Physicochemical Properties of Anthocyanin Extract of Rose Apple (Syzygium malaccensis, (L.) Merryl & Perry) Peel Powder

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Abstract-- Extract of red rose apple (Syzygium malaccensis, (L.) Merryl & Perry) peel was subjected to microencapsulation by spray drying, varying the maltodextrin concentration (5-17.5%) and air inlet temperature (169-205 °C). The quadratic model was not significant for yield, moisture, water activity, wettability, solubility, apparent density, volumetric diameter of 50% of D12 particles, and L and b color parameters, with the mean values for these properties being 63.83% 6.32%, 0.24, 99.49 g/100g, 0.27 g ml−1, 470.71 µm, 68.36 and 10.13, respectively. The model was significant for color and anthocyanins, which exhibited a mean value of 18.90 and 27.92 mg/100g. The maximum concentration of anthocyanin pigments was very low (30 mg/100g), indicating that the conditions used in this study were not adequate for increasing encapsulation efficiency, and the temperature of 190°C and 10% maltodextrin concentration resulted in lowest pigments losses and greatest red color retention.

Index Term-- anthocyanin, rose apple, food quality, fruit, spray drying

INTRODUCTION

Red rose apple (Syzygium malaccensis, (L.) Merryl & Perry) is used for producing jams, jellies and preserves, and its peel, representing 8% of the process, is a source of anthocyanins (300 mg /100g ) (Augusta et al., 2010). Its dehydrated extract serves as a coloring agent, antioxidant and anti-carcinogenic, as has already been documented in the literature for different sources of anthocyanin (Cai and Corke, 2000; Youdim et al.,2000; Hagiwara et al., 2001, Idham et al. 2012).

These pigments may have a greater shelf life when dehydrated, and one of the most efficient and economical methods in dehydration of coloring agents has been encapsulation by spray drying. This method is widely used in food powders due to low temperature and short exposure time and has been applied to high value-added products such as colorings, flavoring agents, and sources of carotenoids, among others (Tonon et al., 2008; Moreira et al., 2009: Souza et al., 2009; Souza et al., 2011; Sensone et al., 2011; Idham et al., 2012; Botrel et al., 2012).

Spray drying is a complex process in which many variables affect the physicochemical properties of the resulting products, and, among them, inlet air temperature and the feed concentration of additives used to improve the performance of this process. The drying inlet air temperature is related to many physical and chemical properties of the product, such as final moisture content, rehydration characteristics (solubility, density, wettability), degradation of the encapsulated substance, colour and morphological properties (Souza et al., 2009; Abadio et al., 2004; Tonon et al., 2009.). The type and concentration of the additive is related to the vitreous transition temperature of the product, increasing it and allowing drying at higher temperatures, avoiding adherence to the walls of the equipment and increasing the yield and indirectly affecting the physical and chemical properties of the reconstituted product. (Tonon et al.,2008; Tonon et al.,2011; Ersus and Yurdagel, 2006, Dibi Táxi et al., 2000).

With a view toward increasing the added value of the subproducts of rose apple processing, the aim of this study was develop a methodology for producing the extract dried by spray drying and verify the effect of drying inlet air temperature and maltodextrin concentration on the physicochemical properties of the extract of rose apple peel.

MATERIALS AND METHODS

Materials

Red rose apples (Syzygium malaccensis, (L.) Merryl & Perry) produced in state of Rio de Janeiro, Brazil, in the period of April and May (2007 to 2011) were used. The fruit was collected manually at the mature stage, taking the coloring of the intense red peel and the sensory characteristics at maturity (taste and aroma) into consideration. It was placed in plastic containers to avoid mechanical injuries and was transported to the food technology laboratory. The fruit was selected, washed in running water, sanitized with chlorinated water (200 mg L−1 of chlorine) for 10 minutes, rinsed and dried at ambient temperature, and the peel was removed and placed in 0.08 mm thick polyethylene bags (27 × 29 cm) and stored in a freezer at -18°C until preparation of the extract and
drying. Fig. 1 shows the block diagram of the experimental procedure.

