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Phenolic acids and flavonoids of fig fruit (*Ficus carica* L.) in the northern Mediterranean region

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Abstract

Phenolics are an important constituent of fruit quality because of their contribution to the taste, colour and nutritional properties of fruit. We have tried to evaluate the phenolic profile of fig fruit, since only limited information on that topic is available in the literature. With the HPLC-PDA system, we have identified the following phenolics: gallic acid, chlorogenic acid, syringic acid, (+)-catechin, (−)-epicatechin and rutin. Phenolics were extracted from three different fig cultivars that are commonly grown in Slovenia's coastal region. These cultivars were 'Škofjotka' ('Zuccherina') a white type fruit, 'Črna petrovka' and 'Miljska figa', both dark type fruit. The fruit from the first and the second crop were collected and compared. In general, fruit from the second crop contained higher values of phenolics than fruit from the first crop. The analysed phenolics present at the highest content were rutin (up to 28.7 mg per 100 g FW), followed by (+)-catechin (up to 4.03 mg per 100 g FW), chlorogenic acid (up to 1.71 mg per 100 g FW), (−)-epicatechin (up to 0.97 mg per 100 g FW), gallic acid (up to 0.38 mg per 100 g FW) and, finally, syringic acid (up to 0.10 mg per 100 g FW). Both cultivars with dark fruit exhibited a higher total level of analysed phenolics, in comparison to the white fruit cultivar 'Škofjotka'. The amounts measured are comparable to those of other fruits grown in this region. The amounts of rutin in particular are quite high and comparable to apples, for example. As a typical, seasonal fresh fruit, figs can be an important constituent of the regional diet.

Keywords: Fig; Phenolics; Seasonal changes; HPLC

1. Introduction

Figs (*Ficus carica* L.) are a widespread species commonly grown, especially in warm, dry climates. The ideal condition for intensive cultivation of figs is a semi-arid climate with irrigation. The world production of figs is about one million tons, and it is mostly concentrated in the Mediterranean. In this area, figs have been grown for centuries and are the most frequently mentioned fruit in the Bible (Slavin, 2006).

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 ripen 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 ripen 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 (Lodhi, Bradley, & Crane, 1969).

Figs are widely consumed fresh, either peeled or not. Fresh fruits naturally have a short, post-harvest life of 7–10 days, but with a combination of cooler conditions and a CO_2-enriched atmosphere, the fruit can be stored for up to 2–4 weeks (Sozzi, Abrajan-Villasenor, Trinchero, & Fraschina, 2005). Figs are also very popular as dried fruit, since drying prolongs their storability.

As a seasonal food, figs represent an important constituent of the Mediterranean diet (Solomon et al., 2006). This

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type of diet is considered one of the healthiest and is associated with longevity (Trichopoulou, Vasilopoulou, Georga, Soukara, & Dilis, 2006). Figs are an excellent source of minerals, vitamins and dietary fibre; they are fat and cholesterol-free and contain a high number of amino acids (Slavin, 2006; Solomon et al., 2006). Similarly to other fruit species, figs contain sugars and organic acids that influence their quality. They also contain phenolic substances, which contribute importantly to their quality, especially because it has been proven that their consumption can have a positive effect on human health. The content level of phenolics is usually influenced not only by the cultivar, but also varies significantly from one fruit part to the other; moreover, it is heavily dependent on the growing technology in the orchard (Veberic et al., 2005).

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 dealing with the phenolic contents of these fruit. The aim of our research was to investigate the influence of one of the northernmost fig fruit growing areas – to which the Slovenian coastal region belongs – on the levels of selected phenolics. We have tried to evaluate the influence of the cultivar as well as the influence of crop timing on the phenolic content level of fresh fig fruit. The data obtained form a good basis for evaluating the nutritional importance of fig fruit.

2. Material and methods

2.1. Plant material

The figs were collected from orchards in the coastal area of Slovenia (northern part of the Mediterranean). All the fruits were picked in their commercial maturity stage, which was determined by the softening of the fruit and development of their typical fruit taste and colour. Owing to successive ripening, the cultivars were picked twice for the first crop (the beginning and middle of July) and twice for the second crop (the beginning and middle of September).

