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DRYING PROCESS AFFECTS BIOACTIVE COMPOUNDS IN HAWTHORN SPECIES

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Abstract. Five different methods of drying (microwave-drying, oven-drying at 50 and 70°C, sun-drying and shade drying) the fresh fruits of two hawthorn species – *Crataegus azarolus* L. (yellow) and *Crataegus orientalis* L. (red) – were investigated in this study to determine its impact on their antioxidant capacity and antioxidant content. The results showed that antioxidant capacity increased, and at the same time the number of total phenolic compounds decreased with increase in the temperature in oven drying, whereas in other drying methods (microwave, sun and shade-drying) the amount of total phenolic compounds increased. It was observed that in all samples the vitamin C content decreased. Samples dried in a microwave appeared to have the strongest antioxidant capacity. Microwave-drying appeared to be the best method for preserving bioactive chemicals.

Key words: antioxidant capacity, flavonoid compounds, different drying methods, vitamin C

INTRODUCTION

The growing interest in wild edible plants such as hawthorn – that cannot be easily cultivated in common orchards – is caused by the presence of specific bioactive substances which have many benefits for human health [Tadic et al. 2008, Liu et al. 2010]. Hawthorn fruits content phenolic compounds (flavonoids, phenolic acid, anthocyanin) which have cleansing, anti-inflammatory, vasorelaxing and hypolipidemic properties [Abdul and Majeed 2013]. Wild edible hawthorn fruits contain large amounts of bioac-

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tive compounds and nutrients compared to other cultivated plant species [Kostic et al. 2012, Ercisli et al. 2015].

In developing countries, particularly in Middle East and Asia, fresh hawthorn fruits are used in food industry. Hawthorn fruits are available seasonally, however, it is possible to provide their year-round availability prolonging their durability. One of the methods to extend the durability of medicinal plants is drying. High temperature air drying is not useful in industrial processes because the heat treatment reduces the amount of vitamin C and phenolic compounds. Drying must be performed to preserve the natural chemical features and nutritional characteristics of the fresh herbs. An inappropriate drying method may reduce the bioactive compounds, or lead to the formation of new chemical compounds as a result of oxidation reactions [Chan et al. 2009]. Drying causes a reduction in fruits weight and volume, and thus enables the storage, packaging and transport of hawthorn fruits at competitive costs [Sobukola et al. 2007].

Attractiveness of the food products for consumers and are connected with the quality of fruits and vegetables [Najda et al. 2014]. The strict rules of the market and high expectations of consumers in relation to the product make fruits of the wrong texture and staining become unattractive and not find purchasers. Therefore, it is vital that the dried fruits are characterized with appropriate nutritional properties and quality as much as possible similar to the fresh fruits (colour, firmness). Plant materials are usually stabilized by drying. Among the methods of drying raw plants we can distinguish convection drying, microwave drying (with the use of atmospheric or lower pressure), vacuum drying, freeze drying and drying consisting of two or more methods. Food products are sensitive to high temperature, as it easily degrades the products and their nutritional properties. The selection of a particular drying method is important for hawthorn fruits conservation and it depends on the type of fresh herbs, fruits' biochemical properties, desired characteristics of the dried products, as well as on the operating conditions and costs [Raghavan and Orsat 2007]. Drying in the sun (natural drying) is slow and time-consuming compared to other drying methods, during which biologically active substances change its quality and quantity [Latapi and Barrett 2006]. Oven drying is one of the most used techniques for medicinal plants dehydration. It is a traditional, inexpensive technique which is used for dehydrating herbs with the use of low temperature [Barba and d'Amore 2012]. Drying at low temperatures protects bioactive compounds against degradation, but the long time required for drying and the ongoing metabolic process may lead to quality loss of the aromatic plants [Madrau et al. 2009, Jing et al. 2010]. Heat treatment results in decrease of the amount of vitamin C and phenolic compounds. High temperatures of drying used in air dehydration method may lead to phenols degradation, while phenolic compounds are significantly reduced because of the exposure to high amounts of oxygen. Guclu et al. [2006] report that fruits dried by this method are characterized with lower antioxidant values compared to the fresh ones. The antioxidant activity of the dried prunes was significantly increased. Piga et al. [2003] reported the increase in the antioxidant capacity in them. The main disadvantage of drying in high temperatures is that it is time consuming and the high temperature may badly affect the taste, color and bioactive compounds of the raw material [Jing et al. 2010]. Relative to the two first methods, microwave drying is fast, more uniform, and reduces space usage. It also loss of natural substances thus maintains the quality of final

