Within each segment, bars with different letters are significantly different

Figure 21. Effect of storage on hue angle
* Within each segment, bars with different letters are significantly different
Moisture Sorption Working Isotherm

Moisture working isotherms of freeze-dried, RW-dried and hot-air dried açai are presented in Figure 23. All the isotherms were sigmoidal in shape, as characteristic of most foods, and presented similar water sorption behavior. The hot-air dried sample exhibited a slightly higher water adsorption capacity than the RW and freeze-dried materials at all $a_w$ values. A type II isotherm was also observed by Maskan et al. (1998) for vacuum dried mulberries and Syamaladevi et al. (2009) for freeze-dried raspberry.

The water sorption data of the dried samples were fitted to the Guggenheim-Anderson-de Boer (GAB) and Brunauer-Emmett-Teller (BET) models. The estimated GAB and BET parameters are presented in Table 4. Both the BET and GAB models showed a good fit to the experimental data, as shown by low root mean square errors (RMSE). The GAB model is an extension of the BET model by introducing the constant $K$. The GAB model can be used to predict the isotherm parameters at a water activity of up to 0.9, whereas BET allows isotherm modeling for $a_w$ up to 0.5. The constants in the GAB equation are temperature dependent. In this experiment the values of $C$ fell between 1 and 20 and $K$ between 0.7 and 1.0, which is in the range of most food products reported in the literature (Rahman 1995).

Both the BET and GAB models are based on the monolayer moisture concept and provide the monolayer moisture content of the product, an important parameter for assuring food stability. As it can be seen from Table 3, the monolayer moisture content values of the

![Figure 22. Effect of storage on chroma](image)

*Within each segment, bars with different letters are significantly different*
three dried açaí samples calculated using the BET model were lower than those obtained from the GAB model, a phenomenon that has been documented in published papers. Timmermann et al. (2001) stated that GAB monolayer moisture content is always higher than BET monolayer.

The moisture content of all dried samples was below their monolayer moisture content value, indicating good product stability over time. Bell et al. (2000) reported that, for most dried foods, the monolayer value is usually at water activity of 0.2-0.4 and, in general, the results of the current project fall between that range (except for hot-air dried samples, which had an average $a_w$ of 0.119). The same authors showed that, for most chemical reactions in aqueous phase, the rate of quality loss begins to increase above $a_w$ 0.2-0.3. Beyond that range, water adsorbed is enough to behave as a solvent, increasing the mobility of the reactants and the rate of degradative reactions. An exception of that is lipid oxidation, for which the rate of reaction increases as the water activity decreases below the monolayer. The occurrence of lipid oxidation will be discussed later.

As previously mentioned, freeze-dried, RW-dried and hot-air dried samples presented a type II isotherm. The monolayer moisture content values obtained for those samples varied from 2.43% to 2.53% according to the BET model and from 2.5% to 2.62% according to the GAB model, depending on the drying method used (Table 4). The monolayer values obtained in this research were lower than the ones previously reported. Tonon et al. (2009) reported a type III isotherm for spray dried açaí at 25°C, probably due to the presence of carrier agents (crystalline molecules). The monolayer moisture content reported by Tonon et al. (2009) varied from 3.1% to 5.8% according to the BET model and from 3.2% to 6.3% when obtained from the GAB model, depending on the carrier agent used. Da Silva et al. (2008) also worked with spray dried açaí and reported a type III isotherm for the product, at all temperatures used (15, 25 and 35°C). The reported monolayer moisture content, according to the BET model, was 7.7% (25°C).
Table 4. Estimated GAB and BET parameters

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Freeze-dried</th>
<th>RW-dried</th>
<th>Hot-air dried</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>7.13</td>
<td>6.82</td>
<td>11.82</td>
</tr>
<tr>
<td>GAB</td>
<td>M₀</td>
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<td></td>
<td>K</td>
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<tr>
<td></td>
<td>RMSE</td>
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<td>0.07</td>
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<td>C</td>
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<td>10.91</td>
</tr>
<tr>
<td>BET</td>
<td>M₀</td>
<td>2.43</td>
<td>2.49</td>
<td>2.53</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
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<td>0.03</td>
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</tr>
</tbody>
</table>

**Anthocyanins**

Cyaniding-3-glucoside (peak 1) and cyaniding-3-rutinoside (peak 2) were found to be the major anthocyanins (ACNs) in all açaí samples, which is in agreement with previous reports of Lichtenthaler et al. (2005), Schauss et al. (2006b), and Vera de Rosso et al. (2008). Of them, cyaniding-3-rutinoside was found to be the predominant ACN, having a concentration of 5 to 30% above the concentration of cyaniding-3-glucoside depending on the drying method. The MS spectral data of these compounds are presented in Table 5 and a typical HPLC
chromatogram for açai juice is shown in Figure 24. HPLC chromatograms for freeze, RW and hot-air dried samples are presented in Figures 32-34 in Appendix A.

Table 5. Identification of anthocyanins

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>(t_R) (min)</th>
<th>MS (m/z)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.4</td>
<td>449</td>
<td>cyanidin-3-glucoside</td>
</tr>
<tr>
<td>2</td>
<td>26.3</td>
<td>595</td>
<td>cyanidin-3-rutinoside</td>
</tr>
</tbody>
</table>

The effect of different drying methods on anthocyanin content (reported as sum of cyanidin-3-glucoside and cyanidin-3-rutinoside) is shown in Figure 25. On day 0, the freeze-dried samples presented an anthocyanin content (5.46 mg/g DW) comparable to that from the açai juice (5.74 mg/g DW), followed by the RW-dried (4.87 mg/g DW) and hot-air dried (2.79 mg/g DW). During storage, the anthocyanin content of freeze dried samples was always significantly higher than that of the RW dried açai, which was significantly higher than that of hot-air dried samples. The anthocyanin concentration of hot-air dried açai was approximately 40-50% lower than that of other açai samples. Freeze drying resulted in the greatest retention of anthocyanins compared to other drying methods, which confirms the superiority of this technique. A better retention of anthocyanins by freeze drying compared to other drying methods was also reported by Nsonzi et al. (1998) for blueberries and Michalczyk et al. (2009)
for raspberry, strawberry and bilberry. Although significantly different, the RW-dried samples showed an anthocyanin content similar to the freeze-dried, indicating that this technique is superior to hot-air drying, with respect to preserving ACNs. Anthocyanins are very unstable and can be easily degraded during hot-air drying due to the use of high temperatures for long time and presence of oxygen (Lohachoompol et al. 2004; Piga et al. 2003).

