CONVECTIVE, VACUUM AND FREEZE DRYING OF BLACK SEEDLESS RAISINS: PHYSICOCHEMICAL PROPERTIES

KONVEKTIVNO, VAKUUM I SUŠENJE ZAMRZAVANJEM CRNOG BESEMENOG GROŽĐA: FIZIČKO-HEMIJSKE KARAKTERISTIKE

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ABSTRACT

Fresh black seedless grapes were dried by convective, vacuum and freeze drying in order to investigate and compare the physical (moisture content, water activity, total colour change and rehydration power) and chemical (total phenolic, flavonoids and monomeric anthocyanin content and antioxidant activity) properties of dried raisin samples. The optimal maximum and minimum values of all the investigated physicochemical parameters were obtained in vacuum dried samples. The vacuum dried sample (70 °C, 20 mbar and 11 h) was characterized as a sample with the most favourable physicochemical properties (namely moisture content, water activity, rehydration power, total phenolic and flavonoid content), whereas convective and freeze dried samples were found to exhibit less favourable results relative to all the investigated physicochemical properties.

Keywords: black seedless raisins, convective drying, vacuum drying, freeze drying, physicochemical properties

REZIME

Proizvodnja sušenog grožđa u Srbiji je veoma popularna. Sušeno grožđe konzumira se kao poslastica ili kao dodatak žitaricama i konditorskim proizvodima. Tehnika sušenja značajno utiče na kvalitet osušenog grožđa. U većini zemalja tradicionalno se primenjuje tehnika sušenja grožđa na suncu. Takođe, veliki broj proizvođača koristi tehniku konvektivnog sušenja toplim vazduhom za dobijanje sušenog grožđa. Nedostaci konvektivnog sušenja, kao što su prisustvo vazduha i visoke temperature vazduha, mogu se uspešno prevazići primenom vakuum sušenja i sušenja smrzavanjem. Sveže besemeno crno grožđe osušeno je konvektivnim sušenjem, vakuum sušenjem i sušenjem zamrzavanjem u cilju poređenja fizičkih (sadržaj vlage, aktivnost vode, ukupna promena boje i sposobnost rehidratacije) i hemijskih (sadržaj ukupnih fenola, flavonoida i monomernih antocijana i antioksidativna aktivnost) osobinasušenog grožđa. Optimalne minimalne i maksimalne vrednosti ispitanih fizičko-hemijskih parametara zabeležene su u vakuum osušenim uzorcima. Vakuum osušen uzorak (70°C; 20 mbar i 11 h) okarakterisan je sa najvećim brojem poželjnih vrednosti ispitivanih parametara (sadržaj vlage, aktivnost vode, sposobnost rehidratacije, sadržaj ukupnih fenola i flavonoida). Konvektivno osušeni uzorci i uzorci osušeni zamrzavanjem pokazali su manje dobre rezultate u poređenju sa vakuum osušenim uzorcima u pogledu ispitivanih fizičko-hemijskih parametara.

Ključne reči: besemeno crno grožđe, konvektivno sušenje, vakuum sušenje, sušenje zamrzavanjem, fizičko-hemijske karakteristike

INTRODUCTION

Black seedless grapes are highly valued for their irresistible taste and the enormous processing potential resulting in products such as raisins, juices, wine and other alcoholic drinks. Black grapes are rich in phenolic compounds, which have been found to possess antioxidant properties (Rice-Evans *et al.*, 1997; Velioglu *et al.*, 1998), as well as in numerous other nutritional compounds. Raisins could be consumed directly or as ingredients in biscuits, chocolates and breads (Xiao *et al.*, 2010). Furthermore, the production of raisins from grapes greatly contributes to the growth of business profit in the grape-growing countries (Pangavhane *et al.*, 1999). During refrigerated storage, a relatively high content of water in fresh grapes affects the microbial spoilage (Xiao *et al.*, 2010). For this reasons, fresh grapes should be consumed or processed into different products. Therefore, drying is the most common way of grape preservation as raisins have a longer shelf life and occupy less storage compared to other grape products. According to Krokida *et al.* (2000), the quality of dehydrated food products is strongly affected by drying processes used for preservation, as well as by the applied set of drying parameters. Almost all raisins are produced by natural drying in sunlight (Li *et al.*, 2010). In order to improve the quality of dried products, traditional drying techniques such as sun drying can be replaced by industrial drying methods such hot air or convective drying (Xiao *et al.*, 2010). Convective drying is a commonly used drying process in