products [Contreras et al. 2008]. Hawthorn fruit are an important dietary ingredient and nutrient for the population in developing countries such as Iraque, Iran, Argentina, Ecuador, Yemen, Libya, Moldova, Peru, Turkey. However, to date, no research has been carried out on technique and parameters of the drying of wild edible fruits. This paper evaluates and compares the effectiveness of five different drying methods based on the change of content of the phenolic compounds and catechin and quercetin affecting the antioxidant capacity and amount of vitamin C content of the dried hawthorn fruits. Optimization of drying process can undoubtedly lead to improvements in the functionality and health promoting capacity of these fruits.

MATERIAL AND METHODS

Plant preparation. 3000 g of the fresh fruits of two species – yellow hawthorn (*Crataegus azarolus* L.) and red hawthorn (*Crataegus orientalis* L.) were collected from the Soran mountains (Halgurd Sakran National Park, Erbil province, Kurdistan region government, Iraq 36 38'14'' N and 44 53'22'' E) before the ripening period in September 2014. These fruits were manually cleaned – washed with water and rinsed off – and left to dry on a tray for 15 min at room temperature (31°C).

Determination of moisture content. The moisture content of the fresh fruits was immediately determined according to the AOAC, [2000] method and found to be 81.38 and 82.43 g water per 100 g sample for yellow and red hawthorn respectively.

Hot-air oven drying. A 100 g of hawthorn fruits were distributed uniformly onto stainless steel trays of size 24.7 × 52.7 cm and dried in a laboratory pilot dryer at 50 and 70°C at a constant air velocity (0.8 m·s) and ambient relative humidity. The drying time required to reach the suitable moisture content for yellow hawthorn fruits was 620 (50°C) and 540 (70°C) min and the moisture content of the dried fruits was 13.63 g (50°C) and 12.42 g (70°C). The drying time required to reach the suitable moisture content for red hawthorn fruits was 560, 510 min and the moisture content of the dried fruits was 11.24 g (50°C) and 12.02 g (70°C). Sampling was done in 5 times. In oven 5 sampling was according to follows: 0 = fresh; 1 = 100 min; 2 = 240 min; 3 = 380 min; 4 = end of drying process. The choice of the drying temperature in the oven was made on the basis of previously conducted trial experiments, which were also the basis for the choice of time after which the measurement was made.

Microwave oven drying. A domestic microwave oven (Sharp R-248E; 800 W) with maximum output was used for the drying experiments. The size of the microwave was 354 × 370 × 185 mm. The microwave's oven consisted of a rotating glass plate with 240 mm diameter at the base of the oven. Time of the drying was regulated with the use of electronic timer located on the microwave. 100 g of hawthorn fruits were spread on the glass plate inside the microwave and left until completely dried. The moisture content of 9.59 g for yellow fruits was reached after 15 min and 8.40 g for red fruits reached after 14 min. Sampling was done 5 times. In microwave 5 sampling was according to the following: 0 = fresh; 1 = 3 min; 2 = 7 min; 3 = 11 min, 4 = end of drying process.

Sun and shade drying. About 100 g of hawthorn fruits were spread on the glass plate inside greenhouse and were left to sun-dry for 10 days with about 11 h of daylight per day. Mid-day temperature in the greenhouse could reach 27°C. The moisture content of the dried fruits reached 13.09 g for yellow and 14.34 g for red hawthorn. The fruits were then shade-dried for 12 days in the laboratory at ambient temperature of 25°C and relative humidity of 34%. The moisture content of the dried fruits was 15.29 and 13.34 g for the yellow and the red hawthorn respectively. Five samplings were done for this case. For both sun and shade drying, sampling was done according to the following procedures: 0 – fresh; 1 – 2 day; 2 – 5 day 3 – 8 day; 4 – end of drying process.

Determination of total phenolic content. Total phenolic content was evaluated in the methanolic extracts, according to the Folin-Ciocalteu method [Barros et al. 2011]. Extracts were diluted 1:1500 or 1:1,000 before incubation at 40°C. Absorption was measured at 755 nm. TPH was expressed as mg of gallic acid mg per 100 g of dry weight.

Vitamin C assay, Vitamin C content was determined by titration according to the instructions of the AOAC [1991].

