Chemical changes caused by air drying of fresh plum fruits

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Abstract

Drying of fresh plums may provide an excellent delicacy, but such technological process is inevitably followed by certain chemical changes. Three plum cultivars were dried at two different temperatures (70°C and 90°C), and the effect of drying procedure on total anthocyanins, flavonoids, phenolics, selected bioactive compounds and antioxidant capacity were monitored. Polyphenolic compounds suffered strong changes, depending on the applied drying temperature. Drying procedure at both 70°C and 90°C influenced to a great extent for total polyphenolic content in the fresh plums of 'Čačanska Rodna' (1.8 and 2.1-fold increase, respectively). The identical drying conditions showed almost no influence on plums of 'Stanley', while drying 'Mildora' at 70°C resulted in significant decrease, but higher temperature caused the opposite effect. Statistical analysis showed high correlation between polyphenolic content and antioxidant activity, in all tested cultivars and for both fresh plums and prunes. Caffeoylquinic acids and caffeic acids suffered certain changes depending on the cultivar and temperature applied. Anthocyanins completely disappeared after drying. Although drying of fresh plums prompted severe chemical changes, prunes might be considered as functional food due to the high level of antioxidant.

Introduction

High consumption of fruits and vegetables could promote an excellent state of health in humans, lower the risk of several chronic diseases such as heart disease, cancer, obesity, ulcer, diabetes, and even slow aging (Oyebode *et al*., 2014; Shahidi and Ambigaipalan, 2015; Rodriguez-Casado, 2016; Van Berleere and Dauchet, 2017). These effects are mainly associated with biologically active components that are naturally present in the produce, such as phenolic compounds (flavonoids, anthocyanins, phenolic acids, etc.), carotenoids, vitamins, minerals and fibres (Crozier *et al*., 2009; Acosta-Estrada *et al*., 2014). Apart from their health benefits, these compounds mainly determine the sensory qualities of the fruits (colour, flavour, taste). More health benefits of daily consumption of whole fruits or vegetables, raw or processed, rather than pharmaceutical supplements of only one of the constituents, is well accepted in public opinions.

Dried fruits, as concentrated form of fresh fruits, are mainly consumed as finger food snacks due to their delicate organoleptic properties and high energy foodstuff. Prunes are dried fruits of certain cultivars of plums (*Prunus domestica* L.). In recent years, they have been recognised as a functional food, due to their high antioxidant activity and favourable effects on human health (Lever *et al*., 2014; Léotoing *et al*., 2016; Wallace, 2017). The benefits of prunes are mainly associated with the high content of polyphenolic compounds (Kayano *et al*., 2004; Chang *et al*., 2016). In terms of total phenolics and antioxidant capacity, prunes are highly ranked, as compared to the other dried fruits and vegetables (Wu *et al*., 2004; Pellegrini *et al*., 2006).

In the present work, prunes were obtained from three plum cultivars: 'Stanley', 'Čačanska Rodna' and 'Mildora'. 'Stanley' cultivar was developed in the New York State Agricultural Experiment Station in the early 20th century from the cross of 'd'Agen' and 'Grand Duke', and is a major plum cultivar in

the USA. Plum cultivars 'Čačanska Rodna' and 'Mildora', intended for drying, were developed at Fruit Research Institute - Čačak, Serbia. 'Čačanska Rodna' cultivar resulted from the cross of 'Stanley' × 'Požegača' in 1961. It was named and released in 1975, and patented in 1991. Fruits are of blue colour, with favourable technological properties suitable for drying (Mitrović *et al*., 2013). 'Mildora' cultivar originated from the cross of 'Large Sugar Prune' × 'Čačanska Lepotica' in 1980, and was named and released in 2004. Fruits are of light purple colour, suitable for drying (Mitrović *et al*., 2006).

The primary objective of the present work was to determine the chemical changes, based on the level of total phenolics, selected phenolic compounds, and antioxidant capacity of plums dried at two different temperatures (70°C and 90°C). In order to analyse the changes that resulted from drying, freshly harvested unprocessed plums were also analysed and served as control. The determination of an optimal drying regime is a crucial step in the production of prunes. Primarily, the entire process should be shortened as much as possible, due to the energy consumption; but on the other hand, shortened drying procedure requires high temperatures, which might cause loss of certain valuable compounds. The cultivar specificity must also be considered. Therefore, the three previously mentioned cultivars and two temperature regimes were chosen in order to optimise the drying process.

