Proximate composition and kinetics drying of sweet pine nuts compared to typical nuts of Araucaria angustifolia

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ABSTRACT: The objective of this research was to determine the proximate composition and kinetics drying of sweet pine nuts compared to typical pine nuts of Araucaria angustifolia. This study is based on the proximate components, color, and duration of pine nuts drying of both types, and the influence of temperature and cutting geometry on the dehydration process. Sweet pine nuts had lower calorific value and carbohydrate content, but higher lipid, dietary fiber, protein, and ash contents when compared to typical pine nuts. Color of sweet pine nuts is light pink whereas the typical pine nut is yellowish-white. Sweet pine nuts were also softer. Drying kinetics of the seeds fit well into the logistic and Thompson models. To accelerate drying rates, we recommend slicing pine nuts into thin cross-sections and drying them at temperatures of 60 °C for typical pine nuts and 70 °C for sweet pine nuts.

Key words: brazilian pine, centesimal composition, gluten free flour, food drying.

INTRODUCTION

The Araucaria angustifolia (Bertol. Kuntze), popularly known as Brazilian pine or Paraná pine, belongs to the Araucariaceae family and found in South America, predominantly in Brazil (WANG & RAN, 2014). This species is considered critically endangered (IUCN 2018) mainly as a consequence of deforestation carried out between 1930 and 1970 (GUERRA et al., 2002). Therefore, incentivizing conservation through the use of pine nuts (Araucaria seed) as a food product can encourage reforestation and reduce extraction pressure on the remaining natural forest (DANNER et al., 2012).

Pine nuts have been one of the main sources of food for indigenous populations in Southern Brazil (BITENCOURT & KRAUSPENHAR, 2006). Additionally, the pine nut has socioeconomic importance due to the commercialization of A. angustifolia and extraction of this plant from several areas where it naturally occurs (SHIBATA et al., 2016). The pine nut is consumed both cooked and
roasted, mainly between April and July throughout the region (CORDENUNSI et al., 2004; COSTA et al., 2013). Pine nuts can also be used in the production of pasta and bread after being processed into flour (WASZCZYNSKY & COSTA, 2014), or incorporated into fruit jams (BOLZAN & PEREIRA, 2017).

The dry matter of pine nuts is mostly composed of starch, which, after dehydration, can be used as gluten-free flour, which has high potential for use in the food industry (CORDENUNSI et al., 2004; CONFORTI & LUPANO, 2008). There is one Araucaria tree that produces pine nuts with higher sugar and lower starch content compared to typical pine nuts. These nuts have greater potential for commercialization and use in food products due to their sweet taste and soft texture (SACHET et al., 2020). Drying pine nuts enables them to be used in the production of food throughout the year. This results in added value and increased consumption, as drying pine nuts facilitates transport, handling, and storage as well as increasing quality and shelf life. Additionally, it limits microbiological contamination and enzymatic and oxidative degradation (MATHLOUTHI, 2001; ERTEKIN & FIRAT, 2017). Studies that define the ideal conditions for pine nut dehydration are necessary to increase the utility of this component in the food industry (ERTEKIN & FIRAT, 2017).

The objective of this research was to determine the proximate composition and drying kinetics of sweet pine nuts compared to typical ones.

MATERIALS AND METHODS

An Araucaria tree characterized by its production of sweet seeds was found on a farm in Pato Branco, Paraná, Brazil (26°12'50” S; 52°38'42” W). Two pine cones were collected from this tree, and in the laboratory the pine nuts were manually peeled. Sweet and typical pine nuts were assessed by a taster who tasted a slice of each seed. Both kinds of pine nuts were assessed, after being processed into flour (WASZCZYNSKY & COSTA, 2014), or incorporated into fruit jams (BOLZAN & PEREIRA, 2017).

For the study of drying kinetics, each of the 54 typical pine nuts and 54 sweet pine nuts were cut in three distinct ways: 1) in 10 circular transverse slices, ~ 4.0 mm thick; 2) in a longitudinal slice of the central part of the nut, ~ 8.0 mm thick; and 3) in two longitudinal slices, ~ 12.0 mm thick. Samples were weighed and distributed in aluminum trays with perforated bottoms and dried in a forced-air oven at three temperatures: 50, 60, or 70 °C. Weight loss readings were measured until the samples reached equilibrium moisture, that is, until they reached a constant weight. Data were expressed as dimensionless moisture ratio (RX) using the equation

\[ RX = \frac{U - U_e}{U_i - U_e} \]