One hundred grams of the fruit were homogenized in an Arno blender (Arno, São Paulo, Brazil) with 200 mL of solvent (ethanol acidified with 1.5 M HCL) and left for 16 hours at a temperature of 5 °C. It was then filtered in porosity sintered glass filter (number 2). For removal of the residues, the extract was centrifuged in a Quimis centrifuge (Rio de Janeiro, Brazil) at 690 g for 10 minutes at ambient temperature. After centrifuging, the extract was concentrated at 38-40°C in a rotary evaporator, Fisaton model 802, Rio de Janeiro, Brazil) until reduction to 50 % of the initial volume.

Spray drying

To around 400 mL of the extract obtained, with a variation from 18 to 20 °Brix, was added 10 DE maltodextrin (Corn do Brasil, Brazil) and was pumped to the Spray Dryer (BUCHI, model 190, Germany), with evaporation capacity of 1L/h. The constant operational conditions used were: feed flow rate: 2.78 10⁻³ m³/s; air pressure:120 psi; 0.3 mm spray nozzle and outlet temperature of 85-96°C. The variables under study were the air inlet temperature and the maltodextrin concentration, according to experimental design.

Experimental design

The following methodology was recommended by Barros Neto et al. (2007) and consisted of a second order rotational factorial design, with 2 variables, 2 levels and 3 replications at the central point. The variables evaluated were: inlet air temperature T(°C) and maltodextrin concentration MD (g/100g) in extract of the rose apple peel, whose levels are found in Table 1.

The data obtained in the design were fitted to the following polynomial (Equation 1).

\[ Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \varepsilon \]  

(1)

Where \( \beta_n \) are the coefficients of regression, \( Y \) is the analyzed response, \( x_1 \) and \( x_2 \) are the independent codified variables (air inlet temperature and maltodextrin concentration, respectively) and \( \varepsilon \) is experimental error.

The results were statistically analyzed with the aid of the Statistic 8.0 software (StatSoft, Tulsa, USA).

Yield (%)  

The yield was calculated based on the dry matter of the powder obtained and of the food submitted to drying, according to equation 2

\[ Y = \frac{p_1}{p_2} \times 100 \]  

(2)

\( p_1 \) = mass of dry sample after drying (g)  

\( p_2 \) = mass of dry sample in feed (g)

Physicochemical analysis

The analysis were performed in triplicate. Moisture content was determined in a vacuum oven (Luferco Instrumentos Científicos, Brazil) at 75 °C, according to technique from the Instituto Adolfo Lutz (2008). The values were expressed in g/100 g dry solids. The monomeric anthocyanins were in accordance with the methodology recommended by Giust and Wrolstad, (2001). One hundred grams of rose apple peel were ground with 200 mL of 96% ethanol and 1.5M HCL mixture (85: 15 v/v) and the ground
residue was repeatedly washed with acidified ethanol up to complete extraction of the anthocyanins. The resulting solution was raised to a final volume of 500 mL. Then 1 mL of the solution was added to 10 mL of pH 1.0 buffer solution. The same procedure was carried out with pH 4.5 solution. A reading of spectrophotometer absorbance was made (Beckman model DU-70, Germany) at 520 nm and 700 nm for the two solutions. The monomeric anthocyanin (AM) content was calculated according to equation 3, using the values of 26,900 L/mol.cm for Molar Absorptivity (ε) and 449.2 g/mol for molecular weight (MM), after determination of the cyanidin 3-O-glucoside anthocyanin as majoritarian by HPLC (high performance liquid chromatography) (Augusta, 2011), for red rose apple extract peel. For the determination these substance in the dehydrated product, 1g of rose apple peel powder was diluted with the 96% ethanol and 1.5 M HCl (85:15 v/v) mixture up to 25 mL in a volumetric flask in the absence of light. Then 1 mL of this solution was added to 10 mL of pH 1.0 buffer solution. The same procedure was carried out with pH 4.5 solution. A reading of spectrophotometer absorbance (Abs) was made at 520 nm and 700 nm for the two solutions and equation 3 was used for determination of the monomeric anthocyanins (ANT).

\[
\text{ANT (mg/100g)} = \left( \frac{\text{Abs (L)}}{\epsilon} \right) \times \text{MM} \times \text{VD} \times \text{FD} \tag{3}
\]

