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POLYPHENOLIC CONTENT AND ANTIOXIDANT CAPACITY IN FRUITS OF PLUM (*PRUNUS DOMESTICA* L.) CULTIVARS "VALJEVKA" AND "MILDORA" AS INFLUENCED BY AIR DRYING

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ABSTRACT

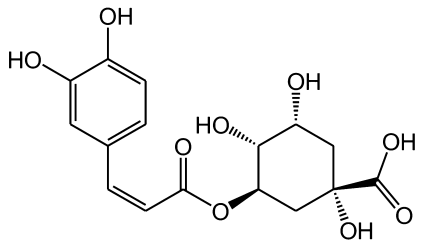
Polyphenolic content and antioxidant capacity of freshly harvested plums cvs. "Valjevka" and "Mildora," and changes caused by drying were analyzed. Plum drying at 90C resulted in significant changes in anthocyanins, flavonoids and phenolics content, and antioxidant capacity in both cultivars examined. Statistical analysis showed that antioxidant capacity of both fresh plums and prunes of "Valjevka" and "Mildora" is strongly influenced by the phenolic constituents of the fruit. The major phenolic compound in fresh plums and prunes is neochlorogenic acid, followed by caffeic acid and chlorogenic acid. After drying, a significant decrease in neochlorogenic acid and an increase in caffeic acid was observed, while chlorogenic acid content decreased in prunes of "Valjevka," and increased in prunes of "Mildora." Rutin and protocatechuic acid contents were slightly decreased after drying, while gallic acid content was dramatically increased. A complete degradation of cyanidin was induced by drying.

PRACTICAL APPLICATIONS

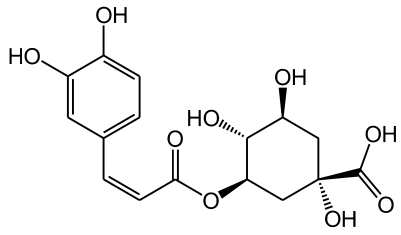
This study is intended to inform producers of dried fruits about changes induced by drying, as well as to highlight the supposition that dried fruits may be considered functional food due to the high level of polyphenolic compounds and increased antioxidant capacity. The scientific results relative to the nutritional profile of prunes, combined with their attractive appearance and favorable flavor, may serve as a commercial strategy, given the increased level of consumers' awareness on the importance of healthy food intake.

INTRODUCTION

Fresh plum fruits are traditionally processed into products with longer shelf life, such as jams, compotes and prunes (dried plums). Prunes – dried fruits of some cultivars of *Prunus domestica* L. – are well known as functional food, and their favorable effects on human health are mainly associated with their high phenolic content and the ensuing high antioxidant activity. Generally, fruits and vegetables are a natural source of antioxidant compounds, such as flavonoids, flavonolignans, lignans, tannins, phenolic acids and the derivatives. The antioxidant activity of prunes is particularly high in comparison with the antioxidant activities of other dried fruits and vegetables (Pellegrini *et al.* 2006). Furthermore, compared with other fruits, prunes were found to have the highest oxygen radical absorbance capacity (ORAC) value (McBride 1999). The major phenolic compounds in prunes are caffeoylquinic acid isomers (chlorogenic and neochlorogenic acid) (Fig. 1) and flavonoids (Raynal *et al.* 1989; Donovan *et al.* 1998; Nakatani *et al.* 2000). These phenolics in prunes are well-known antioxidants toward human low density lipoproteins (LDL)



Chlorogenic acid (5-*O*-caffeoylquinic acid)



Neochlorogenic acid (3-*O*-caffeoylquinic acid)

FIG. 1. STRUCTURE OF CAFFEOYLQUINIC ISOMERS

(Donovan *et al.* 1998; Prior and Cao 2000), scavengers for reactive oxygen and nitrogen species (Crespo *et al.* 2008), and inhibitors preventing formation of conjugated diene from linoleic acid oxidation (Marinova *et al.* 2009). Apart from their positive effect on human health, prunes are primarily used in the diet as an exceptionally tasty delicacy and high energy foodstuff.

Plums cvs. "Valjevka," and "Mildora," intended for drying, were developed at Fruit Research Institute-Čačak, Serbia. "Valjevka" resulted from the cross of cvs. "Agen 707" × "Stanley" in 1959, named and released in 1985, and protected in 1990 (Ogašanović 1990). Fruits are of attractive dark blue color, with favorable technological properties suitable for drying (Ogašanović 1990; Mitrović *et al.* 2006). "Mildora" originated from the cross of cvs. "Large Sugar Prune" × "Čačanska Lepotica" in 1980, named and released in 2004 (Ogašanović *et al.* 2005). "Mildora" is highly tolerant to *Plum pox virus* (Paunović *et al.* 2006), with fruits of light purple colour, suitable for drying (Mitrović *et al.* 2006).