The contents of anthocyanins found in this study, 5.7 mg/g DW for açai juice and 2.8 to 5.5 mg/g DW for dried samples, are different from previously reported data. For açai juice Vera de Rosso et al. (2008) reported around 3.0 mg/g DW, whereas Pacheco-Palencia et al. (2009) reported approximately 13 mg/g DW. Anthocyanin contents of 0.5 mg/g DW and 3.19 mg/g DW have been reported by Gallori et al. (2004) and Schauss et al. (2006b), respectively, for freeze dried açai. Differences in pigment content are to be expected since the level of anthocyanins is affected by factors like climatic conditions, harvesting period, maturity stage and processing techniques, which, in case of açai juice, normally include a thermal pasteurization. Lichtenthaler et al. (2005) reported anthocyanin contents varying between 13 and 463mg/L for different açai juice samples. In fact, the authors also analyzed the juice of fruits collected from the same trees in different years and noticed that anthocyanin levels ranged from 88 to 211mg/L.

Cyaniding-3-glucoside and cyaniding-3-rutinoside account for more than 95% of the total anthocyanins in açai (Pacheco-Palencia et al. 2009; Schauss et al. 2006b). Interestingly, the content of anthocyanins in this fruit is much lower than that of other berries. For instance, wild
blueberries were reported to have around 487 mg/100g FW (~45 mg/g DW), while blackberries and black raspberries were said to have approximately 245 and 687 mg/100g FW (~19 and 46 mg/g DW, respectively) (Wu et al. 2006).

The effect of storage on anthocyanin content of dried samples is presented in Figure 26. The content of ACNs, within each drying method, did not change over the storage period, indicating good stability of those compounds under the experimental conditions of the project.

It has been reported that water activity plays an important role on anthocyanin degradation (Amr et al. 2007; Garzón et al. 2001). High water contents result in high molecular mobility, which facilitates chemical reactions. According to Erlandson et al. (1972) high water activity values results in either hydrolysis of the glycosidic bond to form aglycones, which are unstable, or opening of the pyrillium ring to form a substituted chalcone. The low water activity values, as well as the low moisture contents of below monolayer values, of the açaí powders used in this study may contribute to a relative good retention of ACNs during storage.

Brønnum-Hansen et al. (1985) evaluated the effect of different water activity values and storage on stability of freeze-dried elderberry anthocyanins. They reported that samples stored at or below the monolayer moisture content showed the highest stability, with essentially no loss of anthocyanins after 1 year of storage.

Tonon et al. (2010) studied the effects of water activity (0.328 and 0.529) and storage temperature (25 and 35°C) on anthocyanin stability of spray dried açaí. A higher temperature and water activity led to faster ACN degradation. Since all samples were stored at $a_w$ values below the critical water activity, degradation was not expected. According to the authors, diffusion of oxygen may have caused anthocyanin degradation.

![Figure 26. Effect of storage on anthocyanin content](image)

*Within each segment, bars with different letters are significantly different*
The antioxidant capacity of açai samples against peroxyl radicals was assessed by ORAC assay. The effect of different drying methods on the antioxidant capacity of açai is shown in Figure 27. On day 0, the freeze-dried samples presented an ORAC value (993.12 μmol TE/g DW) comparable to the açai juice (1125.33 μmol TE/g DW), suggesting that this drying method retained most of the bioactive compounds responsible for the antioxidant properties of açai. The RW-dried samples showed an intermediate antioxidant capacity (710.39 μmol TE/g DW) while hot-air dried samples exhibited the lowest ORAC value (528.35 μmol TE/g DW). The ranking for the ORAC among the three drying methods remained the same over the 3-month storage, with the freeze-dried having the highest while the hot-air dried being with the lowest ORAC values.

Schauss et al. (2006a) studied the antioxidant capacity of freeze-dried açai and reported an ORAC value of 996.9 μmol TE/g DW. In the present research, a similar ORAC value, 993.12 μmol TE/g DW, was obtained for the freeze-dried product on day 0. Different results for the antioxidant capacity of açai juice have been reported in the literature. Pacheco-Palencia et al. (2007) recorded an ORAC value of 54.4 μmol TE/mL juice (~453 μmol TE/g DW), while Del Pozo-Insfran et al. (2004) and Pacheco-Palencia et al. (2009) reported 48.6 μmol TE/mL juice (~405 μmol TE/g DW) and 87.4 μmol TE/g juice (~728 μmol TE/g DW), respectively. In this research, the açai juice was found to have an ORAC value of 1125.3 μmol TE/g DW. The differences in antioxidant capacity of açai might be due to differences in polyphenolic composition, which is affected by geographical and seasonal differences as well as by post-harvest practices and the processing method used.

It has been stated that açai has the highest antioxidant capacity, of any fruit reported to date, against peroxyl radicals (Schauss et al. 2006a). In this research, the açai juice (1125.3 μmol TE/g DW) and freeze-dried açai powders (~838 - 993 μmol TE/g DW) were found to have very high antioxidant capacity, being superior to other berries with high ORAC values, such as fresh lowbush blueberries (92.09 μmol TE/g fruit or ~837 μmol TE/g DW) and cranberries (92.56 μmol TE/g fruit or ~718 μmol TE/g DW) (Wu et al. 2004a). Despite of being lower than the freeze-dried product, RW-dried and hot-air dried açai showed ORAC values higher than other fruits, such as fresh blackberries (52.45 μmol TE/g fruit or ~400 μmol TE/g DW), raspberries (47.65 μmol TE/g fruit or ~336 μmol TE/g DW), and strawberries (35.41 μmol TE/g fruit or ~398 μmol TE/g DW) (Wu et al. 2004a).

The effect of storage on the antioxidant capacity of dried products is presented in Figure 28. For all the three dried samples, no discernable changes in antioxidant capacity were
observed over time. These results agree with our previous discussion that anthocyanin content did not change during storage. Anthocyanins have been identified as important antioxidants in açaí, together with other compounds, some of which are yet to be identified.

