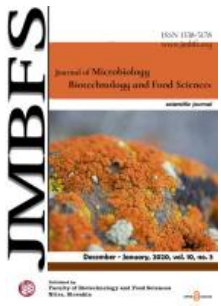

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CAROTENOID AND ANTIOXIDANT RETENTION OF THE DEHYDRATED TOMATO PRODUCTS AFFECTED BY THEIR DIFFERENT TECHNOLOGICAL TREATMENTS

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ABSTRACT

Tomatoes are the most commonly preserved vegetables in the world. Traditional tomato products are tomato juice, puree or ketchup but demand for dried tomatoes is increasing at the market. Drying is one of the oldest methods of preservation and often accompanies the degradation of nutritionally important ingredients. In order to protect nutrients from excessive oxidation during drying, the right choice of the drying temperature and the treatment of the raw material prior to drying are important elements of the manufacturing process. In our work we investigated the impact of various ways of antioxidant treatment of the raw material before drying on the stability of total carotenoids, polyphenols and antioxidant activity of the product. We used Uno Rosso F1 cultivar of tomatoes, dried by air at 70 °C, and the fruits were cut into slices of 3 mm thickness. To increase the stability of phytonutrients, we used the slice treatment prior to drying with 1% potassium bisulphite, ascorbic acid, citric and acetic acid and 5% sucrose and sodium chloride solutions. We found that the 1% solution of ascorbic acid was the most effective in protecting of total carotenoids and polyphenols. In the protection of total polyphenols, acetic acid and potassium bisulphite solutions were equally effective. The most significant increase in antioxidant activity was found to be ascorbic acid solution.

Keywords: drying, tomato, treatment

INTRODUCTION

At the food product market, there has been an increasing demand for dried tomatoes, which are used as flavoring or decorative ingredient in food **(Marfil et al., 2008).** Dried tomatoes, tomato powder, as well as other processed products are subject to scientific studies due to the high antioxidant activity and high carotenoid content especially lycopene (**Chang *et al.*, 2006; Monteiro *et al.*, 2008; Kobori *et al.*, 2010**).
The basic preservative principle of drying is to reduce water activity, limiting microbiological activity, enzymatic processes, and minimizing physical and chemical changes during storage of finished products (**Maskan, 2000; Krokida *et al.*, 2001**).
Karam *et al.* (2016) report that drying is a widespread and widely used process of fruit and vegetables preserving in which the removal of water from the product minimizes the various product degradations caused either by microorganisms or by enzymes that require sufficient water content in the environment. The drying conditions as well as the method of product processing significantly affect the nutritional quality of the product, but also physical, textural and sensory properties. Traditionally, warm air drying techniques are the most widely used, which may have an adverse effect on the quality of the product, especially due to the ongoing physico-chemical changes that occur during drying in the tissues. During drying in tomatoes, changes associated with degradation of nutritionally important components, e.g. vitamin C and lycopene occure. Incorrect choice of drying conditions, especially low or too high temperature or too long drying time, can cause serious damage to the product, especially its taste, color and nutritional content (**Doymaz, 2007; Heredia *et al.*, 2007; Cruz *et al.*, 2012**).
Color change is most often caused by degradation of carotenoids and lycopene and also by processes of non-enzymatic browning in the reaction of sugars and amino acids in the Maillard reaction process (**Marfil *et al.*, 2008**). Several authors studied the optimal drying conditions (**Sacilik *et al.*, 2006; Doymaz, 2007; Sanjinez-Argandoña *et al.*, 2011; Doymaz a Özdemir, 2014**).
Optimizing the tomato drying process can be achieved by providing maximum drying speed and minimizing oxidative and thermal damage. The prerequisite for achieving the desired quality and stability of the colors is the acceleration of the drying process due to the reduction of the cut thickness of the dried tomatoes. It is recommended the fruit to be cut into smaller pieces before drying, eg. slices, quarters. This operation will provide the larger contact area of the dried product with flowing air and will require less time to achieve the same level of moisture removal (**Giovanelli *et al.*, 2002; Sanjinez-Argandoña *et al.*, 2011**).
In order to improve the quality of dried tomatoes, it is recommended that tomatoes should be treated with calcium chloride solutions before the drying process (**Lewicki *et al.*, 2002; Lewicki and Michaluk, 2004**), sodium chloride (**Sacilik *et al.*, 2006**) or sodium metabisulphite (**Akanbi *et al.*, 2002; Santos-Sanchez *et al.*, 2012**).
Latapi and Baret (2006) report that the most widely used food additive in the drying industry is sulfur dioxide used in the gaseous state or as the sulfur dioxide salt used as a solution. **Santos-Sánches *et al.* (2012)** used the solution of 1% sodium metabisulphite in their work. The authors report that sulfur dioxide and sulphites are used as antioxidants to prevent degradation of ascorbic acid and lycopene during drying, but also during storage. **Muratore *et al.* (2008)** recommend tomatoes to be treated with a 1% citric acid solution before drying. **Abreu *et al.* (2011)** used osmotic solutions of sugar and sodium chloride at concentrations of 5 and 10% in order to increase the proportion of soluble substances in the final product and to speed up the drying process.
The aim of this study was to evaluate the efficacy of tomato slice treatment before drying with ascorbic, citric, acetic, potassium disulfite, sucrose and sodium chloride solutions for the stability of total carotenoids, total polyphenols and antioxidant activity.