Where,

\[
\text{Abs} = (A_{510} \text{ pH} 1.0 - A_{700} \text{ pH} 1.0) - (A_{510} \text{ pH} 4.5 - A_{700} \text{ pH} 4.5)
\]

\[
\text{L} = \text{path length in cm} = 1
\]

\[
\text{VD} = \text{dilution volume (500 mL)}
\]

\[
\text{FD} = \text{dilution factor (11)}
\]

Apparent density (DA) was measured according to the method of Bhandari et al. (1993) and expressed in g.mL\(^{-1}\) of powder. Water activity (A\(_w\)) was performed in a water activity analyzer Aqualab Model Series 3 TE (Decagon Devices, Pullman, USA). Colour evaluation was made by reflectance on the ColorQuest XE equipment, (Hunterlab system, USA), with opening of 0.375 mm diameter and D65/10 illuminant. The sample was placed in a 10 mm quartz cuvette to carry out the test. The colour parameters measured were: \(L^* = \text{lightness} \quad (0 = \text{black and 100-white}); \quad a^* = (-80 \text{ up to zero = green, from zero to +100 = red}) \quad b^* = (-100 \text{ up to zero = blue, zero} +70 = \text{yellow})\). Particle size distribution was determined by the laser diffraction technique, using the particle analyzer Analysette 22 Fritsch (Idar-Oberstein, Germany), and diameter expressed as \(D_{3,2}\) (Sauter mean diameter, relating volume/surface). Solubility was determined using the method from IAL (2008), in which 1 g of the sample was weighed in a centrifuge tube previously heated in a laboratory oven to 60 °C, cooled in a desiccator and weighed. Ten mL of distilled water was added, and after homogenization for 15 seconds in a Heidolph agitator at 2.800 rpm, it was left to rest for 3h. The tube was then heater in a water bath at 50°C for 30 minutes and centrifuged at 340 G for 20 minutes. The supernatant was discarded and the residue was once more washed with 10 mL more of distilled water and centrifuged. The tube with residue was dried in a laboratory oven at 60 °C until constant weight. Solubility (SOL) was calculated by equation 4.

\[
\text{SOL} (%) = \frac{100 \times \frac{N}{P}}{x} \tag{4}
\]

\(N = \text{Difference between the grams of the initial sample and grams of the residue}
\]

\(P = \text{grams of the initial sample}
\]

Particle morphology was evaluated by scanning electron microscopy (SEM). The powders were attached to a double-sided adhesive tape mounted on SEM stubs with a diameter of 1 cm and a height of 1 cm, and then coated with gold in a vacuum and examined with an SEM (Hitachi, model TM 3000, Japan), operated at 20 Kv.

**RESULTS AND DISCUSSION**

It may be observed by analysis of variance for all the responses measured (Table 2) that the quadratic model did not fit well for most of the responses, with \(F_{\text{calculated}}\) being less than \(F_{\text{tabulated}}\) for all of them, except for diameter. However, the lack of fit for diameter was very large, due to the large variation of
these data. Through the estimated models (Table 3) with greater coefficients of determination (R²), some responses will be discussed based on the surface generated, and other properties will be compared with the literature in accordance with their

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Sequential sum of squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td></td>
<td>495.1 4.58 0.01 989 0.01 264.07 574.96 59.38 9.63 62168</td>
</tr>
<tr>
<td>Lack -of fit</td>
<td>3</td>
<td>448.2 4.63 0.01 1232 0.01 41.64 743.18 17.72 13.72 1233</td>
</tr>
<tr>
<td>Pure error</td>
<td>3</td>
<td>68.18 0.21 0.00 0.00 0.00 15.27 5.47 0.01 0.16 87838</td>
</tr>
<tr>
<td>R-Sq (%)</td>
<td></td>
<td>62.30 61.20 78.7 59.10 62.10 87.70 55.30 84.50 55.2 55.10</td>
</tr>
<tr>
<td>Fc</td>
<td></td>
<td>1.61 1.48 2.54 1.27 1.46 4.07 1.23 3.16 1.13 5.60</td>
</tr>
</tbody>
</table>

