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Effect of Drying of Figs (Ficus carica L.) on the Contents of Sugars, 1 Organic Acids, and Phenolic Compounds 2

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8 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 9 determined before and after processing. Samples were analyzed three times in a year, and phenolic compounds were determined 10 using high-performance liquid chromatography coupled with mass spectrometry (HPLC-MS). In figs, monomer sugars 11 predominate, which is important nutritional information, and the content of sugars as well as organic acids in fresh figs was lower 12 than in dried fruits. However, the best sugar/organic acid ratio was measured after the sun-drying process. Analysis of individual 13 14 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. 15 With these results it can be concluded that the differences in analyzed compounds in fresh and dried figs are significant. The 16 differences between the sun-dried and oven-dried fruits were determined in organic acids, sugars, chlorogenic acid, catechin, 17 epicatechin, kaempferol-3-O-glucoside, luteolin-8-C-glucoside, and total phenolic contents. The results indicate that properly dried 18 figs can be used as a good source of phenolic compounds. 19

KEYWORDS: bioactive compounds, drying, fig, fresh, sugars, organic acids, phenolics 20

INTRODUCTION 23

Ficus carica L., a deciduous tree belonging to the Moraceae 24 25 family, is one of the earliest cultivated fruit trees. In the northern Mediterranean region, fig trees produce one or two crops per 26 year, depending on the cultivar. The first crop is grown from 27 flowers that were initiated in the previous year, and the fruit 28 ripens at the beginning of summer. The second crop (the main 29 one) is produced from flowers that emerge on the current 30 season's shoots, and the fruit ripens in late summer. Therefore, 31 the development of both crops is marked by different weather 32 conditions. Fruits from the two crops can also differ in size and 33 shape.1 34

The fig is a delicious, nutritive fruit and has medicinal proper-35 ties that may reduce the risk of cancer and heart disease.² Fig fruit 36 is consumed fresh, dried, preserved, canned, and candied. In the 37 Mediterranean region, it is used for alcohol and wine production 38 39 and in Europe for a fig-coffee preparation. Fresh and dried figs are especially rich in fiber, trace minerals, antioxidant polyphenols, 40 proteins, sugars, organic acids, and volatile compounds that 41 provide a pleasant characteristic aroma.³⁻⁶ Dried figs can be 42 stored for 6-8 months.⁷ 43

The consumption of fresh figs is increasing as consumers are 44 showing an interest in fresh quality produce of less familiar 45 fruits.⁸ In some areas, such as California, most fig cultivars have 46 been selected for drying and the growers have little fresh fruit 47 handling experience,⁹ but in some northern Mediterranean 48 conditions, which have sometimes less favorable weather condi-49 tions for drying, most of the figs are consumed fresh and proper 50 conditions for fruit drying have to be established. Sun-drying can 51 ensure proper preservation of figs. However, with traditional 52

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.¹

Therefore, mechanical air dehydration has gained importance because of its many advantages over sun-drying.¹¹These 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

		sampling date		
day	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 78 important bioactive compounds and antioxidant activity of fresh 79 and properly sun-dried and oven-dried figs were determined and 80 compared. The new data present important information on the 81 content of sugars, organic acids, antioxidant activity, total phe-82 nolics, and individual phenolic compounds of the figs subjected 83 to two drying methods as well as give some important nutritional 84 data about the differences of fresh and dried figs' chemical 85 composition. 86

87 MATERIALS AND METHODS

Chemicals. The following standards were used for the quantifica-88 89 tion of sugars and organic acids: sucrose, glucose, and fructose; citric and malic acids from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). 90 The following standards were used for the quantification of phenolic 91 compounds: chlorogenic acid (5-caffeoylquinic acid), rutin (quercetin-92 3-O-rutinoside), and cyanidin-3-O-rutinoside from Sigma-Aldrich; 93 94 (-)-epicatechin, quercetin-3-O-glucoside, and kaempferol from Fluka Chemie (Buchs, Switzerland); and (+)-catechin from Roth (Karlsruhe, 95 Germany). Methanol for the extraction of phenolics was acquired from 96 Sigma-Aldrich. The chemicals for the mobile phases were HPLC-MS 97 grade acetonitrile and formic acid from Fluka Chemie. Water for the 98 mobile phase was twice distilled and purified with the Milli-Q system 99 (Millipore, Bedford, MA). For the total phenolic content, Folin-100 Ciocalteu phenol reagent (Fluka Chemie), sodium carbonate (Merck, 101 Darmstadt, Germany), and gallic acid and methanol (Sigma-Aldrich) 102 were used. For the determination of antioxidant capacity 1,1-diphenyl-2-103 picrylhydrazyl (DPPH), ascorbic acid, and methanol were purchased 104 105 from Sigma.