Materials and methods

Fruit collections

Plum fruits (*Prunus domestica* L.) of 'Stanley', 'Čačanska Rodna' and 'Mildora' cultivars grafted on rootstock *P. cerasifera* L. were collected at appropriate maturity stages for drying (early-September) from an experimental orchard established in 1996 in the village Preljina (43°55'26"N, 20°26'52"E), Serbia. Samples were collected as follows: 300 samples of each plum cultivar (with no mechanical injuries or disease manifestation) were selected from 10 trees (30 fruits per tree). Centrally positioned plum trees in the orchard were used for the experiment. After harvesting, one third of the fruits were stored at -20°C for no longer than 1 w before analyses were performed. The remaining two thirds of fruits were dried at 70°C and 90°C. After drying, prunes were stored at room temperature for two months prior to examination. The whole edible part of the fruit was used in the present work. Fresh plums and prunes were carefully cut in halves and pits manually removed by hand. Mesocarp and exocarp were frozen by pouring into liquid nitrogen and homogenised using a stainless-steel blender.

Experimental drying unit

The drying of fresh plum fruits was conducted in a laboratory convective air dryer (Figure 1) (Kandić *et al*., 2006). The drying procedure was as follows: (i) ambient air was channelled in by inlet vent (1) and moved to the preparation joint (2), where it was heated up to the desired temperature, and turned either towards the valve V1 or V2; (ii) air was moved to the one of inlet joint (3a or 3b) and through the drying chamber (6), where the fruits were placed; (iii) a certain portion of used air was removed from the system by an outlet joint (5), while the rest was moved back to the dryer by recirculation joint (4); (iv) this air portion was moved back to the inlet vent (1), where it was mixed/refreshed with ambient air (Figure 1).

Constant air drying velocity of 1 ms^{-1} (measured by anemometer) is provided by the centrifugal fan, with a power of 1.5 kW at 220 V. Air was heated by electrical heater, with a maximum power of 12 kW at 220 V. Control of the air temperature was enabled by K (NiCr-Ni) type thermocouples connected with an Omega digital thermometer type 2809 (Ωmega Engineering, Inc., Stanford, CT, USA), which allowed continuous measurement. Drying trays, which are made of stainless-steel braided wire with a 400 × 400 mm stainless steel frame, were parallelly placed into the drying chamber. Fresh plum fruits were positioned onto the drying trays in a single layer formation, while the heated air was introduced vertically across the trays.
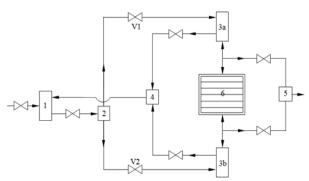

Figure 1. Laboratory convective air dryer scheme.

Drying procedure

Equally sized fruits with equal solid soluble content were placed on trays. The fruit weight of 'Stanley' cultivar was about 50 g (20 fruits/kg; pit: 3.5%), 'Čačanska Rodna' cultivar was 40 g (25 fruits/kg; pit: 4.6%), and 'Mildora' cultivar was 25 g (40 fruits/kg; pit: 4.1%). Uniform drying conditions were provided by setting the fruits up on double symmetrically laid trays, with total capacity

of 3 kg. The drying was performed in a convective air dryer where the air intake and fruit inlet are at the same end of the tunnel. The predetermined air-drying temperature was either 70°C or 90°C, and was maintained throughout the entire drying process, with the air velocity of 1 ms^{-1}. At 60 minintervals, moisture losses from plum fruits were checked by a digital balance, and the direction of the vertical air flow was alternated to ensure uniformity of drying. Drying was concluded when dry matter content was lowered down to about 75%.

Determination of soluble solid content, dry matter content, sugar content and titratable acidity

The soluble solid content of the fresh fruits was determined on a manual refractometer (3828, Carl Zeiss, Germany). The dry matter content was determined by drying at 105°C until constant mass. Titratable acidity was determined by neutralisation of fruit extract with 0.1 N NaOH to pH 8.2, using phenolphthalein as indicator. Acidity was expressed as mg malic acid equivalents /100 g dry matter. Sucrose, inverted sugars, and total sugars content were determined by Luff-Schoorl method (Tanner and Brunner, 1979).

