

Effect of Drying of Figs (*Ficus carica* L.) on the Contents of Sugars, Organic Acids, and Phenolic Compounds

Ana Slatnar,^{*,†} Urska Klancar,[‡] Franci Stampar,[†] and Robert Veberic[†]

[†]Agronomy Department, Chair for Fruit, Wine and Vegetable Growing, Biotechnical faculty, University of Ljubljana, Jamnikarjeva 101, SI-1000 Ljubljana, Slovenia

[‡]Science and Research Center of Koper, Institute for Mediterranean Agriculture and Olive Growing, University of Primorska, Garibaldijska 1, SI-6000 Koper, Slovenia

ABSTRACT: Fresh figs were subjected to two different drying processes: sun-drying and oven-drying. To assess their effect on the nutritional and health-related properties of figs, sugars, organic acids, single phenolics, total phenolics, and antioxidant activity were determined before and after processing. Samples were analyzed three times in a year, and phenolic compounds were determined using high-performance liquid chromatography coupled with mass spectrometry (HPLC-MS). In figs, monomer sugars predominate, which is important nutritional information, and the content of sugars as well as organic acids in fresh figs was lower than in dried fruits. However, the best sugar/organic acid ratio was measured after the sun-drying process. Analysis of individual phenolic compounds revealed a higher content of all phenolic groups determined after the oven-drying process, with the exception of cyanidin-3-*O*-rutinoside. Similarly, higher total phenolic content and antioxidant activity were detected after the drying process. With these results it can be concluded that the differences in analyzed compounds in fresh and dried figs are significant. The differences between the sun-dried and oven-dried fruits were determined in organic acids, sugars, chlorogenic acid, catechin, epicatechin, kaempferol-3-*O*-glucoside, luteolin-8-*C*-glucoside, and total phenolic contents. The results indicate that properly dried figs can be used as a good source of phenolic compounds.

KEYWORDS: bioactive compounds, drying, fig, fresh, sugars, organic acids, phenolics

INTRODUCTION

Ficus carica L., a deciduous tree belonging to the Moraceae family, is one of the earliest cultivated fruit trees. In the northern Mediterranean region, fig trees produce one or two crops per year, depending on the cultivar. The first crop is grown from flowers that were initiated in the previous year, and the fruit ripens at the beginning of summer. The second crop (the main one) is produced from flowers that emerge on the current season's shoots, and the fruit ripens in late summer. Therefore, the development of both crops is marked by different weather conditions. Fruits from the two crops can also differ in size and shape.¹

The fig is a delicious, nutritive fruit and has medicinal properties that may reduce the risk of cancer and heart disease.² Fig fruit is consumed fresh, dried, preserved, canned, and candied. In the Mediterranean region, it is used for alcohol and wine production and in Europe for a fig-coffee preparation. Fresh and dried figs are especially rich in fiber, trace minerals, antioxidant polyphenols, proteins, sugars, organic acids, and volatile compounds that provide a pleasant characteristic aroma.^{3–6} Dried figs can be stored for 6–8 months.⁷

The consumption of fresh figs is increasing as consumers are showing an interest in fresh quality produce of less familiar fruits.⁸ In some areas, such as California, most fig cultivars have been selected for drying and the growers have little fresh fruit handling experience,⁹ but in some northern Mediterranean conditions, which have sometimes less favorable weather conditions for drying, most of the figs are consumed fresh and proper conditions for fruit drying have to be established. Sun-drying can ensure proper preservation of figs. However, with traditional

drying methods prior selection of the produce with respect to maturity, size, condition, and state of ripeness does not exist. Moreover, the produce is exposed to direct solar irradiation and as the drying parameters cannot be controlled, the product quality is low. Sun-drying is, therefore, not homogeneous, and the final product is caramelized and crusted. Direct exposure to the sun also destroys the color, vitamins, and oven-dried flavor of the figs.¹⁰

Therefore, mechanical air dehydration has gained importance because of its many advantages over sun-drying.¹¹ These include the following: (A) The process is under better sanitary conditions, because of a reduction in contamination by dust and other foreign matter. (B) Drying parameters can be accurately set, controlled, and changed over the entire processing time; thus, a more consistently uniform product can be achieved with less quality degradation. (C) Dehydration is not conditioned by rain or weather changes. (D) When a constant rate of dehydration is reached, increasing the air flow can result in shorter drying times. (E) Labor costs are lower.

Although figs are an important fresh fruit variety in many countries, as well as a delicious dried fruit consumed in most parts of the world, there are only a few reports about phenolic content in fresh or dried figs. However, there is no comparison made in the phenolic content between fresh and dried fruit. Fresh figs are not available all year round, so many consumers often

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Table 1. Average Day Temperatures (°C) in a 7 Day Period of Sun-Drying Figs

day	sampling date		
	July 9	July 15	Sept 11
1	21.3	23.6	22.4
2	21.4	24.3	22.4
3	18.5	24.7	22.6
4	20.1	24.3	22.0
5	22.5	19.3	21.6
6	23.3	20.9	21.7
7	23.6	21.9	21.8

choose dried fruit instead. Therefore, the contents of the same important bioactive compounds and antioxidant activity of fresh and properly sun-dried and oven-dried figs were determined and compared. The new data present important information on the content of sugars, organic acids, antioxidant activity, total phenolics, and individual phenolic compounds of the figs subjected to two drying methods as well as give some important nutritional data about the differences of fresh and dried figs' chemical composition.