Determination of DPPH capacity radical–scavenging activity. Antioxidant capacity was determined by DPPH Antioxidant capacity (%), evaluated based on the ability to neutralize the DPPH radicals by means of spectrophotometry according to Brand-Williams et al. [1995]: to do this, water extracts were then evaporated until dry and lyophilized. Analyses were performed for 20 $\mu g \times ml^{-1}$ concentration. The absorbance measurements were made at $\lambda = 517$ nm wavelength using spectrophotometer (HITACI U-2900). Inhibition percentage for each sample was calculated as follows:

$$\% \text{ inhibition} = 100 (A_0 - A_x) / A_0$$

Where A_0 is the absorbance of a DPPH blank and A_x is the absorbance of juice solution.

Polyphenols compositions. Polyphenols compositions (quercetin and catechin) were determined using high-performance liquid chromatography (HPLC) method as described by Bakhshi and Arakawa [2006]. Samples of 5 g of chopped fresh hawthorn fruits and 1 g of powdered dry hawthorn berries were weighed and transferred quantitatively to 50 ml round-bottom flasks and immersed in 20 ml of methanol. The extraction was carried out in a 70°C for 3 hours. Then, extracts were stored in the refrigerator for 24 hours. After that time, the obtained supernatants were filtered through 0.45 μm Waters-Millex syringe filter. The qualitative and quantitative analysis of poliphenoles was performed using a liquid chromatograph with a column: Waters Symentery C18 5 μm 4.6 × 150 mm (Waters, Dublin Ireland) filled with silica gel, equipped with a UV-Visible detector (Waters Dual λ Absorbance 2487). Mobile phase consisted of methanol and acetic acid (85:15, v/v). Polyphenols of injected samples were compared with standards of catechin purchased from Sigma-Aldrich and Quercetin 3-galactoside was obtained from Extrasynthese, France. Quercetin and catechin was determined immediately in each of the method and during the drying process.

Statistical analysis. The results were presented as means ± SE. The experiment was conducted using a completely randomized design with three replications. Data were analyzed as a 2-factor linear model using the PROC ANOVA procedure (SAS software

ver. 9.2 for windows) with drying method and time as the factors. Significant differences were calculated according to Tukey multiple range tests. Differences at $P < 0.05$ were considered statistically significant.

RESULTS AND DISCUSSION

Effects of drying methods on moisture content and some bioactive compounds. Moisture content was significantly affected by drying methods ($p \leq 0.05$), but no differences were found between time 0 and 1. Decreasing speed in sampling time 0 and 1 in all of drying method was lowest than in sampling time 2, 3 and 4 sampling times (fig. 1). Like in the case of yellow hawthorn, the moisture content in red hawthorn was significantly affected by interaction between drying methods and sampling time $p \leq 0.05$ (fig. 2). In the sun- and shade-drying methods, decreasing level of moisture content was lower than in other drying methods. The lowest moisture content was recorded in the case of microwave drying method (9.78 g), whereas the highest moisture content was recorded in the case of sun and shade-drying method.

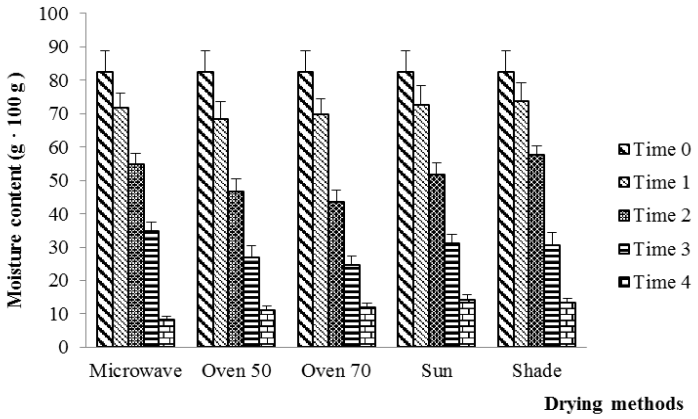

Fig. 1. Moisture change in the yellow hawthorn fruits in different drying methods and parameters

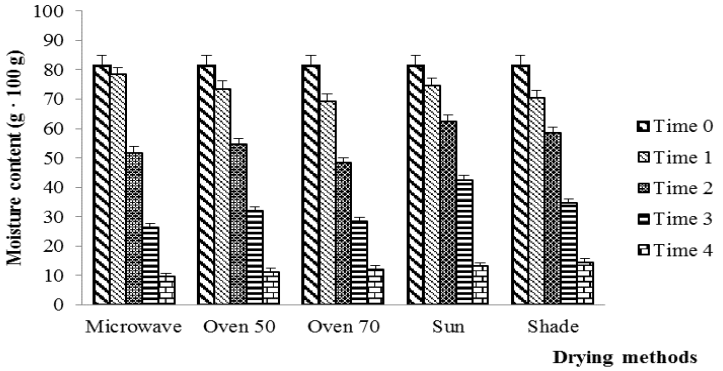

Fig. 2. Moisture change in the red hawthorn fruits in different drying methods and parameters