Prunes of the "Valjevka" are highly merited among consumers of dried fruits. They are extremely dark in color, almost coal-black, with harmonious sweet-acid flavor typical of prunes. On the other hand, amber-like prunes of "Mildora" are of a sweet-honey flavor, which is markedly nontypical of prunes.

The primary objective of this study was to determine the level of total phenolics, the concentration of each selected phenolic compound, and antioxidant capacity of prunes ("Valjevka" and "Mildora"), dried at 90C. In order to analyze changes resulting from drying, freshly harvested unprocessed plums were also analyzed.

MATERIALS AND METHODS

Fruit Collections

Fruits of "Valjevka," and "Mildora" (*Prunus domestica* L.) grafted on rootstock *Prunus cerasifera* L. were collected from an experimental orchard established in 1996 in Preljina, the village situated in a plum-growing region of Čačak, Serbia (43°55′26″N, 20°26′52″E). Fruits were collected in early September 2010 at a maturity stage suitable for drying, based on a predetermined fruit classification. Harvesting time depended on the form of fruit utilization (Childers 1949).

Sampling involved three hundred samples of each plum cultivar (with no mechanical injuries or disease indications) selected from 10 trees (30 fruits per tree). Plum trees located in the middle of the row were used for the experiment. After harvesting, 2 kg of fresh fruits of each plum cultivar were stored at −20C for a maximum of 1 week prior to conducting chemical analyses, while the remaining fresh plums were dried the very same day. Dried fruits of each cultivar were packed in heat-sealed polyethylene bags (90 μm thick), and stored at room temperature (18–20C) for 2 months before examination. The whole edible part of the fruit was used in the study. Fresh plums or prunes were carefully cut in halves and pits removed manually. Mesocarp and exocarp were frozen by pouring into liquid nitrogen and homogenized using a stainless steel blender. Soluble solid content, dry matter contents, sugar contents and titratable acidity were determined by Tanner and Brunner (1979).

Experimental Drying Unit

The experiments were conducted in a laboratory convective air dryer, as the most common method practiced industrially (Kandić *et al.* 2006). The experimental setup consists of three basic units: the preparation and air heating unit, drying chamber, and air recirculation and air vent unit. The centrifugal fan, with a power of 1.5 kW at 220 V, ensures constant 1 m/s air drying velocity (measured by anemometer). The air is heated using the electrical heater, with a maximum power of 12 kW at 220 V. This equipment is provided with a data acquisition system allowing control of the air drying conditions, such as the drying temperature, controlled by K (NiCr-Ni)-type thermocouples connected to an Omega digital thermometer type 2809 (Ωmega Engineering, Inc., Stanford, CT).

The major element of the experimental dryer is the drying chamber containing drying trays. The trays are made of braided stainless steel wire with a 400 × 400-mm stainless steel frame that holds a single layer of fruits. At the very

beginning of the drying process, the trays with fruits are placed directly into the drying chamber in a batch. A stream of heated air of predefined characteristics is introduced vertically across the trays. During the drying process, the direction of the vertical air flow was periodically alternated at 60-min intervals, ensuring uniform drying at all six trays.

Drying Procedure

Fruits of a uniform size (counting fruits in 1 kg) and uniform soluble solid content were placed on trays. The fruit weight of "Valjevka" ranged between 40 and 44 g (22–25 fruits in 1 kg), the tray capacity being 3,500 g, whereas fruit weight of "Mildora" was 25 g (40 fruits in 1 kg), the tray capacity being 3 kg. The samples were spread out on the drying tray in a thin-layer form, so that the airflow could pass across the trays. Fruits of each plum cultivar were placed on two symmetrically laid trays, which ensured uniform drying conditions. The drying was performed in a convective air dryer that simulates parallel-flow configuration, where the air intake and fruit inlet are at the same end of the tunnel. This drying configuration requires exposure to a higher temperature (Sabarez and Price 1999). Furthermore, since prunes are industrially produced by dehydration of plums at temperatures of 85–90C (Wilford *et al.* 1997; Piga *et al.* 2003; Becalski *et al.* 2011), the predetermined air drying temperature in our trials was 90C, and was maintained throughout the drying process along with the air velocity of 1 m/s. During the drying process, moisture losses from plum fruits were recorded at 60 min intervals by a digital balance. Drying was terminated when the dry matter content of samples was about 75%.

Determination of Anthocyanin Content

Twenty grams of grinded fruit was blended with 40 mL of extracting solvent (95% ethanol/1.5 N HCl, 85:15). The extract was collected through filtration with an additional 30 mL of solvent washing. The residue was soaked with 70 mL of extracting solvent, and the extract was collected after 2 h. The total extracts were pooled and brought up to 200 mL. The monomeric anthocyanin pigment content of the aqueous extracts was determined using the pH-differential method described previously (Liu *et al.* 2002). Pigment content was calculated as milligrams of cyanidin-3-glucoside equivalents/100 g dm, using an extinction coefficient of 26,900 L/cm/mol and molecular weight of 449.2 g/mol.

