Scientific Papers. Series A. Agronomy, Vol. LIX, 2016
ISSN 2285-5785; ISSN CD-ROM 2285-5793; ISSN Online 2285-5807; ISSN-L 2285-5785

INFLUENCE OF DRYING PROCESS ON PHENOLIC CONTENT AND ANTIOXIDANT ACTIVITY OF TWO DIFFERENT AUTOCHTHONOUS ALBANIAN FIG VARIETIES

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Abstract

This paper aimed to evaluate the drying effect on phenolic content and antioxidant activity of two autochthonous fig varieties (Roshnik and Malakuq) with different colour taken respectively from Berat and Elbasan region in Albania. For drying of samples were applied sun-drying and hot air dehydration processes. Before processing fig varieties were analyzed for their total polyphenolics content, flavonoids and anthocyanins content separately in the whole fresh fruit, pulp and peel., also determinations were done in the dried fruits after sun-drying and hot air dehydration process. Antioxidant activity was evaluated using DPPH (1,1-diphenyl-2-picryl hydrazyl) and ABTS (2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) radical scavenging assays. Total polyphenolic content in whole fresh fruit, pulp, and peel and dried figs ranged 81.30-214.59 mg GAE 100 g^{-1} DM^{-1}, anthocyanins content ranged 0.0-17.76 mg C3G 100 g^{-1} DM^{-1}, and flavonoids content ranged 19.17-95.66 mg CE 100 g^{-1} DM^{-1} of sample. Antioxidant activity evaluated using DPPH assay results ranged from 3.09 to 6.48 mol TE 100 g^{-1} DM^{-1}, and from ABTS assay values ranged from 14.04 to 34.88 mol AAE 100 g^{-1} DM^{-1} of sample. The data obtained showed that autochthonous fig varieties are good source of antioxidants, and selected red fig variety showed higher phenolic content, compared to yellow fig variety. It was seen that peel showed higher antioxidant activity than pulp, as it resulted with higher total polyphenolic, flavonoids and anthocyanins content. Both drying processes influenced on increasing the total phenolic content and antioxidant activity, but hot air dehydration process influenced more in increasing total phenolic content and antioxidant activity, also influenced more in lowering moisture content and pH, and increasing total acidity of final dried product compared to sun-drying process.

Key words*: antioxidants, autochthonous, drying influence, fig.*

INTRODUCTION

Ficus carica is a tropic and subtropical plant produced in all Mediterranean basin and countries that have similar climate conditions. Albania is very rich in biodiversity of fig trees, and there are a lot of varieties, forms, ecotypes, and genotypes of figs (Koka, 1999).

Berat and Elbasan are the most known regions in Albania for fig growing, due to their geographical position and climate condition. These regions are known especially for figs that have good qualities for drying.

Fig fruit has high water activity, so it is highly perishable, even in refrigerated conditions (Hardenburg et al., 1986; Piga et al., 1995), and thus nearly all the world production is preserved in the dried form.

In Albania sun drying is the conventional method commonly used that requires low capital, simple equipment and low energy input.

There are concerns about the safety of the final product, and these concerns can be overcome by artificial drying (Piga et al., 2004). Nonetheless, hot air dehydration has gained importance because it has many advantages over sun-drying (Barbosa-Ca´ novas & Vega-Mercado, 1996), these include: (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) labour costs are lower.

For millennium, figs have been a typical component in the health promoting Mediterranean diet (Solomon et al., 2006).

The beneficial effects of figs are associated with the constitutive presence in the products of biologically active components, like carotenoids, phenolics, some vitamins and fibres.

Phenolics are an important constituent of fruit quality because of their contribution to the taste, color and nutritional properties of fruit. The functionality of these compounds is mainly expressed in their scavenging free oxygen radicals, which are involved in many pathological conditions (Briviba and Sies, 1994; Tadić et al., 2008; Hasan et al., 2010).

Rababah et al. (2005) reported that the levels of total phenolic compounds were higher in dried fruits (apple, strawberry, and peach) followed by pureed and fresh products.