Kiranoudis et al. [1997] studied the influence of temperature of drying with hot air-drying of some fruits (apple, pear, kiwi and banana) and determined the moisture content of these fruits. They found out that increasing the air temperature decreases the moisture content and the total drying time what has been also reported by Abasi et al. [2009].

Antioxidant capacity. The antioxidant capacity in yellow hawthorn was significantly affected by interaction between methods and time of drying $p \leq 0.05$ (tab. 1). In the case of microwave drying, the antioxidant capacity increased by 59.5% until the sampling time 3 and decreases thereafter to 49.9%. Oven drying method at 50°C and 70°C showed an increasing in antioxidant capacity (72.28 and 60.78% respectively) until the sampling time 3, followed by a decrease after the sampling time 3. Finally, the sun-drying method showed an increasing value in antioxidant capacity (56.96%). Theshade-drying method showed similar trend of increasing antioxidant capacity until time 3 by 66.46%. The antioxidant capacity in red hawthorn was significantly affected by interaction between drying methods and sampling time $p \leq 0.05$. Our results showed that antioxidant capacity increased in all of thermal drying methods (tab. 2). Oven drying at 50°C showed no significant change in antioxidant capacity. Likewise, the sun-drying method showed a significant increase (68.36%) in antioxidant capacity until the sampling time 2 and also decrease (41.65%) in antioxidant capacity thereafter until the end of the drying process.

Dewanto et al. [2002] stated that an increase in antioxidant compounds in drying process may be due to this compounds being mostly attached to the fruit peel and insoluble fiber and that heat drying process may cause an increase of antioxidant compounds from the cell matrix. When heat is applied during dehydration process, it can induce the formation of compounds such as melanoidins in the Maillard reaction, which can increase antioxidant compounds [Puupponen-Pimiä et al. 2003]. Increasing antioxidant activity with increasing total phenolics content has been reported during dehydration of vegetables [Volden et al. 2008]. Based on our results, changes in total phenolics are useful predictors to changes antioxidant capacity of hawthorn fruits. Thus, hawthorn fruits could be considered as an important source of biologically active components with high antioxidant capacity. Zhang and Hamauzu [2004] reported reduction of 72% total phenolics, 66% ascorbic and 65% antioxidant activity when broccoli florets were exposed to heat for 5 minutes.

Total phenolic compounds. Total phenolic compounds in yellow hawthorn were significantly affected by interaction between drying methods and sampling time $p \leq 0.05$ (tab. 1). In microwave drying method from the first sampling time to the sampling time 4, an increasing value of total phenolic compounds was observed (135.95 mg·100 g^{-1}). In oven 50°C and 70°C total phenolic compounds was decreased while this decreasing in oven 50°C was more than oven 70°C. Sun drying method caused that total phenolic content at the beginning increased but at the end of time total it slowly decreased. In shade drying methods total phenolic content at the beginning showed an increasing value (140.35 mg·100 g^{-1}) but after sampling time 3 total phenolic content was slowly decreasing (108.77 mg·100 g^{-1}). According to Table 2, total phenolic compound in red hawthorn were significantly affected by interaction between drying methods and sampling times ($p \leq 0.05$). In microwave sampling time 1 the amount of total phenolic compounds was the biggest (mg·100 g^{-1}). Also, in sun drying methods the increase of content was observed in sampling time 1 (136.63 mg·100 g^{-1}). On the other hand, shade drying

methods showed the biggest amount of total phenolic compounds in sampling time 3 (129.03 mg·100 g^{-1}). In oven 50 and 70°C total phenolic compound from the beginning to the end of drying process was decreasing. The highest total phenolic compound at the end of drying process in red hawthorn was recorded in shade drying method with sampling time 4 (119.38 mg·100 g^{-1}). Microwave increased total phenolic compound at the end of yellow hawthorn drying process (135.95 mg·100 g^{-1}). As in Table 1 and 2, the oven drying method had showed a decrease in total phenolic content in both yellow and red hawthorn. This may be due to breakdown of phenolic compounds during the drying process. Meyer et al. [1998] reported that variation in phenolic compounds significantly depend on structure and is primarily related to their hydroxylation and methylation patterns. Increase of temperature in hot-air drying not significantly increased the total phenolic and flavonoids contents of dried hawthorn fruits. Similar actions were reported for apricot by Madrau et al. [2009].

