

Dehydration of “dedo de moça” pepper: kinetics and phytochemical concentration

Desidratação de pimentas dedo-de-moça: cinética e concentração de fitoquímicos

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Abstract

Red pepper is rich in vitamin C and other phytochemicals and can be consumed as a dehydrated product. The evaluation of the best drying conditions can ensure a better quality product. This study aimed to investigate the effect of air temperature (55, 65, and 75 °C) on drying kinetics of red peppers and on vitamin C, total phenolic content, and color of dried pepper as compared to the fresh product. Dehydration was carried out in a forced convection oven. Drying kinetics was determined by periodic weighting until constant weight. The moisture content of the fresh pepper was approximately 86%. The drying curves were fitted to three different models available in the literature. The Page model showed the best fit for this process. Analysis of variance revealed that the air drying temperature significantly influenced ($p < 0.05$) the quality parameters (vitamin C content, total phenolic content, and color) of the dried pepper as compared to the fresh pepper. After drying, the vitamin C retention increased with reduced air-drying temperature. In general, products dried at lower temperatures exhibited better quality due to reduced losses of bioactive compounds.

Keywords: “dedo de moça” pepper; drying curves; mathematical models; quality parameters.

Resumo

A pimenta vermelha é rica em vitamina C e outros fitoquímicos e pode ser consumida como produto desidratado. A avaliação das melhores condições de secagem pode garantir melhor qualidade do produto. Assim, o objetivo deste trabalho foi estudar o efeito da temperatura do ar de secagem (55, 65, 75 °C) sobre a cinética de secagem, conteúdos de vitamina C e fenólicos totais e cor do produto desidratado, comparando-os à pimenta *in natura*. A desidratação foi feita por convecção forçada em estufa. A cinética de secagem foi determinada por pesagens periódicas até peso constante. A umidade da pimenta *in natura* foi de aproximadamente 86%. As curvas de secagem foram ajustadas por três modelos diferentes, avaliados na literatura. O modelo de Page apresentou o melhor ajuste para este processo. A análise de variância mostrou que a temperatura de secagem influenciou significativamente ($p < 0,05$) os parâmetros de qualidade (conteúdo de vitamina C, conteúdo de fenólicos totais, cor) da pimenta desidratada quando comparados aos da pimenta *in natura*. Após a secagem, a retenção de vitamina C aumentou com a redução da temperatura de secagem. De maneira geral, a qualidade do produto foi favorecida na secagem com menor temperatura, devido à redução nas perdas de compostos bioativos.

Palavras-chave: pimenta dedo de moça; curvas de secagem; modelos matemáticos; parâmetros de qualidade.

1 Introduction

Peppers are widely used in food products such as sauces, meats, jellies, cakes, chocolates, and sweets due to their spicy and pungent flavor caused by the presence of capsaicins (CARVALHO et al., 2006). Besides being used as a spice, peppers also have a preservative effect because they are rich in capsaicin exhibiting high antioxidant and antimicrobial properties (REIFSCHNEIDER, 2000).

Among the various varieties of pepper, when dried and ground to flakes, “dedo-de-moça” pepper (*Capsicum baccatum* var. *pendulum*) is known as *red pepper*, *deer antler pepper* or *pepperoni*, is one of the most widely consumed peppers in Brazil, mainly in the states of Rio Grande do Sul, São Paulo, and Goiás. It is cultivated by small, medium, and large producers and perfectly fits into the model of family farming and small

farmer-agribusiness integration (CARVALHO; RIBEIRO; HENZ, 2009).

Pepper is an abundant and cheap source of vitamins, minerals, and fiber (TUNDE-AKINTUDE; AKINTUDE; FAGBEJA, 2011). They are naturally rich in ascorbic acid, provitamin A carotenoids (SIMONNE et al., 1997), tocopherols, flavonoids, and phenolic acids, and capsaicin, which is the most important component (ISHIKAWA et al., 1998). These compounds are powerful antioxidants with a very important function of neutralizing the free radicals in the human body, thus reducing the risk of diseases such as arthritis, cardiovascular diseases, and cancer and delay the aging process (FAUSTINO; BARROCA; GUINÉ, 2007). However, its high moisture content makes it susceptible to deterioration.