Determination of Flavonoid Content, Total Phenolic Content and Antioxidant Capacity

Grinded sample (4.0 g) was vigorously stirred with 40 mL of extraction solution consisting of methanol and distilled water (80% v/v) for 2 h in the dark at room temperature. The mixture was centrifuged in two sequential times for 15 min at 3,500 rpm, and supernatant was filtered through a 0.45 μm Minisart filter before analysis. The extracts obtained were used for the determination of the flavonoid and total phenolic contents, and antioxidant capacity. Total flavonoid content was determined by a colorimetric method described previously (Liu *et al.* 2002). The results were expressed as milligrams of catechin equivalents/100 g dm. The total phenolic content was determined using a modified Folin-Ciocalteu colorimetric method (Singleton *et al.* 1999; Liu *et al.* 2002), whereby the results expressed as milligrams of gallic acid equivalents/100 g dm.

Antioxidant properties were determined by the ABTS assays. ABTS•+ radical cation scavenging activity was determined according to the method described by Re *et al.* (1999). Results were expressed as Trolox equivalent antioxidant capacity (mmol TE/100 g dm).

Extraction and HPLC-DAD Analysis

Samples were prepared according to the method described by Escarpa and González (2000). Shortly, 10 g of fresh plum sample or 5 g of prune sample was extracted with 25 mL of methanol containing 1% HCl and 1% of *tert*-butylhydroquinone, using an ultrasonic bath. Samples were analyzed using an Agilent 1260 series HPLC (Agilent Technologies, Santa Clara, CA) equipped with diode array detector (DAD), and linked to a ChemStation data handling system. A ZORBAX Eclipse Plus C18 column (4.6 × 150 mm, 3.5 μm particles) was used. Injection volume was 5 μL, and the temperature was set at 25C. The elution solvents were aqueous 0.01 M phosphoric acid (A) and 100% methanol (B). The samples were eluted according to the linear gradient described by Escarpa and González (2000). Phenolic compounds were detected at 260 nm (protocatechuic acid), 280 nm (gallic acid), 329 nm (neochlorogenic acid, chlorogenic acid, and caffeic acid) and 360 nm (rutin).

Due to the lack of anthocyanin standards (anthocyanidins-3-glycoside), and in order to determine the cyanidin content in plums and prunes, samples were also prepared according to the method of Hertog *et al.* (1992), and were further analyzed using the same HPLC system. Injection volume was 5 μL, the temperature was set at 30C and the flow rate was 0.5 mL/min. Solvent A was 1% formic acid and solvent B was acetonitrile. The gradient used was as follows: 0–10 min, 10% 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. Cyanidin was detected at 520 nm.

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.

TABLE 1. CHEMICAL PROPERTIES OF FRUITS (FRESH AND DRIED) OF TWO PLUM CULTIVARS

	cv. "Valjevka"			cv. "Mildora"		
	ANOVA	Fresh	Dried	ANOVA	Fresh	Dried
Dry matter content (%)	***	18.9 b	77.9 a	***	25.3 B	74.4 A
Soluble solid content (%)		17.5	–		23.6	–
Total sugar (g/100 g dm)	*	71.1 a	54.1 b	*	64.2 A	57.4 B
Invert sugar (g/100 g dm)	ns	39.9	47.6	*	39.8 B	50.3 A
Sucrose (g/100 g dm)	***	29.7 a	6.2 b	***	23.2 A	6.7 B
Titratable acidity (g/100 g dm)	ns	3.5	3.8	ns	1.6	1.6
pH		3.8	–		4.4	–
Sugar/acid radio	*	20.4 a	14.5 b	*	40.3 A	35.0 B

Values with a different letters within each cultivar denote statistically significant differences (Duncan's test, $P < 0.05$).
ns, *, **, ***: nonsignificant or significant at $P < 0.05$, 0.01, 0.001, respectively.

Statistical Analysis

In all the experiments, three samples were analyzed, and all the assays were carried out in triplicate. Data were analyzed by one-way analysis of variance (ANOVA), using Statistica 7 (StatSoft, Inc., Tulsa, OK). The pairwise comparisons between different parameters were done using Duncan's test ($P < 0.05$). Correlation coefficients between fruit phenolic constituents (anthocyanins, flavonoids and polyphenols) and antioxidant capacity were determined.

RESULTS AND DISCUSSION

Chemical Changes During Drying of Plums

Table 1 shows the chemical properties of fresh plums and changes observed after the drying. Fresh fruits of "Valjevka" had higher content of total sugar, sucrose, and titratable acidity, compared to fruits of "Mildora." On the other hand, fresh fruits of "Mildora" had higher dry matter content, soluble solid content, and more importantly, twice as high sugar/acid ratio than those of "Valjevka." As for invert sugar, no significant differences were evidenced between the cultivars examined.