MATERIALS AND METHODS

Chemicals. The following standards were used for the quantification of sugars and organic acids: sucrose, glucose, and fructose; citric and malic acids from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). The following standards were used for the quantification of phenolic compounds: chlorogenic acid (5-caffeoylquinic acid), rutin (quercetin-3-O-rutinoside), and cyanidin-3-O-rutinoside from Sigma-Aldrich; (–)-epicatechin, quercetin-3-O-glucoside, and kaempferol from Fluka Chemie (Buchs, Switzerland); and (+)-catechin from Roth (Karlsruhe, Germany). Methanol for the extraction of phenolics was acquired from Sigma-Aldrich. The chemicals for the mobile phases were HPLC-MS grade acetonitrile and formic acid from Fluka Chemie. Water for the mobile phase was twice distilled and purified with the Milli-Q system (Millipore, Bedford, MA). For the total phenolic content, Folin–Ciocalteu phenol reagent (Fluka Chemie), sodium carbonate (Merck, Darmstadt, Germany), and gallic acid and methanol (Sigma-Aldrich) were used. For the determination of antioxidant capacity 1,1-diphenyl-2-picrylhydrazyl (DPPH), ascorbic acid, and methanol were purchased from Sigma.

Plant Material and Experimental Design. The orchard of a local cultivar of *F. carica* L. called 'Bela petrovka' was planted in Glem (altitude 303 m, latitude 45° 29' 21" N, longitude 13° 47' 18" E), a hilly part of Slovenian Istria, in 1998. All trees were managed according to integrated cultivation protocols and trained as an open vase with a 5 × 4 m spacing. Fresh figs were picked by hand two times in the summer (July) and once in the autumn (September) of 2009. At each picking term three samples of physiologically mature fruits were collected (seven to eight fruit per sample, total weight approximately 0.5 kg). One sample was immediately transferred on ice to a freezer and then to laboratory facilities, where the figs were subjected to analysis. Two other remaining samples were used for drying. For both drying protocols fruits were cut in half and uniformly distributed on a sample tray in a single layer (a homemade device made of wire mesh surrounded with a wooden frame). Half was immediately exposed to the sun at a height of 1 m from the ground surface and placed indoors at night. The other tray was placed in an air-dryer. All experiments of sun-dried figs were set on the day of harvest and took 7 days; figs dried in a dryer took 24 h. In the days

after harvest average day temperature was monitored for the duration of the sun-drying and remained approximately the same throughout the experiment (Table 1). The air-drying experiment was conducted in a specially made wooden dryer 1.5 × 1.3 × 1.3 m in size, connected to an oil-fired furnace blowing hot air. Drying air temperature ranged between 62 and 64 °C.¹² Air relative humidity ranged between approximately 40% (at the beginning) and 10% (at the end).

Analysis of Individual Sugars and Organic Acids. The samples were analyzed for their content levels of sugars (sucrose, glucose, and fructose) and organic acids (malic and citric). Figs were cut into small pieces, and 15 g of the fresh mass or 15 g of the dry mass was immersed in 20 or 40 mL of twice-distilled water and homogenized with a T-25 Ultra-Turrax (Ika-Labortechnik, Stauden, Germany). The samples were left for extraction for 0.5 h at room temperature with frequent stirring at 150 rpm (Grant Bio POS-300, Grant Instruments, Cambridge, U.K.), and the extracted samples were centrifuged at 10000 rpm for 7 min at 10 °C (Eppendorf Centrifuge 5810R, Hamburg, Germany). The supernatants were filtered through a 0.45 μm filter (Macherey-Nagel, Düren, Germany) and transferred to a vial.

Samples were analyzed according to the method described by Sturm et al.¹³ using high-performance liquid chromatography (HPLC; Thermo Scientific, Finnigan Spectra System, Waltham, MA). For each analysis 20 μL of sample was used. Analysis of sugars was carried out using a Rezex RCM-monosaccharide column (300 × 7.8 mm; Phenomenex, Torrance, CA) with a flow of 0.6 mL min⁻¹, and column temperature was maintained at 65 °C. For the mobile phase, twice-distilled water was used and an refractive index (RI) detector for identification. Organic acids were analyzed using a Rezex ROA-organic acid column (300 × 7.8 mm; Phenomenex), and the UV detector was set at 210 nm with a flow of 0.6 mL min⁻¹, maintaining the column temperature at 65 °C. For the mobile phase, 4 mM sulfuric acid (H₂SO₄) was used. The concentrations of carbohydrates and organic acids were calculated with the help of corresponding external standards. The concentrations were expressed in grams per kilogram of fresh weight (FW) or dry weight (DW).

Extraction and Determination of Individual Phenolic Compounds. The extraction of fruit samples was done as described by Petkovsek et al.,¹⁴ with some modification. Fresh or dry fig samples were ground to a fine powder in a mortar chilled with liquid nitrogen. The samples of 10 g fresh or 2.5 g dry fruit were extracted with 20 or 10 mL of methanol containing 1% (w/v) 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 3% (v/v) formic acid in a cooled ultrasonic bath for 1 h. The treated samples were centrifuged for 7 min at 10000 rpm. The supernatant was filtered through a Chromafil AO-45/25 polyamide filter (Macherey-Nagel) and transferred to a vial prior to injection into a HPLC system. Samples were analyzed using a Thermo Finnigan Surveyor HPLC system (Thermo Scientific, San Jose, CA) with a diode array detector at 280 nm (hydroxycinnamic acids and flavan-3-ols), 350 nm (flavonols), and 530 nm (anthocyanins). A Phenomenex HPLC column C18 (150 × 4.6 mm, Gemini 3 μ) protected with a Phenomenex security guard column operated at 25 °C was used. The injection volume was 20 μL, and the flow rate was maintained at 1 mL min⁻¹. The elution solvents were aqueous 1% formic acid (A) and 100% acetonitrile (B). Samples were eluted according to the gradient described by Marks et al.:¹⁵ 0–5 min, 3–9% B; 5–15 min, 9–16% B; 15–45 min, 16–50% B; 45–50 min, 50% isocratic; and finally washing and reconditioning of the column. Identification of compounds was achieved by comparing retention times and their UV–vis spectra from 200 to 600 nm, as well as by the addition of an external standard. Compounds were identified and quantified using a mass spectrometer (Thermo Scientific, LCQDeca XP MAX) with an electrospray ionization (ESI) operating in negative/positive ion mode (Table 2). The analyses were carried out using full-scan data-dependent MSⁿ scanning from *m/z* 115 to 2000. The capillary temperature was 250 °C, the sheath gas and auxiliary gas were