Plant Material and Experimental Design. The orchard of a 106 local cultivar of F. carica L. called 'Bela petrovka' was planted in Glem 107 (altitude 303 m, latitude 45° 29′ 21″ N, longitude 13° 47′ 18″ E), a hilly 108 part of Slovenian Istria, in 1998. All trees were managed according to 109 integrated cultivation protocols and trained as an open vase with a 5×4 m 110 111 spacing. Fresh figs were picked by hand two times in the summer (July) and once in the autumn (September) of 2009. At each picking 112 term three samples of physiologically mature fruits were collected (seven 113 to eight fruit per sample, total weight approximately 0.5 kg). One sample 114 was immediately transferred on ice to a freezer and then to laboratory 115 facilities, where the figs were subjected to analysis. Two other remaining 116 117 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 118 homemade device made of wire mesh surrounded with a wooden 119 frame). Half was immediately exposed to the sun at a height of 1 m 120 from the ground surface and placed indoors at night. The other tray was 121 placed in an air-dryer. All experiments of sun-dried figs were set on the 122 day of harvest and took 7 days; figs dried in a dryer took 24 h. In the days 123

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after harvest average day temperature was monitored for the duration of124the sun-drying and remained approximately the same throughout the125experiment (Table 1). The air-drying experiment was conducted in a126specially made wooden dryer $1.5 \times 1.3 \times 1.3$ m in size, connected to an127oil-fired furnace blowing hot air. Drying air temperature ranged between12862 and 64 °C.¹² Air relative humidity ranged between approximately12940% (at the beginning) and 10% (at the end).130

Analysis of Individual Sugars and Organic Acids. The 131 samples were analyzed for their content levels of sugars (sucrose, 132 glucose, and fructose) and organic acids (malic and citric). Figs were 133 cut into small pieces, and 15 g of the fresh mass or 15 g of the dry mass 134 was immersed in 20 or 40 mL of twice-distilled water and homogenized 135 with a T-25 Ultra-Turrax (Ika-Labortechnik, Stauden, Germany). The 136 samples were left for extraction for 0.5 h at room temperature with 137 frequent stirring at 150 rpm (Grant Bio POS-300, Grant Instruments, 138 Cambridge, U.K.), and the extracted samples were centrifuged at 139 10000 rpm for 7 min at 10 °C (Eppendorf Centrifuge 5810R, Hamburg, 140 Germany). The supernatants were filtered through a 0.45 μ m filter 141 (Macherey-Nagel, Düren, Germany) and transferred to a vial. 142

Samples were analyzed according to the method described by Sturm 143 et al.¹³ using high -performance liquid chromatography (HPLC; Thermo 144 Scientific, Finnigan Spectra System, Waltham, MA). For each analysis 145 20 μ L of sample was used. Analysis of sugars was carried out using a 146 Rezex RCM-monosaccharide column (300×7.8 mm; Phenomenex, 147 Torrance, CA) with a flow of 0.6 mL min⁻¹, and column temperature 148 was maintained at 65 °C. For the mobile phase, twice-distilled water 149 was used and an refractive index (RI) detector for identification. 150 Organic acids were analyzed using a Rezex ROA-organic acid column 151 $(300 \times 7.8 \text{ mm}; \text{Phenomenex})$, and the UV detector was set at 210 nm 152 with a flow of 0.6 mL min⁻¹, maintaining the column temperature at 153 65 °C. For the mobile phase, 4 mM sulfuric acid (H₂SO₄) was used. 154 The concentrations of carbohydrates and organic acids were calculated 155 with the help of corresponding external standards. The concentrations 156 were expressed in grams per kilogram of fresh weight (FW) or dry 157 weight (DW). 158