Figure 27. Effect of different drying methods on antioxidant capacity
* Within each segment, bars with different letters are significantly different

Figure 28. Effect of storage on antioxidant capacity
* Within each segment, bars with different letters are significantly different
Açaí Juice

Predominant odorants of açaí juice were identified by means of AEDA and are presented in Table 6. Twenty-six neutral/basic and 4 acidic compounds were identified, with flavor dilution (FD) factors ranging from 9 to 2187. All compounds were positively identified by RI, MS and odor.

Esters are important flavor compounds of many fruits and fruit juices. Interestingly, only one ester, ethyl butyrate, was identified in açaí juice. Ethyl butyrate is an important odor-active compound found in many foods, being significant in fruit juices such as orange, apple and strawberry. It is actually described as the most important odorant in orange juice, being responsible for fruity, pineapple notes (Nisperos-Carriedo et al. 1990; Perez-Cacho et al. 2008). Similar to açaí juice, watermelon is another fruit that do not have many esters in its volatile composition (Beaulieu et al. 2006).

The most important flavor compounds identified in açaí juice were (E,Z) 2,6-nonadienal, α-ionone, and 2-phenylethanol and/or β-ionone, with FD factors of 2187. (E,Z) 2,6-nonadienal was most likely derived from lipoxygenase activity on linolenic acid (Tressl et al. 1981). It could also have been produced by autoxidation of methyl linolenate (Ullrich et al. 1988b). This compound is the main volatile in cucumber, being also important in melon and watermelon (Buescher et al. 2001; Perry et al. 2009; Pino et al. 2003). Alfa-ionone, a norisoprenoid, is a product of degradation of carotenoids. Mahattanatawee et al. (2005), working with orange juice, reported that this compound is formed by oxidative cleavage of double bonds in α-carotene and α-cryptoxanthin. This odorant is responsible for a floral note and is an important constituent in other fruits, such as raspberries (Hampel et al. 2007) and blackberries (Qian et al. 2005). 2-phenylethanol and β-ionone were probably co-eluted and it was not possible to identify which compound was the major responsible for the additional floral notes found in açaí juice. Since β-ionone has a much lower threshold compared to 2-phenylethanol, this volatile may be the most important one. 2-phenylethanol is derived from phenylalanine and the pathway for its biosynthesis in plants is not well understood yet (Tieman et al. 2007). The compound is the major aroma volatile in roses (Sakai et al. 2007) and it is also of great importance for the flavor of lychee and apple cider (Ong et al. 1998; Xu et al. 2007). Beta-ionone, like α-ionone, is a norisoprenoid and has been reported as an important volatile in other fruits, such as blackberries and raspberries (Du et al. 2010; Klesk et al. 2004).
Many aldehydes derived from lipid oxidation were identified in the açaí juice. It is well known that the disruption of plant tissues induces lipoxygenase activity, leading to the formation of hydroperoxides. By action of hydroperoxide lyases, hydroperoxides are then converted into volatile aldehydes. Thermal oxidation, autoxidation and photo-oxidation are also responsible for the formation of fatty acid derived aldehydes (Tressl et al. 1981). As previously mentioned, açaí has a high lipid content and, probably, both pathways were responsible for the formation of those compounds in açaí juice. Volatile production most likely occurred during post-harvest, processing (mainly) and storage. Among the aldehydes identified, \((E,Z)\) 2,6-nonadienal (already discussed above), \((E,E,Z)\) 2,4,6-nonatrienal, \((E)\) 2-nonenal, \((E,E)\) 2,4-nonadienal, and \((E,E)\) 2,4-decadial showed the highest FD factors. \((E,E,Z)\) 2,4,6-nonatrienal can be formed by enzymatic degradation and autoxidation of linolenic acid (Schuh et al. 2005); \((E)\) 2-nonenal has been reported as a product of thermal decomposition of hydroperoxides from linoleic and linolenic acids (Lozano et al. 2007a); and \((E,E)\) 2,4-nonadienal and \((E,E)\) 2,4-decadial can be formed by oxidation of linoleic acid (Frankel 1983).

Lipid oxidation-derived aldehydes may be further reduced to alcohols by alcohol dehydrogenases. This may be the mechanism behind the formation of \((Z)\) 3-hexen-1-ol. This volatile has been reported as a product of the metabolism of linolenic acid hydroperoxides by hydroperoxide lyases and alcohol dehydrogenases (Angerosa et al. 1999). \((Z)\) 3-hexen-1-ol is responsible for fresh green and grassy odors. The compound is one of the main contributors to the characteristic odor of green leaves. It has also been detected in elderberry juice and grapes (Fan et al. 2010; Hatanaka 1993; Jensen et al. 2001).

The ketones \(1\)-octen-3-one and \((Z)\) \(1,5\)-octadien-3-one may also have been derived from lipid oxidation, probably of linoleic acid (Tressl et al. 1981). \((Z)\) \(1,5\)-octadien-3-one imparted a plastic, styrene flavor, whereas \(1\)-octen-3-one was characterized as mushroom-like or metallic. These compounds constitute important odorants in mushrooms. \(1\)-octen-3-one has been also identified in lychees and elderberry juice (Mahattanatawee et al. 2007; Jensen et al. 2001).

Some thermally generated volatiles were as well identified. Methional is formed by Strecker degradation reaction involving methionine. The compound is responsible for a potato-like note (Di et al. 2003). Phenylacetaldehyde is a Strecker aldehyde of phenylalanine, with a characteristic floral note (Hofmann et al. 2000). Vanillin (4-hydroxy-3-methoxybenzaldehyde) has been reported to be a thermally induced decomposition product of ferulic acid and contributes with a pleasant vanilla, sweet note (Peleg et al. 1992). Those compounds might have been generated, or had their concentration increased, during pasteurization of the juice.
In addition, two phenolic compounds, guaiacol and isoeugenol, were present in the açaí juice, showing relatively high FD factors. Guaiacol is responsible for smoky, medicinal and/or phenolic notes, and is usually characterized as an off-flavor in fruit juices. The presence of this compound in juices has been related to product spoilage, mainly by *Alicyclobacillus acidoterrestris*. The spores of this microorganism are resistant to pasteurization and can grow over a wide range of temperatures, producing off-flavors (Eisele *et al.* 2005; Perez-Cacho *et al.* 2007). In the case of açaí, spoilage might have occurred in the juice or in the fruit, before processing, since the elevated temperatures and relative humidity of the harvesting/production area may favor microbial growth. On the other hand, isoeugenol provides a pleasant floral scent. The compound is one of the main volatiles of the petunia flower and was also detected in blueberries (Dexter *et al.* 2007; Su *et al.* 2010). Moreover, an unknown compound (no. 4), with high FD factor (729) was detected in açaí juice. This odorant was responsible for green, apple notes.