Determination of anthocyanin content, flavonoid contents and total phenolics

The monomeric anthocyanin pigment content of the aqueous extracts was determined using the pH-differential method previously (described Prior *et al.*, 1998; Liu *et al.*, 2002). The results were expressed as mg cyanidin-3-glucoside equivalents/100 g dry matter (mg C3GE/100 g dm). Total flavonoid content was determined by a colorimetric method previously described (Zhishen *et al.*, 1999; Liu *et al.*, 2002). The results were expressed as mg of catechin equivalents/100 g dry matter (mg CE/100 g dm). The total phenolic content was determined using a modified Folin-Ciocalteau colorimetric method (Singleton *et al.*, 1999; Liu *et al.*, 2002), with results expressed as mg of gallic acid equivalents/100 g dry matter (mg GAE/100 g dm).

Antioxidant activity

Antioxidant properties were determined by the ABTS radical scavenging assay, as previously described (Re *et al.*, 1999). Results were expressed as Trolox equivalent antioxidant capacity/100 g dry matter (mmol TE/100 g dm).

Extraction and HPLC-DAD analysis

Samples were prepared based on the method previously described (Miletić *et al.*, 2013). In order to analyse the individual polyphenolic compounds, plums and prunes extracts were analysed by Agilent 1260 series HPLC (Agilent Technologies, Santa Clara, CA, USA) equipped with diode array detector (DAD), and linked to a ChemStation data handling system. Injection volume was 5 µL and the flow rate was 0.5 mL/min. A ZORBAX Eclipse Plus C18 column (4.6 × 150 mm, 3.5 µm particles) was used, with temperature set at 25°C. Spectra were acquired at 260, 280, 329 and 360 nm. In order to determine cyanidin content in plums and prunes, samples were also prepared according to the method of Hertog *et al.* (1992) and were further analysed using the same HPLC system. Injection volume, column type and a flow rate were intact, while the temperature was set at 30°C. A spectrum was acquired at 520 nm. For both extraction methods, the same solvents (A: 1% formic acid, B: acetonitrile) and gradient (0-10 min, 15% of B in A; 10-25 min, 15-50% of B in A; 25-30 min, 50-80% of B in A; 30-32 min, 10% of B in A) were used. Phenolic compounds were identified according to peak retention time and UV/Vis spectra by comparing them with those of the standards. The quantities of the different phenolic compounds were based on peak areas, and expressed as mg/100 g dm.

Statistical analysis

For all the experiments, three samples were analysed and all the assays were carried out in triplicate. The results are expressed as mean values and standard deviation. Data were analysed by one-way and two-way analyses of variance (ANOVA) to examine differences among the cultivars and drying temperatures, using Statistica 7 (StatSoft, Inc., Tulsa, OK, USA). The pairwise comparisons between different parameters were performed out using Duncan's test ($p < 0.05$).

Results and discussion

Chemical properties of fresh plum fruits

Fruit flavour is mainly determined by chemical composition. Chemical properties of fresh plum cultivars were analysed and are presented in Table 1. Parameters related to the sugar content (total sugars, inverted sugars and sucrose) showed no statistically significant differences between the tested cultivars. Other measured traits showed great variation in different fresh plum cultivars. It is noteworthy to emphasise that a significantly lower titratable acidity of 'Mildora' cultivar (1.60 g/100 g dm) was observed as compared to the other two cultivars with almost even acidities. Furthermore, the dry matter content and soluble solid content of 'Mildora' fresh plums

were higher to those of 'Stanley' and 'Čačanska Rodna' cultivars. All these parameters contribute to the high sweet sensation during fresh 'Mildora' consumption.

High content of polyphenolic compounds in fresh plums are well documented (Jaiswal et al., 2013; Igwe and Charlton, 2016). Table 1 represents also the polyphenolic composition of fresh plums analysed in the present work. Apart from gallic acid content, with no significant difference among the tested cultivars, all other individual polyphenol compounds varied greatly. Major phenolic compounds of fresh plums are hydroxycinnamic acids (Jaiswal et al., 2013; Celik et al., 2017). In our tested cultivars, neochlorogenic acid (3 O-caffeoylquinic acid), chlorogenic acid (5 O-caffeoylquinic acid) and caffeic acid were identified. The most abundant hydroxycinnamic acid was neochlorogenic acid, which accounted for 37.91 mg/100 g dm ('Stanley'), 11.78 mg/100 g dm ('Čačanska Rodna') and 3.05 mg/100 g dm ('Mildora'), followed by caffeic acid (16.71, 5.58 and 2.03 mg/100 g dm, respectively) and chlorogenic acid (3.08, 0.87 and 0.80 mg/100 g dm, respectively). As compared to the other cultivars, neochlorogenic acid and chlorogenic acid contents were generally lower, which is probably due to the cultivar specificities (Kim et al., 2003; Piga et al., 2003; Del Caro et al., 2004;