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One of the most common methods of pepper preservation is dehydration. Nevertheless, this process usually results in loss of nutrients and other undesirable changes, which include discoloration and darkening according to the process conditions (KIM et al., 2006). Although dried products have reduced nutritional quality (MIRANDA et al., 2009), the quality of these products depends on the drying conditions (TUNDE-AKINTUDE; AKINTUDE; FAGBEJA, 2011).

Several studies on drying kinetics of peppers can be found in the literature (REIS et al., 2011; VEGA et al., 2007; TUNDE-AKINTUDE; AFOLABI, AKINTUDE, 2005; GUPTA et al., 2002). Other studies focused on product quality aimed to investigate the effect of the temperature on the composition of pepper (FAUSTINO; BARROCA; GUINÉ, 2007), especially with respect to vitamin C, phenolic compounds, carotenoids (DI SCALA; CRAPISTE, 2008; COSTA et al., 2010; MONTES et al., 2010), color, and antioxidant properties (ARSLAN; ÖZCAN, 2011).

The objective of this paper was to study the effect of air temperature (55, 65, and 75 °C) on drying kinetics of red peppers and on vitamin C, total phenolic content and color of dried pepper as compared to the fresh product.

2 Materials and methods

2.1 Material

Ripe fruits of “dedo-de-moça” pepper (*Capsicum baccatum* var. pendulum) were purchased from the local market in Pirassununga/SP. The reagents 2,6-dichlorophenol indophenol (Sigma-Aldrich), oxalic acid (Vetec), and ascorbic acid (Sigma-Aldrich) were used to quantify the vitamin C and the Folin-Ciocalteu reagent (Sigma-Aldrich), and sodium carbonate (Synth) were used for determination of total phenolic contents.

2.2 Methods

Drying kinetics

The fresh peppers were washed, cut in half lengthwise, and the seeds were removed. The peppers were laid out in rectangular trays covered with aluminum screen, previously weighed, with the rind (epicarp) placed down until a single layer of product has been completed. The trays were placed in a forced air drying circulation oven (0.55 m/s) with temperature control (Marconi) at 55, 65, and 75 °C. The trays were weighed periodically (every 20 minutes) until their weight changed by less than 5% in the last three weighing. The drying experiment was performed in triplicate with two repetitions.

The drying curves were obtained by plotting the moisture ratio as a function of time, and also by plotting the drying rate as a function of moisture. Among the several empirical models usually found in the literature and used to describe the drying kinetics of agricultural products, the models presented below (Equations 1-3) were chosen to fit the experimental data:

a) Lewis Model (AYENSU, 1997; ARSLAN; ÖZCAN, 2011):

$$Y = \exp(-kt) \quad (1)$$

b) Page Model (ARSLAN; ÖZCAN, 2011; DOYMAZ, 2005):

$$Y = \exp(-kt^n) \quad (2)$$

c) Henderson-Pabis Model (ARSLAN; ÖZCAN, 2011; DOYMAZ, 2004):

$$Y = a \exp(-kt) \quad (3)$$

Where, Y is the moisture ratio (Equation 4, dimensionless), t is time (hour), and a , k (h^{-1}) and n are empirical parameters of these models. These parameters were calculated by non linear regression.

$$Y = \frac{m_t - m_{wc}}{m_i - m_{wc}} \quad (4)$$

where m_p , m_i , and m_{wc} correspond respectively to moisture at time t , time zero, and equilibrium.

Moreover, the drying rate of the red peppers was calculated as the first derivate of the equation that presented the best fitting parameters.

Raw material characterization

The “dedo-de-moça” peppers (*Capsicum baccatum* var. pendulum) were obtained from Jun/2011 to Feb/2012 and subjected to analysis for determination of moisture, protein, fat, and ash. These analyses were performed according to recommendations of the Association of Official Analytical Chemists (ASSOCIATION..., 1990), and the results expressed the mean values obtained for different batches. The moisture content of fresh and dried peppers was determined by the gravimetric method at 105 °C/24 h. The protein content was determined by the Kjeldahl method (conversion factor of 6.25). The lipid content was determined by Soxhlet extraction. The ash content was determined by incineration in a muffle furnace at 550 °C.