Extraction and Determination of Individual Phenolic 159 Compounds. The extraction of fruit samples was done as described 160 by Petkovsek et al.,¹⁴ with some modification. Fresh or dry fig samples 161 were ground to a fine powder in a mortar chilled with liquid nitrogen. 162 The samples of 10 g fresh or 2.5 g dry fruit were extracted with 20 or 163 10 mL of methanol containing 1% (w/v) 2,6-di-tert-butyl-4-methylphe-164 nol (BHT) and 3% (v/v) formic acid in a cooled ultrasonic bath for 1 h. 165 The treated samples were centrifuged for 7 min at 10000 rpm. The 166 supernatant was filtered through a Chromafil AO-45/25 polyamide filter 167 (Macherey-Nagel) and transferred to a vial prior to injection into a 168 HPLC system. Samples were analyzed using a Thermo Finnigan 169 Surveyor HPLC system (Thermo Scientific, San Jose, CA) with a diode 170 array detector at 280 nm (hydroxycinnamic acids and flavan-3-ols), 171 350 nm (flavonols), and 530 nm (anthocyanins). A Phenomenex HPLC 172 column C18 (150×4.6 mm, Gemini 3μ) protected with a Phenomenex 173 security guard column operated at 25 °C was used. The injection volume 174 was 20 μ L, and the flow rate was maintained at 1 mL min⁻¹. The elution 175 solvents were aqueous 1% formic acid (A) and 100% acetonitrile (B). 176 Samples were eluted according to the gradient described by Marks 177 et al.:¹⁵ 0–5 min, 3–9% B; 5–15 min, 9–16% B; 15–45 min, 16–50% 178 B; 45-50 min, 50% isocratic; and finally washing and reconditioning of 179 the column. Identification of compounds was achieved by comparing 180 retention times and their UV-vis spectra from 200 to 600 nm, as well as 181 by the addition of an external standard. Compounds were identified and 182 quantified using a mass spectrometer (Thermo Scientific, LCQ Deca XP 183 MAX) with an electrospray ionization (ESI) operating in negative/ 184 positive ion mode (Table 2). The analyses were carried out using fullscan data-dependent MS^n scanning from m/z 115 to 2000. The capil-186 lary temperature was 250 °C, the sheath gas and auxiliary gas were 187

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compound	peak	$t_{\rm R}$ (min)	$[\mathrm{M}-\mathrm{H}]^-~(m/z)$	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
$a \left[M + H \right]^+ (m/z).$					

Table 2. Retention Time and MS^n Fragmentation Data of Major Phenols Detected in Fig $([M - H]^- Molecular Ion)$

20 and 7 units, respectively, and the source voltage was 4 kV for negative 188 ionization and 0.1 kV for positive ionization. Quantification was 189 achieved according to the concentrations of a corresponding external 190 standard. 191

Concentrations of phenolic compounds were calculated from the 192 peak areas of the sample and the corresponding standards. The 193 concentrations were expressed in milligrams per 100 g of FW or DW. 194 For compounds lacking standards, quantification was carried out using 195 compounds similar to standards. Thus, kaempferol-3-O-glucoside and 196 luteolin-8-C-glucoside were quantified in equivalents of quercetin-3-O-197 glucoside. 198

Determination of Total Phenolic Content. The extraction of 199 fruit samples for the determination of total phenolic content (TPC) was 2.00 made according to the same protocol as for individual phenolics, with 201 the difference that no BHT and formic acid were added. TPC of the 202 extracts was assessed using the Folin-Ciocalteu phenol reagent 203 method.¹⁶ Six milliliters of twice-distilled water and 500 µL of Folin-204 Ciocalteu reagent were added to $100 \,\mu\text{L}$ of the sample extracts, and after 205 between 8 s and 8 min at room temperature, 1.5 mL of sodium carbonate 206 (20% w/v) and 1.9 mL of twice distilled water were added. The extracts 207 were mixed and allowed to stand for 30 min at 40 °C before the 2.08 absorbance at 765 nm was measured on a Lambda Bio 20 UV-vis 209 spectrophotometer (Perkin-Elmer, Waltham, MA). A mixture of water 210 and reagents was used as a blank. The TPC was expressed as gallic acid 211 212 equivalents (GAE) in milligrams per kilogram of FW or DW. Absorp-213 tions were measured in three replicates.