Usenik et al., 2009; Jaiswal et al., 2013;). Jaiswal et al. (2013) analysed 11 fresh plum cultivars and chlorogenic acid content varied between 0 and 37.4 µg/g fw, while neochlorogenic acid content was up to 521.8 µg/g fw. Among these cultivars, 'Čačanska Rodna' was also analysed, and the obtained values for chlorogenic and neochlorogenic acid contents were 16.3 and 71.8 µg/g fw, respectively, which is also higher as compared to our results for the same cultivar (1.94 and 26.33 µg/g fw). These differences might be attributed to the different agrotechnical treatments and climate conditions. Nevertheless, it was revealed that chlorogenic acid and neochlorogenic acid are the predominant hydroxycinnamic acids, mostly concentrated in plum fruits skin (Sójka et al., 2015).

As for the caffeic acid, Fu et al. (2011) detected 0.51 g/100 g fw in red plum (no cultivar indicated) and no traces of caffeic acid in black plum (no cultivar indicated). Ozturk et al. (2012) determined 1.355 mg of caffeic acid in 100 g fw of 'Black Amber' fresh plum, which is quite lower as compared to our fruits of 'Stanley' (3.205 mg/100 g fw), but higher as compared to 'Čačanska Rodna' and 'Mildora' (1.247 and 0.513 mg/100 g fw, respectively). Piga et al. (2003) found no traces of caffeic acid in fresh plum fruits. Protocatechuic acid was detected in our plum samples, in the range slightly lower as compared to

Table 1. Chemical profile of fresh plum fruit cultivars.

		'Stanley'	'Čačanska Rodna'	'Mildora'
	ANOVA	fresh	fresh	fresh
Dry matter content (%)	***	19.18 ± 0.27[c]	22.35 ± 0.69[b]	25.25 ± 0.89[a]
Soluble solid content (%)	***	16.20 ± 0.56[c]	20.88 ± 1.08[b]	23.58 ± 0.68[a]
Total sugars (g/100 g dm)	ns	64.91 ± 1.02	64.68 ± 1.01	64.18 ± 2.31
Inverted sugars (g/100 g dm)	ns	40.49 ± 0.44	40.76 ± 0.91	39.81 ± 2.56
Sucrose (g/100 g dm)	ns	23.20 ± 1.07	22.73 ± 1.55	23.15 ± 0.35
Titratable acidity (g/100 g dm)	***	3.27 ± 0.31[a]	3.62 ± 0.15[a]	1.60 ± 0.09[b]
pH	*	3.86 ± 0.09[b]	3.58 ± 0.34[b]	4.36 ± 0.13[a]
Sugar/acid ratio	***	19.97 ± 2.00[b]	17.87 ± 0.82[b]	40.29 ± 2.81[a]
Rutin	***	2.54 ± 0.04[b]	3.92 ± 0.10[a]	2.03 ± 0.07[c]
Neochlorogenic acid	***	37.91 ± 0.69[a]	11.78 ± 0.50[b]	3.05 ± 0.07[c]
Chlorogenic acid	***	3.08 ± 0.05[a]	0.87 ± 0.03[b]	0.80 ± 0.02[b]
Caffeic acid	***	16.71 ± 0.25[a]	5.58 ± 0.21[b]	2.03 ± 0.06[c]
Protocatechuic acid	***	1.45 ± 0.02[a]	1.48 ± 0.04[a]	1.07 ± 0.03[b]
Gallic acid	ns	3.43 ± 0.49	4.27 ± 0.87	3.46 ± 0.09
Cyanidin	***	6.98 ± 0.12[a]	6.55 ± 0.26[b]	0.44 ± 0.22[c]
Total anthocyanins (mg/100 g dm)	***	107.75 ± 1.51[a]	28.03 ± 0.89[b]	0.81 ± 0.81[c]
Total flavonoids (mg/100 g dm)	***	345.67 ± 15.90[a]	125.78 ± 6.13[b]	100.45 ± 2.00[c]
Total phenolics (mg/100 g dm)	***	643.12 ± 1.97[a]	215.34 ± 6.12[c]	312.87 ± 7.74[b]
Antioxidant capacity (ABTS; mol TE/100 g dm)	***	2.66 ± 0.18[a]	0.734 ± 0.087[c]	0.978 ± 0.091[b]

Data are means ± SD. Means with different superscripts were statistically significant (Duncan's test, $p < 0.05$). ns, *, **, ***: non-significant or significant at $p < 0.05$, 0.01, 0.001, respectively.

the previously reported data (Kayano *et al.*, 2004; Wang *et al.*, 2018).