MATERIAL AND METHODS

The experiment was performed using Uno Rosso F1 cultivar of tomatoes It is medium early determinate variety, suitable for mechanized harvesting. It has

strong growth with high fertility. The fruits are small, slightly elongated, they weighs 60 - 70 grams and are resistant to cracking in more frequent rainfall and irrigation. The fruits are particularly suitable for industrial processing.

Drying was performed in the laboratory oven (MEMMERT UF 160) with the possibility of controlling drying conditions, the drying temperature was 70 °C (**Mendelová *et al*., 2014; Andrejiová and Mendelová, 2016**). Drying was performed until the moisture content of the product was less than 18%. The final moisture content was monitored at (KERN MRS 120-3) moisture analyzer. The average drying time was 17 hours.

We dried the fruit into slices of 3 mm thickness. Before drying, we used the treatment of slices with antioxidant solutions. Based on recommendations such as **Latapi and Barret (2006), Hasan and El Hana (2008), Muratore *et al.* (2008)**, **Abreu *et al.* (2011), Hasturk *et al.* (2011), Santos-Sánchez *et al.* (2012), Doymaz and Özdemir (2014), Azzez *et al.* (2017),** we prepared: 1% potassium metabisulphite solution, 1% ascorbic acid solution, 1% citric acid solution, 1% acetic acid solution, 5% sucrose solution and 5% sodium chloride solution. Treatment with solutions of organic acids and potassium metabisulphite was performed for 5 minutes, treatment with osmotic solutions for 60 minutes. After treatment, the excess moisture of the fruits was removed on the filter paper and then placed on a dryer.

The total carotenoid content was determined by the methodology of **Hegedűsová *et al.* (2016**). Sample preparation for analysis consisted of homogenization at BOSH MKN 6003 mill for 3 minutes. Carotene extraction from the homogenized samples was performed with acetone. The acetone extract obtained was shaken repeatedly with petroleum ether, and the layers were phased with distilled water. Subsequently, the carotene-saturated petroleum ether phase was dried over anhydrous sodium sulfate, transferred quantitatively to a volumetric flask and made up to the specified volume with 25 ml petroleum ether. The absorbance of the samples was measured spectrophotometrically at JENWAY spectrophotometer (6405 UV / VIS) at 450 nm.

The determination of total polyphenols was performed by the Folin-Ciocalteau method of **Lachman *et al.* (2003)**. The method is based on the reaction of Folin-Ciocalteu reagent with polyphenols present in the analyzed sample to produce a blue color product. Sample preparation for polyphenol analysis consisted of homogenization and extraction in 80% ethanol at HEIDOLPH GSL 3006 shaker at 150 rpm for 24 hours. The polyphenol content was measured spectrophotometrically at 765 nm used JENWAY spectrophotometer (6405 UV / VIS). The total polyphenols content was calculated from calibration curve (GAE) of the gallic acid at concentration 50-800 mg/L.

The antioxidant activity was determined by the Phosphomolybdenum method (**Prieto *et al*., 1999**). The principle of the method is based on the reduction of Mo (VI) to Mo (V) by the reducing components of the sample and subsequent formation of the phosphate complex Mo (V) in acid pH with varying intensity of green color. The preparation of samples for analysis was consistent with the preparation of the sample for analysis of total polyphenols. The absorbance of the samples was measured at JENWAY (6405 UV / VIS) spectrophotometer at 695 nm. The reducing ability of the sample was calculated from the ascorbic acid calibration curve prepared from solutions with ascorbic acid (AAE) concentrations of 40-300 mg/L.

The experiment was performed in three replicates. To assess statistically significant differences among tomato variants treated before drying, we used the Tukey HSD multiple comparison test at P <0.05.

RESULTS AND DISCUSSION

Several scientific works (**Kerkhofs *et al*., 2005; Chang *et al*., 2006; Santos-Sánches *et al*., 2012; Gümüsay *et al*., 2015**) state that in practice the most frequent air drying causes a significant decrease in nutritional quality. In order to minimize losses during such drying and improve the nutritional quality of the final product, an important technological step is the antioxidant treatment of the material prior to drying.