Determination of vitamin C content

The vitamin C content was obtained according to the method of Tillmans modified by Benassi and Antunes (1988), who used oxalic acid solution as solvent to replace metaphosphoric acid. One gram of pepper was added to 50 mL oxalic acid solution, followed by 1:10 dilution. The vitamin C content was expressed as mg AA/100 g dry matter. The retention of vitamin C was expressed relative to its initial content in the fresh pepper.

Determination of total phenolic content

The content of phenolic compounds was determined by the Folin-Ciocalteu method as described by Vega-Galvez et al. (2009). The color reaction occurred within 2 hours, always in the dark, and the absorbance was measured at 765 nm using a spectrophotometer (PerkinElmer Lambda 35). The total phenolic content was determined using a standard curve of

galic acid (Vetec) in the range of 50-500 ppm. The results were expressed as mg galic acid equivalents (GAE)/100 g dry matter.

Color measurement

The color of the fresh and dried peppers was measured using a colorimeter Miniscan XE (Hunterlab) working with standard illuminant D65 and a measuring cell with an opening of 30 mm. Color was expressed in CIE L* (whiteness or brightness), a* (redness/greenness), and b* (yellowness/blueness) coordinates (VEGA-GÁLVEZ et al., 2008). Five replicate measurements were performed, and the results were averaged.

Statistical analysis

The modeling of drying kinetics was performed by nonlinear regression using the Statistics Software (version 11, Statsoft Company, NC, USA). The data on color parameters, vitamin C, and phenolics compounds were statistically analyzed by analysis of variance (ANOVA) and by Tukey test ($\alpha = 5\%$), for comparison of means, using the SAS software (version 9.2, SAS Institute Inc, Cary, NC, USA).

In addition to the correlation coefficient (R^2), other statistical parameters were used to evaluate the best model to describe the drying curves, namely the reduced sum square error (SSE, Equation 5) and root mean square error (RMSE, Equation 6). The lowest SSE and RMSE with the highest R^2 values were selected as optimal criteria to evaluate the fit quality of the proposed model (VEGA et al., 2007; FAUSTINO; BARROCA; GUINÉ, 2007).

$$SSE = \frac{1}{N} \sum_{i=1}^N (Y_{\text{exp}i} - Y_{\text{mod}i})^2 \quad (5)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (Y_{\text{exp}i} - Y_{\text{mod}i})^2} \quad (6)$$

where N is the number of observations and $Y_{\text{exp}i}$ and $Y_{\text{mod}i}$ are the experimental and predicted values for the observation i , respectively.

3 Results and discussion

3.1 Characterization of raw materials and drying kinetics

The fresh “dedo-de-moça” red pepper had 85.68 ± 1.06 g water/100 g of sample; 1.66 ± 0.16 g protein/100 g sample; 0.59 ± 0.04 g total lipids/100 g sample; and 4.79 ± 0.16 g ash/100 g sample. These results were similar to those obtained by Vega-Gálvez et al. (2009) for fresh red peppers, from Chile, which were submitted to different drying conditions (50-90 °C).

Examples of drying curves of “dedo-de-moça” red pepper at three temperatures and a constant air velocity of 0.55 m/s are shown in Figure 1. The drying kinetics represented as drying rates as a function of the moisture content is also shown in Figure 2. It can be observed that the drying kinetics were dependent on the air temperature, as expected (BABALIS et al.,