It is well known that cyanidin is the most dominant anthocyanidin in plum fruits (Usenik *et al.*, 2009; Sahamishirazi *et al.*, 2017). The comparable amount of cyanidin was detected in 'Stanley' and 'Čačanska Rodna' cultivars (6.98 and 6.55 mg/100 g dm, respectively), while significantly lower amount was determined in 'Mildora' cultivar (0.44 mg/100 g dm), which was expected due to its light purple colour. The content of rutin, as the main flavonol in plum fruits, in our fresh plum samples was comparable with data from previously reported studies (Piga *et al.*, 2003; Miletić *et al.*, 2013; Usenik *et al.*, 2013).

Generally, fresh plums of 'Mildora' cultivar showed the lowest content of individual polyphenols, as compared to the other two cultivars. The lowest amount of anthocyanins (0.81 mg/100 g dm) and flavonoids (100.5 mg/100 g dm) were also observed in fresh fruits of 'Mildora', cultivar as compared to 'Stanley' (107.8 and 345.7 mg/100 g dm, respectively) and 'Čačanska Rodna' (28.0 and 125.8 mg/100 g dm, respectively) cultivars. The similar order in polyphenolic content was also expected. Nevertheless, the highest amount of polyphenols was detected in fresh fruits of 'Stanley' cultivar followed primarily by 'Mildora' and then by 'Čačanska Rodna' cultivars (Table 1). Consequently, the highest antioxidant capacity of fresh fruits of 'Stanley' cultivar, followed by 'Mildora' and 'Čačanska Rodna' cultivars was observed. Ozturk *et al.* (2012) determined the total phenolic content in 'Black Amber' fresh plums of 39 mg/100 g fw, which is quite lower as compared to all three cultivars analysed in the present work. Kim a*et al.* (2003) analysed total flavonoid and total phenolic contents in 11 fresh plum cultivars. In general, all those cultivars contained higher amount of flavonoids and phenolics, as compared to our tested cultivars. For instance, they determined total content of flavonoids and phenolics in fresh fruit of 'Stanley' cultivar of 110.0 and 181.3 mg/100 g fw, respectively, while our results for the same cultivar revealed the contents of 66.3 and 123.4 mg/100 g fw, respectively. According to the classification given by Sahamishirazi *et al.* (2017), all our fresh plum fruits belong to the category of low phenolic content cultivars (i.e. below 150 mg/100 g fw).

Chemical changes of plums caused by air drying

Drying of plums certainly causes great impact on chemical composition. In the present work, two different drying temperatures, 70°C and 90°C, were applied and the consequent chemical changes are given in Figure 2. Total sugar content in prunes slightly decreased in all three cultivars by drying at 70°C and 90°C. Drying at higher temperature caused a slightly higher impact on total sugars. On the other hand, the content of inverted sugars increased by drying at both drying temperatures, while the content of sucrose significantly diminished, most likely due to sucrose hydrolysis. Titratable acidity showed different behaviour related to the cultivar. For 'Stanley' and 'Čačanska Rodna' cultivars, titratable acidity decreased at both drying temperatures as compared to the fresh plum fruits, but these decreases were more pronounced at 70°C. In contrast, drying fresh plums of 'Mildora' at both temperatures caused higher acidity as compared to the fresh fruits.
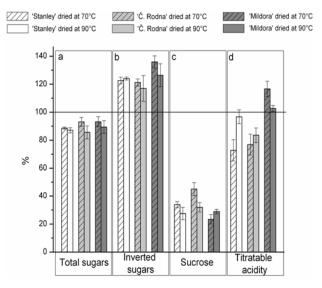

Figure 2. Chemical changes of prunes air-dried at 70°C and 90°C: (a) total sugars, (b) inverted sugars, (c) sucrose, and (d) titratable acidity. All values were calculated by assigning a value of 100% to the determined chemical parameters of freshly harvested plums (horizontal line at 100%), and the changes in all prune samples as compared to fresh plums were then calculated.