Table 1. Effects of drying methods and their parameters on the antioxidant activity and chemical compounds of yellow hawthorn fruit

Methods	Time	Antioxidant capacity (DPPH %)	Total phenolics (mg GAE·100 g)	Vitamin C (mg·100 g)	Quercitin (µg·100 g)	Catechin (µg·100 g)
Microwave	0	16.71 ±1.10f*	89.22 ±1.27ef	131.23 ±5.34a	37.00 ±2.78cd	45.13 ±3.02c
	1	28.20 ±0.95de	140.08 ±1.24a	62.67 ±8.15d	57.03 ±4.18ab	65.23 ±2.45a
	2	50.03 ±1.35bc	135.34 ±1.36ab	55.53 ±2.45d	66.38 ±2.65a	50.00 ±1.48b
	3	59.50 ±4.34b	126.07 ±1.34bc	50.70 ±3.27de	40.34 ±4.41c	41.93 ±2.12c
	4	49.80 ±2.05bc	135.95 ±1.3ab	45.80 ±2.93de	43.43 ±6.61c	35.36 ±5.79d
Oven 50°C	0	16.71 ±1.1f0	89.22 ±1.27ef	131.23 ±5.34a	37.00 ±2.78cd	45.13 ±3.02c
	1	75.89 ±6.39a	144.43 ±4,02a	117.63 ±2.35a	40.64 ±1.89c	54.00 ±4.13ab
	2	72.28 ±3.35cd	105.65 ±1.32de	90.20 ±3.26bc	33.00 ±4.57d	42.00 ±3.53c
	3	42.60 ±8.34c	87.22 ±0.56ef	76.67 ±6.62c	29.00 ±2.12d	37.36 ±4.75cd
	4	38.78 ±3.27c	74.356 ±6.21g	41.38 ±6.22e	25.37 ±3.38de	44.00 ±3.67c
Oven 70°C	0	16.71 ±1.10f	89.22 ±1.27ef	131.23 ±5.34a	37.00 ±2.78cd	45.13 ±3.02c
	1	55.98 ±4.39bc	115.38 ±6.78cd	81.39 ±4.28bc	61.76 ±2.38a	40.26 ±2.96cd
	2	60.78 ±8.49e	110.62 ±0.79d	73.23 ±6.88c	43.66 ±8.09c	36.26 ±3.55d
	3	55.54 ±2.13bc	101.22 ±1.1de	44.13 ±6.76de	40.23 ±5.34c	30.34 ±3.24d
	4	23.63 ±2.93b	98.15 ±1.69de	32.06 ±5.02ef	28.56 ±8.73de	33.67 ±2.65d
Sun	0	16.71 ±1.10f	89.22 ±1.27ef	131.23 ±5.34a	37.00 ±2.78cd	45.13 ±3.02c
	1	23.29 ±1.33e	131.36 ±2.38b	73.30 ±6.88c	50.81 ±2.65bc	66.00 ±1.76a
	2	51.86 ±1.43bc	134.45 ±0.22bc	68.47 ±9.26cd	38.46 ±3.34cd	53.98 ±1.18b
	3	52.10 ±2.21bc	121.61 ±1.56ab	49.40 ±5.81de	25.36 ±3.11de	59.00 ±0.9ab
	4	56.96 ±1.59bc	100.46 ±5.18de	31.83 ±9.00f	20.67 ±2.56e	46.41 ±1.56bc
Shade	0	16.71 ±1.10f	89.22 ±1.27ef	131.23 ±5.34a	37.00 ±2.78cd	45.13 ±3.02c
	1	39.62 ±3.97cd	98.88 ±8.52de	81.35 ±6.18c	55.63 ±5.00b	66.00 ±2.07a
	2	31.95 ±0.83d	140.35 ±1.27a	73.62 ±11.18c	47.00 ±3.02bc	46.73 ±0.58bc
	3	46.04 ±1.56c	132.58 ±3.61b	71.31 ±7.15cd	39.00 ±2.69c	46.36 ±2.23bc
	4	66.46 ±1.42ab	108.77 ±2.03d	40.27 ±8.45e	32.61 ±6.36d	38.66 ±3.59cd