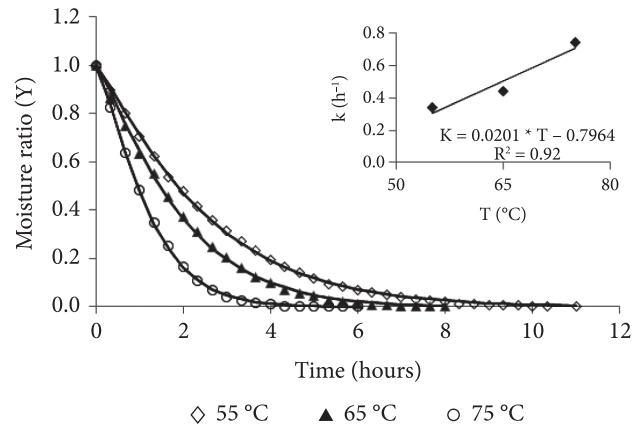


Figure 1. Drying curves at different temperatures. Symbol - experimental points, line - Page model. (\diamond) 55 °C, (\blacktriangle) 65 °C, (\circ) 75 °C. Figure inside: variation of k (from Page model) as a function of air temperature.

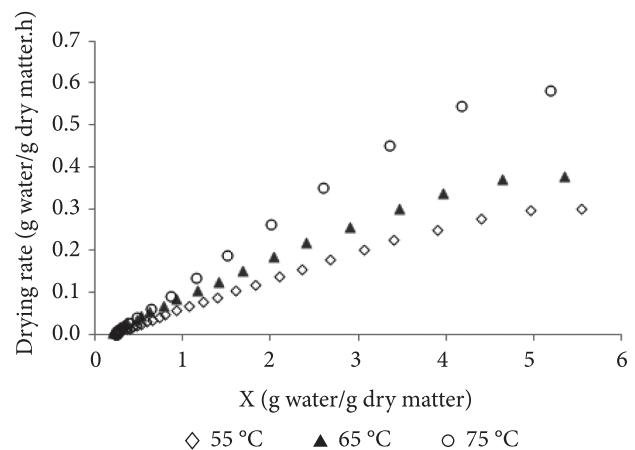


Figure 2. Drying rate curves for red pepper at different temperatures: (\diamond) 55 °C, (\blacktriangle) 65 °C, (\circ) 75 °C.

2006; VEGA et al., 2007; DI SCALA; CRAPISTE, 2008). The increase in temperature resulted in increased drying rates and consequently in reducing drying time, such behavior is typical of agricultural products (REIS et al., 2011; ARSLAN; ÖZCAN, 2011).

The time needed to reach a moisture content of about 14 g of water/100 g of sample, which could be considered as a final moisture content, was 10.7, 7.3, and 6 hours when the air drying temperature was 55, 65 and 75 °C, respectively. This means that decreasing air temperature from 75 to 55 °C may increase drying time by about 75%.

The drying rate curves (Figure 2) showed that drying kinetics corresponded to a period of constant drying rate, which decreased with increasing temperature, followed by a falling rate period. At the first stage of the drying process, moisture moves to the surface by capillary suction rapidly enough to maintain a uniformly wet surface, and thus the drying rate is constant (TUNDE-AKINTUDE; AFOLABI; AKINTUDE, 2005). In the

last stage of the drying process, water is inside of the porous, and consequently the wet area on the food surface decreases gradually and the falling rate period starts (BAKER, 1997).

The behavior of the drying rate curves (Figure 2) is in agreement with the studies of Turhan, Turhan and Sahbaz (1997), who found the constant rate period during drying of blanched chili peppers. However, the behavior observed in this study was contrary to that found by Akpinar, Bicer and Yildiz (2003), who observed that the drying of red pepper occurred only in the falling rate period at 55, 60, and 70 °C. The difference between the results obtained in this study and those of Akpinar, Bicer and Yildiz (2003) at 55 °C may be due to the composition and geometry of the fruit and the velocity of drying air (1.5 m/s), which was approximately 3 times higher than that used in this study (0.55 m/s). Higher air drying velocity causes higher mass transfer of the solid surface to the air. Thus, the drying process becomes controlled by water diffusion through the solid matrix, which results in the falling rate period. On the other hand, the length of the drying period at a constant rate in the samples dried at different temperatures may be due to the strong shrinkage of the samples during the drying process, which also varies with temperature and changes the mass transfer surface of the samples.