A decrease in total sugar, sucrose content and sugar/acid ratio, and an increase in dry matter content and invert sugar were generally observed at drying at 90C. As for titratable acidity, no statistically significant difference was found (Table 1 and Fig. 2). These results are in full agreement with literature data relative to fruit processing. The dried plums generally showed an increased concentration of total sugar in comparison with fresh plum fruits, accompanied by a different proportion of individual sugars (Stacewicz-Sapuntzakis *et al.* 2001). The most striking change is the almost complete disappearance of sucrose, which is hydrolyzed to glucose and fructose (invert sugar) (Fig. 2). This

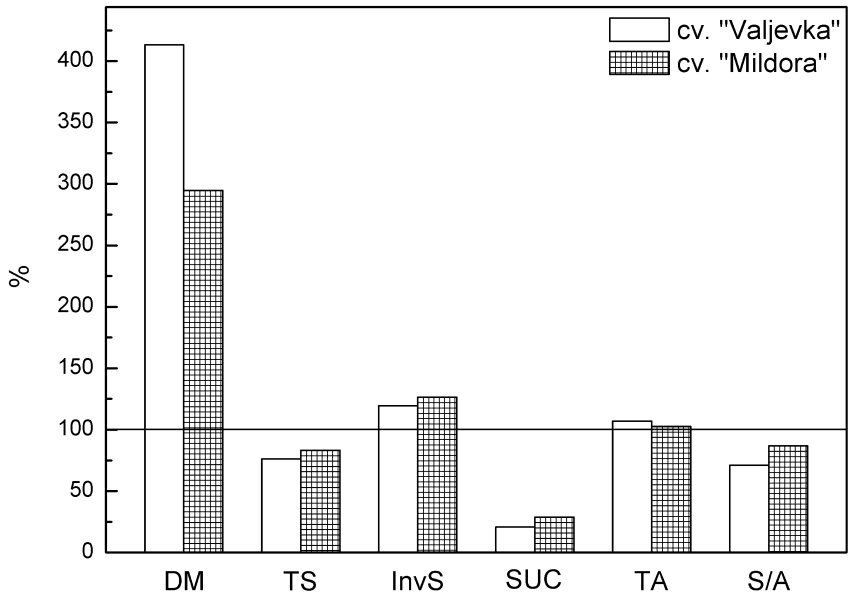


FIG. 2. CHANGES OF CHEMICAL PROPERTIES CAUSED BY AIR DRYING OF PLUMS AT 90C
Dry matter (DM), total sugar (TS), invert sugar (InvS), sucrose (SUC), titratable acidity (TA) and sugar/acid ratio (S/A). All values were calculated by assigning a value of 100% to the determined chemical parameters of freshly harvested plums (horizontal line at 100%), and then calculating the changes in all prune samples compared with fresh plums.

conversion occurs within the first hours of drying, when the high temperature disrupts the cell structure and releases the fruit acids and invertase that act as catalysts of the process (Wilford *et al.* 1997). On the other hand, prolonged drying can cause some loss of glucose and fructose due to the formation of browning compounds with amino acids (Maillard reaction) and sucrose caramelization.

Prunes of different cultivars also differ in physicochemical properties. Prunes of "Mildora" had slightly higher total sugar, invert sugar, and sucrose contents, compared with those of "Valjevka." On the other hand, titratable acidity in prunes of "Valjevka" was 2.3-fold higher than that in prunes of "Mildora." Therefore, 2.4-fold higher sugar/acid ratio of prunes of "Mildora" (34.97) compared with that of prunes of "Valjevka" (14.50) was anticipated.

Phenolic Composition of Plums and Prunes

Plums and prunes are rich sources of phenolic compounds, many of them being concentrated in the exocarp (Raynal and Moutounet 1989; Raynal *et al.* 1989). Table 2 shows the polyphenolic composition of fresh fruits and changes after drying at 90C. Compared with "Mildora," fruits of "Valjevka" had significantly higher content of all polyphenols (except gallic acid). Major phenolic compounds of fresh plums of "Valjevka" and "Mildora" are hydroxycinnamic acids, as reported previously for other plum cultivars (Tomás-Barberán *et al.* 2001; Piga *et al.* 2003; Madrau *et al.* 2010). The most common hydroxycinnamic acid is neochlorogenic acid, which accounted for 24.97 mg/100 g dm ("Valjevka") and 3.05 mg/100 g dm ("Mildora"), followed by free caffeic acid (10.72 and 2.03 mg/100 g dm, respectively), and chlorogenic acid (1.67 and 0.80 mg/100 g dm, respectively). Compared with the data reported for other cultivars (Kim *et al.* 2003; Piga *et al.* 2003; Caro *et al.* 2004; Usenik *et al.* 2008), neochlorogenic acid and chlorogenic acid contents were generally lower, which is probably attributed to cultivar specificities. Piga *et al.* (2003) found 195 and 382 mg/100 g dm of neochlorogenic acid, and 58 and 54 mg/100 g dm of chlorogenic acid in "Sugar" and "President" cultivars, respectively. On the other hand, in the study, no caffeic acid in plums and prunes of these cultivars was detected. Neochlorogenic acid, its content ranging from 19.3 to 120 mg/100 g fw in four different plum cultivars, was reported by Usenik *et al.* (2008). Kim *et al.* (2003) reported the contents of neochlorogenic acid (from 18.1 to 215.4 mg/100 g fw) and chlorogenic acid (0.9–21.0 mg/100 g fw) in fresh fruits of 11 plum cultivars. Very low concentration of free caffeic acid, present in both the pulp (5.5 mg/100 g dm) and exocarp (3.6 mg/100 g dm) in fruits of plums of "d'Agen," was reported by Raynal *et al.* (1989).