Based on the measured results in total carotenoid content, total polyphenol content and antioxidant activity, we found that treatment of tomato fruit before drying showed better results in all treatments and parameters than drying without pretreatment.

In terms of the overall carotenoid content assessment, ascorbic acid treatment was determined to be the most appropriate treatment method, with the highest increase in total carotenoid content (29.94 mg/100 g DM) compared to the untreated control. This claim was also supported by the results of the Tukey HSD assay, in which ascorbic acid treatment was statistically significant (P <0.05) the best treatment. The Tukey HSD test did not show the statistically significant difference within the effect of the remaining treatments (1% potassium metabisulphite, 5% sodium chloride, 5% sucrose, 1% citric acid, 1% acetic acid) on total carotenoid content in dried tomato slices (Table 1).

Table 1 Means and homogeneous groups for the total carotenoid, polyphenol and antioxidant activity content at each pre-drying treatment based on multiple comparison from the Tukey HSD test

Treatment	Total carotenoid content (mg/100 g DM)	Total polyphenol content (mg GAE/100 g DM)	Antioxidant activity (mg AAE/100 g) DM
control (no treatment)	126.85 ±0.29a	204.44 ±6.93a	351.37 ±16.59a
citric acid 1%	130.33 ±0.42ab	218.90 ±4.22ab	388.05 ±0.29b
sucrose 5%	134.79 ±0.40ab	226.35 ±5.44bc	411.22 ±10.15bc
sodium chloride 5%	143.92 ±0.08ab	234.55 ±2.75c	419.04 ±6.79bc
acetic acid 1%	151.42 ±2.26ab	235.36 ±4.11cd	430.21 ±5.24c
potassium metabisulphite 1%	152.43 ±17,64ab	235.38 ±7.25cd	434.29 ±15.59c
ascorbic acid 1%	156.79 ±19.53b	250.25 ±6.87d	540.98 ±20.47d

- different letters at mean represent statistically significant differences among treatments (P <0.05)

By evaluating the total polyphenol content we found, similarly to the total carotenoid content, statistically significant (P<0.05) the highest total polyphenol content after treatment with 1% ascorbic acid (250.25 mg GAE/100 g DM). Compared to the control sample with no treatment (204.44 mg GAE/100 g DM), it is the highest difference (45.81 mg GAE/100 g DM). There were statistically significant (P<0.05) different 11 test pairs. Treatment with 1% ascorbic acid was not statistically significant different (P>0.05) comparing to the treatment with 1% acetic acid and 1% potassium metabisulphite (Table 1).

Treatments with 1% citric acid solution and 5% sodium chloride solution were evaluated to be the less effective treatments for polyphenol protection. Treatment with 5% sucrose solution (218.90 mg GAE/100 g DM) was not statistically significant (P>0.05) different from the untreated control sample (204.44 mg GAE/100 g DM) in total content polyphenols in dried tomato slices.

As the statistically significant (P <0.05) the most effective in antioxidant protection was the solution of 1% ascorbic acid again. Ascorbic acid is considered to be the significant antioxidant, it increased the antioxidant potential of dried tomatoes, that can be seen on the high antioxidant activity (540.98 mg AAE/100 g DM). Based on the one-way ANOVA and post-hoc Tukey HSD tests, it can be concluded that all 5 pre-drying treatments applied showed the statistically significant (P <0.05) positive effect on antioxidant activity of dried tomato slices (Table 1).

Table 1 shows positive effect of the individual treatments on the antioxidant activity of the dried slices. Relatively similar in antioxidant protection of dried tomato slices were solutions of potassium metabisulphite, acetic acid, sodium chloride and citric acid, among which we did not find any statistically significant difference (P> 0.05). Statistically significant (P<0.05) the lowest effect in antioxidant protection showed the sucrose solution (388.05 mg AAE/100 g DM), but even this solution showed no statistically different (P<0,05) results compared to the citric acid solution (411.22 mg AAE/100 g DM) and sodium chloride (419.04 mg AAE/100 g DM).

Muratore *et al.* (2008) investigated the effect of drying and treatment temperature on changes in lycopene, β-carotene and ascorbic acid, during drying at various temperatures as well as the effect of fruit treatment prior to drying. Cherry tomato fruits were treated with 1% sodium chloride solution and 1% citric acid prior to drying. Drying was performed at 40, 60 and 80 °C. They dried the samples to the relatively high residual moisture up to 40% and named the product as semi-dry cherry tomatoes. They found that the temperature of 80 °C was the most suitable for the stability of lycopene and β-carotene for both untreated and treated samples. The fresh sample contained 99.8 mg/100 g DM of lycopene, and only 58.5 mg of 100 g^{-1} DM was retained in 40 ° C dried sample and in the sample dried at 80 °C, 76.4 mg/100 g DM. In the treated samples, the authors did not find significantly higher contents of lycopene or β-carotene compared to untreated samples. However, the positive effect of the treatment was shown in relation to ascorbic acid. In the fresh sample of tomatoes, they detected 433.5 mg/100 g DM, in the untreated sample dried at 40 °C, the ascorbic acid content was 311.5 mg/100 g DM and in the treated sample 368.1 mg/100 g DM.