The increase in drying rate with increased temperature would be expected, and the higher the drying temperature, the higher the diffusion coefficient. This occurs because the higher air-drying temperatures result in greater vapor gradients at the food surface, which will invariably lead to a higher rate of moisture evaporation at the food/air interface. This higher moisture evaporation rate will cause a higher rate of moisture diffusion from the internal regions of the pepper to the surface, which increases the diffusion coefficients (AKPINAR; BICER; YILDIZ, 2003).

The values of the model parameters (k , n , and a) for the three models (Equations 1-3) calculated by nonlinear regression are shown in the Table 1. It was observed that the constant k (h^{-1}) increased with increase in the air-drying temperature for all models (example Small graph depicted on the right-hand

side in Figure 1). However, n (Equation 2) and a (Equation 3) values are substantially constant with temperature (Table 1).

Under all studied temperatures, the correlation coefficient (R^2) of the models fitted to experimental data was higher than 0.98 (Table 2). However, to select a representative model of drying kinetics, the sum square error (SSE) and root mean square error (RMSE) were also evaluated since the analysis of R^2 is not enough to evaluate nonlinear models (MADAMBABA; DRISCOLL; BUCKLE, 1996). Models are considered suitable to describe the drying behavior of an agricultural product when the mean relative errors are less than 10% (MOHAPATRA; RAO, 2005). Thus, a good fit could be observed in all models since high R^2 values (>0.98), and low SSE (<0.06), RMSE (<0.02) values were obtained. Several authors have obtained good results when applying these models in drying kinetics of food, such as Reis et al. (2011), Vega et al. (2007), Miranda et al. (2009), Babalis et al. (2006), Simal et al. (2005) and Doymaz and Pala (2002).

The Page model was chosen to represent the experimental data (Figure 1) because it presented the highest R^2 values (>0.99) and the lowest SSE (<0.00003) and RMSE (0.01) values, followed by Henderson-Pabis and Lewis models in order of importance (Table 2). Faustino, Barroca and Guiné (2007) also considered the Page model as the best model to describe the behavior of dehydration process of green bell pepper. Similar results were also obtained by Arslan and Özcan (2011) for red pepper dried at 50 and 70 °C.

3.2 Vitamin C content

The content of vitamin C can be considered as a quality indicator of food processing due to its low stability during thermal processes (SANTOS, SILVA, 2008). The initial vitamin C content expressed as ascorbic acid (AA) in “dedo-de-moça” red pepper was 144.84 ± 7.36 mg AA /100 g of sample; this value is close to that obtained by Vega-Gálvez et al. (2009) (188.2 ± 4.5 mg AA/100 g of sample) for fresh red pepper (*Capsicum annuum* L. var Hungarian), and it is within the range of values obtained for red peppers, which is between 75 and 277 mg AA/100 g of sample (CASTRO et al., 2008).

The drying-air temperature significantly influenced the vitamin C content in dried pepper since an increase in temperature has a negative effect on vitamin C content. The retention of vitamin C in the dried product corresponded to about 51, 34, and 21% of the initial value when the air drying temperature was 55, 65, and 75 °C, respectively (Figure 3). These values were higher than those obtained by Di Scala and Crapeste (2008), who used air temperatures between 50 and 70 °C and

Table 1. Empirical constants of the models presented in Equations 1-3.

T (°C)	Lewis		Page		Henderson and Pabis	
	k		k	n	k	a
55	0.4109		0.3402	1.1381	0.4282	1.0504
65	0.5282		0.4408	1.1931	0.5636	1.0466
75	0.8300		0.7414	1.2793	0.8709	1.0560

Table 2. Statistical analysis for Kinetic models for different air drying temperatures.