Other compounds detected in the fruit samples in our study were rutin, protocatechuic acid, gallic acid, and cyanidin. Rutin content in our samples was lower or comparable with that in previously reported data (Raynal *et al.* 1989; Donovan *et al.* 1998; Kim *et al.* 2003; Piga *et al.* 2003; Caro *et al.* 2004). Protocatechuic acid and gallic acid were detected in prunes by Fang *et al.* (2002). Concentration of cyanidin in fruits of "Valjevka" (21.36 mg/100 g dm) was markedly higher than in fruits of "Mildora" (0.44 mg/100 g dm). Such a result was expected, given the deep blue color of fresh fruits of "Valjevka" and light purple of fruits of "Mildora." Other peaks were not recognized in the study.

Although the phenolic pool plays a key role in the health-promoting action of plums, the concentration of phenolic compounds can be significantly changed during the initial stage of drying (Raynal *et al.* 1989). Table 2 and Fig. 3 show the concentration of phenolic compounds in prunes.

After drying, prunes of both cultivars showed a significant decrease in neochlorogenic acid and an increase in caffeic acid, while chlorogenic acid content decreased in prunes of "Valjevka," and increased in prunes of "Mildora." Generally, the phenolic acids are degraded by activation of peroxidase and polyphenol oxidase, especially in the high presence of air/oxygen. On the other hand, high drying temperatures may cause a low enzymes activity, resulting in low polyphenolics loss in dried fruits (Raynal *et al.* 1989). Piga *et al.* (2003) found no significant changes in the

TABLE 2. CONTENT OF SELECTED PHENOLICS (MG/100 G DM) IN TWO CULTIVARS OF FRESH AND DRIED PLUMS

	cv. "Valjevka"			cv. "Mildora"		
	ANOVA	Fresh	Dried	ANOVA	Fresh	Dried
Rutin (mg/100 g dm)	***	5.21 a	3.56 b	***	2.03 A	0.99 B
Neochlorogenic acid (mg/100 g dm)	***	24.97 a	18.67 b	***	3.05 A	2.66 B
Chlorogenic acid (mg/100 g dm)	*	1.67 b	1.76 a	**	0.80 A	0.57 B
Caffeic acid (mg/100 g dm)	***	10.72 b	11.94 a	***	2.03 B	2.41 A
Protocatechuic acid (mg/100 g dm)	***	2.14 a	1.23 b	***	1.07 A	0.77 B
Gallic acid (mg/100 g dm)	***	2.56 b	11.44 a	***	3.46 B	13.65 A
Cyanidin (mg/100 g dm)	***	21.36 a	0.00 b	***	0.44 A	0.00 B

Values with a different letters within each cultivar denote statistically significant differences (Duncan's test, $P < 0.05$).

ns, *, **, ***: nonsignificant or significant at $P < 0.05$, 0.01, 0.001, respectively.