* significant at p <0.05  ** Ft=4.96

<table>
<thead>
<tr>
<th>Equations with significatives e non significatives coefficients</th>
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<tbody>
<tr>
<td>Y = 63.83 + 3.32 x₁ + 0.63 x₂ + 11.11 x₃ - 14.86 x₄ - 0.30 x₉</td>
</tr>
<tr>
<td>MC = 6.32 - 0.55 x₁ - 0.16 x₂ + 0.65 x₃ - 2.17 x₄² + 0.07 x₅ x₆</td>
</tr>
<tr>
<td>Aw = 0.24 - 0.002 x₁ + 0.02 x₂² - 0.002 x₃ - 0.01 x₄</td>
</tr>
<tr>
<td>Sol = 99.49 + 0.09 x₁ + 6.20 x₂ + 17.46 x₃ - 18.90 x₄² + 0.32 x₅ x₆</td>
</tr>
<tr>
<td>DA = 0.27 - 0.02 x₁ + 0.02 x₂² + 0.05 x₃ - 0.05 x₄² - 0.01 x₅ x₆</td>
</tr>
<tr>
<td>ANT = 27.92 - 8.39 x₁ - 5.68 x₂² + 3.10 x₃ - 8.60 x₄² - 1.38 x₅ x₆</td>
</tr>
<tr>
<td>L = 68.36 - 8.00 x₁ - 4.43 x₂ + 13.11 x₃ - 11.09 x₄² - 4.67 x₅ x₆</td>
</tr>
<tr>
<td>a = 18.90 - 0.52 x₁ - 0.96 x₂² + 3.02 x₃ - 5.55 x₄² - 2.27 x₅ x₆</td>
</tr>
<tr>
<td>b = 10.13 - 0.20 x₁ - 0.44 x₂² + 1.66 x₃ - 1.96 x₄² - 0.26 x₅ x₆</td>
</tr>
<tr>
<td>D₁/₂ = 470.71 + 60.42 x₁ - 37.99 x₂² + 137.70 x₃ - 130.53 x₄² + 57.43 x₅ x₆</td>
</tr>
</tbody>
</table>

Yield (Y), moisture content (MC), water activity (Aw), solubility(Sol), apparent density particle(DA ), antocianin content (ANT), color parameters (L,a,b), D₃,2 (volume-surface,mean Sauter)x₁ (inlet temperature),x₂ (maltodextrin concentration)

mean value ($β₀$ coefficient), or by trying to explain the tendencies by the signs of the coefficients of the independent variables.

Yield ranged from 52 to 68%, exhibiting a mean value of 63.83, which may be considered medium in relation to similar studies in the literature, which ranged from 85-75%, for bixin (Barbosa et al., 2005); 62-71% for nutraceutical extracts (Sanson et al., 2011); 73-91.5% for lycopene (Shu et al., 2006). This property is positively influenced by the increase in temperature and maltodextrin concentration, since these values result in lower product moisture and also greater vitreous transition temperature (Bhandari and Howes, 1999; Moreira et al., 2009), which minimize adherence of this product to the walls of the equipment. However, according to Shu et al. (2006), the influence of temperature is maximized up to the point at which it causes fissures in the capsules and compromises the stability of the pigments.

The moisture content ranged from 4.3-6.76, typical values of foods dehydrated by spray drying, corroborating results reached for amaranth, a source of anthocyanins (Cai and Corke, 2000); tomato pulp, a source of lycopene (Souza et al., 2009); and anthocyanins of grape pomace (Valduga et al., 2008). They were greater than those found by Tonon et al., 2011, for açai pulp, a source of anthocyanin (0.51-2.23).

In general in the literature, it is reported that the increase in maltodextrin concentration and temperature reduce product moisture content due to highest water evaporation rate at more concentrated solution (Cai and Corke, 2000, Abadio et al., 2004). In a study performed by Tonon et al. (2009), it was observed that the increase of maltodextrin solution did not have a significant effect on the moisture level of açai powder.

From the low values of the coefficients, the activity was little affected by the levels of the variables under analysis, which was from 0.2-0.28. Similar results were obtained by Tonon et al. (2011) and Valduga et al. (2008) in drying of anthocyanin extracts. These results ensure the conservation of these products for an extended period of time when correctly re-packaged, in relation to products of greater water activity.

Solubility also did not much variation, and its high value is due to the hydrophilicity of the maltodextrin because
the anthocyanins extracted (Augusta et al., 2010) are also hydrophilic substances, according to Idhan et al., 2012. This solubility is comparable to fruit dehydrated by this process (Abadio et al., 2004; Tonon et al., 2009).