Several acids were also identified. Acetic acid contributed to vinegar, sour notes, while butanoic and 3-methyl butanoic acids were responsible for cheesy, sweaty notes. Butanoic and 3-methyl butanoic acids are volatile short-chain fatty acids and provide important notes for the characteristic flavor of cheeses (Innocente *et al.* 2000).
Table 6. Odor-active compounds of açaí juice identified by AEDA

<table>
<thead>
<tr>
<th>no.</th>
<th>compound</th>
<th>aroma</th>
<th>Stabilwax</th>
<th>RTX-5</th>
<th>FD factor</th>
<th>fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,3-butanedione</td>
<td>buttery</td>
<td>969</td>
<td>&lt;700</td>
<td>9</td>
<td>NB</td>
</tr>
<tr>
<td>2</td>
<td>ethyl butyrate</td>
<td>fruity, bubble gum</td>
<td>1036</td>
<td>801</td>
<td>27</td>
<td>NB</td>
</tr>
<tr>
<td>3</td>
<td>hexanal</td>
<td>green, cut-leaf</td>
<td>1078</td>
<td>796</td>
<td>27</td>
<td>NB</td>
</tr>
<tr>
<td>4</td>
<td>unknown</td>
<td>green, apple</td>
<td>1135</td>
<td>—</td>
<td>729</td>
<td>NB</td>
</tr>
<tr>
<td>5</td>
<td>octanal</td>
<td>orange, pungent, citrus</td>
<td>1287</td>
<td>1003</td>
<td>9</td>
<td>NB</td>
</tr>
<tr>
<td>6</td>
<td>1-octen-3-one</td>
<td>mushroom, metallic</td>
<td>1295</td>
<td>976</td>
<td>243</td>
<td>NB</td>
</tr>
<tr>
<td>7</td>
<td>unknown</td>
<td>green, floral</td>
<td>1348</td>
<td>—</td>
<td>9</td>
<td>NB</td>
</tr>
<tr>
<td>8</td>
<td>(Z)1,5-octadien-3-one</td>
<td>plastic, styrene</td>
<td>1367</td>
<td>981</td>
<td>27</td>
<td>NB</td>
</tr>
<tr>
<td>9</td>
<td>(Z) 3-hexen-1-ol</td>
<td>green leaf</td>
<td>1381</td>
<td>859</td>
<td>729</td>
<td>NB</td>
</tr>
<tr>
<td>10</td>
<td>acetic acid</td>
<td>vinegar</td>
<td>1429</td>
<td>&lt;700</td>
<td>27</td>
<td>AC</td>
</tr>
<tr>
<td>11</td>
<td>methional</td>
<td>potato</td>
<td>1443</td>
<td>906</td>
<td>27</td>
<td>NB</td>
</tr>
<tr>
<td>12</td>
<td>(Z) 2-nonenal</td>
<td>hay, stale</td>
<td>1495</td>
<td>1147</td>
<td>27</td>
<td>NB</td>
</tr>
<tr>
<td>13</td>
<td>(E) 2-nonenal</td>
<td>hay, stale</td>
<td>1524</td>
<td>1160</td>
<td>729</td>
<td>NB</td>
</tr>
<tr>
<td>14</td>
<td>(E,Z) 2,6-nonadienal</td>
<td>fatty, cucumber</td>
<td>1574</td>
<td>1152</td>
<td>2187</td>
<td>NB</td>
</tr>
<tr>
<td>15</td>
<td>butanoic acid</td>
<td>cheesy, fecal</td>
<td>1615</td>
<td>820</td>
<td>27</td>
<td>AC</td>
</tr>
<tr>
<td>16</td>
<td>phenylacetaldehyde</td>
<td>rosy, floral</td>
<td>1626</td>
<td>1045</td>
<td>27</td>
<td>NB</td>
</tr>
<tr>
<td>17</td>
<td>3-methyl butanoic acid</td>
<td>cheesy, sweaty</td>
<td>1652</td>
<td>862</td>
<td>27</td>
<td>AC</td>
</tr>
<tr>
<td>18</td>
<td>(E,E) 2,4-nonadienal</td>
<td>fatty, fried</td>
<td>1687</td>
<td>1217</td>
<td>243</td>
<td>NB</td>
</tr>
<tr>
<td>19</td>
<td>unknown</td>
<td>stale, hay, fatty</td>
<td>1715</td>
<td>—</td>
<td>27</td>
<td>NB</td>
</tr>
<tr>
<td>20</td>
<td>(E,Z) 2,4-decadien</td>
<td>cucumber, fatty</td>
<td>1756</td>
<td>1291</td>
<td>27</td>
<td>NB</td>
</tr>
<tr>
<td>21</td>
<td>(E,E) 2,4-decadien</td>
<td>fried, fatty</td>
<td>1796</td>
<td>1320</td>
<td>243</td>
<td>NB</td>
</tr>
<tr>
<td>22</td>
<td>β-damascenone</td>
<td>apple sauce, honey</td>
<td>1807</td>
<td>1380</td>
<td>9</td>
<td>NB</td>
</tr>
<tr>
<td>23</td>
<td>α-ionone</td>
<td>floral, wine-like</td>
<td>1835</td>
<td>—</td>
<td>2187</td>
<td>NB</td>
</tr>
<tr>
<td>24</td>
<td>2-methoxy phenol (guaiacol)</td>
<td>smoky, hospital</td>
<td>1841</td>
<td>1087</td>
<td>243</td>
<td>NB/AC</td>
</tr>
<tr>
<td>25</td>
<td>(E,E,Z) 2,4,6-nonatrienal</td>
<td>oats, fatty</td>
<td>1858</td>
<td>1238</td>
<td>729</td>
<td>NB</td>
</tr>
<tr>
<td>26</td>
<td>2-phenylethanol</td>
<td>rosy, wine-like</td>
<td>1892</td>
<td>1115</td>
<td>2187 *</td>
<td>NB</td>
</tr>
<tr>
<td>27</td>
<td>β-ionone</td>
<td>rosy</td>
<td>1901</td>
<td>—</td>
<td>2187</td>
<td>NB</td>
</tr>
<tr>
<td>28</td>
<td>eugenol</td>
<td>cloves, cinnamon</td>
<td>2146</td>
<td>1359</td>
<td>81</td>
<td>NB</td>
</tr>
<tr>
<td>29</td>
<td>isoeugenol</td>
<td>cloves</td>
<td>2319</td>
<td>1455</td>
<td>729</td>
<td>NB</td>
</tr>
<tr>
<td>30</td>
<td>vanillin</td>
<td>vanilla</td>
<td>2531</td>
<td>1421</td>
<td>27</td>
<td>AC</td>
</tr>
</tbody>
</table>