Determination of Antioxidant Activity with the DPPH 214 Radical Scavenging Method. The extraction of fruit samples for 215 the determination of antioxidant activity was made according to the 216 same protocol as for total phenolics. The free radical scavenging activity 217 of fig extracts was measured according to the DPPH method reported by 218 Brand-Williams et al.¹⁷ with some modifications. A methanolic solution 219 $(50 \,\mu\text{L})$ of extract was placed in 96-well microplates, and 200 μL of a 0.1 220 mmol L^{-1} methanolic solution of DPPH was added and allowed to react 221 in the dark at room temperature. The decrease in absorbance of DPPH 222 at 520 nm was measured at 5 min intervals by a spectrophotometer 223 (MRX Dynex Technologies), until the absorbance stabilized (30 min). 224 Methanol was used as blank solution, and a DPPH solution without test 225 samples served as the control. All sample analyses were performed in 226 triplicate. The DPPH radical scavenging activity of fig methanolic 227 extracts was expressed as milligrams of ascorbic acid equivalents per 228 100 g (AEAC = ascorbic acid equivalent antioxidant capacity) in 30 min 2.2.9 of reaction time. Identification of the antioxidant capacities of the 230 samples at various concentrations was made using the standard curves 231 of ascorbic acid. 232

Statistical aAnalysis. The data were analyzed using the Stat-233 graphics Plus 4.0 program (Manugistics, Inc., Rockville, MD). Differ-234 ences between treatments were analyzed independently for each 235 sampling date with a one-way analysis of variance (ANOVA). Significant 236

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	$121.48\pm4.60b$	$96.90\pm9.93b$	$116.42 \pm 12.75 \mathrm{b}$	
oven-drying	$215.88\pm14.18c$	$106.64 \pm 11.93 \text{b}$	$105.28\pm9.76b$	
fresh	$29.24\pm1.34a$	$38.17\pm4.61a$	$25.03\pm2.61a$	
	F	ructose		
sun-drying	$103.72\pm3.97b$	$82.53\pm8.07b$	$103.12\pm11.14\mathrm{b}$	
oven-drying	$195.57\pm12.43c$	$95.38\pm10.31b$	$99.45\pm8.14b$	
fresh	$26.53\pm1.22a$	$34.02\pm4.32a$	$23.43\pm2.48a$	
	S	ucrose		
sun-drying	$4.53\pm0.32b$	$5.75\pm0.44b$	$2.49\pm0.47b$	
oven-drying	$7.40\pm0.44c$	$4.44\pm0.65b$	$5.26\pm0.22c$	
fresh	$0.59\pm0.06a$	$0.88\pm0.15a$	$0.98\pm0.42a$	
Total Sugars				
sun-drying	$229.73\pm8.47b$	$185.18 \pm 18.28b$	$222.03\pm24.36b$	
oven-drying	$418.85\pm27.05c$	$206.47 \pm 22.89 b$	$209.98\pm18.10b$	
fresh	$56.36\pm2.58a$	$73.07\pm9.05a$	$50.63\pm6.05a$	

^{*a*} Mean \pm 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, su-240 crose, and total sugar content levels (g kg⁻¹) of physiologically 241 mature figs and physiologically mature figs dried by two different 242 techniques are presented in Table 2. Fructose (\sim 52%) and 243 glucose (\sim 46%) were found to be the dominant sugars in all 244 accessions analyzed; on the other hand, sucrose levels were very 245 low (\sim 2%), which is in accordance with the results of Veberic 246 et al.¹⁸ The contents of individual and total sugars were statis-247 tically lower in fresh figs compared to dried fruit at all samplings. 248 At the first sampling date the difference in the sugar content was 249 also statistically significant when fruits of the two drying methods were compared; however, at the other two samplings the 251 differences were not detected (Table 3). The glucose/fructose 252 T3