where RX = product water ratio (dimensionless); U = water content of product at time t (decimal dry basis); U_i: initial product water content (decimal dry basis); U_e: product equilibrium water content (decimal dry basis).
Experimental data were fit by four mathematical models: three nonlinear regression models, logarithmic (CHHINNAN, 1984), Thompson (THOMPSON et al., 1968), and Newton (LEWIS, 1921), and Wang’s and Singh linear regression model (WANG & SINGH, 1978). Parameters were estimated based on the Gauss-Newton iterative method, an algorithm based on minimizing the squared sum of the residuals. To check the quality of the models’ fit to the experimental data, the adjusted coefficients of determination for the mean (R²), the corrected Akaike Information Criterion (AIC) and the chi-square test (χ²) values were calculated and the model that presented higher R² and lower AIC and χ² values were selected to represent the drying kinetics data (FERNANDES et al., 2014). The selected model was used to produce the drying curve (RX x Time) and relative drying rate (TAS x Time) graphs. The absolute drying rate was obtained by the equation TAS = \(\frac{\text{MT}_t + \text{MT}_{t+dt}}{d_t}\), where:

- \(\text{MT}_t\) = moisture at time \(t\);
- \(\text{MT}_{t+dt}\) = moisture at time \(t+dt\); and
- \(d_t\) = time interval. It was also possible to infer changes in the drying process, indicating the moments of increased or decreased water loss. All analyses were performed using R (R CORE TEAM, 2019).

## RESULTS

The largest differences observed between sweet and typical pine nuts in the proximate composition analysis were in lipid and dietary fiber content, which were, respectively, 71 and 258% higher in sweet pine nuts both in natura and pine nut flour. Sweet pine nuts also had higher total and lower available carbohydrate content than typical pine nuts. Both sweet and typical pine nuts in natura showed no significant difference in ash content and protein, but these components were significantly higher in sweet pine nut flour when compared to typical pine nut flour (Table 1).

There were differences in additional parameters between the types of pine nuts. \(L^*\) values were smaller for sweet pine nuts (Table 2), indicated by darker bars when compared to typical pine nuts. The highest \(C^*\) value was recorded in sweet pine nuts, by darker bars when compared to typical pine nuts. The highest \(h\) values, indicating the darker hue of typical pine nuts.

Hardness did not vary significantly for the three positions within the sweet pine nuts. Overall, the typical pine nuts were harder than the sweet pine nuts and the hardness showed significant differences between three parts, decreasing from base to apex (Table 3).

### Table 1 - Proximate composition of sweet and typical pine nuts in natura and pine nut flour.

<table>
<thead>
<tr>
<th>Component (g 100 g⁻¹)</th>
<th>Sweet pine nut</th>
<th>Typical pine nut</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet base</td>
<td>Dry base</td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>62.51 (0.43)</td>
<td>69.23 (0.18)</td>
<td>37.4**</td>
</tr>
<tr>
<td>Ash</td>
<td>1.68 (0.03)</td>
<td>1.07 (0.04)</td>
<td>27.8**</td>
</tr>
<tr>
<td>Lipids</td>
<td>2.47 (0.01)</td>
<td>1.62 (0.05)</td>
<td>35.3**</td>
</tr>
<tr>
<td>Proteins</td>
<td>3.86 (0.08)</td>
<td>3.78 (0.08)</td>
<td>-</td>
</tr>
<tr>
<td>DF</td>
<td>3.23 (0.06)</td>
<td>3.23 (0.06)</td>
<td>0.0%</td>
</tr>
<tr>
<td>TC</td>
<td>29.48 (0.39)</td>
<td>29.48 (0.39)</td>
<td>0.0%</td>
</tr>
<tr>
<td>AC</td>
<td>26.25 (0.34)</td>
<td>26.25 (0.34)</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>Wet base</td>
<td>Dry base</td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>11.94 (0.31)</td>
<td>8.61 (0.01)</td>
<td>258.0**</td>
</tr>
<tr>
<td>Ash</td>
<td>3.95 (0.04)</td>
<td>2.61 (0.04)</td>
<td>51.8**</td>
</tr>
<tr>
<td>Lipids</td>
<td>5.81 (0.09)</td>
<td>4.60 (0.09)</td>
<td>35.3**</td>
</tr>
<tr>
<td>Proteins</td>
<td>9.07 (0.22)</td>
<td>7.02 (0.28)</td>
<td>29.2**</td>
</tr>
<tr>
<td>DF</td>
<td>7.58 (0.04)</td>
<td>3.13 (0.19)</td>
<td>142.1**</td>
</tr>
<tr>
<td>TC</td>
<td>69.23 (0.18)</td>
<td>79.41 (0.41)</td>
<td>-12.8**</td>
</tr>
<tr>
<td>AC</td>
<td>61.65 (0.17)</td>
<td>76.28 (0.30)</td>
<td>-19.2**</td>
</tr>
</tbody>
</table>