Vinson et al. (2005) 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.

Phenolics, flavonoids, anthocyanins, and related total antioxidant activities based on chemical extraction have typically been measured using methanol or methanol/water mixtures (Solomon et al., 2006; Veberic et al., 2008; Çaliskan & Polat., 2011; Del Caro and Piga, 2008; Duenas et al., 2008).

There are no studies investigating phenolic content of these two autochthonous Albanian fig cultivars. Comparison of total phenolic content and antioxidant activity of two different fig varieties have been taken under consideration too. Also this work attempt to compare influences on quality of dried fig fruit parameters, applying two drying methods, as sun-drying and hot air dehydration processes.

MATERIALS AND METHODS

For experiments were selected two different autochthonous fig varieties, traditionally used as dried products: "*Roshnik*" (yellow colour) harvested from Berat region (40°42'51.56"N 19°58'48.02"E) and "*Malakuq*" (red colour) of Elbasan region (40°59'56.31"N 20°10'55.04"E) in Albania. In September 2015, fruits were harvested at their optimal ripening time and for further analyses, were transported immediately to the laboratory.

Fig fruits were preselected based on their weight, appearance, maturity, and health conditions, before drying process and were not pre-treated; no chemicals used before. For natural sun-drying 50 fruits were set on a tray, three repetitions, for about 7 days, the average temperature during the day was 37^{o}C. Hot air dehydrator was a closed cabinet with a fan inside to blow the air "horizontally" across the trays (fruits were set on trays inside the drying chamber). Once the air was heated electrically, temperature of the heater was adjusted to 60^{o}C, air relative humidity was approximately 40% (at the beginning) and 10% (at the end), and the process duration was about 24 h.

Methanol extracts were prepared by extracting 1 ± 0.001 g grinded fig samples with 10 ml of aqueous methanol 80% (v/v), homogenized for 1 minute using Ultra-Turrax T-25 (Ika-Labortechnik, GR), with speed set 11000 1/min, and centrifuged using centrifuge Eba 21 (Hettich, GR) for 15 min at 4500 rpm, and this process was repeated three times and supernatants were collected and analyzed. Extracts of whole fresh fruit, pulp, peel, and dried fig samples were prepared separately. All samples were analyzed in triplicate.

Fresh and dried fruits were analyzed for physico-chemical parameters. Moisture content (%) were determined according to method AOAC (2002), pH value was determined using pH meter UB-10 (UltraBasic, Denver Instrumet) (AOAC, 2000), total acidity (% citric acid) by titrating with 0.1N NaOH (AOAC, 2000).

Total phenolic content of the extracts was determined according to the method of Singleton and Rossi's (1965) with some modification and results were expressed as *gallic acid equivalents* (mg GAE 100 g^{-1} DM^{-1} (dry matter) of sample). The absorbance was measured at 760 nm using UV/Vis spectrophotometer Libra S22 (Bichrom, UK).

Total flavonoid content was measured using $AlCl_3$, a colorimetric method (Zubair et al., 2013). The absorbance was measured at 510 nm using the spectrophotometer Libra S22 (Bichrom, UK), and results were expressed as

(+) catechin equivalents (mg CE 100 g^{-1} DM^{-1} of sample).

Total anthocyanins content was measured according to the pH differential method (Cheng and Bren, 1991). Absorbance of extracts was measured at 520 nm and 700 nm in buffers at pH 1.0 and pH 4.5 where absorbance was:

$A = (A_{520}–A_{700})_{pH\ 1.0} –(A_{520}–A_{700})_{pH\ 4.5,}$ (with molar extinction coefficient of 26.900 and molecular weight of 449.2). Results were expressed as *cyanidin-3-glucoside equivalents* (mg C3G 100 g^{-1} DM^{-1} of sample).