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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	
	Mal	ic Acid		
sun-drying	$3.11\pm0.32\mathrm{b}$	$2.26\pm0.33a$	1.84 ± 0.39 a	
oven-drying	$8.71\pm1.23\mathrm{c}$	$9.07\pm0.92b$	$6.29\pm0.79b$	
fresh	$0.76\pm0.05a$	$0.52\pm0.04a$	$0.66\pm0.19a$	
Citric Acid				
sun-drying	$4.66\pm0.53a$	$4.36\pm0.43b$	$3.33\pm0.21b$	
oven-drying	$10.54\pm1.82b$	$6.98\pm0.50c$	$7.00\pm0.42c$	
fresh	$1.83\pm0.18a$	$1.57\pm0.12a$	$1.36\pm0.22a$	
Total Organic Acids				
sun-drying	$7.77\pm0.85b$	$6.37\pm0.68b$	$5.16\pm0.55b$	
oven-drying	$19.25\pm1.51c$	$15.45\pm1.18c$	$13.58\pm1.03c$	
fresh	$2.59\pm0.22a$	$2.10\pm0.15a$	$2.02\pm0.40a$	
Sugars/Organic Acids				
sun-drying	$31.34\pm4.12b$	$27.99\pm2.89b$	$43.02\pm0.73b$	
oven-drying	$21.75\pm2.00a$	$13.64\pm1.42a$	$18.12\pm0.96a$	
fresh	$22.14\pm1.23a$	$35.34\pm4.37b$	$23.57\pm3.76a$	

^{*a*} Mean \pm 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), regard-253 less of the type of drying, which is important as the sugar 254 composition of fig fruit influences the perceived fruit sweetness. 2.55 Fructose has a higher relative sweetness than glucose.¹⁹ There-256 fore, the perception of sweetness in fig accessions is likely due to 257 the prevalence of fructose, and our results indicate that the figs 258 dried in the sun do not taste sweeter than figs dried in a 259 drying room. 260

In fig fruits, malic and citric acids were determined among 261 organic acids. Malic acid was the main compound in fig samples, 262 representing 24.7-58.7% of the total organic acids content. The 263 content of organic acids in dried samples was from 2.4- to 5.6-fold 2.64 higher for citric acid and from 2.8- to 17.4-fold higher for malic 265 acid (Table 4) compared to fresh fruit. A similar content of T4 266 organic acid in figs was reported by Pande and Akoh.²⁰ At all 267 sampling dates a statistically higher content of individual and 268 269 total organic acids was determined in samples dried in a drying room compared to other treatments (Table 4). These results are 270 expected, because dried fruit samples contain less water, which 271 means that the organic acids are more concentrated in dried figs. 272

The ratio between the analyzed sugars and organic acids in 273 fresh and dried figs (Table 4) is a common quality index and a 274 good indicator of internal fruit quality. The optimal ratio differs 275 between cultivars and is crucial for a harmonious flavor. Although 276 277 organic acids are present in lower concentrations in fig fruit than sugars, their effect on the fruit flavor is considerable. The higher 278 the ratio, the sweeter the fruits; the lower the ratio, the more sour 279 tasting.²¹ The statistically highest sugar/organic acid ratio was 280 281 calculated for figs dried in the sun and fresh figs at the second 282 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, 283 on the other hand, had a low content of sugars and a rather high 284