Table 2. Retention Time and MSⁿ Fragmentation Data of Major Phenols Detected in Fig ([M – H][–] Molecular Ion)

compound	peak	t _R (min)	[M – H] [–] (m/z)	MS/MS ions (m/z)	comparison with standard
(+)-catechin	1	12.4	289	245	yes
chlorogenic acid	2	12.8	353	191	yes
(–)-epicatechin	3	15.5	289	245	yes
cyanidin-3-O-rutinoside ^a	4	14.0	595	449, 287	yes
luteolin-8-C-glucoside	5	20.2	447	357, 327, 285	no
rutin	6	22.7	609	301	yes
quercetin-3-O-glucoside	7	23.5	463	301	yes
kaempferol-3-O-glucoside	8	25.4	447	284	no

^a [M + H]⁺ (m/z).

20 and 7 units, respectively, and the source voltage was 4 kV for negative ionization and 0.1 kV for positive ionization. Quantification was achieved according to the concentrations of a corresponding external standard.

Concentrations of phenolic compounds were calculated from the peak areas of the sample and the corresponding standards. The concentrations were expressed in milligrams per 100 g of FW or DW. For compounds lacking standards, quantification was carried out using compounds similar to standards. Thus, kaempferol-3-O-glucoside and luteolin-8-C-glucoside were quantified in equivalents of quercetin-3-O-glucoside.

Determination of Total Phenolic Content. The extraction of fruit samples for the determination of total phenolic content (TPC) was made according to the same protocol as for individual phenolics, with the difference that no BHT and formic acid were added. TPC of the extracts was assessed using the Folin–Ciocalteu phenol reagent method.¹⁶ Six milliliters of twice-distilled water and 500 μL of Folin–Ciocalteu reagent were added to 100 μL of the sample extracts, and after between 8 s and 8 min at room temperature, 1.5 mL of sodium carbonate (20% w/v) and 1.9 mL of twice distilled water were added. The extracts were mixed and allowed to stand for 30 min at 40 °C before the absorbance at 765 nm was measured on a Lambda Bio 20 UV–vis spectrophotometer (Perkin-Elmer, Waltham, MA). A mixture of water and reagents was used as a blank. The TPC was expressed as gallic acid equivalents (GAE) in milligrams per kilogram of FW or DW. Absorptions were measured in three replicates.

Determination of Antioxidant Activity with the DPPH Radical Scavenging Method. The extraction of fruit samples for the determination of antioxidant activity was made according to the same protocol as for total phenolics. The free radical scavenging activity of fig extracts was measured according to the DPPH method reported by Brand-Williams et al.¹⁷ with some modifications. A methanolic solution (50 μL) of extract was placed in 96-well microplates, and 200 μL of a 0.1 mmol L^{–1} methanolic solution of DPPH was added and allowed to react in the dark at room temperature. The decrease in absorbance of DPPH at 520 nm was measured at 5 min intervals by a spectrophotometer (MRX Dynex Technologies), until the absorbance stabilized (30 min). Methanol was used as blank solution, and a DPPH solution without test samples served as the control. All sample analyses were performed in triplicate. The DPPH radical scavenging activity of fig methanolic extracts was expressed as milligrams of ascorbic acid equivalents per 100 g (AEAC = ascorbic acid equivalent antioxidant capacity) in 30 min of reaction time. Identification of the antioxidant capacities of the samples at various concentrations was made using the standard curves of ascorbic acid.

Statistical Analysis. The data were analyzed using the Statgraphics Plus 4.0 program (Manugistics, Inc., Rockville, MD). Differences between treatments were analyzed independently for each sampling date with a one-way analysis of variance (ANOVA). Significant

Table 3. Content of Sugars (g kg^{–1}) in Fresh Fruit and Dried Fruit of Two Drying Methods at Different Sampling Dates^a

	sampling date		
	July 9	July 15	Sept 11
Glucose			
sun-drying	121.48 ± 4.60 b	96.90 ± 9.93 b	116.42 ± 12.75 b
oven-drying	215.88 ± 14.18 c	106.64 ± 11.93 b	105.28 ± 9.76 b
fresh	29.24 ± 1.34 a	38.17 ± 4.61 a	25.03 ± 2.61 a
Fructose			
sun-drying	103.72 ± 3.97 b	82.53 ± 8.07 b	103.12 ± 11.14 b
oven-drying	195.57 ± 12.43 c	95.38 ± 10.31 b	99.45 ± 8.14 b
fresh	26.53 ± 1.22 a	34.02 ± 4.32 a	23.43 ± 2.48 a
Sucrose			
sun-drying	4.53 ± 0.32 b	5.75 ± 0.44 b	2.49 ± 0.47 b
oven-drying	7.40 ± 0.44 c	4.44 ± 0.65 b	5.26 ± 0.22 c
fresh	0.59 ± 0.06 a	0.88 ± 0.15 a	0.98 ± 0.42 a
Total Sugars			
sun-drying	229.73 ± 8.47 b	185.18 ± 18.28 b	222.03 ± 24.36 b
oven-drying	418.85 ± 27.05 c	206.47 ± 22.89 b	209.98 ± 18.10 b
fresh	56.36 ± 2.58 a	73.07 ± 9.05 a	50.63 ± 6.05 a