Antioxidant activity of extracts was determined using ABTS radical scavenging assay (Re. et al., 1999). ABTS and potassium persulfate mixture was kept in the dark at room temperature for 16 h before use. For the analysis, the stock solution was diluted in aqueous methanol 80% (v/v) until the absorption at 734 nm was 0.7± 0.02. 10 µl of extract was mixed with 990 µl of ABTS reagent. The absorption was measured after 6 min of incubation, and the result was expressed as *ascorbic acid equivalents* (mol AAE 100 g^{-1} DM^{-1} of sample).

DPPH radical scavenging assay was used for determination of antioxidant activity of fig extracts, according to the method of Sun et al. (2007) with some modifications. A series of sample extracts (15, 30, 45 µl) were completed to 2 ml with 0.1 mM DPPH and the absorption was measured (A_{sample}) the absorbance of DPPH was $A_{control}$. 2 ml of 80% aqueous methanol was used as a blank solution. The percentage of inhibition was calculated as: Inhibition % = $(A_{control}–A_{sample})/A_{control}$. The amount of sample necessary to decrease the absorbance of DPPH by 50% (IC_{50}) was calculated graphically. The antioxidant activity was expressed as *Trolox equivalents* (mol TE 100 g^{-1} DM^{-1} of sample).

RESULTS AND DISCUSSIONS

Reduction rate of fig moisture content was increased with the prolongation of time of drying process, increasing air temperature and thickness of skin. The increased water-holding capacity of the heated air is a key factor of drying process.

The weight (Table 1) of pre-selected fig fruits was 25±1.2 g ("*Roshnik*" variety) and 45±0.5g ("*Malakuq*" variety).

Both drying processes had decreasing effect on moisture content, where initial moisture ranged 67.92-69.81% and after sun-drying (SD) decreased from 18.36 to 25.6%, while after hot air dehydration (HAD) process decreased from 18.36 to 18.78%. "*Malakuq*" variety had lower moisture content in fresh state and resulted with higher dry matter after both drying methods; even it has bigger fruit size. Titratable acidity expressed as citric acid, predominant organic acid in fig fruit, ranged from 0.38%-0.62% citric acid in fresh fruits, after drying processes process it was increased to 0.64-1.024% citric acid, this because the dried fig fruit samples contain less water, more concentrated are organic acids in dried figs. "*Malakuq*" fig variety showed highest values of acidity, both in fresh and dried state (MF had 0.62 % g citric acid, MSD and MHAD had same values of acidity 1.024 % citric acid). Accordingly, after drying process the pH values were decreased with increscent of total acidity. "*Malakuq*" variety showed lowest pH values both in fresh (MF resulted 4.67) and dried samples (MSD resulted 4.19 and MHAD resulted 4.21).

Table 1. Characteristics of fresh and dried fig fruits

Cultivar	Color	Weight[a] (g)	Sample	Code	Dry matter[a] (%)	pH[a]	Acidity[a] (% citric acid)
Roshnik	yellow	25±1.2	fresh	RF	30.19±0.01	4.76±0.005	0.38±0.01
			sun-dried	RSD	74.4±0.7	4.35±0.02	0.64±0.001
			hot air dried	RHAD	81.22±0.93	4.35±0.01	0.83±0.002
Malakuq	red	45±0.5	fresh	MF	32.08±0.09	4.67±0.03	0.62±0.02
			sun-dried	MSD	81.64±0.12	4.21±0.02	1.024±0.09
			hot air dried	MHAD	83.31±0.41	4.19±0.03	1.024±0.001

(a: mean values with standard deviation, n=3)