* – mean in each column followed by the same letters are not significantly different at $P < 0.05$ according to Tukey's multiple range test. Data expressed as means ±SE

Table 2. Effects of drying methods and their parameters on the antioxidant activity and chemical compounds of red hawthorn fruit

Methods	Time	Antioxidant capacity (DPPH %)	Total phenolics (mg GAE·100 g)	Vitamin C (mg·100 g)	Quercitin (μg·100 g)	Catechin (μg·100 g)
Microwave	0	21.96 ±2.65ef	91.74 ±1.67ef	83.35 ±3.24a	58.53 ±3.02b	36.67 ±1.48b
	1	56.90 ±2.62b	137.52 ±0.77a	66.40 ±5.39b	69.53 ±2.45a	56.40 ±1.18a
	2	60.88 ±0.85ab	130.4 ±0.52ab	55.20 ±4.59c	52.76 ±5.00bc	46.60 ±2.12ab
	3	57.13 ±0.69b	124.96 ±1.24b	42.66 ±3.24d	44.00 ±3.67c	34.26 ±1.48bc
	4	61.70 ±1.7ab	115.55 ±.0.99c	37.50 ±2.66de	37.66 ±0.89d	30.13 ±1.22c
Oven 50°C	0	21.96 ±2.65ef	91.74 ±1.67ef	83.35 ±3.24a	58.53 ±3.02b	36.67 ±1.48b
	1	30.79 ±4.09d	133.57 ±4.31ab	59.60 ±4.71bc	51.66 ±4.79bc	39.30 ±2.12b
	2	37.34 ±1.55cd	128.90 ±0.47b	48.26 ±5.07cd	48.00 ±4.44c	47.43 ±1.22ab
	3	35.65 ±3.04d	91.74 ±1.67ef	42.23 ±5.56d	33.26 ±3.24de	41.68 ±2.45b
	4	33.47 ±2.45d	78.02 ±1.69g	32.20 ±3.85e	26.36 ±2.06e	32.63 ±4.26bc
Oven 70°C	0	21.96±2.65ef	91.74 ±1.67ef	83.35 ±3.24a	58.53 ±3.02b	36.67 ±1.48b
	1	46.08 ±2.28c	120.21 ±4.23bc	54.30 ±5.39c	27.46 ±3.34de	46.66 ±1.8ab
	2	50.67 ±1.89bc	97.57 ±2.01e	48.00 ±3.53cd	51.66 ±2.38bc	51.33 ±0.9a
	3	51.69 ±1.28bc	94.72 ±10.8e	42.50 ±2.12d	34.00 ±2.94de	42.30 ±0.59b
	4	57.03 ±1.88b	81.74 ±1.67g	25.33 ±2.61ef	29.36 ±1.79e	36.40 ±2.35b
Sun	0	21.96 ±2.65ef	91.74 ±1.67ef	83.35 ±3.24a	58.53 ±3.02b	36.67 ±1.48b
	1	53.48 ±1.38bc	136.63 ±1.87a	61.37 ±2.22bc	26.23 ±2.06e	40.53 ±2.23b
	2	68.36 ±2.91cd	115.05 ±6.44de	47.06 ±5.12cd	19.33 ±1.22ef	39.07 ±4.12b
	3	40.37 ±4.35a	101.14 ±10.94c	40.69 ±2.06de	17.73 ±2.23f	45.60 ±7.51ab
	4	41.65 ±1.71cd	95.61 ±0.67e	24.35 ±3.59ef	20.86 ±2.06ef	35.66 ±2.9bc
Shade	0	21.96 ±2.65ef	91.74 ±1.67ef	83.35 ±3.24a	58.53 ±3.02b	36.67 ±1.48b
	1	21.37 ±2.48ef	116.59 ±3.21c	29.36 ±3.02ef	34.83 ±2.22de	55.04 ±1.18a
	2	30.56 ±2.09de	121.63 ±1.02bc	30.26 ±2.22ef	31.93 ±3.91de	43.61 ±1.48ab
	3	33.67 ±1.19d	129.03 ±2.04ab	22.30 ±3.27f	21.43 ±4.34ef	35.10 ±3.58bc
	4	42.23 ±1.94cd	119.38 ±0.52bc	20.43 ±2.80f	18.00 ±3.53ef	26.33 ±1.89e