^a Mean ± SE, n = 5. Different letters in columns indicate statistically significant differences in the contents of individual compounds between the treatments for each set of sampling dates at p < 0.05.

differences among means were determined by the least significant difference (LSD) with a significance level of 0.05.

RESULTS AND DISCUSSION

Sugar and Organic Acid Contents. Glucose, fructose, sucrose, and total sugar content levels (g kg^{–1}) of physiologically mature figs and physiologically mature figs dried by two different techniques are presented in Table 2. Fructose (~52%) and glucose (~46%) were found to be the dominant sugars in all accessions analyzed; on the other hand, sucrose levels were very low (~2%), which is in accordance with the results of Veberic et al.¹⁸ The contents of individual and total sugars were statistically lower in fresh figs compared to dried fruit at all samplings. At the first sampling date the difference in the sugar content was also statistically significant when fruits of the two drying methods were compared; however, at the other two samplings the differences were not detected (Table 3). The glucose/fructose

Table 4. Content of Organic Acids (g kg⁻¹) in Fresh Fruit and Dried Fruit of Two Drying Methods and the Ratio of Sugars/Organic Acids at Different Sampling Dates^a

	sampling date		
	July 9	July 15	Sept 11
Malic Acid			
sun-drying	3.11 ± 0.32 b	2.26 ± 0.33 a	1.84 ± 0.39 a
oven-drying	8.71 ± 1.23 c	9.07 ± 0.92 b	6.29 ± 0.79 b
fresh	0.76 ± 0.05 a	0.52 ± 0.04 a	0.66 ± 0.19 a
Citric Acid			
sun-drying	4.66 ± 0.53 a	4.36 ± 0.43 b	3.33 ± 0.21 b
oven-drying	10.54 ± 1.82 b	6.98 ± 0.50 c	7.00 ± 0.42 c
fresh	1.83 ± 0.18 a	1.57 ± 0.12 a	1.36 ± 0.22 a
Total Organic Acids			
sun-drying	7.77 ± 0.85 b	6.37 ± 0.68 b	5.16 ± 0.55 b
oven-drying	19.25 ± 1.51 c	15.45 ± 1.18 c	13.58 ± 1.03 c
fresh	2.59 ± 0.22 a	2.10 ± 0.15 a	2.02 ± 0.40 a
Sugars/Organic Acids			
sun-drying	31.34 ± 4.12 b	27.99 ± 2.89 b	43.02 ± 0.73 b
oven-drying	21.75 ± 2.00 a	13.64 ± 1.42 a	18.12 ± 0.96 a
fresh	22.14 ± 1.23 a	35.34 ± 4.37 b	23.57 ± 3.76 a

^a Mean ± SE, *n* = 5. Different letters in columns indicate statistically significant differences in the contents of individual compounds between the treatments for each set of sampling dates at *p* < 0.05.

ratio was quite constant in the present study (1.1–1.2), regardless of the type of drying, which is important as the sugar composition of fig fruit influences the perceived fruit sweetness. Fructose has a higher relative sweetness than glucose.¹⁹ Therefore, the perception of sweetness in fig accessions is likely due to the prevalence of fructose, and our results indicate that the figs dried in the sun do not taste sweeter than figs dried in a drying room.

In fig fruits, malic and citric acids were determined among organic acids. Malic acid was the main compound in fig samples, representing 24.7–58.7% of the total organic acids content. The content of organic acids in dried samples was from 2.4- to 5.6-fold higher for citric acid and from 2.8- to 17.4-fold higher for malic acid (Table 4) compared to fresh fruit. A similar content of organic acid in figs was reported by Pande and Akoh.²⁰ At all sampling dates a statistically higher content of individual and total organic acids was determined in samples dried in a drying room compared to other treatments (Table 4). These results are expected, because dried fruit samples contain less water, which means that the organic acids are more concentrated in dried figs.

The ratio between the analyzed sugars and organic acids in fresh and dried figs (Table 4) is a common quality index and a good indicator of internal fruit quality. The optimal ratio differs between cultivars and is crucial for a harmonious flavor. Although organic acids are present in lower concentrations in fig fruit than sugars, their effect on the fruit flavor is considerable. The higher the ratio, the sweeter the fruits; the lower the ratio, the more sour tasting.²¹ The statistically highest sugar/organic acid ratio was calculated for figs dried in the sun and fresh figs at the second sampling date, which had a high content of sugars and a very low content of organic acids (Table 4). Figs dried in the drying room, on the other hand, had a low content of sugars and a rather high