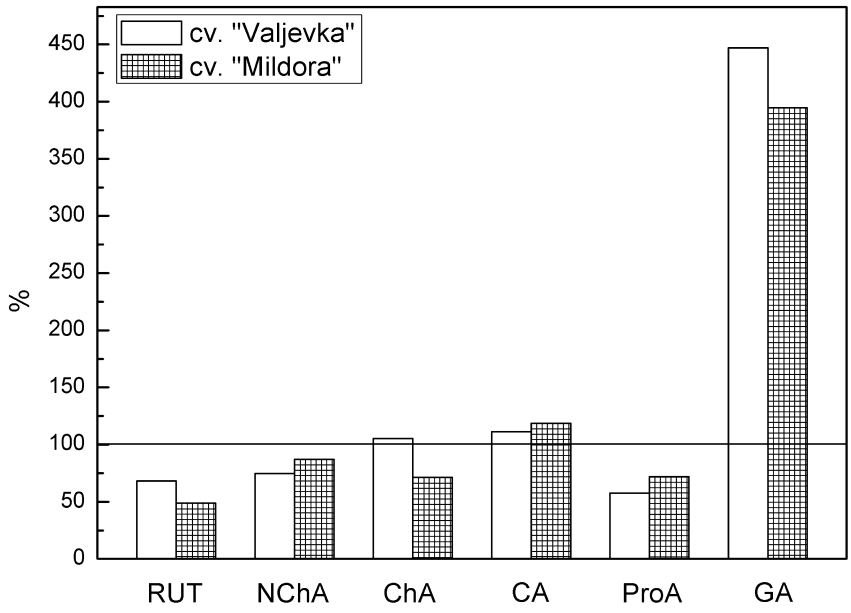


FIG. 3. CHANGES OF POLYPHENOLICS CONTENT CAUSED BY AIR DRYING OF PLUMS AT 90C
Rutin (RUT), neochlorogenic acid (NChA), chlorogenic acid (ChA), caffeic acid (CA), protocatechuic acid (ProA) and gallic acid (GA). All values were calculated by assigning a value of 100% to the determined chemical parameters of freshly harvested plums (horizontal line at 100%), and then calculating the changes in all prune samples compared with fresh plums.

amount of neochlorogenic and chlorogenic acids at drying at 85C. In contrast, Madrau *et al.* (2010) detected an increase in neochlorogenic acid content after drying at 85C, while the concentration of chlorogenic acid remained unaffected.

A drying-caused increase in caffeic acid in prunes of "Valjevka" and "Mildora" was noticed. Similarly, Donovan *et al.* (1998) recorded no caffeic acid in fresh prune-making plums of "French," while caffeic acid content in pitted prunes and extra-large prunes with pits were 9 ± 8 and 10 ± 5 mg/kg, respectively. Most likely, such increase in caffeic acid content stem from the hydrolysis of hydroxycinnamic acids (neochlorogenic acid and chlorogenic acid), especially favoured by higher temperatures and mild acidic conditions (pH of plums of "Valjevka" and "Mildora" were 3.8 and 4.4, respectively).

Drying the fresh fruits of "Valjevka" and "Mildora" resulted in a decrease in protocatechuic acid concentration, and a significant increase in gallic acid concentration. Such increase in gallic acid content after drying is most likely due to the thermal degradation of polyphenolic compounds, such as gallotannins, which are esters of gallic acid and sugars (Muchuweti *et al.* 2005).

Regarding the flavonols, fruits dried at 90C had significantly lower amount of rutin in both cultivars examined. A drying-induced decrease in rutin content in plum fruits was reported in some earlier publishing (Raynal *et al.* 1989; Piga *et al.* 2003; Madrau *et al.* 2010). Raynal *et al.* (1989) showed that degradation of rutin increased as the drying temperature rose, so that after drying for two hours at 95C, only 36% of the rutin remained in the "d'Agen" fruits.

Cyanidin was not detected in any of the dried samples. As the one responsible for the purple color typical of plum fruits, anthocyanins are mainly contained in the skin. Anthocyanin molecules, being generally unstable, are particularly sensitive to technological processing, especially in those involving higher temperatures (Raynal and Moutounet 1989; Yue and Xu 2008). During plum drying, degradation rate in the exocarp is much higher than in the pulp, and thus anthocyanins are almost absent in prunes.

The degradation of rutin and anthocyanins is not directly associated with the denaturation of polyphenol oxidase, since the content of these compounds lowers more rapidly with the rise in temperature. Flavonoids and anthocyanins are therefore not degraded by the same mechanism as phenolic acids, since they are not direct substrates of the oxidases (Baruah and Swain 1959; Walker 1964).

Prunes of "Valjevka" had much higher content of all polyphenols (except gallic acid) with respect to prunes of "Mildora." As for hydroxycinnamic acids, the concentration of neochlorogenic, caffeic and chlorogenic acid in prunes of "Valjevka" were seven, five and three times higher, respectively, than in those of "Mildora." In contrast, gallic acid content in prunes of "Mildora" (13.65 mg/100 g dm) was higher compared with those of "Valjevka" (11.44 mg/100 g dm). *P*-coumaric acid was not found in any samples tested, as reported previously (Donovan *et al.* 1998; Madrau *et al.* 2010).