*Average (standard deviation) (n = 3), ** non-significant and *** significant difference by t-test (P≤0.01), comparing sweet and typical (not sweet) araucaria nuts. DF: dietary fiber; TC: total carbohydrates; AC: available carbohydrates.
In regards to the drying kinetics, among the four models evaluated to predict the pine nut drying phenomenon, the logarithmic and Thompson equations best fit the experimental data of moisture content reduction versus drying time. R² values were higher than 0.98 in all pine nut cutting geometries, both in sweet and typical pine nuts, and in all three temperatures tested. Moreover, the AIC and χ² test values were lower for these two models in all cases (three temperatures, two types of pine nut and three cutting geometries). In general, Newton’s nonlinear regression also generated a good fit but had reduced efficiency in interpreting the drying results of the pine nut samples at 70 °C. The smallest adjustments to the data were made using Wang and Singh’s linear regression equation (Table 4). Thus, considering the three statistics (higher R², lower AIC, and lower χ²) a graphical representation of drying kinetics of sweet and typical pine nuts can be made using either the Logarithmic or Thompson model.

Using the Logarithmic model, it was reported that higher temperatures promoted a reduction of drying time more significantly when the cutting geometry was more fractionated (transverse cuts in slices of ~ 4.0 mm) when compared to the other two longitudinal cuts which generated thicker slices. In order to reach 10% moisture, the seeds cut in thinner slices had reduced drying times at 50 °C.

The sweet pine nuts took longer to dry (25 and 40 min for typical and sweet pine nut samples, respectively), which is explained by the higher initial moisture content, differences in chemical composition and structural conditions of the sweet pine nuts. No significant difference in drying time was observed between the type of slices at higher temperatures (60 and 70 °C). When the seeds were cut in half, generating two thick pieces (~ 12.0 mm), the drying time increased to 60 min at 70 °C (Figure 1).

In regard to the average relative rate of drying generated by the logarithmic model, the amount of water extracted per minute increased as temperature increased. This was especially true in sweet pine nuts, which have a higher initial water content. However, in the case of typical pine nuts, there was a significant increase in the drying rate when temperatures increased from 50 to 60 °C, but when the temperature was increased from 70 °C the increase in drying rate was negligible (Figure 2).

**DISCUSSION**

In this research, for the first time, we compared the proximate composition between typical (non-sweet) pine nuts and sweet pine nuts, which have a sweet taste due to the greater reduction sugar content and total sugars (915% and 466%) and
lower starch content (54.8%) than typical pine nuts (SACHET et al., 2020). To date, sweet pine nuts have been detected in only one *A. angustifolia* matrix, which was used for seed collection by these authors and in the present research.

The appearance of sweet pine nuts may have arisen from the same physiological mechanism as that observed in sweet corn. A deficiency of enzymes responsible for the transformation of phytoglycogen into amylopectin dramatically reduces starch concentration and increases sugars (glucose, fructose, and sucrose) in sweet corn compared to typical corn (208.2 kcal). Special attention has been given to research on the nutritional use of starch-rich *A. angustifolia* seeds to promote the use of processed pine nuts (pre-cooked, dehydrated, vacuum packed, etc.) or pine nut flour (after drying and milling) to make gluten-free bread and pasta (CORDENUNSI et al., 2004; CONFORTI & LUPANO, 2008; SHIBATA et al., 2016; ZORTÉA-GUIDOLIN et al., 2017).

Special emphasis is given to the fiber content of sweet pine nuts, as fiber contributes to nutrient metabolism and disease regulation (BRENNAN, 2005). This reveals the excellent nutritional value of sweet pine nuts, with its functional attributes and lesser carbohydrates content than typical pine nuts (CORDENUNSI et al., 2004; CONFORTI & LUPANO, 2008; SHIBATA et al., 2016; ZORTÉA-GUIDOLIN et al., 2017).

Coloration is a parameter that directly influences sensory analysis and consumer preference.
for food products. Sweet pine nuts presented L’ values of 80 which is lower than typical pine nuts (L’ = ~ 85), indicating a slightly darker hue; although, still close to white (0 indicates a totally dark color sample and 100 is an all-white sample) (MINOLTA, 1998; SPADA et al., 2012). The component that most influences color differentiation is sugar (GONÇALVES et al., 2014) and sweet pine nuts are so named because they have a higher total and reducing sugar content than typical pine nuts (SACHET et al., 2020). By evaluating hue (SPADA et al., 2012), we demonstrated the light pink color of sweet pine nuts and the light yellow of typical pine nuts.

The typical pine nut samples were harder than sweet pine nuts, which showed that it is necessary to use more force to compress and break the seed (GUSMÃO et al., 2018). The increased hardness in the base of the seed compared to the center and apex of typical pine nuts may be the effect of differences in proximate composition along the seed, verified by the higher starch and lower lipid content in the base as compared to the apex (COSTA et al., 2013). The greater softness detected in sweet pine nuts is explained by the lower starch content (SACHET et al., 2020), which should make it easier to cook and/or grind these pine nuts, which is advantageous for the production of flour and other derivatives in the food industry.