Table 5. Content of Phenolic Compounds (mg 100 g⁻¹) in Fresh Fruit and Dried Fruit of Two Drying Methods at Different Sampling Dates^a

	sampling date		
	July 9	July 15	Sept 11
Chlorogenic Acid			
sun-drying	9.84 ± 1.41 b	15.88 ± 1.07 b	3.42 ± 0.54 a
oven-drying	13.96 ± 1.48 c	32.42 ± 0.89 c	19.92 ± 2.56 b
fresh	1.33 ± 0.15 a	2.78 ± 0.46 a	4.91 ± 1.00 a
Catechin			
sun-drying	11.46 ± 2.45 b	5.88 ± 0.60 b	6.60 ± 1.18 b
oven-drying	16.16 ± 1.32 b	15.57 ± 2.04 c	19.75 ± 0.68 c
fresh	1.36 ± 0.24 a	2.67 ± 0.17 a	2.88 ± 0.18 a
Epicatechin			
sun-drying	23.30 ± 3.12 b	20.37 ± 0.70 b	10.44 ± 0.86 b
oven-drying	34.65 ± 2.63 c	36.65 ± 2.46 c	26.66 ± 1.85 c
fresh	7.58 ± 1.64 a	8.67 ± 1.12 a	7.11 ± 0.54 a
Kaempferol-3-O-glucoside			
sun-drying	0.46 ± 0.04 b	0.31 ± 0.04 b	0.59 ± 0.06 b
oven-drying	0.99 ± 0.09 c	0.56 ± 0.05 c	1.43 ± 0.07 c
fresh	0.04 ± 0.00 a	0.10 ± 0.00 a	0.13 ± 0.01 a
Luteolin-8-C-glucoside			
sun-drying	0.15 ± 0.02	0.13 ± 0.01	0.16 ± 0.02
oven-drying	0.39 ± 0.03	0.21 ± 0.02	0.45 ± 0.04
fresh	nd ^b	nd	nd
Rutin			
sun-drying	6.66 ± 1.39 b	12.06 ± 1.00 b	1.38 ± 0.37 a
oven-drying	7.03 ± 1.03 b	14.62 ± 1.81 b	3.75 ± 0.29 b
fresh	0.61 ± 0.14 a	1.86 ± 0.63 a	0.89 ± 0.20 a
Quercetin-3-O-glucoside			
sun-drying	2.40 ± 0.46 b	3.35 ± 0.19 b	0.56 ± 0.12 a
oven-drying	2.23 ± 0.24 b	2.98 ± 0.27 b	1.10 ± 0.06 b
fresh	0.18 ± 0.04 a	0.60 ± 0.17 a	0.41 ± 0.09 a
Cyanidin-3-O-rutinoside			
sun-drying	0.26 ± 0.06 a	0.12 ± 0.01 a	0.13 ± 0.05 a
oven-drying	0.16 ± 0.02 a	0.12 ± 0.01 a	0.31 ± 0.05 b
fresh	0.21 ± 0.05 a	0.31 ± 0.05 b	0.62 ± 0.04 c

^a Mean ± SE, *n* = 5. Different letters in columns indicate statistically significant differences in the contents of individual compounds between the treatments for each set of sampling dates at *p* < 0.05. ^b nd, not detected.

content of organic acids, and thus the lowest sugar/organic ratio. That result was expected, because one of the factors of sweetness was also the glucose/fructose ratio, which was high in sun-dried figs.

Phenolic Compounds. A number of studies have shown that the presence of phenolics in food and especially in fruit can be particularly important for consumers, because of their beneficial health properties. Besides antioxidant effects, phenolic compounds possess a wide spectrum of biochemical properties and can also have a beneficial effect in preventing the development of diseases such as cancer and cardiovascular diseases.²² In our study eight phenolics in fresh and dried figs, belonging to four

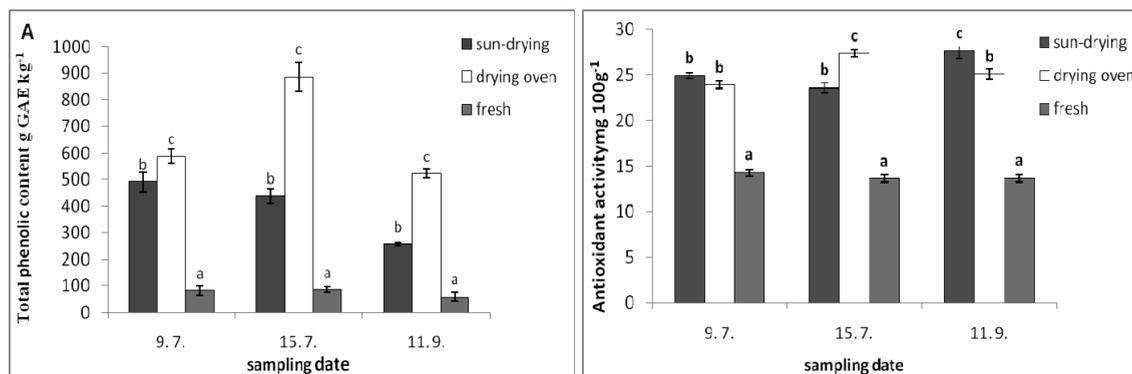


Figure 1. Total phenolic content (mean \pm SE in g kg^{-1}) and antioxidant activity (mean \pm SE in $\text{mg } 100 \text{ g}^{-1}$) of fresh fruit and dried fruit of two drying methods.