T (°C)	Lewis			Page			Henderson and Pabis		
	R^2	SSE	RMSE	R^2	SSE	RMSE	R^2	SSE	RMSE
55	0.996	4.7×10^{-4}	2.2×10^{-2}	0.999	3.6×10^{-5}	6.2×10^{-3}	0.997	3.3×10^{-4}	1.8×10^{-2}
65	0.997	8.0×10^{-4}	2.8×10^{-2}	0.999	9.8×10^{-5}	1.0×10^{-2}	0.995	6.8×10^{-4}	2.6×10^{-2}
75	0.988	5.7×10^{-2}	2.4×10^{-1}	0.997	3.0×10^{-5}	5.5×10^{-3}	0.992	8.6×10^{-4}	2.3×10^{-2}

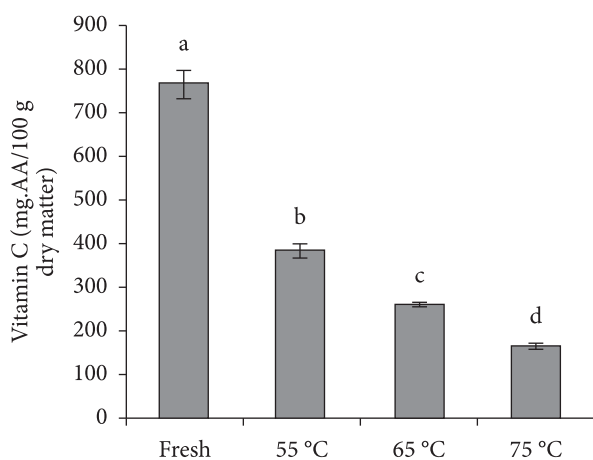


Figure 3. Vitamin C content as function of air-drying temperature. Different letters mean significant difference ($p < 0.05$) of vitamin C content.

air velocity of 0.2 and 1.2 m/s to dry red peppers and found residual values of vitamin C from 12 to 18% of the initial value. On the other hand, the values obtained in this study were similar to those obtained by Sigge, Hansmann and Joubert (1999), who dehydrated green peppers using air drying temperature of 55-75 °C and velocity of 2 m/s, and found vitamin C values between 25 and 40%. The degradation of vitamin C during the drying process may be associated with its heat stability and oxidation reaction since it presents antioxidant characteristics (VEGA-GÁLVEZ et al., 2009).

3.3 Total phenolic content

Phenolic compounds comprise a wide variety of chemical compounds including capsinoids, which can act as free radical scavengers minimizing lipid oxidation and in some cases as chelating metal agents (COSTA et al., 2010). The functionality of these compounds in food products can be changed by the processing conditions. In this study, the initial total phenolic content was 240 ± 27 mg galic acid equivalents/100 g sample, which was very close to the value obtained by Oboh and Rocha (2007) (218 mg/100 g of sample) and higher than the value found by Hassimotto, Genovese and Lajolo (2005) (131 mg/100 g sample) in methanolic extract of *C. annuum*. Costa et al. (2010) also found lower values of total phenolic content in four different types of peppers (chillies, Magali red, cambuci, and cumari peppers), when analyzing pepper extract using different solvents (hexane, chloroform, and ethyl acetate). Deepa et al. (2007) found total phenolic content between 323 and 852 mg/100 g sample for 10 different species of *C. annuum* L., and Howard et al. (2000) found values ranging from 284.6 to 570.7 mg/100 g in ripe fruits of four species of *C. annuum*. Unfortunately, studies on the effect of drying conditions on capsinoids content have not been found in the specialized literature.

The total phenolic content values expressed as galic acid equivalents per 100 g of dried sample under different air drying temperatures are shown in Figure 4. The drying

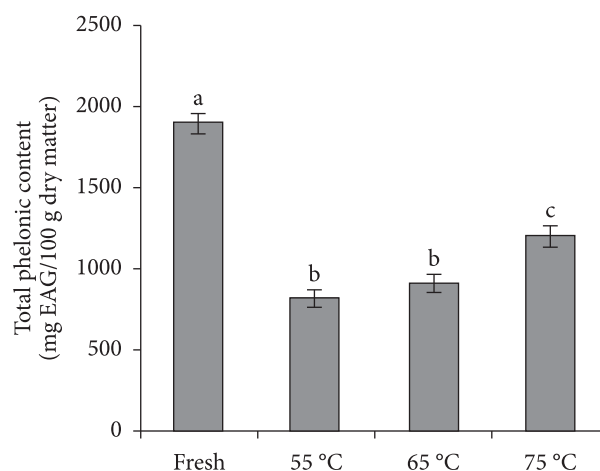


Figure 4. Total phenolic content as a function of air-drying temperature of fresh pepper. Different letters mean significant difference ($p < 0.05$) of total phenolic content.