which products are dried using a stream of heated air under controlled conditions (Vakula *et al.*, 2015). In addition to convective drying, fruit drying can also be performed by vacuum and freeze drying, thus supplanting a stream of heated air (used for drying) by lower temperatures and lower oxygen contents. These techniques and mild drying conditions favour the temperature sensitive fruit drying and reduce negative chemical reactions, thus preserving highly valuable bioactive compounds in fruit during the drying process (Joshi *et al.*, 2011). The primary purpose of this study was to compare convective, vacuum and freeze dried black seedless raisins according to their physicochemical properties. The physical properties examined encompassed moisture content, water activity, total colour change and rehydration power, whereas the chemical properties examined involved total phenolics, flavonoids and monomeric anthocyanins contents, as well as the antioxidant activity of dried products.

MATERIAL AND METHOD

Sample

Fresh black seedless grapes (variety SK 00-3/40) were purchased at the Faculty of Agriculture, University of Novi Sad in September (2016). After purchasing, the samples were frozen and stored at -20 °C until drying.

Chemicals

1,1-Diphenyl-2-picryl-hydrazyl-hydrate (DPPH) and (-)-catechin were purchased from Sigma Aldrich (Germany); Folin–

Ciocalteu reagent and gallic acid were purchased from Merck (Germany). All the other chemicals were of the analytical and HPLC reagent grade.

Drying procedures

Vacuum drying was performed in a vacuum dryer prototype (described in detail by Šumić et al. (2013)), whereas the convective and freeze drying procedure used were described in detail by Šumić et al. (2016).

Analysis of the physicochemical properties

Moisture content was determined by drying the samples at 105 °C until the constant weight and water activity was measured using an a_w meter. Total colour change was obtained by determining the CIE $L^*a^*b^*$ color coordinates and it is expressed as ΔE , which presents the difference between the color of fresh and dried black seedless raisins. The rehydration power of dried samples was obtained by immersing 2.0 g of chopped dried samples in 50 mL of distilled water for 24 h. The volume of excess water, unabsorbed by dried samples, was measured. After deducting this amount of water from the initial 50 mL, the results obtained were expressed as a percentage (%). The total phenolic and the total flavonoid contents were determined using the Folin-Ciocalteu colorimetric assay (Singleton and Rossi 1965; Kähkönen et al. 1999) and the aluminum chloride assay (Harborne, 1984) respectively, whereas the total monomeric anthocyanins was determined using the pH differential method (Bakar et al., 2009). Antioxidant activity was obtained using the DPPH assay (Espín et al., 2000). A description of the analysis performed (moisture content, water activity, total colour change, rehydration power, total phenolic, flavonoid and monomeric anthocyanins content and antioxidant activity) was shown in detail by Šumić et al. (2016).

Experimental design

Nine samples of fresh black seedless grapes, each weighing 300 g, were used in the experiments. Four physical parameters (moisture content, water activity, total colour change and rehydration capability) and four chemical parameters (total phenolic, flavonoid and monomeric anthocyanin content and antioxidant activity) were obtained for three convective dried samples (C1-3), five vacuum dried samples (V1-5) and one freeze dried sample (F1). The conditions of drying methods are presented in Table 1.

Table 1. Convective, vacuum and freeze drying conditions

Dried sample	Temperature [°C]	Pressure [mbar]	Drying time [h]
C1	55	1000	24
C2	60	1000	18
C3	70	1000	10
V1	40	20	26
V2	48	20	25
V3	55	20	17
V4	63	20	24
V5	70	20	11
F1	-30	0.01	120

*Convective dried (CD) sample

*Vacuum dried (VD) sample

*Freeze dried (FD) sample

Statistical analysis

The analysis of variance (ANOVA, $p < 0.05$) was applied in order to differentiate between the samples using the $\alpha = 0.05$ criterion and the Tukey's multiple comparison test.

RESULTS AND DISCUSSION

Characterization of fresh black seedless grapes

Two physical (moisture content (MC) and water activity (a_w)) and four chemical parameters (total phenolic (TPC), flavonoid (TFC) and monomeric anthocyanin content (TMAC)

and antioxidant activity (AA)) were observed in fresh black seedless grapes. The results obtained are presented in Table 2.