297 groups of hydroxycinnamic acids, flavan-3-ols, flavonols, and
 298 anthocyanins, were identified. The predominant phenolic com-
 299 pound was epicatechin; in very small amounts luteolin-8-
 300 C-glucoside was detected (Table 5). The highest content of individ-
 301 ual phenolics was recorded at the second sampling of the first
 302 crop for most phenols (Table 5). These results show that the
 303 selection of the right crop in two fruiting figs is of high
 304 importance and that the ideal ripeness of fig fruit is equally
 305 significant as it ensures a high content of substances in fresh and
 306 dried figs that are vital for human health. A difference in the
 307 amount of phenolic compounds in cultivars that bear fruit twice a
 308 year has also been reported previously.²³

309 In the group of hydroxycinnamic acids chlorogenic acid was
 310 determined. The amount of chlorogenic acid in fresh figs ranged
 311 between 1.3 and 4.9 $\text{mg } 100 \text{ g}^{-1}$ and that in dried figs between 3.4
 312 and 32.4 $\text{mg } 100 \text{ g}^{-1}$ (Table 5). Our results for fresh figs are in
 313 agreement with those reported by Veberic et al. and Del Caro
 314 et al.^{23,24} Statistically significant differences in the content of
 315 chlorogenic acid between the fresh or two types of dried figs
 316 occurred at almost every sampling date. In all cases, statistically
 317 higher amounts of chlorogenic acid were measured in figs dried in
 318 the drying oven (Table 5). These results are expected because in
 319 the drying room constant conditions can be reached, as opposed to
 320 the sun-drying, during which the conditions vary greatly.

321 Both (-)-epicatechin and (+)-catechin from the group of
 322 flavan-3-ols were determined in fresh and dried figs. Epicatechin
 323 was the predominant analyzed phenolic compound in our study,
 324 ranging from 7.8 $\text{mg } 100 \text{ g}^{-1}$ FW in fresh figs to 25.4 $\text{mg } 100 \text{ g}^{-1}$
 325 DW in dried figs. In all samples, the content of catechin was lower
 326 than that of epicatechin. In previous studies higher contents of
 327 these flavan-3-ols in figs were reported by Pande and Akoh;²⁰ on
 328 the other hand, Veberic et al.²³ measured a much lower content
 329 of epicatechin and catechin. These differences may be cultivar
 330 specific and also due to agroecological specifics of the studies.
 331 However, according to the data presented, fresh figs belong to
 332 fruit rich in both constituents, in comparison to apple pulp¹⁴ and
 333 sweet cherry.²⁵ A statistically higher content of both epicatechin
 334 and catechin was measured in figs dried in the air oven (Table 5).
 335 Previous results of a study on sun-dried pear show that as a result
 336 of the drying process monomeric catechin and epicatechin
 337 decreased between 91 and 96%,²⁶ which is in contrast to our
 338 results as the contents of both these monomers were higher in
 339 dried figs. Devic et al.²⁷ reported that procyanidins are better
 340 preserved by the drying process than hydroxycinnamic acids or
 341 monomeric catechin. Indeed, these latter groups of polyphenols

were initially involved in enzymatic browning but can also diffuse
 more easily as their molecular weight is lower.

The following compounds from the group of flavonols were
 determined: kaempferol-3-O-glucoside, luteolin-8-C-glucoside, rutin,
 and quercetin-3-O-glucoside. Luteolin-8-C-glucoside was not
 detected in fresh figs, and its content was also low in dried figs.
 Likewise, statistically higher contents of kaempferol-3-O-glucoside,
 rutin, and quercetin-3-O-glucoside were determined in the fig sample
 dried in the drying oven (Table 5). In the case of kaempferol-3-
 O-glucoside the difference between the drying methods was
 observed (Table 5). The drying processes had a similar influence
 on the content of phenolic compounds from the group of flavonols
 than on the other groups of phenolic compounds.

From the group of anthocyanins only cyanidin-3-O-rutinoside
 was determined in cultivar 'Bela petrovka'. According to the
 literature, cyanidin-3-O-rutinoside is the main anthocyanin in
 figs,²⁸ with its content ranging between 0.12 and 0.62 $\text{mg } 100 \text{ g}^{-1}$
 FW. The content of total anthocyanins in yellow cultivars ranges
 from 0.06 to 2.97 $\text{mg } 100 \text{ g}^{-1}$,²⁹ which is in agreement with the
 data reported in our study. A statistically lower content of
 cyanidin-3-O-rutinoside was detected in the dried fruit of the
 second and third sampling dates (Table 5). A higher concentra-
 tion of total anthocyanins after drying of strawberry, apple, and
 peach fruit was previously reported by Rababah et al.³⁰ On
 the contrary, our results indicate that the drying process has a
 negative influence on the content of anthocyanins, which was
 also reported by Sablani et al.³¹ and Wojdylo et al.³²

Total Phenolic Content and Antioxidant Activity. Total
 phenolics were in the range from 74.9 mg GAE kg^{-1} FW in fresh
 figs to 530.2 mg GAE kg^{-1} DW in dried figs (Figure 1A). A
 statistically higher TPC was determined in figs dried in the drying
 oven at all sampling dates (Figure 1A). Veberic et al.¹⁸ measured
 similar TPC compared to our results. A much higher TPC
 (1189.0 mg GAE kg^{-1}) has been reported in fresh fig fruits in
 the research of Çaliskan and Aytekin Polat.²⁹ In comparison with
 sweet cherry, which contains from 443 to 879 mg GAE kg^{-1}
 FW,²⁵ and apple, of which the pulp contained 422.5 mg GAE
 kg^{-1} FW and the peel 1754.6 mg GAE kg^{-1} FW,¹⁴ our analysis of
 figs showed similar TPC in fresh fruit to that of sweet cherry and
 apple pulp. Rababah et al.³⁰ reported that the levels of total
 phenolics were higher in dried fruits (apple, strawberry, and
 peach) followed by pureed and fresh products.