process significantly affected the total phenolic content when compared to that of fresh red pepper. There was no significant difference between the values obtained at 55 and 65 °C, but the total phenolic content of products dried at 75 °C were higher ($p < 0.05$) than those verified at 55 and 65 °C. Probably, the high retention of phenolic compounds at 75 °C was due to the considerable reduction of drying time at this temperature, as described in 3.1 (Figure 1). It is well known that deterioration rates usually result from the time-temperature relationship. The formation of phenolic compounds at 75 °C might be due to the availability of precursors of phenolic molecules by interconversion mechanism between phenolic molecules (QUE et al., 2008; VEGA-GÁLVEZ et al., 2009).

3.4 Color parameters

Color is one of the most important criteria for evaluation of food by consumers. Undesirable changes in color may lead to a decrease in product quality and marketing value (DOYMAZ; PALA, 2002). Red peppers are considered excellent sources of natural pigments. The effect of the drying-air temperature was evaluated on the color parameters L^* , a^* , and b^* and compared to those of fresh red pepper (Figure 5). The parameters L^* and b^* presented no significant difference ($p < 0.05$) for the drying-air temperatures of 55 and 65 °C as compared to those of fresh pepper. The air drying temperature of 75 °C showed the highest variation in the parameters L^* , a^* , and b^* as compared to those of the fresh sample.

The increase in L^* value indicates a discoloration of the pepper at 75 °C as compared to the fresh pepper (Figure 5). This result differs from those obtained by Arslan and Özcan (2011), who observed lower L^* values for the dried pepper at 70 °C and attributed this behavior to brown pigment formation. The brown pigment in dried pepper may be due to the development of the Maillard reaction (reducing sugars and protein). Vega-Gálvez et al. (2009) found no significant difference between L^* values for peppers dried at 50-70 °C temperature interval.