The apparent density was low in relation to other products dehydrated by this process, such as powdered tomato extract: 0.60 mg/l (Souza et al.; 2009) and powdered pineapple juice: 0.59 (Abadio et al. 2004), nearer to the results obtained by Tonon et al. (2011) for açai juice. It is a very important property for product marketing, reconstitution of the product and packaging, generally being affected by the conditions of the process, which affect the moisture content, size distribution and particle morphology. It generally decreases with the increase in drying temperature due to rapid drying, which causes particle expansion by the increase in volume. The increase in concentration leads to lower moisture concentration, and since the solid material has lower density than water, density decreases (Gharsallaoui et al., 2007).

The anthocyanin content ranged from 4.5-33.39 mg/100g, values much below those obtained from other sources, such as black carrots (300-500 mg/100g) Ersus and Yurdazel, 2007; grape pomace (159.9 mg/100g) Valduga et al., 2008; and açaí (3436, mg/100g), Tonon et al. 2010. In relation to the original content of the peel extract after concentration (80 mg/100g) the drying conditions provided the maximum retention of 42% and maximum losses of 90%, showing that the maltodextrin concentration was not sufficient for retaining this pigment and the temperature was high for the process. In relation to original content of the peel extract (300mg/100g) (Augusta et al., 2010), the vacuum concentration reduced 73%, indicating a great loss in this process.

In relation to the effects of the variables, it may be noted through Fig. 2 that the maximum value of encapsulated anthocyanin is near the central drying conditions, because high temperatures degrade this pigment and high maltodextrin concentrations may lead to the quantity dilution effect, as already documented in various studies with anthocyanin sources (Cai and Corke, 2000; Shu et al., 2006; Ersus and Yurdagel; 2007; Tonon et al., 2008).

In relation to color parameters, it is observed that for lightness and parameter b, the models did not fit. It is observed by the coefficient sign that lightness decreased with an increase in temperature and increased with the addition of maltodextrin, due to darkening reactions promoted by oxidation of the pigments and effect of the white color of maltodextrin, respectively. In relation to parameter a, which measures the intensity of red colouring, typical of the anthocyanin of the rose apple extract, a tendency and explanations similar to the anthocyanin concentration may be seen in Fig. 3, because it is this pigment which is the main responsible for the red coloring of the powder extract. Similar results were found by the aforementioned authors in retention of anthocyanin pigments.

In relation to diameter, curves were of the bimodal type, exhibiting bands of 8.05-65 μm and 150- 500 μm, and an average volumetric diameter of 50% of 470 μm particles. The model did not fit, but it may be seen by the signs of the coefficients that the diameter increases with increase in temperature and concentration of maltodextrins. These results already expected and obtained in various studies (Cai and Corke, 2000; Ersus and Yurdagel, 2007; Tonon et al., 2008 b) due to the expansion of the particles caused by rapid drying and by increase of viscosity of the solution with the addition of maltodextrin, increasing the size of the drop and consequent size of the particle (Gharsallaoui et al., 2007).

In relation to morphology, it may be observed by Fig. 4 that it was not altered by the change in air inlet temperature or maltodextrin concentration, observing larger particles with a smooth surface surrounded by smaller particles, showing the polydispersity of particle size. There was no evidence of fissures and folding, which are results of rapid drying, combining effects of high temperature and concentration of solids, which decreases the stability of the product during storage (Cai and Corke, 2000). These results are commonly
found in various research results already cited in the discussion.

![Fig. 3. Surface response for parameter a](image)

![Fig. 4. Morphology of the extract of powdered rose apple under different drying conditions: (a) 175°C/15% MD, (b) 190°C/10% MD](image)

Generally, high temperatures lead to greater sized particles by the expansion of water vapors formed and high concentration of solids by the increase in drop size (Alamilla-Beltran, 2005).

**CONCLUSIONS**

Although the yield was good in some trials (70%), the maximum concentration of anthocyanin pigments was very low (30 mg/100g), indicating that the conditions used were not adequate for increasing encapsulation efficiency. Among the conditions studied, a temperature of 190°C and 10% maltodextrin concentration is suggested, which resulted in lower pigment loss and greater red colour retention for carrying out further studies.

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