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	$9.84\pm1.41\mathrm{b}$	$15.88 \pm 1.07 \mathrm{b}$	$3.42\pm0.54a$
oven-drying	$13.96\pm1.48c$	$32.42\pm0.89c$	$19.92\pm2.56b$
fresh	$1.33\pm0.15a$	$2.78\pm0.46a$	$4.91\pm1.00a$
	Ca	techin	
sun-drying	$11.46\pm2.45\mathrm{b}$	$5.88\pm0.60b$	$6.60\pm1.18b$
oven-drying	$16.16\pm1.32b$	$15.57\pm2.04c$	$19.75\pm0.68c$
fresh	$1.36\pm0.24a$	$2.67\pm0.17a$	$2.88\pm0.18a$
	Epic	atechin	
sun-drying	$23.30\pm3.12b$	$20.37\pm0.70b$	$10.44\pm0.86b$
oven-drying	$34.65\pm2.63c$	$36.65\pm2.46c$	$26.66\pm1.85c$
fresh	$7.58\pm1.64a$	$8.67\pm1.12a$	$7.11\pm0.54a$
	Kaempferol	-3-O-glucoside	
sun-drying	$0.46\pm0.04\mathrm{b}$	$0.31 \pm 0.04 \mathrm{b}$	$0.59\pm0.06b$
oven-drying	$0.99\pm0.09c$	$0.56\pm0.05c$	$1.43\pm0.07c$
fresh	$0.04\pm0.00a$	$0.10\pm0.00a$	$0.13\pm0.01a$
	Luteolin-8	3-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	$6.66\pm1.39b$	$12.06\pm1.00\mathrm{b}$	$1.38\pm0.37a$
oven-drying	$7.03\pm1.03b$	$14.62\pm1.81\mathrm{b}$	$3.75\pm0.29b$
fresh	$0.61\pm0.14a$	$1.86\pm0.63a$	$0.89\pm0.20a$
Quercetin-3-O-glucoside			
sun-drying	$2.40\pm0.46b$	$3.35\pm0.19b$	$0.56\pm0.12a$
oven-drying	$2.23\pm0.24b$	$2.98\pm0.27b$	$1.10\pm0.06b$
fresh	$0.18\pm0.04a$	$0.60\pm0.17a$	$0.41\pm0.09a$
Cyanidin-3-O-rutinoside			
sun-drying	$0.26\pm0.06a$	$0.12\pm0.01~a$	$0.13\pm0.05a$
oven-drying	$0.16\pm0.02a$	$0.12\pm0.01~a$	$0.31\pm0.05b$
fresh	$0.21\pm0.05a$	$0.31\pm0.05b$	$0.62\pm0.04c$
$^{\prime}$ Mean \pm SE, $_{\prime}$	n = 5. Different let	tters in columns in	dicate statistically

^{*a*} Mean \pm 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 sundried figs.

Phenolic Compounds. A number of studies have shown that289the presence of phenolics in food and especially in fruit can be290particularly important for consumers, because of their beneficial291health properties. Besides antioxidant effects, phenolic com-292pounds possess a wide spectrum of biochemical properties and293can also have a beneficial effect in preventing the development of294diseases such as cancer and cardiovascular diseases.²² In our295study eight phenolics in fresh and dried figs, belonging to four296

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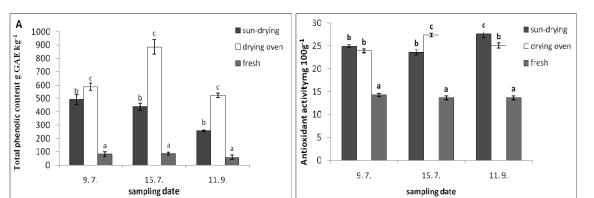


Figure 1. Total phenolic content (mean \pm SE in g kg⁻¹) and antioxidant activity (mean \pm SE in mg 100 g⁻¹) of fresh fruit and dried fruit of two drying methods.

297 groups of hydroxycinnamic acids, flavan-3-ols, flavonols, and 298 anthocyans, were identified. The predominant phenolic compound was epicatechin; in very small amounts luteolin-8-299 *C*-glucoside was detected (Table 5). The higest content of indivi-T5 300 dual phenolics was recorded at the second sampling of the first 301 crop for most phenols (Table 5). These results show that the 302 selection of the right crop in two fruiting figs is of high 303 importance and that the ideal ripeness of fig fruit is equally 304 significant as it ensures a high content of substances in fresh and 305 dried figs that are vital for human health. A difference in the 306 amount of phenolic compounds in cultivars that bear fruit twice a 307 year has also been reported previously.²³ 308