Abreu *et al.* (2011) used 5 and 10% osmotic solutions of sucrose and sodium chloride as well as various combinations prior to tomato drying. They used Bonus variety, the treatment with osmotic solutions was performed for 120 minutes, followed by drying at 65 °C for 12 hours. Treatment with osmotic solutions after drying resulted in the higher soluble dry matter content, especially in solutions with 10% sucrose content. They found interesting results in the evaluation of lycopene retention in dried samples. Sucrose solution showed the best results. After treatment with this solution, they detected an increase in the lycopene content in the sample by 5.63%. The lycopene content increased from 446.85 μg/g DM to 472.02 μg/g DM. 10% sucrose solution and 5% sodium chloride solution were also found to be suitable solutions for treating of tomatoes

prior to drying to improve lycopene stability. In the case of 10% sucrose solution, the lycopene content after drying was 43.5% higher than in the control sample and 34.1% in the case of 5% sodium chloride solution. In our work, comparing to 5% solution of sucrose and 5% sodium chloride solution, we found better results with sodium chloride solution in relation to the stability of total carotenoids, even though it is far from being such a high retention percentage as reported by the authors. In case of 5% sodium chloride solution, the total carotenoid content was higher by 13.8% compared to the control sample and 6.8% by the 5% sucrose solution.

Hastur Sahim *et al.* (2011) compared the effect of different ways of drying in tomato slices: in the sun, in a hot air dryer at 65, 75 and 85 °C under vacuum, by lyophilization and also by treatment before drying with 1% ascorbic acid + 1% citric acid + 4% potassium carbonate solution + 2% sodium metabisulphite on the stability of lycopene and the color properties of dried tomatoes. Authors found that treatment with the prepared solution showed the positive effect on the retention of lycopene in dried tomatoes in all hot air drying processes as well as in vacuum drying and lyophilization. By evaluation of the drying in a hot-air dryer as the most commonly used drying method in practice, the drying at 65 ° C after the previous treatment the highest stability of lycopene was positively evaluated.

Latapi and Barret (2006a) dried tomatoes in direct sunlight at an average daily temperature of 30 °C for 9 days. In order to protect the nutritionally important components, they treated tomatoes before drying with 10% sodium chloride solution, 8% sodium metabisulphite solution and solution obtained by mixing of a basic solution of sodium chloride and potassium metabisulphite. They showed positive effect on the stability of lycopene, not only during the drying process, but also during the subsequent storage of the finished products. By assessing the impact on the stability of ascorbic acid, authors noted the inadequate effect of the solutions used, as the ascorbic acid content of the dried samples decreased from the original value of 3.37 mg/g to less than 0.4 mg/g in the treated samples. With only sodium chloride treatment, ascorbic acid content was reduced by 97.3%, almost to zero content.

Doymaz and Özdemir (2014) treated tomatoes with 3% potassium carbonate solution and 2% solution of oleic acid and ethanol. They used the drying temperature of 60, 68 and 76 °C, and the tomatoes were cut in half, quarter and eighth. In their conclusions they note the positive effect of the drying temperature and the fruit treatment before drying on the drying rate.

CONCLUSION

Based on the results, we can conclude that all pre-drying treatments used, showed positive effect on the resulting nutritional quality of the dried tomato slices. In assessing the effect of treatment on carotenoid stability, we found the highest total carotenoid content after treatment with 1% ascorbic acid solution, but based on the results of the Tukey test, this treatment was not statistically significant (P> 0.05) compared remaining treatments. By evaluating the effect of the pre-drying treatment on the stability of the total polyphenol content, treatment with 1% ascorbic acid solution was the most effective treatment, but 1% acetic and potassium metabisulphite solutions were equally effective, with no statistically significant difference (P> 0.05). The weakest effect on polyphenol stability showed the 5% sucrose solution.

The ascorbic acid solution was also proven to be effective as pre-drying treatment regarding the antioxidant activity, and contributed to increasing the antioxidant potential of dried tomato slices as well. Less effective than 1% ascorbic acid solution appeared to be 1% acetic acid solution and 1% potassium metabisulphite solution as in the case of polyphenol protection, with no statistical difference. The decreasing gradient in the antioxidant protection effect during drying showed solutions of sodium chloride, citric acid and sucrose, among which we found no statistically significant (P> 0.05) difference.

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