Total polyphenolic (TP) content (Figure 1) was determined in fresh figs, and TP in the whole fruit ranged 83.61-120.25 mg GAE 100 g^{-1} DM^{-1}, in pulp ranged 81.3-109.78 mg GAE 100 g^{-1} DM^{-1}, and in peel ranged 97.86-137.44 mg GAE 100 g^{-1} DM^{-1}. From the data was noted that polyphenols were more concentrated in the peel than in pulp. "*Malakuq*" variety had higher TP content in both fresh and dried state (MF had 120.25 mg GAE 100 g^{-1} DM^{-1}, MSD had 160.04 mg GAE 100 g^{-1} DM^{-1} and MHAD had 214.59 mg GAE 100 g^{-1} DM^{-1} of sample). Drying methods applied had different influences on TP content in both fig varieties, where HAD had an increasing effect on phenolic content compared to SD. It was noted that after hot air dehydration fruits had higher TP content compared to sun-drying (TP after HAD ranged 168.42-214.59 mg GAE 100 g^{-1} DM^{-1}, while after SD ranged 110.31-160.04 mg GAE 100 g^{-1} DM^{-1} of sample).

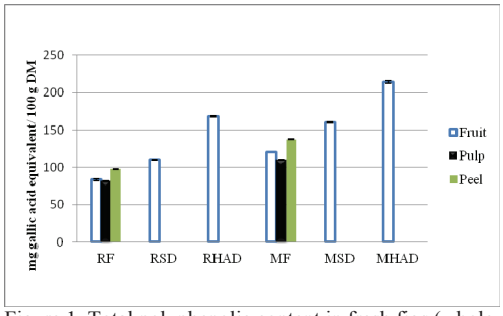

Figure 1. Total polyphenolic content in fresh figs (whole, fruit, pulp and peel) and dried figs

Total anthocyanins (TA) content ranged 0.0-17.76 mg C3G 100 g^{-1} DM^{-1} of sample (Figure 2). Anthocyanins were detected in fresh figs, while in dried figs were depleted. Yellow variety showed moderate content in pulp, and not in peel, so the presence in the whole fruit came from anthocyanins in the peel. Due to its red colour, "*Malakuq*" variety showed the presence on anthocyanins both in pulp and peel.

Total flavonoid content (TF) in fresh figs (Figure 3) ranged in whole fruit 20.27-32.23 mg CE 100 g^{-1} DM^{-1}, in pulp 19.17-31.94 mg CE 100 g^{-1} DM^{-1} and peel 26.90-37.65 mg CE 100 g^{-1} DM^{-1} of sample. In dried fruit TF after SD ranged 27.11-49.30 mg CE 100 g^{-1} DM^{-1} of sample, and after HAD ranged 51.95-95.66 mg CE 100 g^{-1} DM^{-1} of sample.

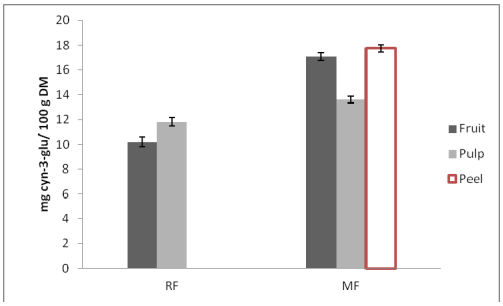

Figure 2. Total anthocyanins content in fresh figs varieties

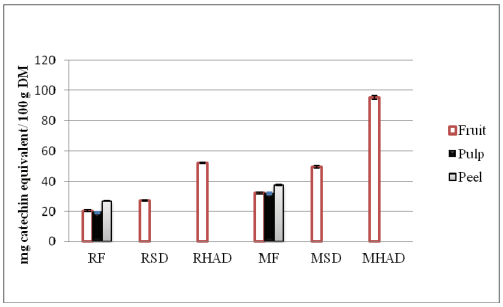

Figure 3. Total flavonoid content in fresh figs (whole, fruit, pulp and peel) and dried figs

Antioxidant activity was determined using ABTS (Figure 4) and DPPH (Figure 5) radical scavenging assay. From both assays was noted that highest antioxidant activity resulted in peel 14.63-24.14 mol AAE 100 g^{-1} DM^{-1}, and 3.60-4.45 mol TE 100 g^{-1} DM^{-1} of sample) than in pulp (14.05-16.05 mol AAE 100 g^{-1} DM^{-1} of sample and 3.09-3.71 mol TE 100 g^{-1} DM^{-1} of sample).