Changes in the contents of total flavonoids, total phenolics and antioxidant activity (as ABTS test) prompted by drying at two different temperatures are given in Figure 3. The changes of anthocyanins were not given, since the amount of anthocyanins in prunes were negligible. Total phenolic content in fruits of 'Stanley' cultivar was almost not affected by drying. A decrease was observed in fruits of 'Mildora' cultivar by drying at 70°C, while drying at 90°C caused a slight increase in polyphenolic content. In contrast, content of polyphenolics increased dramatically in fruits of 'Čačanska Rodna' after drying at both 70°C and 90°C. Such behaviour cannot be clearly explained, due to the complexity of the drying process. There are several mechanisms that play important roles in this phenomenon (Miletić

et al., 2013). First, cultivar specificity must be emphasised. Anthocyanins are thermally unstable molecules, which are completely decomposed during drying procedure (Patras *et al.*, 2010). Then, polyphenol oxidase, as naturally abundant enzyme in fruits, gradually degrades polyphenolic compounds. But simultaneously, polyphenol oxidase is subjected to denaturation, due to the high temperature exposure (Raynal and Moutounet, 1989). According to previously published studies, phenolic compounds in stone fruits are mostly concentrated in the fruit's skin (Raynal and Moutounet, 1989; Tomás-Barberán *et al.*, 2001), which is the region mostly exposed to the heat. Taking into consideration all these phenomena, it is clear that any prediction or explanation requires much deeper research.

Convective air drying is the oldest fruit drying method. Although plenty of new methods have been developed, fruits dried at high temperatures are still most abundant in the market, due to the low cost of production, and the most acceptable among consumers in Europe. Michalska *et al.* (2016a) analysed plum powders obtained by five different drying methods (freeze-drying (FD), vacuum drying (VD), convective drying at 60°C and 70°C (CD), microwave-vacuum drying (MVD) and combination of convective pre-drying and microwave drying (CPD-MVD)) of fresh plums of 'Valor' cultivar. The levels of total phenolic in these prune powders follows the order: MVD (4.8 Wg^{-1}) < MVD (4.8/1.2 Wg^{-1}) < CPD VMD (60°C/1.2 Wg^{-1}) < CD (70°C) < CD (60°C) < VD < FD < MVD (1.2 Wg^{-1}) < CPD-VMD (70°C/1.2 Wg^{-1}). Preservation of total phenolics in dried fruits obtained by convective drying method is not at the highest level, but still quite efficient, and strongly depending on the operating temperature.

Antioxidant capacity is mainly attributed to polyphenolic content. Therefore, the ABTS test profile (Figure 3c) to the great extent resembles the total phenolic profile (Figure 3b). The statistical analysis showed a significant correlation between antioxidant capacity and total phenolics of all three cultivars in fresh plum ($R^2 = 0.979$), dried at 70°C ($R^2 = 0.991$) and dried at 90°C ($R^2 = 0.806$). Taking into account all three cultivars of fresh plums and prunes, correlation was quite high ($R^2 = 0.903$). On the other hand, correlation between antioxidant capacity and total flavonoids of all three cultivars in fresh plums, prunes dried at 70°C and prunes dried at 90°C was statistically significant ($R^2 = 0.912$, 0.980 and 0.924, respectively). Slightly lower coefficient of determination was obtained by considering points of all three cultivars of fresh plums and prunes ($R^2 = 0.745$). These results infer that the antioxidant

capacity of fresh plums and prunes of 'Stanley', 'Čačanska Rodna' and 'Mildora' cultivars appeared to be to a great extent influenced by fruit phenolics.
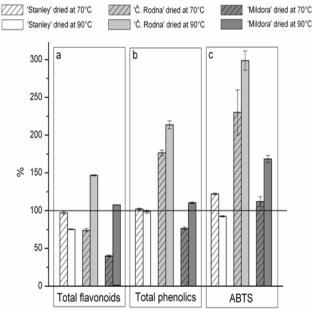

Figure 3. Changes in total flavonoids (a), total phenolics (b) and antioxidant capacity (ABTS) (c) of prunes air-dried at 70°C and 90°C. All values were calculated by assigning a value of 100% to the determined chemical parameters of freshly harvested plums (horizontal line at 100%), and the changes in all prune samples as compared to fresh plums were then calculated.