Explanations: see Table 1

According to Mrad et al. [2012] the decrease in total phenolic content during hot drying methods can be due to the binding of polyphenols with other compounds (proteins) and change in the chemical structure of polyphenols which cannot be extracted or determined by available methods. De Ancos et al. [2000] suggested that the content of polyphenolic compounds can be changed depending on many factors other than heat treatment. These included the activity of polyphenol oxidase, organic acid content, sugar concentration and pH. The increase in total phenolic compounds showed that the hawthorn fruit could be the result of changes in cell structure and the chemical degradation associated with low temperature compared to oven drying [Susana et al. 2014]. Since this increase may be due to originating from the disruption of cell walls during processing or the breakdown of insoluble phenolic compounds, it could have led to better extractability of these compounds.

Vitamin C. According to results, vitamin C in yellow hawthorn significantly ($p \leq 0.05$) was affected by interaction between drying methods and sampling time (tab. 1). According to results showed in Table 1 at the entire drying method, vitamin C content was decreased slowly. At the end of drying methods the highest vitamin C content was found in microwave drying method (45.80 mg·100 g^{-1}) while the lowest was found in sun drying method (31.83 mg·100 g^{-1}). In the case of red hawthorn fruits results showed that vitamin C content was significantly ($p \leq 0.05$) affected by interaction between drying methods and sampling times (tab. 2). In all of the drying methods, from the beginning vitamin C content was decreasing slowly. Lowest vitamin C content was found in shade drying method with sampling time 4 (20 mg·100 g^{-1}). The highest vitamin C content at the end of drying process was observed in microwave drying method (37.50 mg·100 g^{-1}). At the beginning decrease of vitamin C was slow, this is probably due to water content that was still remaining in fruits (tabs 1 and 2). Vitamin C or ascorbic acid stability could be affected by several factors such as moisture content, temperature, and oxygen. As the moisture content decreases, its concentration also decreases. High temperature and exposure to oxygen could also affect its sudden decrease. In general, the longer the drying period (low temperatures, high relative humidity, thick products), the lower the retention of vitamin C [Santos and Silva 2008]. Microwave provides high retention of vitamin C, due to shorter time other than different methods, reduced mobility of reactants, and reduced partial pressure of O_2. Vitamin C retention is also improved by all drying processes under an inert atmosphere, which reduce of the presence of O_2. Naggy [1980] found vitamin C responses to increasing temperatures to be dependent on the acid content of the fruits and vitamin C loss was lower in citrus than in other fruits because it is stable to heat under acidic conditions.

Qing-Guo et al. [2006] determined the quality parameters, such as vitamin changes of edamames dried by a convective drying, vacuum microwave drying, convective-vacuum microwave drying, and freeze drying, and the differences among the methods were compared and discussed. Degradation of vitamin C increased with raising drying air temperature. On the other hand, the distribution of vitamin C is reduced with increasing relative humidity of the drying air. Similar correlations were observed during drying of various fruits Al-Zubaidy and Khalil [2007] and Madrau et al. [2009]. High vitamin C content may be a protective strategy against drought injury. In general, quick drying retains larger quantity of vitamin C than slow drying. Therefore, the vitamin C content of fruits obviously reduced during the sun and hot air drying [Jayaraman and Das-Gupta 1995].

Phenolic compounds (catechin and quercetin). Results showed that catechin and quercetin content in yellow hawthorn was significantly ($p \leq 0.05$) affected by the interaction between drying methods and sampling time (tab. 1). Quercetin content was increased with microwave, oven 70°C and sun drying methods at the beginning but after that quercetin content decreased. In shade and oven 50°C drying method quercetin content at beginning time to end of drying process decreased slowly (fig. 3). Lowest quercetin content was recorded in sun drying method with sampling time 4 (20.67 μg·100 g^{-1}). Catechin content in microwave, oven 50°C, sun and shade drying methods at the beginning increased but after this time, catechin content decreased slowly (tab. 1). In oven 70°C, catechin content decreased at beginning and no increase of the content was observed. The highest catechin content was found in sun and shade drying method with sampling time 1