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

Both (-)-epicatechin and (+)-catechin from the group of 32.1 flavan-3-ols were determined in fresh and dried figs. Epicatechin 322 was the predominant analyzed phenolic compound in our study, 323 ranging from 7.8 mg 100 g⁻¹ FW in fresh figs to 25.4 mg 100 g⁻¹ DW in dried figs. In all samples, the content of catechin was lower 324 325 326 than that of epicatechin. In previous studies higher contents of these flavan-3-ols in figs were reported by Pande and Akoh;²⁰ on 327 the other hand, Veberic et al.²³ measured a much lower content 328 of epicatechin and catechin. These differences may be cultivar 329 specific and also due to agroecological specifics of the studies. 330 However, according to the data presented, fresh figs belong to 331 fruit rich in both constituents, in comparison to apple pulp¹⁴ and 332 sweet cherry.²⁵ A statistically higer content of both epicatechin 333 and catechin was measured in figs dried in the air oven (Table 5). 334 Previous results of a study on sun-dried pear show that as a result 335 of the drying process monomeric catechin and epicatechin 336 decreased between 91 and 96%,²⁶ which is in contrast to our 337 338 results as the contents of both these monomers were higher in dried figs. Devic et al.²⁷ reported that procyanidins are better 339 preserved by the drying process than hydroxycinnamic acids or 340 monomeric catechin. Indeed, these latter groups of polyphenols 341

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 kampferol-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 mg 100 g $^-$ FW. The content of total anthocyanins in yellow cultivars ranges from 0.06 to 2.97 mg 100 $g^{-1,29}$ 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 concentration 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 369 phenolics were in the range from 74.9 mg GAE kg^{-1} FW in fresh 370 figs to 530.2 mg GAE kg^{-1} DW in dried figs (Figure 1A). A 371 FI statistically higher TPC was determined in figs dried in the drying 372 oven at all sampling dates (Figure 1A). Veberic et al.¹⁸ measured 373 similar TPC compared to our results. A much higher TPC 374 (1189.0 mg GAE kg^{-1}) has been reported in fresh fig fruits in 375 the research of Çaliskan and Aytekin Polat.²⁹ In comparison with 376 sweet cherry, which contains from 443 to 879 mg GAE kg⁻¹ 377 FW,²⁵ and apple, of which the pulp contained 422.5 mg GAE 378 kg^{-1} FW and the peel 1754.6 mg GAE kg^{-1} FW,¹⁴ our analysis of 379 figs showed similar TPC in fresh fruit to that of sweet cherry and 380 apple pulp. Rababah et al.³⁰ reported that the levels of total 381 phenolics were higher in dried fruits (apple, strawberry, and 382 peach) followed by pureed and fresh products. 383

Antioxidant potential, expressed as AEAC, is presented in 384 Figure 1B. AEAC was significantly higher in all dried figs ana-385 lyzed, with almost 2-fold higher values detected as in fresh figs. 386

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Between the two drying methods, only the differences at the 387 388 second and third sampling dates were significant (Figure 1B). The antioxidant capacity of phenolic compounds is based on 389 their ability to scavenge free radicals, chelate pro-oxidant metal 390 ions, and inhibit some enzymes.³³ Nevertheless, the contribution 391 of organic acids cannot be ignored. Total phenolic content seems 392 393 to be a good indicator of the antioxidant potential in fruit, and 394 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, 395 396 are an excellent source of nutrients and are in vivo antioxidants; 397 the antioxidant capacity of human plasma increased significantly 398 for hours after their consumption. 399

Conclusion. To our knowledge, this is the first study compar-400 ing the contents of selected primary (sugars and organic acids) 401 and secondary (phenols) metabolites in figs subjected to differ-402 ent drying methods with those of fresh fig fruit. Changes in the 403 phenolic compounds and the degradation mechanisms de-404 pended on the drying process applied and on the type of phenolic 405 406 compounds studied. In all cases, phenolic compounds were relatively well preserved. The difference in the contents of primary 407 and secondary metabolites was significant when fresh and dried figs 408 were compared. Also, between the drying processes a big difference 409 was detected in the contents of secondary metabolites, and the 410 oven-dried figs were richer in these compounds. Considering the 411 absolute amounts of individual chemical compounds constituting 412 fig fruit, it can be demonstrated that significantly more primary 413 metabolites than secondary metabolites are present in both fresh 414 and dried figs. When fresh figs are not available, properly dried figs 415 could thus be used as a valuable substitute in diets that aim to 416 prevent certain diseases. In our further studies, it would be 417 interesting to concentrate on the effect drying has on various fig 418 cultivars and to include a different treatment such as the addition of 419 sulfur to the dried fruit or blanching process. 420

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