Fresh plums fruits sustained a great impact while being dried at high temperatures, which is greatly reflected on concentration of the individual phenolic constituents (Table 2). The highest content of all selected phenolics (rutin, neochlorogenic acid, chlorogenic acid, caffeic acid, protocatechuic acid and gallic acid) in prunes of 'Stanley' cultivar was dominant as compared to the prunes of 'Čačanska Rodna' and 'Mildora', cultivars regardless the drying temperature (as showed in Table 2, Cultivar (A)). Apart from gallic acid, the content of all other individual phenolics in prunes dried at 70°C was significantly higher as compared to the prunes dried at 90°C, regardless the plum cultivar (Table 2, Drying temperature (B)).

Drying fresh plum fruits of 'Stanley' cultivar at both temperatures resulted in a decrease in neochlorogenic acid and chlorogenic acid content, while the content of gallic acid significantly increased. Protocatechuic acid content was hugely increased by drying, as compared to the fresh plums (1.45 mg/100 g dm), but drying at 90°C decreased the content of protocatechuic acid as compared to the one at 70°C. Caffeic acid content increased when dried at 70°C as compared to the fresh fruits (from 16.71 to 19.41 mg/100 g dm), but drying at higher temperature caused

Table 2. Content of selected phenolics (mg/100 g dm) of prunes dried at 70°C and 90°C.

		Rutin	Neochlorogenic acid	Chlorogenic acid	Caffeic acid	Protocatechuic acid	Gallic acid
Cultivar (A)		***	***	***	***	***	***
'Stanley'		2.89 ± 1.49[a]	24.94 ± 3.31[a]	2.77 ± 0.03[a]	17.88 ± 1.69[a]	2.33 ± 0.54[a]	20.68 ± 4.68[a]
'Čačanska Rodna'		0.64 ± 0.13[c]	11.77 ± 2.75[b]	1.29 ± 0.11[b]	8.69 ± 0.13[b]	0.96 ± 0.10[b]	13.84 ± 1.63[b]
'Mildora'		0.79 ± 0.22[b]	2.05 ± 0.67[c]	0.70 ± 0.15[c]	1.87 ± 0.59[c]	0.70 ± 0.08[c]	13.25 ± 0.75[b]
Drying temperature (B)		***	Ns	Ns	***	***	***
70°C		1.79 ± 1.85[a]	12.88 ± 11.80	1.60 ± 0.89	9.82 ± 7.87[a]	1.44 ± 1.04[a]	14.86 ± 1.60[b]
90°C		1.09 ± 0.36[b]	12.96 ± 8.41	1.58 ± 0.97	9.14 ± 6.05[b]	1.22 ± 0.48[b]	16.99 ± 6.01[a]
A × B		***	***	***	***	***	***
'Stanley'	70°C	4.25 ± 0.15[a]	27.94 ± 0.19[a]	2.77 ± 0.02[a]	19.41 ± 0.13[a]	2.82 ± 0.07[a]	16.42 ± 0.17[b]
	90°C	1.54 ± 0.03[b]	21.93 ± 0.47[b]	2.78 ± 0.05[a]	16.35 ± 0.30[b]	1.84 ± 0.01[b]	24.94 ± 0.50[a]
'Čačanska Rodna'	70°C	0.53 ± 0.01[f]	9.27 ± 0.08[d]	1.19 ± 0.03[c]	8.73 ± 0.17[c]	0.87 ± 0.01[d]	15.31 ± 0.34[c]
	90°C	0.74 ± 0.10[d]	14.28 ± 0.12[c]	1.39 ± 0.02[b]	8.66 ± 0.09[d]	1.05 ± 0.03[c]	12.37 ± 0.17[e]
'Mildora'	70°C	0.58 ± 0.01[e]	1.43 ± 0.05[f]	0.79 ± 0.01[d]	1.33 ± 0.04[f]	0.64 ± 0.01[f]	12.84 ± 0.22[de]
	90°C	0.99 ± 0.02[c]	2.66 ± 0.01[e]	0.57 ± 0.8[e]	2.41 ± 0.02[e]	0.77 ± 0.04[e]	13.65 ± 0.94[d]

Data are means ± SD. Means with different superscripts were statistically significant (Duncan's test, $p < 0.05$). ns, *, **, ***: non-significant or significant at $p < 0.05, 0.01, 0.001$, respectively.