Changes in Antioxidant Activity After Drying of Plums

As mentioned above, the content of all individual polyphenols in fresh fruits of "Valjevka" was higher than in fruits of "Mildora," which consequently resulted in higher total flavonoids (207.9 and 100.4 mg/100 g dm in "Valjevka" and

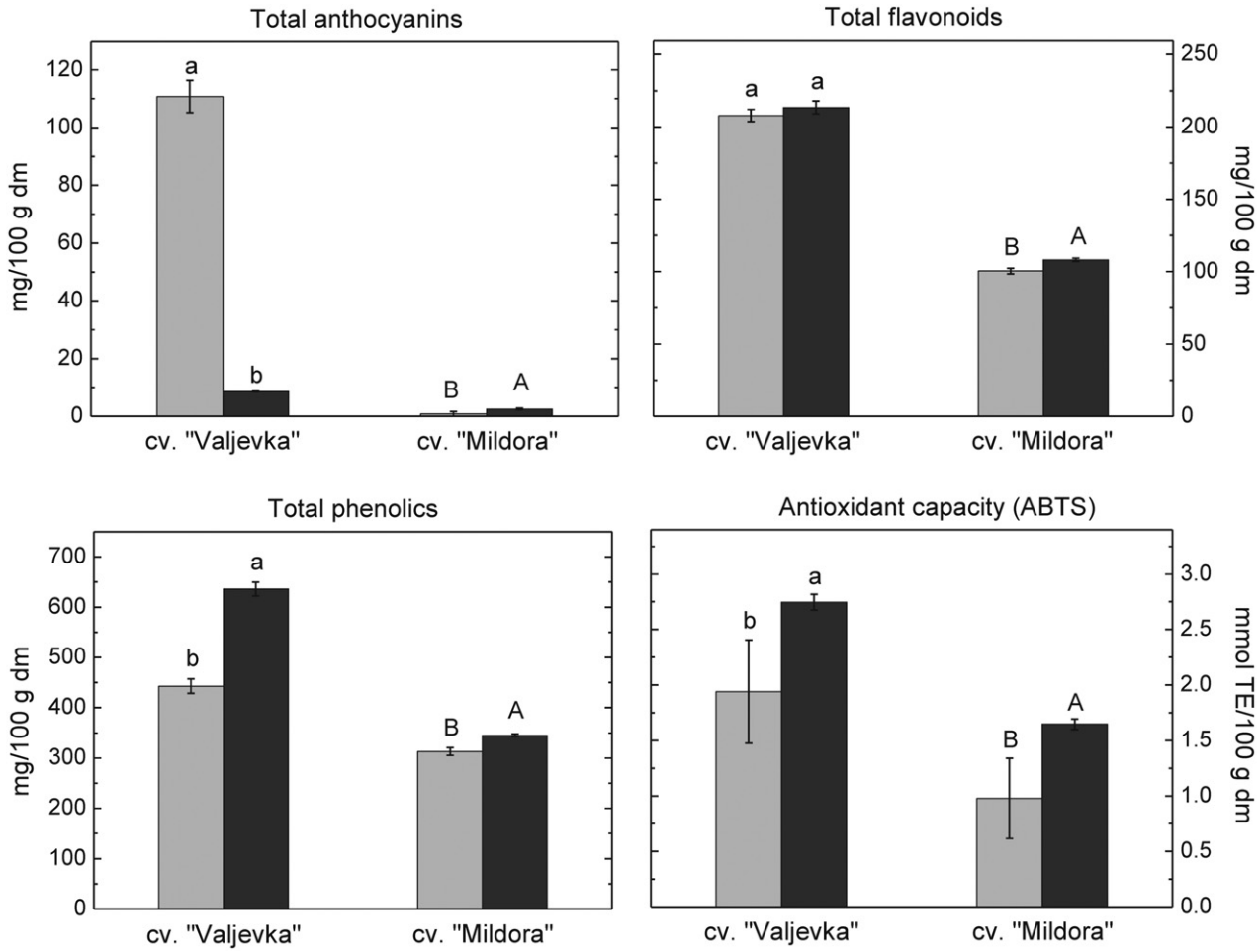


FIG. 4. CHANGES IN TOTAL ANTHOCYANINS, TOTAL FLAVONOIDS, TOTAL PHENOLICS AND ANTIOXIDANT CAPACITY IN PLUMS DRIED AT 90C
Data are the mean of three determinations. *Different letters* within each cultivar mean statistical difference by Duncan's test ($P < 0.05$). Gray and black rectangles represent fresh plums and prunes, respectively.

"Mildora," respectively) and total phenolics (442.8 and 312.9 mg/100 g dm in "Valjevka" and "Mildora," respectively) (Fig. 4). This was particularly emphasized in total anthocyanins content (110.7 and 0.81 mg/100 g dm in "Valjevka" and "Mildora," respectively). Consequently, higher antioxidant capacity of fruits of "Valjevka" (1.941 and 0.978 mmol TE/100 g dm in "Valjevka" and "Mildora," respectively) was also observed. Kim *et al.* (2003) determined total phenolics, total flavonoids and antioxidant capacity of fresh fruits of 11 cultivars. In the study, total flavonoids varied between 64.8 and 257.5 mg/100 g of fw, while total phenolics content were in a wide range from 125.0 to 372.6 mg/100 g fw.