Table 2. Investigated properties of fresh black seedless grape samples

Analysis	Raw sample
MC [%]	72.25
a_w	0.960
TPC [mg GAE/100 g]	82.71
TFC [mg CE/100 g]	18.36
TMAC [mg CGE/100 g]	225.79
IC ₅₀ [μg/mL]	1.8663

Physical properties

The moisture content (MC) (Table 3) of convective dried samples varied between 8.47 and 28.35 %. It can be seen that higher temperatures used during convective drying significantly influence the MC reduction. The lowest MC of vacuum dried samples was also the lowest MC of all the investigated dried samples. Such a low MC of the V5 sample (70 °C; 20 mbar and 11 h) was probably caused by high temperature in a combination with low pressure used during vacuum drying. Furthermore, F1 (-30 °C, 1000 mbar and 120 h) had the highest MC of all the dried samples. The raisin MC obtained by Williamson and Carughi (2010) was 17.7 %, which is in the range of the MC values obtained in this paper. The water activity (a_w) (Table 3) of convective dried samples was in the range from 0.39 to 0.74, whereas the water activity of vacuum dried samples ranged between 0.28 and 0.87. As in the case of MC, the lowest and the highest a_w values of all the dried samples were obtained in the V5 (70 °C, 20 mbar and 11 h) and F1 (-30 °C, 1000 mbar and 120 h) samples, respectively. Such results were expected as these two parameters are in correlation.

Table 3. Experimentally obtained parameter values of the dried samples examined

Sample	Moisture content [%]	Wateractivity	ΔE [%]	Rehydration power [%]
C1	28.35	0.74	3.07	30.00
C2	27.22	0.62	2.96	25.00
C3	8.47	0.39	5.76	36.25
V1	21.53	0.68	0.89	37.50
V2	17.67	0.87	0.90	37.50
V3	20.23	0.87	0.64	33.75
V4	11.45	0.38	3.30	40.00
V5	5.03	0.28	1.65	47.50
F1	49.48	0.88	3.93	14.10

Color is considered to be one of the most important quality indicators of dried products (Radojčin et al., 2010). The lowest total colour change (ΔE) (Table 3) of convective dried samples was obtained in C1 (55 °C, 1000 mbar and 24 h), whereas the highest ΔE was recorded in C3 (70 °C, 1000 mbar and 10 h). Consequently, higher temperatures used during the convective drying of the C3 sample negatively influenced the preservation of the original fresh fruit colour. The ΔE value of the C3 sample was also the highest compared to all the other dried samples. Accordingly, the lowest ΔE value of vacuum dried samples observed in V3 (55 °C, 20 mbar and 17 h) was also the lowest ΔE value obtained in all the samples dried. Such a low ΔE value indicates a positive influence of the following drying parameters on colour preservation: 55 °C, 20 mbar and 17 h. The ΔE of F1 was also rather high, indicating that long drying time caused an increase in ΔE in the freeze dried sample.

The rehydration power (RP) (Table 3) of convective dried samples varied between 25 % and 36.25 %, whereas the RP of vacuum dried samples was in the range from 33.75 % and 47.50

%. The highest value of rehydration power was obtained in V5 (70 °C, 20 mbar and 11 h), whereas the lowest and highest RP values of all the dried samples were obtained in the F1 and V5 samples, respectively. Moreover, the F1 and V5 samples were found to exhibit the highest and lowest MC and a_w values, respectively. Such results were expected as there is no direct correlation between these parameters.