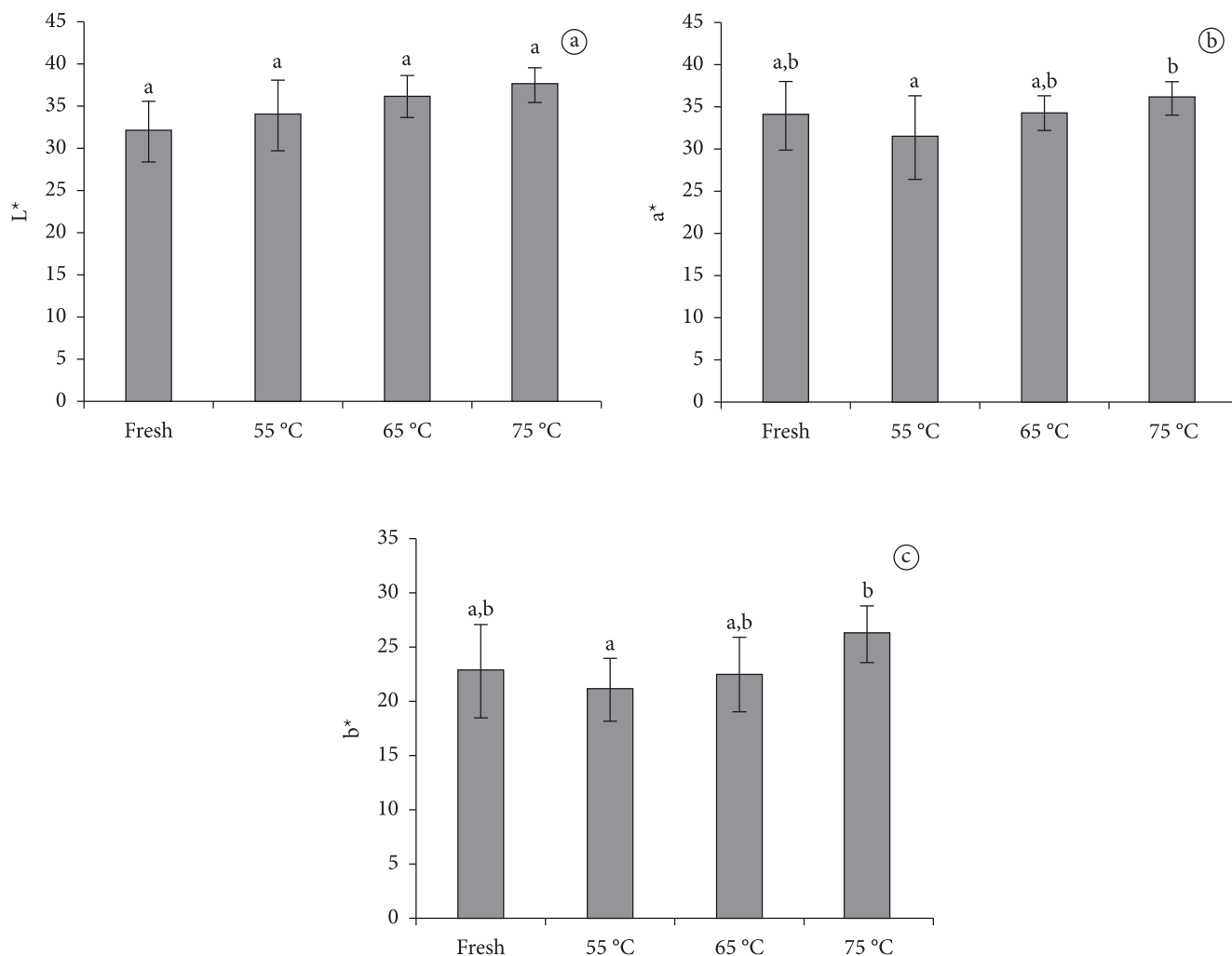


Figure 5. Effect of air drying temperature on the color parameters: L* (a), a* (b), and b* (c). Different letters mean significant difference ($p < 0.05$) of color parameters.

Changes in the chromatic coordinates a^* ($-a^*$ = green; $+a^*$ = red) and b^* ($-b^*$ = blue; $+b^*$ = yellow) are shown in Figure 5. The values of a^* increased with higher temperatures; however there was little variation in this parameter for the dried samples at different temperatures as compared to those of the fresh sample. The increase in chromatic coordinate b^* at 75 °C may be due to the formation of brown products in non-enzymatic reactions. Vega-Gálvez et al. (2009) observed an increase in b^* parameter with the increase in the air drying temperature as compared to the fresh sample.

Changes in color of dried pepper are mainly attributed to non-enzymatic browning and loss of carotenoids (PÉREZ-GÁLVEZ; HORNERO-MÉNDES; MÍNGUEZ-MOSQUERA, 2005, KIM et al., 2006). Some authors argue that the formation of brown compounds may be related to the loss of color since Maillard reactions normally occur upon the reduction of sugar and amino acids (MIRANDA et al., 2009). The discoloration of carotenoids during drying processing might occur through enzymatic or non-enzymatic oxidation (VEGA-GÁLVEZ et al., 2009).

4 Conclusions

The drying curves show similar behavior for most agricultural products. A constant drying rate period was observed at 55 °C during the first 90 minutes of process. After this period and under other temperatures, the drying process occurred in the falling rate period. The empirical model proposed by Page was considered as the one that best represented the drying kinetics of “dedo-de-moça” pepper. Therefore, it represents an excellent tool for estimating the drying time.

At air temperature of 75 °C, there was further degradation of color parameters and lower retention of vitamin C in dried peppers. The quality of the final product was higher when lower drying temperatures were employed due to less degradation of bioactive compounds. The present results may be useful to optimize the drying process to obtain dried red pepper with higher nutritional and functional values (vitamin C retention and total phenolics) and physical properties (color).

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