Plum drying at 90C resulted in an increase in total phenolics in both cultivars. Total flavonoid content in fruits of "Valjevka" was not affected by drying, while a slight increase was observed in fruits of "Mildora." Total anthocyanin content dramatically decreased in fruits of "Valjevka" after drying (from 110.7 to 8.6 mg/100 g dm), while a negligible drying-induced increase in total anthocyanins was observed in fruits of "Mildora" (from 0.81 to 2.5 mg/100 g dm). These alternations in the concentration of phenolics, flavonoids and anthocyanins caused by drying are the result of the simultaneous effect of a few phenomena. First, partial degradation of phenolic acids prompted by polyphenol oxidase decreases the concentration. However, the fact that the denaturation of these enzymes also occurs, especially at temperatures higher than 75C (Raynal *et al.* 1989), should also be considered. Second, flavonoids and anthocyanins are not affected by polyphenol oxidase, since these compounds disappear more rapidly as the temperature rises. Regarding these phenomena, it is difficult to predict the changes that may occur during processing, since the chemical composition of dried fruits is the result of complex mechanisms. In the study of commercial prunes (*Prunus domestica* L. cv. "French"), Donovan *et al.* (1998) recorded that mean

concentrations of phenolics were 1,840 mg/kg in pitted prunes, 1,397 mg/kg in extra-large prunes with pits and 1,107 mg/kg in fresh prune-making plums. The authors did not detect anthocyanins in prunes examined. On the other hand, some reports revealed a decrease in total phenolics after drying (Piga *et al.* 2003; Vinson *et al.* 2005; Madrau *et al.* 2010).

The phenolics in plums and prunes govern antioxidant activity at various levels. As shown in Fig. 4, antioxidant capacity was highly influenced by air drying. Namely, antioxidant capacity increased significantly with drying in both cultivars examined (increase of 41.5 and 68.3% in "Valjevka" and "Mildora," respectively). Similar results were previously reported. Madrau *et al.* (2010) recorded an increase in antioxidant activity in prunes of "President" obtained by drying at 60 and 85C, despite the significant decrease in polyphenols. Similarly, Caro *et al.* (2004) showed that fruits of "Sugar" and "President" dried at 85C had substantially higher antioxidant capacities than freshly harvested plums.

The comparison of prunes of the two cultivars examined revealed higher anthocyanins, flavonoids and polyphenols content in fruits of "Valjevka" (8.6, 213.5 and 636.1 mg/100 g dm, respectively) than in prunes of "Mildora" (2.5, 108.1 and 345.2 mg/100 g dm, respectively). Consequently, antioxidant capacity of prunes of "Valjevka" was also higher (2.747 mmol TE/100 g dm) than that in prunes of "Mildora" (1.646 mmol TE/100 g dm).

The statistical analysis showed a significant correlation between total anthocyanins and total flavonoids in fresh plums of both cultivars examined and antioxidant capacity ($R = 0.821$, and 0.823, respectively, $P < 0.05$). Slightly lower correlation coefficient was obtained between total phenolic content in fresh plums of both cultivars and antioxidant capacity ($R = 0.778$). On the other hand, the correlation coefficients between total anthocyanins, total flavonoids and total phenolics in prunes of both cultivars examined and antioxidant capacity are statistically significant ($R = 0.993$, 0.998 and 0.999, respectively, $P < 0.05$). These results infer that the antioxidant capacity of fresh plums and prunes of "Valjevka" and "Mildora" appears to be to a great extent influenced by all fruit phenolic constituents (anthocyanins, flavonoids and polyphenols).

CONCLUSIONS

Air drying of freshly harvested plums of "Valjevka" and "Mildora" at 90C causes significant changes in the chemical composition of the fruit. These changes include a decrease in total sugar, sucrose content and sugar/acid ratio, as well as an increase in dry matter content and invert sugar, while no statistically significant difference was found in the titratable acidity. The use of the HPLC technique revealed that the hydroxycinnamic acids (neochlorogenic acid, chlorogenic acid and caffeic acid) are the major phenolic compounds of fresh plums and prunes alike. The prunes obtained by processing plums showed a significant decrease in neochlorogenic acid and an increase in caffeic acid in both cultivars, while chlorogenic acid content decreased in prunes of "Valjevka" and increased in prunes of "Mildora." Other compounds detected were rutin, benzoic acids and cyanidin.

Drying of plums at 90C resulted in an increase in total phenolics in both cultivars. While the drying had no effect on the total flavonoid content of the "Valjevka" fruits, this value was slightly increased in the fruits of "Mildora." Anthocyanins, being molecules very unstable and sensitive to technological processing, almost disappeared after drying.

Statistical analysis showed a significant correlation between fruit phenolic constituents and antioxidant capacity of plums and prunes of both cultivars examined, inferring the strong influence of anthocyanins, flavonoids and polyphenols on antioxidant capacity.

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