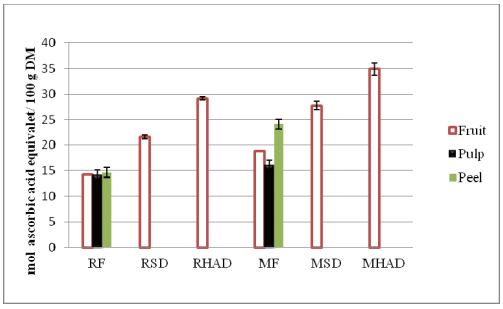

Figure 4. Antioxidant activity in fresh and dried figs, ABTS assay

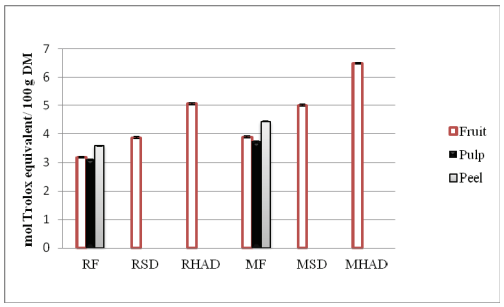

Figure 5. Antioxidant activity in fresh and dried fig fruit, DPPH assay

"*Malakuq*" variety showed highest values of antioxidants activity both in fresh and dried state. Antioxidant activity determined with both assays resulted higher at all dried figs varieties, compared to fresh figs. Also, it was noted that antioxidant activity of samples hot air dried resulted higher compared to sun dried.

Total phenolic content seems to be a good indicator of the fruit antioxidant potential and other authors have reported a correlation between these parameters. Nevertheless, the contribution of organic acids cannot be denied.

In our study dried fig showed higher content of phenolic content compared to fresh figs. Also, between the two drying processes applied, had different influences on phenolic content and antioxidant activity. Phenolic content and antioxidant activity of hot air dried fig samples resulted higher compared to sun-dried samples.

CONCLUSIONS

Based on the results between two selected fig varieties were seen differences on physicochemical parameters, which may be due to genotypic factor and the region of cultivation. Comparing two varieties taken under study "*Malakuq*" variety expressed higher values of dry matter (32.08% fresh, and 83.31% dried samples), correspondingly lower water activity, and about 20-38% higher acidity and lower pH values, which indicates that as a dried product may be more stable from microorganism contamination. Two varieties showed differences on phenolic content, also antioxidant compounds were about 25 % more concentrated in peel, than in pulp. "*Malakuq*" variety showed about 1.5-fold higher antioxidant activity, also related with its higher values on phenolic, anthocyanins and flavonoids content compared to "*Roshnik*" variety.

Comparing the influence of two drying methods applied resulted that hot air dried product achieved lower moisture content compared to sun-dried product, also application of hot air dehydration had an increasing effect on total acidity for "*Roshnik*" variety more than sun-drying process, indeed for "*Malakuq*" variety this parameter was not affected, as final products were nearest in values, pH was decreased but not affected by the drying process applied. Between two dried varieties "*Malakuq*" showed about 30% higher potential of antioxidant compounds compared to "*Roshnik*" variety, while anthocyanins were depleted at both dried varieties. Hot air dehydration processes influenced differently on the phenolic content, showing an increasing effect about 25-35% on phenolic content compared to sun-drying.

This study showed that both autochthonous Albanian fig varieties, besides fresh consumption showed high potential to be processed as dried products, but "*Malakuq*" variety showed better quality for drying compared to "*Roshnik*" variety even it had bigger fruit size, also it resulted with higher dry matter content, higher acidity, lower pH, higher phenolic content and antioxidant activity compared to "*Roshnik*" variety.

This work may suggest that hot air dehydration process should be taken under consideration for application to food industries as more suitable method for fig drying, relating this with its influence in improving the quality of final dried product, and influenced more in lowering moisture content and pH, increasing acidity, also increasing phenolic content and antioxidant activity compared to sun-drying process.

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