All compounds identified by RI, MS and odor
* Compounds were co-eluted

Dried Açaí

To evaluate the effect of drying and storage on the flavor of açaí the SPME technique was employed and three groups of odor-active compounds were selected for analysis. 2-methyl butanal, 3-methyl butanal, benzaldehyde and phenylacetaldehyde were chosen as indicators of Maillard reaction; pentanal, hexanal, heptanal, (E) 2-hexenal, (E,E) 2,4-heptadienal and (E,E) 2,4-decadienal were used as indicators of lipid oxidation; and 2-phenylethanol, (Z) 3-hexen-1-ol and octanal were selected as characteristic flavor compounds identified in açaí juice by AEDA (named as “target compounds”).

Table 7 presents the concentration of the analyzed volatile compounds in each product on day 0. It can be seen that dehydration changed the flavor of the açaí juice. In general, the
concentration of Strecker aldehydes was higher in dried samples, indicating the occurrence of Maillard reaction during drying. The majority of lipid oxidation compounds also had their concentration increased with drying. This was expected since açaí juice is rich in lipids and the application of heat during processing would most likely induce lipid oxidation and the release of volatile aldehydes. All the Maillard reaction indicators and three indicators of lipid oxidation were detected in açaí juice. These compounds might be either originally present in açaí, being characteristic of the fruit flavor, or might have been produced during juice pasteurization and storage. Lower concentrations of (Z) 3-hexen-1-ol were found in dried products, suggesting that this volatile was lost during drying. It has been reported that the small size of the molecule and its polarity are factors that cause C6 alcohols to evaporate together with water (De Torres et al. 2010). The concentration of octanal did not change due to processing whereas 2-phenylethanol presented contradictory results (significantly higher in freeze-dried samples, lower in RW-dried samples and equal to açaí juice for hot-air dried samples).

Table 7. Concentration of volatile compounds in açaí juice and powders on day 0 (expressed in μg/L)

<table>
<thead>
<tr>
<th></th>
<th>Juice</th>
<th>FD</th>
<th>RW</th>
<th>HAD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strecker Aldehydes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methyl butanal</td>
<td>85 ± 18 b</td>
<td>212 ± 66 a</td>
<td>91 ± 27 b</td>
<td>175 ± 36 ab</td>
</tr>
<tr>
<td>3-methyl butanal</td>
<td>147 ± 32 b</td>
<td>278 ± 65 ab</td>
<td>234 ± 66 ab</td>
<td>404 ± 94 a</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>23 ± 4 bc</td>
<td>133 ± 18 a</td>
<td>14 ± 3.4 c</td>
<td>43 ± 11 b</td>
</tr>
<tr>
<td>phenylacetaldehyde</td>
<td>235 ± 123 bc</td>
<td>456 ± 77 ab</td>
<td>119 ± 35 c</td>
<td>669 ± 155 a</td>
</tr>
<tr>
<td><strong>Lipid Oxidation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pentanal</td>
<td>233 ± 93 a</td>
<td>200 ± 67 ab</td>
<td>49 ± 5 c</td>
<td>55 ± 12 bc</td>
</tr>
<tr>
<td>hexanal</td>
<td>3.4 ± 1.4 b</td>
<td>7.3 ± 0.5 a</td>
<td>2.8 ± 0.8 b</td>
<td>9.8 ± 2.2 a</td>
</tr>
<tr>
<td>(E) 2-hexenal</td>
<td>118 ± 48 a</td>
<td>95 ± 14 a</td>
<td>52 ± 5.5 ab</td>
<td>24 ± 11 b</td>
</tr>
<tr>
<td>(E,E) 2,4-heptadienal</td>
<td>0 b</td>
<td>50 ± 7.3 a</td>
<td>4.7 ± 0.4 b</td>
<td>6.4 ± 1 b</td>
</tr>
<tr>
<td>(E,E) 2,4-decadienal</td>
<td>0 b</td>
<td>161 ± 29 a</td>
<td>0 b</td>
<td>0 b</td>
</tr>
<tr>
<td><strong>Target compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>octanal</td>
<td>3.9 ± 1.1 a</td>
<td>5.6 ± 1.4 a</td>
<td>4.5 ± 0.6 a</td>
<td>5.4 ± 2.8 a</td>
</tr>
<tr>
<td>(Z) 3-hexen-1-ol</td>
<td>1172 ± 373 a</td>
<td>106 ± 18 b</td>
<td>22 ± 5.8 b</td>
<td>43 ± 15 b</td>
</tr>
<tr>
<td>2-phenylethanol</td>
<td>276 ± 81 b</td>
<td>613 ± 145 a</td>
<td>41 ± 8.7 c</td>
<td>158 ± 35 bc</td>
</tr>
</tbody>
</table>

* Within each row, bars with different letters are significantly different

Comparison among the three dried products on day 0 revealed that, in general, RW and hot-air dried samples had a lower volatile concentration compared to freeze-dried samples. This may not mean that RW and hot-air drying resulted in less Maillard reaction and/or lipid
oxidation. As previously described, both techniques expose the product to oxygen and relatively high temperatures. In case of hot-air drying, the exposure occurs during a long time. Therefore, the lower concentration of odorants might have been caused by evaporation / loss of volatiles.