At 50 °C, cutting the seed into several thin slices (~ 4.0 mm) increased the evaporation rate of water due to increased surface area, resulting in decreased time to reach equilibrium moisture. Cutting geometry has been shown to influence the drying rate of tomatoes, because cutting them into four parts is more advantageous than cut in half (SANJINEZ-ARGANDOÑA et al., 2011). However, cutting pine nut slices requires more time to perform and when the temperature was raised to 60 and 70 °C, there was no significant difference in drying rates between the three types of slices. The use of higher temperatures (70 °C) increased the rate of water removal from sweet pine nuts, accelerating the drying process; this is due to the fact that a higher amount of heat transferred from the air to the material, with a consequent increase in the migration speed of the water within the pine nuts to the product surface (REIS et al., 2013). This considerably reduces the time required to reach equilibrium moisture, resulting in greater time savings compared to the use of lower temperatures (50 or 60 °C). However, for typical pine nuts, the drying temperature of 60 °C can be used...
since there was no increase in the drying rate from 60 to 70 °C. This generates energy savings for drying typical pine nuts.

The initial moisture content of the seed types (45.5 and 62.5% for typical and sweet pine nuts, respectively) influenced the time of drying. At 50 °C, the typical pine nuts have been dried more slowly. This may be due to the fact that seeds with lower water content have higher binding forces between water molecules and require more energy to dry than those with a higher water content (AVIARA & AJIBOLA, 2002). At 60 °C, the sweet pine nuts dried more slowly, probably due to the higher temperature being sufficient to accelerate the evaporation of water at the beginning of the drying process, but afterwards, the higher lipid content of sweet pine nuts may have acted as a limiting factor. Lipids, which are large nonpolar and hydrophobic molecules, may have acted as a physical barrier for heat transfer and limited the diffusion of water from the interior to the seed surface (REIS et al., 2018).

At 70 °C, both the typical and sweet pine nuts dried at similar rates. If the drying process is not properly conducted, it can cause constituent losses (HO et al., 2016). However, in our research, the removal of water in preparation for flour production led to a product with a higher concentration of sugar. Therefore, dehydration under these conditions is a sound method of storage without loss of nutritional characteristics (FADIMU et al., 2018). The higher moisture and sugar content of the sweet pine nuts can reduce their preservation potential and accelerate their deterioration. Even for typical *A. angustifolia* seeds, due to their high water content, controlled drying is necessary to avoid the development of microorganisms (CONFORTI & LUPANO, 2008). Processing *Araucaria* seeds to produce flour allows for off-season consumption (March to July).

The results of this research should be useful for the utilization of sweet pine nuts in the food industry, either to produce pre-cooked pine nuts or flour and can be used to make gluten-free breads and pastas. In addition to highlighting this type of pine nut for its sweet taste and soft texture, as already described in Sachet et al. (2020), the present study highlighted the greater nutritional potential of these pine nuts in relation to typical pine nuts. Sweet pine nuts have higher nutritional value than typical pine nuts, with higher lipid, dietary fiber, protein and ash content, lower total carbohydrate content and lower caloric value. Sweet pine nuts are also softer, which makes them easier to grind.

**Figure 2 - Relative drying rate with data adjusted by the Logarithmic equation in typical and sweet pine nuts with three cutting geometries and submitted to three drying temperatures.**

Sample type - 1 and 2: Typical and sweet pine nuts cut into slices of ~ 4.0 mm thickness, respectively; 3 and 4: Typical and sweet pine nuts cut into a slice of the central part of the pineion, ~ 8.0 mm thickness, respectively; 5 and 6: Typical and sweet pine nuts cut into two longitudinal slices ~ 12.0 mm thickness, respectively.
We also delimit the best form of drying: thinner sliced pine nuts (~ 4.0 mm) can be dried at a temperature of 50 °C, while pine nuts thicker than 8.0 mm should be dried at a temperature of 60 °C for typical pine nuts and 70 °C for sweet pine nuts. The Logarithmic and Thompson models can be used to predict the drying kinetics of typical and sweet pine nuts in the temperature range of 50 to 70 °C. To accelerate the drying rate, the pine nuts can be cut into thinner slices (~ 4.0 mm) and dried at 70 °C.

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DECLARATION OF CONFLICT OF INTERESTS

The authors declare no conflict of interest.

AUTHORS’ CONTRIBUTIONS

BVG, APCM, MRS, and MFR performed the experiments and carried out the lab analyses. MRS and RHP performed statistical analyses of experimental data. EAP and MAD conceived and designed experiments and supervised and coordinated the lab analyses. AR, EAP and MAD prepared the draft of the manuscript. All authors critically revised the manuscript, and in the decision to publish the results.

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