Antioxidant potential, expressed as AEAC, is presented in
 Figure 1B. AEAC was significantly higher in all dried figs ana-
 lyzed, with almost 2-fold higher values detected as in fresh figs.

Between the two drying methods, only the differences at the second and third sampling dates were significant (Figure 1B). The antioxidant capacity of phenolic compounds is based on their ability to scavenge free radicals, chelate pro-oxidant metal ions, and inhibit some enzymes.³³ Nevertheless, the contribution of organic acids cannot be ignored. Total phenolic content seems to be a good indicator of the antioxidant potential in fruit, and several authors have reported a correlation between these parameters in peaches³⁴ and nectarines,³⁵ which was also confirmed by our study. Vinson et al.³⁶ reported that figs, especially dried ones, are an excellent source of nutrients and are in vivo antioxidants; the antioxidant capacity of human plasma increased significantly for hours after their consumption.

Conclusion. To our knowledge, this is the first study comparing the contents of selected primary (sugars and organic acids) and secondary (phenols) metabolites in figs subjected to different drying methods with those of fresh fig fruit. Changes in the phenolic compounds and the degradation mechanisms depended on the drying process applied and on the type of phenolic compounds studied. In all cases, phenolic compounds were relatively well preserved. The difference in the contents of primary and secondary metabolites was significant when fresh and dried figs were compared. Also, between the drying processes a big difference was detected in the contents of secondary metabolites, and the oven-dried figs were richer in these compounds. Considering the absolute amounts of individual chemical compounds constituting fig fruit, it can be demonstrated that significantly more primary metabolites than secondary metabolites are present in both fresh and dried figs. When fresh figs are not available, properly dried figs could thus be used as a valuable substitute in diets that aim to prevent certain diseases. In our further studies, it would be interesting to concentrate on the effect drying has on various fig cultivars and to include a different treatment such as the addition of sulfur to the dried fruit or blanching process.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ana.slatnar@bf.uni-lj.si. Fax: +386 1 256 57 82' Phone: +386 1 320 31 10.

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REFERENCES

- (1) Lodhil, F.; Bradley, M. V.; Crane, J. C. Auxins and gibberellin-like substances in parthenocarpic and non-parthenocarpic syconia of *Ficus carica* L., CV. King. *Plant Physiol.* **1969**, *44*, 555–561.
- (2) Vinson, J. A. The functional food properties of fig. *Cereal Foods World* **1999**, *44*, 82–87.
- (3) Slavin, J. L. Figs: past, present and future. *Nutr. Today* **2006**, *41*, 180–184.
- (4) Oliveira, A. P.; Silva, L. R.; Andrade, P. B.; Valentao, P.; Silva, B. M.; Pereira, J. A.; de Pinho, P. G. Determination of low molecular weight volatiles in *Ficus carica* using HS-SPME and GC/FID. *Food Chem.* **2010**, *121*, 1289–1295.
- (5) Oliveira, A. P.; Silva, L. R.; de Pinho, P. G.; Gil-Izquierdo, A.; Valentao, P.; Silva, B. M.; Pereira, J. A.; Andrade, P. B. Volatile profiling of *Ficus carica* varieties by HS-SPME and GC-IT-MS. *Food Chem.* **2010**, *123*, 548–557.
- (6) Oliveira, A. P.; Valentao, P.; Pereira, J. A.; Silva, B. M.; Tavares, F.; Andrade, P. B. *Ficus carica* L.: metabolic and biological screening. *Food Chem. Toxicol.* **2009**, *47*, 2841–2846.