The volatile composition of each dried product was monitored during storage and results are presented in Table 8. All dried samples showed a significant increase in the concentration of lipid oxidation-derived compounds after 3 months of storage. These results indicate that lipid oxidation was, probably, the most important reaction that took place in açai powders. It is well known that oxidation rate at low water activity, which is the case of dried açai samples, is high, because no enough water is available to reduce free radical concentration (Angelo 1992).

Storage of dried samples also resulted in an increase in the concentration of all Strecker aldehydes, suggesting the occurrence of Maillard reaction. However, this increase in volatile concentration was significant only for RW-dried products. RW-dried açai showed the highest water activity values. This may help explain the higher extent of Maillard reaction in those samples. With respect to the target compounds, in general, the concentration of (Z) 3-hexen-1-ol and 2-phenylethanol did not change during storage. However, the concentration of octanal was significantly higher after 3 months. Octanal is also a lipid oxidation derivative, which might explain the increase in its concentration during storage.

Table 8. Concentration of volatile compounds in freeze, RW and hot-air dried açai on day 0 and after 3 months of storage (expressed in μg/L)

<table>
<thead>
<tr>
<th></th>
<th>FD day 0</th>
<th></th>
<th>3M</th>
<th></th>
<th>FD day 0</th>
<th></th>
<th>3M</th>
<th></th>
<th>FD day 0</th>
<th></th>
<th>3M</th>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>Strecker Aldehydes</strong></td>
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<tr>
<td>2-methyl butanal</td>
<td>212 ± 66 a</td>
<td>247 ± 95 a</td>
<td></td>
<td>91 ± 27 b</td>
<td>221 ± 47 a</td>
<td></td>
<td>175 ± 36 a</td>
<td>241 ± 56 a</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>3-methyl butanal</td>
<td>278 ± 65 a</td>
<td>468 ± 206 a</td>
<td></td>
<td>234 ± 66 b</td>
<td>561 ± 103 a</td>
<td></td>
<td>404 ± 94 a</td>
<td>552 ± 108 a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>133 ± 18 a</td>
<td>206 ± 78 a</td>
<td></td>
<td>14 ± 3.4 b</td>
<td>82 ± 25 a</td>
<td></td>
<td>43 ± 11 a</td>
<td>73 ± 15 a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenylacetaldehyde</td>
<td>456 ± 77 a</td>
<td>592 ± 236 a</td>
<td></td>
<td>119 ± 35 b</td>
<td>461 ± 105 a</td>
<td></td>
<td>669 ± 155 a</td>
<td>719 ± 77 a</td>
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<tr>
<td><strong>Lipid Oxidation</strong></td>
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<tr>
<td>pentanal</td>
<td>126 ± 8.3 b</td>
<td>466 ± 170 a</td>
<td></td>
<td>204 ± 99 a</td>
<td>335 ± 39 a</td>
<td></td>
<td>151 ± 105 b</td>
<td>510 ± 130 a</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>hexanal</td>
<td>200 ± 67 b</td>
<td>1363 ± 516 a</td>
<td></td>
<td>49 ± 5 b</td>
<td>522 ± 82 a</td>
<td></td>
<td>55 ± 12 b</td>
<td>912 ± 194 a</td>
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<tr>
<td>heptanal</td>
<td>7.3 ± 0.5 b</td>
<td>37 ± 11 a</td>
<td></td>
<td>2.8 ± 0.8 b</td>
<td>12 ± 1.4 a</td>
<td></td>
<td>9.8 ± 2.2 b</td>
<td>17 ± 4 a</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(E) 2-hexenal</td>
<td>95 ± 14 a</td>
<td>108 ± 40 a</td>
<td></td>
<td>52 ± 5.5 b</td>
<td>110 ± 18 a</td>
<td></td>
<td>24 ± 11 b</td>
<td>60 ± 10 a</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(E,E) 2,4-heptadienal</td>
<td>50 ± 7.3 b</td>
<td>135 ± 41 a</td>
<td></td>
<td>4.7 ± 0.4 b</td>
<td>83 ± 17 a</td>
<td></td>
<td>6.4 ± 1 b</td>
<td>96 ± 20 a</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(E,E) 2,4-decadinal</td>
<td>161 ± 29 b</td>
<td>212 ± 14 a</td>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
<td>0</td>
<td>0</td>
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<tr>
<td><strong>Target compounds</strong></td>
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<tr>
<td>octanal</td>
<td>5.6 ± 1.4 b</td>
<td>52 ± 21 a</td>
<td></td>
<td>4.5 ± 0.6 b</td>
<td>11 ± 1.4 a</td>
<td></td>
<td>5.4 ± 2.8 b</td>
<td>16 ± 4.2 a</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(Z) 3-hexen-1-ol</td>
<td>106 ± 18 a</td>
<td>112 ± 32 a</td>
<td></td>
<td>22 ± 5.8 a</td>
<td>29 ± 4.7 a</td>
<td></td>
<td>43 ± 15 a</td>
<td>51 ± 5.1 a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-phenylethanol</td>
<td>613 ± 145 a</td>
<td>771 ± 285 a</td>
<td></td>
<td>41 ± 8.7 b</td>
<td>76 ± 11 a</td>
<td></td>
<td>158 ± 35 a</td>
<td>145 ± 7.5 a</td>
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</tbody>
</table>

* Within each segment, bars with different letters are significantly different
At the end of storage, the concentrations of the selected flavor compounds in all dried samples were compared (Table 9). In general, all açaí powders showed similar concentration of Strecker aldehydes. Freeze-dried samples showed significantly higher concentration of three lipid oxidation indicators (hexanal, heptanal and \((E,E)\) 2,4-decadienal) and all target compounds. Additional research is necessary in order to better understand the occurrence of Maillard and lipid oxidation during storage. Also a consumer test should be performed to find out consumer preferences. Some of the results reported for flavor could as well be due to matrix effects.

Table 9. Concentration of volatile compounds in açaí powders after a 3-month storage (expressed in μg/L).