a decrease (16.35 mg/100 g dm). Prunes of 'Čačanska Rodna' cultivar, dried at both 70°C and 90°C, showed a significant increase in chlorogenic acid, caffeic acid and gallic acid content, and a decrease in rutin and protocatechuic acid contents. In the same cultivar, content of neochlorogenic acid decreased when dried at 70°C (from 11.77 to 9.27 mg/100 g dm), but drying at 90°C caused an increase (14.28 mg/100 g dm). As for 'Mildora' cultivar, except of gallic acid, drying at both temperatures prompted a decrease in contents of rutin, neochlorogenic acid, chlorogenic acid and protocatechuic acid. The content of caffeic acid in prunes of 'Mildora' cultivar decreased after drying at 70°C (from 2.03 in fresh fruits to 1.33 mg/100 g dm), but drying at 90°C caused an increase (2.41 mg/100 g dm).

It is well documented that phenolic compounds of fresh fruits suffer great changes while being dried (Raynal and Moutounet, 1989; Chang *et al.*, 2016; Michalska *et al.*, 2016b). Del Caro *et al.* (2004) analysed the polyphenolic content of prunes of 'President' and 'Sugar' cultivars, dried by high temperatures (70 - 85°C) and low temperature (60°C). It was showed that drying procedure (i.e. drying temperature) played a crucial role in polyphenolic profile of prunes. Namely, contents of neochlorogenic acid and chlorogenic acid in prunes dried at higher temperature were significantly higher as compared to prunes dried at lower temperature, in both tested cultivars. Piga *et al.* (2003) found no significant changes in the amount of neochlorogenic and chlorogenic acids between fresh plums and prunes dried at 85°C, while significantly lower

content was detected when being dried at 60°C.

The content of caffeic acid in our prunes are in line with previously published papers (Donovan *et al.*, 1998; Nakatani *et al.*, 2000; Del Caro *et al.*, 2004). Nakatani *et al.* (2000) detected 2.6 mg/100 g fw of caffeic acid in prunes, which is similar to our results (from 0.34 to 3.72 mg/100 g fw). On the other hand, some authors found no traces of caffeic acid in prunes (Donovan *et al.*, 1998; Piga *et al.*, 2003; Prior *et al.*, 2007). While being dried, content of caffeic acid is changed, due to the two simultaneous processes: thermal degradation of caffeic acid and hydrolysis of hydroxycinnamic acids (neochlorogenic acid and chlorogenic acid), especially favoured by higher temperatures and mild acidic conditions. Therefore, caffeic acid content in our dried samples varied, being dependent on cultivar and drying temperature. Del Caro *et al.* (2004) found no traces of caffeic acid in prunes dried at 60°C, but 3.51 mg/kg dm in prunes dried at higher temperatures.

For all the three tested plum cultivars, drying procedure resulted in a huge increase in gallic acid content, which is most likely associated with a thermal degradation of gallotannins, as naturally present in plum fruits.

Conclusion

Air-drying of freshly harvested plums caused significant changes in chemical composition of the fruits, especially in total sugar and sucrose reduction, and invert sugar growth. Drying 'Stanley' cultivar had no effect on total phenolic content, while

fresh fruits of 'Čačanska Rodna' cultivar sustained dramatic increase at both drying temperatures. 'Mildora' cultivar showed variations in total phenolic content, such as decrease in prunes dried at 70°C, to an increase in prunes dried at 90°C. Being thermally unstable, the amount of anthocyanins in all prunes was negligible.

Drying plums of 'Stanley' cultivar at both 70°C and 90°C caused a reduced content in neochlorogenic and chlorogenic acid, while caffeic acid content increased after drying at 70°C. Regardless of the drying temperature, prunes of 'Čačanska Rodna' cultivar showed a significant increase in chlorogenic acid and caffeic acid contents, and a decrease in rutin and protocatechuic acid contents, as compared to the fresh plums. The contents of rutin, neochlorogenic, chlorogenic acid and protocatechuic acid in prunes of 'Mildora' cultivar were reduced by both drying regimes. Drying at both temperatures also prompted a decrease in the contents of rutin, neochlorogenic acid, chlorogenic acid and protocatechuic acid in 'Mildora' cultivar. The high correlation between antioxidant capacity and total phenolic content was evident, and strongly depended on the drying temperature.

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