Fig cultivars included in the study are well adapted to the environmental conditions of the north Mediterranean climate. They are probably closely related to other cultivars grown in the Mediterranean Basin, but they represent local types of figs. The cultivars included were the following:

- ‘Škofjotka’ (with the synonym ‘Zuccherina’) is a white type of fig with yellow flesh, which is sweet-tasting and very juicy; the fruit have good size and are quite resistant to rain;
- ‘Miljska figa’ (a dark type) yielded only the main crop in September. The fruit are middle-sized, round, and purple in colour with red pulp; their taste is sweet, and the fruit are juicy;
- ‘Črna petrovka’ is a dark type, middle-sized, purple coloured fig with sweet, juicy fruit.

The fruit were harvested at the optimal ripening time in the year 2005. Phenolic compounds were analysed for the whole fruit. For every cultivar, five repetitions were carried out ($n = 5$); each repetition included 10 fruit sampled from five trees. The fruit were stored at −20 °C until the preparation of samples.

2.2. Extraction and the HPLC analysis

The samples were prepared according to the method described by Escarpa and Gonzalez (1998): 10 g of whole fruit were extracted with methanol containing 1% 2,6-di-tert-butyl-4-methylphenol (BHT), using an ultrasonic bath. Samples were extracted with 10 ml of solvent for 1 h, 10 ml for 30 min, and finally 5 ml for 30 min. The three extraction fractions were combined into a final volume of 25 ml and filtered through a 0.25 μm membrane filter (Macherey-Nagel) prior to their injection onto the HPLC. BHT was added to the samples to prevent oxidation during the extraction.

The samples were analysed on the Thermo Finnigan Surveyor HPLC system with a diode array detector at 280 nm. The spectra of compounds were also recorded between 210 and 350 nm. 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 Gonzalez (1998). The injection amount was 20 μl, and the flow rate was 1 ml/min. The column used was a Phenomenex Synergi 4u MAX – RP 80 A, operated at 25 °C.

The following phenolic compounds were identified: gallic acid, chlorogenic acid (5-*O*-caffeoylquinic acid), (−)-epicatechin, (+)-catechin, syringic acid, and rutin (quercetin-3-*O*-rutinoside). Identification of compounds was achieved by comparing the retention times and the spectra as well as by the addition of standards. The concentrations of phenolic compounds were calculated with the help of a corresponding external standard. The sum of the individual phenolics that were determined in the study was expressed as the total analysed phenolics.

2.3. Statistical analysis

The analysis of data was performed as an analysis of variance (ANOVA) using the Statgraphics Plus 4.0 program. The differences between the cultivars and between picking times were estimated using the Tukey HSD test at $p < 0.05$.

3. Results and discussion

Besides sugars and organic acids, phenolics as secondary metabolites can also contribute to sweet, bitter or astringent flavours of fruit to a certain extent, while they can also contribute to aroma (Tomas-Barberan & Espin, 2001). 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. The two main groups of phenolics in apples are phenolic acids and flavonoids. Lee, Kim, Kim, Lee, and Lee (2003) report that some of these compounds have an even stronger antioxidant activity than, for instance, ascorbic acid. 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 like cancer and cardiovascular diseases (Lattanzio, 2003). The phenolics analysed in our experiment were gallic acid, catechin, epicatechin, chlorogenic acid, syringic acid and rutin (Table 1).

In the group of phenolic acids, the highest amounts were exhibited in the case of chlorogenic acid, followed by gallic acid, with trace amounts of syringic acid. High amounts of gallic acid were noted in the 'Miljska figa' cultivar and in both crops of 'Črna petrovka'. The lowest values were recorded in the first crop of the 'Škofjotka' cultivar, and similar values were also recorded in the second crop. Gallic acid and its glycosides are characteristic of some berry crops, like currant, raspberry or strawberry, in similar or higher amounts in strawberry than shown here for figs (Hakkinen et al., 1999). It has been proven that grape seeds and skins are good sources of gallic acid; the seeds contain especially high values (Yilmaz & Toledo, 2004). Amounts of gallic acid comparable to the data achieved for figs were also identified in some tropical fruit and persimmon (Gorinstein et al., 1999). Gallic acid is extremely well absorbed into the human body, compared with other polyphenols (Manach, Williamson, Morand, Scalbert, & Rémésy, 2005). In the review by Tomas-Barberan and Clifford (2000) gallic acid was shown to have a positive effect under *in vitro* conditions against cancer cells.