<table>
<thead>
<tr>
<th></th>
<th>FD</th>
<th>RW</th>
<th>HAD</th>
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<tbody>
<tr>
<td><strong>Strecker Aldehydes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>2-methyl butanal</td>
<td>247 ± 95 a</td>
<td>221 ± 47 a</td>
<td>241 ± 56 a</td>
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<td>3-methyl butanal</td>
<td>468 ± 206 a</td>
<td>561 ± 103 a</td>
<td>552 ± 108 a</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>206 ± 78 a</td>
<td>82 ± 25 b</td>
<td>73 ± 15 b</td>
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<tr>
<td>phenylacetaldehyde</td>
<td>592 ± 236 a</td>
<td>461 ± 105 a</td>
<td>719 ± 77 a</td>
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<tr>
<td><strong>Lipid Oxidation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pentanal</td>
<td>466 ± 170 a</td>
<td>335 ± 39 a</td>
<td>510 ± 130 a</td>
</tr>
<tr>
<td>hexanal</td>
<td>1363 ± 516 a</td>
<td>522 ± 82 b</td>
<td>912 ± 194 ab</td>
</tr>
<tr>
<td>heptanal</td>
<td>37 ± 11 a</td>
<td>12 ± 1.4 b</td>
<td>17 ± 4 b</td>
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<td>((E)) 2-hexenal</td>
<td>108 ± 40 a</td>
<td>110 ± 18 a</td>
<td>60 ± 10 a</td>
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<tr>
<td>((E,E)) 2,4-heptadienal</td>
<td>135 ± 41 a</td>
<td>83 ± 17 a</td>
<td>96 ± 20 a</td>
</tr>
<tr>
<td>((E,E)) 2,4-decadienal</td>
<td>212 ± 14 a</td>
<td>0 b</td>
<td>0 b</td>
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<tr>
<td><strong>Target compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>octanal</td>
<td>52 ± 21 a</td>
<td>11 ± 1.4 b</td>
<td>16 ± 4.2 b</td>
</tr>
<tr>
<td>((Z)) 3-hexen-1-ol</td>
<td>112 ± 32 a</td>
<td>29 ± 4.7 b</td>
<td>51 ± 5.1 b</td>
</tr>
<tr>
<td>2-phenylethanol</td>
<td>771 ± 285 a</td>
<td>76 ± 11 b</td>
<td>145 ± 7.5 b</td>
</tr>
</tbody>
</table>

* Within each row, bars with different letters are significantly different

**Glass Transition Temperature (T_g)**

Knowledge of glass transition temperature is important because this parameter has been related to food stability. Glass transition of amorphous food systems has been found to cause structural and textural changes, which increases molecular mobility and decreases product stability. In general, amorphous foods are more stable in the glassy state, in which mobility and, therefore, degradative reactions are limited (Slade et al. 1991).
In this project, the glass transition temperature was studied using differential scanning calorimetry (DSC). A typical DSC thermogram is presented in Figure 29 for the freeze-dried sample. Thermograms for RW-dried and hot-air dried samples can be found in Figures 35 and 38 (Appendix B). Similar curves were obtained for all dried samples. All DSC thermograms showed three major endothermic peaks: the first one between -5 and -3°C, the second between 10 and 12°C and the third between 150 and 200°C. The last endothermic peak was probably due to sample decomposition. We hypothesized that the first two endothermic peaks were caused by melting of lipids. There seemed to be glass transition between 50 and 60°C.

![DSC thermogram for freeze-dried açaí](image)

**Figure 29.** DSC thermogram for freeze-dried açaí

In order to confirm our hypothesis and due to the uncertainty of finding the product's glass transition temperature, samples were subjected to an oil extraction and then both the oil and solids fractions were used for a second DSC analysis. Figure 30 shows the thermogram for the oil of freeze-dried açaí. Thermograms for the oil of RW-dried and hot-air dried açaí are shown in Figures 36 and 39, respectively (Appendix B). Once again, the curves for the oil of all dried samples were similar. Interestingly, the thermograms for the oil fractions were
characterized by the same first two endothermic peaks found in the dried samples, validating our hypothesis.

Figure 30. DSC thermogram for freeze-dried açaí oil

Since the lipids present in dried açaí melt into two endothermic peaks at relatively low temperatures, it is possible to conclude that they are liquid at room temperature. Being liquid gives them higher mobility to participate in degradative reactions, such as lipid oxidation. This agrees with the results discussed previously for flavor, which indicated the occurrence of lipid oxidation during storage of açaí powders. For higher stability against this reaction, addition of carrier agents, such as maltodextrin, prior to drying would be very important. Those compounds would form a “more glassy” matrix, encapsulating the oil and protecting it from degradation.

Schauss et al. (2006b) studied the fatty acid composition of freeze-dried açaí and found that the predominant fatty acid was oleic acid (56.2%), followed by palmitic acid (24.1%) and linoleic acid (12.5%). The melting points of those individual fatty acids are around 13°C, 63°C and -5°C, respectively. The same authors reported that ~74% of the total fatty acids present in freeze-dried açaí is composed by unsaturated fatty acids. This helps explain the low melting temperature of the endotherms.
Fatty acids are, probably, present in açaí powders in the form of triacylglycerol (TAG). TAG polymorphism may have influenced the shape and position of the melting peaks. In most thermograms, for both the whole sample (Figures 29, 35 and 38) and the oil (Figures 30, 36 and 39), it is possible to notice that if a line is drawn between the baseline of the first melting peak and the baseline of the second melting peak, an exothermic peak appears between the two endothermic peaks. This might be due to TAG conversion to a more stable stable polymorph via recrystallization (exothermic peak). These more stable polymorphs will later melt together with other forms to give the second endothermic peak. Different TAG composition, due to different drying methods (Gutiérrez et al. 2008), and TAG polymorphs may result in slightly different melting temperatures and bigger or smaller exothermic peaks. It would be interesting to further investigate the lipid fraction of açaí powders in order to better describe their melting behavior.

In preliminary studies, crimped pans were used in DSC analysis. Comparing the thermograms obtained when using crimped pans with those obtained when using hermetically sealed pans revealed the same first two endothermic peaks. However, since crimped pans permit moisture evaporation, an evaporation peak was found and no decomposition peak was observed up to 250°C. When using hermetically sealed pans, the decomposition peak was present between 150 and 200°C. This indicates that the presence of water allows decomposition to begin at lower temperatures.