- (7) Venkatartnam, L. *Packaging of Figs. A Souvenir on Packaging of Fruits and Vegetables in India*; Agriculture Horticultural Society Public Gardner: Hyderabad, India, 1988.
- (8) Stover, E.; Aradhya M.; Crisosto C.; L., F. Overview of the California fig industry and new interest in varieties for fresh fruit. In *Proceedings of the California Plant and Soil Conference: Opportunities for California Agriculture*, Sacramento, CA, 2007; pp 169–175.
- (9) Crisosto, C. H.; Bremer, V.; Ferguson, L.; Crisosto, G. M. Evaluating quality attributes of four fresh fig (*Ficus carica* L.) cultivars harvested at two maturity stages. *HortScience* **2010**, *45*, 707–710.
- (10) Chimi, H.; Ouauich, A.; Semmar, M.; Tayebi, S. Industrial processing of figs by solar drying in Morocco. *Acta Hortic.* **2008**, *798*, 331–334.
- (11) Barbosa-Cánovas, G. V.; Vega-Mercado, H. Other methods of dehydration of foods and packaging aspects. In *Dehydration of Foods*; Barbosa-Cánovas, G. V., Vega-Mercado, H., Eds.; Chapman & Hall: New York, 1996; pp 289–320.
- (12) Piga, A.; Agabbio, M.; Farris, G. A. Dehydration performance of local fig cultivars. *Acta Hortic.* **2003**, *605*, 241–245.
- (13) Sturm, K.; Koron, D.; Stampar, F. The composition of fruit of different strawberry varieties depending on maturity stage. *Food Chem.* **2003**, *83*, 417–422.
- (14) Petkovsek, M. M.; Stampar, F.; Veberic, R. Parameters of inner quality of the apple scab resistant and susceptible apple cultivars (*Malus domestica* Borkh.). *Sci. Hortic.* **2007**, *114*, 37–44.
- (15) Marks, S. C.; Mullen, W.; Crozier, A. Flavonoid and chlorogenic acid profiles of English cider apples. *J. Sci. Food Agric.* **2007**, *87*, 719–728.
- (16) Singleton, V. L.; Rossi, J. A. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *Am. J. Enol. Vitic.* **1965**, *16*, 144–158.
- (17) Brand-Williams, W.; Cuvelier, M. E.; Berset, C. Use of a free-radical method to evaluate antioxidant activity. *Food Sci. Technol.* **1995**, *28*, 25–30.
- (18) Veberic, R.; Jakopic, J.; Stampar, F. Internal fruit quality of figs (*Ficus carica* L.) in the northern Mediterranean region. *Ital. J. Food Sci.* **2008**, *20*, 255–262.
- (19) Redlinger, P. A.; Setser, C. S. Sensory quality of selected sweeteners – aqueous and lipid model systems. *J. Food Sci.* **1987**, *52*, 451–454.
- (20) Pande, G.; Akoh, C. C. Organic acids, antioxidant capacity, phenolic content and lipid characterisation of Georgia-grown underutilized fruit crops. *Food Chem.* **2010**, *120*, 1067–1075.
- (21) Colaric, M.; Veberic, R.; Stampar, F.; Hudina, M. Evaluation of peach and nectarine fruit quality and correlations between sensory and chemical attributes. *J. Sci. Food Agric.* **2005**, *85*, 2611–2616.
- (22) Lattanzio, V. Bioactive polyphenols: their role in quality and storability of fruit and vegetables. *J. Appl. Bot. Food Qual.* **2003**, *77*, 128–146.
- (23) Veberic, R.; Colaric, M.; Stampar, F. Phenolic acids and flavonoids of fig fruit (*Ficus carica* L.) in the northern Mediterranean region. *Food Chem.* **2008**, *106*, 153–157.
- (24) Del Caro, A.; Piga, A. Polyphenol composition of peel and pulp of two Italian fresh fig fruits cultivars (*Ficus carica* L.). *Eur. Food Res. Technol.* **2008**, *226*, 715–719.
- (25) Usenik, V.; Fabčić, J.; Stampar, F. Sugars, organic acids, phenolic composition and antioxidant activity of sweet cherry (*Prunus avium* L.). *Food Chem.* **2008**, *107*, 185–192.
- (26) Ferreira, D.; Guyot, S.; Marnet, N.; Delgado, I.; Renard, C.; Coimbra, M. A. Composition of phenolic compounds in a Portuguese pear (*Pyrus communis* L. var. S. Bartolomeu) and changes after sun-drying. *J. Agric. Food Chem.* **2002**, *50*, 4537–4544.
- (27) Devic, E.; Guyot, S.; Daudin, J. D.; Bonazzi, C. Kinetics of polyphenol losses during soaking and drying of cider apples. *Food Bioprocess. Technol.* **2010**, *3*, 867–877.
- (28) Solomon, A.; Golubowicz, S.; Yablowicz, Z.; Grossman, S.; Bergman, M.; Gottlieb, H. E.; Altman, A.; Kerem, Z.; Flaishman, M. A. Antioxidant activities and anthocyanin content of fresh fruits of common fig (*Ficus carica* L.). *J. Agric. Food Chem.* **2006**, *54*, 7717–7723.

- 515 (29) Çaliskan, O.; AYTEKIN POLAT, A. Phytochemical and antioxidant
516 properties of selected fig (*Ficus carica* L.) accessions from the eastern
517 Mediterranean region of Turkey. *Sci. Hort.* **2011**, *128*, 473–478.
- 518 (30) Rababah, T. M.; Ereifej, K. I.; Howard, L. Effect of ascorbic acid
519 and dehydration on concentrations of total phenolics, antioxidant
520 capacity, anthocyanins, and color in fruits. *J. Agric. Food Chem.* **2005**,
521 *53*, 4444–4447.
- 522 (31) Sablani, S. S.; Andrews, P. K.; Davies, N. M.; Walters, T.; Saez,
523 H.; Bastarrachea, L. Effects of air and freeze drying on phytochemical
524 content of conventional and organic berries. *Dry. Technol.* **2011**,
525 *29*, 205–216.
- 526 (32) Wojdylo, A.; Figiel, A.; Oszmianski, J. Effect of drying methods
527 with the application of vacuum microwaves on the bioactive compounds,
528 color, and antioxidant activity of strawberry fruits. *J. Agric. Food Chem.*
529 **2009**, *57*, 1337–1343.
- 530 (33) Silva, B. M.; Andrade, P. B.; Valentao, P.; Ferreres, F.; Seabra,
531 R. M.; Ferreira, M. A. Quince (*Cydonia oblonga* Miller) fruit (pulp, peel,
532 and seed) and jam: antioxidant activity. *J. Agric. Food Chem.* **2004**,
533 *52*, 4705–4712.
- 534 (34) Scalzo, J.; Politi, A.; Pellegrini, N.; Mezzetti, B.; Battino, M.
535 Plant genotype affects total antioxidant capacity and phenolic contents
536 in fruit. *Nutrition* **2005**, *21*, 207–213.
- 537 (35) Cantin, C. M.; Moreno, M. A.; Gogorcena, Y. Evaluation of the
538 antioxidant capacity, phenolic compounds, and vitamin C content of
539 different peach and nectarine *Prunus persica* (L.) Batsch breeding
540 progenies. *J. Agric. Food Chem.* **2009**, *57*, 4586–4592.
- 541 (36) Vinson, J. A.; Zubik, L.; Bose, P.; Samman, N.; Proch, J. Dried
542 fruits: excellent in vitro and in vivo antioxidants. *J. Am. Coll. Nutr.* **2005**,
543 *24*, 44–50.