Chlorogenic acid is a phenolic acid, which is very common in different parts of plants and fruit as well. Teixeira, Patão, Coelho, and Teixeira da Costa (2006) identified chlorogenic acid in fig leaves. In our study, the highest values were achieved in the fruit of 'Miljska figa', which produces only the main crop in September. High amounts were also achieved in the second crop of the 'Škofjotka' cultivar. The first crop of the same cultivar exhibited rather low values, which were also comparable to the first crop of the 'Črna petrovka' cultivar. It seems that the first crops of dissimilar cultivars result in lower amounts of chlorogenic acid. Similar values to those attained in the case of figs were also achieved in the pulp (minus the skin) of certain apple cultivars, as reported by Veberic et al. (2005), while in the majority of apple cultivars, the content level of chlorogenic acid in the apple peel was much higher. The pulp and peel of apricots and peaches, as well as whole cherries also contained higher values of chlorogenic acid (Veberic & Stampar, 2005). Higher values were also reported in the pear cultivar 'Williams' (Colaric, Stampar, Solar, & Hudina, 2006), while kernels of various walnut cultivars (Colaric, Veberic, Solar, & Stampar, 2005) exhibited similar values to cultivar 'Miljska figa'. Chlorogenic acid is an antioxidant; Graziani et al. (2005) showed that catechin and chlorogenic acid were equally effective as apple extracts in preventing oxidative injury to human gastric epithelial cells *in vitro*. However, chlorogenic acid is poorly absorbed in the human body and is metabolised by colonic microflora (Olthof, Hollman, Buijsman, van Amelsvoort, & Katan, 2003).

In our research, syringic acid appeared in quite low levels. The highest values were found in 'Črna petrovka', especially in the first crop. The other two cultivars had much lower concentrations. Colaric et al. (2005) report that

Table 1
Content of various phenolics in fig fruit (mg per 100 g fresh weight) of the first and the second crop in July and September (means ± standard errors are presented)

Cultivar	Sampling	Gallic acid	Chlorogenic acid	Syringic acid	(−)-Epicatechin	(+)-Catechin	Rutin
Škofjotka	July 1	0.15a ±0.01	0.46a ±0.14	0.022a ±0.003	0.34a ±0.01	1.19ab ±0.04	4.89a ±0.14
	July 2	0.14a ±0.01	0.56a ±0.03	0.027a ±0.002	0.41a ±0.02	1.49bc ±0.04	5.38a ±0.27
	September 1	0.18ab ±0.02	1.28bcd ±0.14	0.032a ±0.004	0.61b ±0.03	1.07a ±0.04	6.63ab ±0.40
	September 2	0.23b ±0.03	1.44cde ±0.11	0.033a ±0.003	0.66b ±0.04	1.27ab ±0.09	8.52ab ±0.75
Črna petrovka	July 2	0.38d ±0.03	0.71a ±0.056	0.104c ±0.004	0.43a ±0.03	4.03e ±0.26	10.4b ±0.42
	September 1	0.30c ±0.03	1.24bc ±0.06	0.082b ±0.006	0.57b ±0.02	2.29d ±0.09	15.6c ±0.71
	September 2	0.30c ±0.01	1.05b ±0.10	0.079b ±0.006	0.58b ±0.04	2.30d ±0.20	15.0c ±1.15
Miljska figa	September 1	0.29c ±0.02	1.71e ±0.14	0.027a ±0.002	0.94c ±0.09	1.71c ±0.08	27.3d ±2.28
	September 2	0.30c ±0.02	1.57de ±0.15	0.034a ±0.003	0.97c ±0.06	1.8c ±0.08	28.7d ±2.12

Different letters for individual phenolic compound indicate statistically significant differences at $p < 0.05$.

syringic acid was the most abundant phenolic among the phenolics analysed in the kernel and pellicle of walnut (*Juglans regia* L.). They reported concentration levels several times higher than what we noticed in our study. Syringic acid can act as an antioxidant. In the study of Que, Mao, and Pan (2006) it was shown that syringic acid was highly correlated with antioxidant activities in rice wines.

Both (−)-epicatechin and (+)-catechin belong to the group of catechins. Auger et al. (2004) report that this is a very important group of compounds in the Mediterranean diet. However, according to the data presented, figs do not belong to fruit rich in both constituents, in comparison to plums, apples or various kinds of berries. Figs analysed in our study contained more (+)-catechin than (−)-epicatechin. The highest values of (+)-catechin were achieved in the first crop of 'Črna petrovka' followed by somewhat lower values in the second crop. The lowest values were achieved in the 'Škofjotka' cultivar, which also showed the lowest values for (−)-epicatechin. The highest values for (−)-epicatechin were achieved in the second crop of 'Miljska figa'.