Figure 31 shows the thermogram for freeze-dried açaí solids. Thermograms for RW and hot-air dried solids are presented in Figures 37 and 40 (Appendix B). Interestingly, the thermograms for the solid fractions showed a very subtle step change in the heat flow between 50 and 60°C, which may indicate the occurrence of a glass transition around that temperature. This step change can be more easily visualized in the thermogram of RW-dried solids. The magnitude of change in heat capacity is proportional to the amount of amorphous material undergoing glass transition. The subtle step change observed in the thermograms might be due to the small amount of amorphous material in the samples undergoing glass transition. In addition, due to the complexity of food products, it is usually difficult to determine their $T_g$. Glass transition usually occurs over a range of temperatures. Further studies are required in order to better identify the $T_g$ of the product.
Figure 31. DSC thermogram for freeze-dried açaí solids

References


Grosch, W. and Schwarz, J.M. 1971. Linoleic and linolenic acid as precursors of the cucumber flavor. Lipids. 6, 351-352.


Qian, M.C. and Wang, Y. 2005. Seasonal variation of volatile composition and odor activity value of 'Marion' (Rubus spp. hyb) and 'Thornless Evergreen' (R. lacinatus L.) blackberries. J. Food Sci. 70, 13-20.


Ullrich, F. and Grosch, W. 1988b. Identification of the most intense odor compounds formed during autoxidation of methyl linolenate at room temperature. J. Am. Oil Chem. Soc. 65, 1313-1317.


Chapter 4: 
Conclusions

This project evaluated the impact of three different drying methods (freeze drying, RW drying, and hot-air drying) and subsequent storage on the quality of açaí. To accomplish the objective, anthocyanin content, antioxidant capacity, moisture content, water activity, moisture sorption isotherm, glass transition temperature, flavor and color were analyzed.

All three methods produced dried samples with low moisture contents, in the range of monolayer values, thus having a low water activity and relatively good product stability during storage. The dried powders showed a sigmoidal shape isotherm, with hot-air dried açaí sorbing slightly more water than the other samples at all $a_w$ values. The GAB and BET models both produced a good fit to the isotherm data.

DSC analysis showed a very subtle step change in heat flow for the solid fraction of all dried samples, suggesting the occurrence of a glass transition for the oil-free solid between 50 and 60°C. Thermograms for the oil fractions revealed that the lipids present in açaí powders are liquid at room temperature, which will increase their mobility, making them more prone to degradative reactions, such as lipid oxidation.

Drying definitely affected the color of açaí. All dried samples exhibited higher lightness and lower hue angle and chroma compared to açaí juice. Comparison among the treatments revealed that RW-dried açaí had the highest lightness and chroma values. In general, no significant difference was observed for hue angle. The color of the RW-dried samples was probably influenced by the açaí oil, which made comparison with other dried samples difficult. Color changes during storage were marked by a decrease in lightness and an increase in hue angle and chroma for all dried samples. The color changes during storage might have been caused by the formation of brown pigments due to Maillard reaction and/or polymerization of oxidized phenolic compounds. A consumer test would have to be performed in order to determine which dried sample has the most representative color of açaí.

Analysis of the flavor of açaí juice identified ($E,Z$) 2,6-nonadienal, $\alpha$-ionone and $\beta$-ionone and/or 2-phenylethanol as the most important odorants. A number of thermally generated compounds and aldehydes derived from lipid oxidation were also identified. These compounds may either be characteristic of the fruit or might have been formed during thermal pasteurization, drying, and storage. The effects of drying and storage on the flavor of acaí were also remarkable. The concentrations of Strecker aldehydes and lipid oxidation compounds in dried samples were higher in dried powders compared to that in açaí juice, indicating the
occurrence of Maillard reaction and lipid oxidation during drying. In general, RW and hot-air dried samples showed a lower concentration of Strecker aldehydes and lipid oxidation compounds compared to freeze-dried açaí. It is possible that loss of volatiles occurred during RW and hot-air drying, resulting in lower concentrations of those odorants. During storage, all dried samples showed an increase in lipid oxidation compounds, indicating the occurrence of that reaction. Significant increase in Maillard reaction products was observed only in RW-dried samples. At the end of the storage period, all three dried powders showed similar volatile concentration. It would be important to perform a consumer test in order to verify which dried sample has the most representative flavor of açaí juice and to find out if consumers can perceive the changes that occurred during storage.

The anthocyanin concentrations in the freeze-dried açaí were comparable to those in the açaí juice, suggesting that this drying method preserved most of the pigments. The RW-dried açaí showed intermediate anthocyanin content whereas hot-air dried samples recorded the lowest pigment concentration. During storage, anthocyanin content did not change within each treatment.

For antioxidant capacity, the highest ORAC value (993.12 μmol TE/g DW) was obtained in the freeze-dried samples, being again comparable to açaí juice. The RW-dried açaí had a medium ORAC value while the hot-air dried samples presented the lowest antioxidant capacity. The ranking for antioxidant capacity is in the same sequence as that for the anthocyanin content (FD>RW>HAD), indicating that freeze drying preserved the majority of the bioactive compounds present in açaí. All dried samples maintained their antioxidant capacity during storage.

In general, the results presented in this work indicate that the freeze-dried açaí retained the antioxidant properties of the raw material to a higher degree compared to other dried powders. Therefore, lyophilisates can probably satisfy the need for a more shelf stable product with a better retention of bioactive compounds. The RW-dried samples showed superior quality compared to the hot-air dried samples. Moreover, an economic analysis taking into consideration of capital investment or operation costs of each drying method is needed when doing drying method selection for açaí preservation.
Appendix A: HPLC Chromatograms

Figure 32. HPLC chromatogram for freeze dried açaí on day 0
Figure 33. HPLC chromatogram for RW-dried açaí on day 0
Figure 34. HPLC chromatogram for hot-air dried açaí on day 0
Figure 35. DSC thermogram for RW-dried açaí
Figure 36. DSC thermogram for RW-dried açaí oil
Figure 37. DSC thermogram for RW-dried açaí solids
Figure 38. DSC thermogram for hot-air dried açai
Figure 39. DSC thermogram for hot-air dried açaí oil
Figure 40. DSC thermogram for hot-air dried açaí solids