Chemical properties

The lowest total phenolic content (TPC) (Figure 1) of convective dried samples was recorded in C1 (55 °C, 1000 mbar and 24 h), whereas the highest TPC value was recorded in C2 (60 °C, 1000 mbar and 18 h). The range of the TPC values obtained for convective dried samples approximates to the TPC values observed in vacuum dried samples. The TPC values of V1-V5 varied between 263.13 mg and 382.08 mg GAE/100 g DW, indicating that the combination of high temperature and short vacuum drying time is more desirable for the TPC preservation in raisins than the combination of low temperature and long vacuum drying time. According to Meng et al. (2011), the total polyphenolic content in raisins varied between 193.3 and 678.4 mg GAE/100g DW, whereas Breksa et al. (2010) recorded a variation between 316.3 mg and 1,141.3 mg GAE/100 g DW. The total phenolic content of raisins recorded in the study of Rababah et al. (2012) was 401.5 mg GAE/100g DW. The highest TPC of vacuum dried samples was obtained in the V5 sample, in addition to the lowest MC and a_w and the highest RP. Furthermore, the V5 sample was also found to exhibit the highest TPC value of all the dried samples. The lowest TPC value of all the investigated samples was recorded in F1 (-30 °C; 0.01 mbar and 120 h). The highest total flavonoid content (TFC) (Figure 2) of convective dried samples was obtained in C2 (60 °C, 1000 mbar and 18 h), which was expected as flavonoids represent the subgroup of polyphenolic compounds. However, the range of TFC values obtained in vacuum dried samples was between 100.32 and 150.64 mg CE/100 g DW, which is in accordance with the results obtained by Meng et al. (2011) (the authors recorded a total flavonoid content in raisins of 106.2-522 mg CE/100 g DW). The lowest TFC value of vacuum dried samples was obtained in V4 (63 °C, 20 mbar and 24 h), which also exhibited the highest TPC of all the dried samples. As in the instance of TPC, the sample with the lowest TFC, i.e. the F1 sample, was found to have the highest MC, a_w and the lowest RP value. The range of the total monomeric anthocyanin content (TMAC) (Figure 3) of convective dried samples was from 41.93 mg to 138.00 mg CGE/100 g DW. These results approximate to the result obtained by Rababah et al. (2012), who recorded an anthocyanin content of 41.8 mg CGE/100 g DW in raisin samples. The lowest TMAC of convective and all the other dried samples were observed in C3 (70 °C, 1000 mbar and 10 h). Consequently, in addition to shorter drying time, high temperatures used during convective drying negatively influenced the preservation of TMC in the sample C3. In like fashion, the combination of high temperature and short vacuum drying time is more desirable for both TPC and TFC preservation than the use of low temperature and long vacuum drying time. However, the F1 sample had significantly higher TMAC values than the sample C3 with the lowest TMAC value obtained. The highest IC₅₀ (Figure 4), i.e. the lowest antioxidant activity (AA) value of all convective dried samples was obtained in the sample C1 (55 °C, 1,000 mbar and 24 h). This was also the lowest AA of all the dried samples. Long drying time and the presence of oxygen during convective drying negatively influenced the antioxidant activity of dried samples. The highest AA, TPC and TMAC results of vacuum and all the other dried samples was recorded in the sample V5

(70 °C, 20 mbar and 11 h). As in the instance of TFC, the F1 sample had significantly high AA values compared to the lowest AA values obtained in the sample C1. According to Breksa et al. (2010), the antioxidant activity of raisins ranged from 7.7 to 60.9 $\mu\text{mol Trolox/g DW}$.

Fig. 1. Total phenolic content (TPC) recorded in CD, VD and FD samples; *Means that do not share letters are significantly different ($p < 0.05$)

Fig. 2. Total flavonoid content (TFC) recorded in CD, VD and FD samples; *Means that do not share letters are significantly different ($p < 0.05$)

Fig. 3. Total monomeric anthocyanins content (TMAC) recorded in CD, VD and FD sample; *Means that do not share letters are significantly different ($p < 0.05$)

Fig. 4. IC₅₀ values recorded in CD, VD and FD samples

*Means that do not share letters are significantly different ($p < 0.05$)

CONCLUSION

Based on the results obtained, i.e. the physicochemical parameter values of black seedless raisins (moisture content, water activity, total colour change, rehydration capability, total phenolic, flavonoid and monomeric anthocyanin compounds, and antioxidant activity) dried by convective, vacuum and freeze drying, it can be concluded that the lowest moisture content and water activity were recorded in the vacuum dried sample V5 (70 °C, 20 mbar and 11 h), as well as the highest rehydration power, total phenolic and monomeric anthocyanins contents, and the highest antioxidant activity. Therefore, the vacuum dried sample V5 was characterized as a sample with the greatest number of desirable physicochemical properties. The lowest total colour change and the highest total flavonoid content were observed in the vacuum dried samples V3 (55 °C, 20 mbar and 17 h) and V2 (48 °C, 20 mbar and 25 h). All desirable (maximum and minimum) physicochemical parameter values were obtained in vacuum-dried samples. In addition to the highest moisture content and water activity, the lowest rehydration power and total phenolic and flavonoid contents were observed in the freeze dried sample F1 (30 °C, 0.01 mbar and 120 h). The lowest monomeric anthocyanin content and the highest total colour change were recorded in the convective dried sample C3 (70 °C, 1000 mbar and 10 h), whereas the lowest antioxidant activity was obtained in the sample C1 (55 °C, 1000 mbar and 24 h). On balance, convective and freeze dried samples were found to exhibit less desirable physicochemical properties than vacuum dried samples.

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