Rutin was present in the highest concentrations among all the phenolics analysed. Based on our previous experiments (Veberic et al., 2005), we have noticed that with this analytical method, other quercetin glycosides sometimes co-elute with rutin, probably because of their similar structure. The cultivar containing the highest level of rutin was 'Miljska figa'. This cultivar had values of rutin almost double, compared to the fruit of the 'Črna petrovka' cultivar and more than three times higher compared to fruit of the 'Škofjotka' cultivar, picked at the same time. Teixeira et al. (2006) also identified rutin in fig leaves; however, they did not quantify it. The amounts of rutin analysed in our study, especially in the 'Miljska figa' cultivar, are higher than those analysed in sweet cherries, peaches and apricots, as reported by Veberic and Stampar (2005). The amounts of rutin established in figs are comparable, or in some cases even higher than, the rutin values in apple peel documented in the study by Veberic et al. (2005). Lee et al. (2003) reported that quercetin is an important phenol with antioxidative properties, however it is much more easily taken up by the human body in the form of glycosides, which are afterwards transformed into quercetin. Therefore, the amount of quercetin glycosides like rutin could be important for the nutritional value of figs.

Regarding the total of the analysed phenolics (Fig. 1), which were highly influenced by the content level of rutin, we have observed that 'Miljska figa' was the cultivar with the highest content. It contained nearly three times the content of the 'Škofjotka' cultivar, which proved to be the poorest in the phenolics analysed. Among cultivars that bear two crops, the second crop was somewhat higher in the content of total analysed phenolics. This could be explained by the fact that the fruit develop in warmer, drier and sunnier environmental conditions than the first crop. These weather conditions could be the trigger for higher phenolic synthesis.

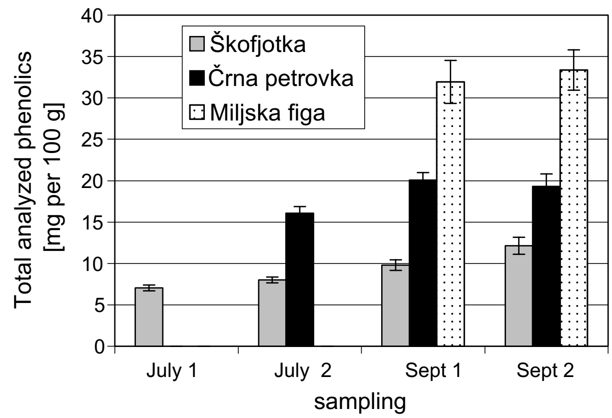

Fig. 1. Total of analysed phenolics in three fig cultivars. Bars represent the mean ± standard error for each cultivar at four sampling dates. The sampling dates July 1 and July 2 represent the fruits of the first crop and the September dates the fruits of the second crop.

Table 2
Monthly meteorological data from April to September 2005 in the littoral region of Slovenia (http://www.arso.gov.si/o%20agenciji/knjižnica/publikacije/Mesecni_bilten-2005.html)

Month	Average air temperature/°C	Total rainfall/mm	Total sunshine/h
April	11.3	77	219
May	16.9	63	291
June	21.2	57	320
July	22.7	63	326
August	20.1	152	238
September	18.4	71	230

The weather conditions in 2005 were favourable for the growth and development of figs (Table 2). The only month with slightly less favourable weather conditions was August. The temperatures in the months from April to September were, with the exception of April and August, above the long-term average measured for this region. Also the number of sun hours was, with the exception of August, above average, which again is favourable for fig growth. On the other hand, the amount of rainfall was lower (again with the exception of August), but there was still enough water provided for the needs of fig trees. We can conclude that in 2005 the weather conditions were favourable for growing figs, with the exception of the first picking of the second crop, which occurred at the beginning of September and was therefore marked by cooler and moister weather conditions with less sunshine, which occurred in August.

Regarding the phenolic levels, figs can contribute to the local diet as a typical seasonal fruit. It can be pointed out that in cultivars which bear fruit twice a year some differences in the amount of phenolics between the two crops can occur. According to our results, the second crop had somewhat higher concentrations than the first one, perhaps due to more stressful conditions during the ripening period. The amounts of phenolics measured are comparable to those of other fruit grown in this region. The levels of rutin, in particular, are quite high and comparable, for example, to apples. Further research into the content levels of phenolics should also be done on dried figs, which are popular and represent a healthy alternative to confectionary.

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