(66 μg·100 g^{-1}). According to results, quercetin and catechin content in red hawthorn was significantly ($p \leq 0.05$) affected by interaction between drying methods and sampling time (tab. 2). In all of the drying methods (except sun) at the beginning time quercetin content increased, then in sampling time 3 slowly decreased. Highest quercetin content at the end of drying process was found in microwave method (37.66 μg·100 g^{-1}) and lowest quercetin content was observed in shade methods (18 μg·100 g^{-1}). Figure 4 illustrated chromatogram of the identified polyphenols in fruits of yellow hawthorn subjected to microwave drying for a period of 4 min. Catechin content increased at the beginning, then decreased at the end of drying process. The highest decrease in catechin content was found in shade drying method (26.33 μg·100 g^{-1}). Oven 70 method preserved catechin content higher (36.4 μg·100 g^{-1}) than other methods. The result is probably due to the temperature and time used in the drying techniques. According to Schieber [2001] the loss of flavonoids during heat treatment might be due to the harsh drying conditions, in particular, the temperature and duration used. Similarly, Davey et al. [2000] reported that wet thermal processing can affect the phytochemicals by thermal breakdown that affect the integrity of the cell structure which then results in the migration of components, leading to losses by leakage or breakdown in various chemical reactions involving enzymes, light and oxygen. Using convection drying methods decreases polyphones content, which was reported in strawberry and blueberry. For this fruits decreasing variation depended mainly on the temperature applied and drying time [López et al. 2010]. Rodríguez et al. [2014] reported that the retention of the polyphenolic compounds depend on the technique applied and primarily on the temperature used for drying. Susana et al. [2014] expressed that the quercetin content decreased significantly in the dried fruit compared to the fresh fruits and also reported that the degradation of the quercetin during the drying process can be due to formation of other polyphenolic compounds such as catechin. In this research both of two hawthorn species showed a significant decrease in quercetin content but in catechin at the beginning the content was increased and then decreased in all of drying methods.

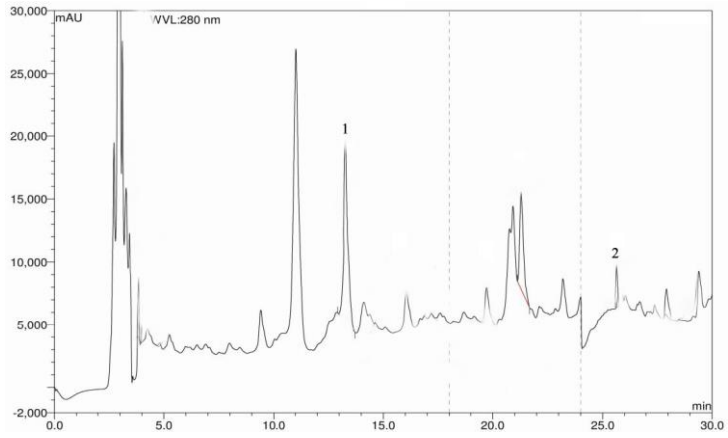

Fig. 3. HPLC chromatogram of the identified polyphenols in fruits of red hawthorn subjected to microwave drying for a period of 4 min. 1: catechin 2: quercetin

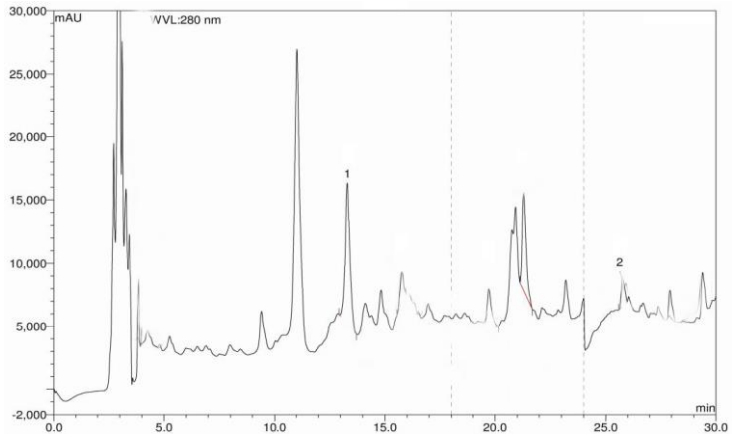

Fig. 4. HPLC chromatogram of the identified polyphenols in fruits of yellow hawthorn subjected to microwave drying for a period of 4 min. 1: catechin 2: quercetin

CONCLUSIONS

Our study demonstrates that the drying method had significant effects on antioxidant capacity, total phenolic compounds, vitamin C, quercetin, catechin and moisture percent in both yellow and red hawthorn fruits. Microwave drying methods maintained better fruits quality and offer better performance relative to other drying techniques. Because of long time needed for drying, the fruits quality decreased more at the end of drying process in the case of the sun- and shade-drying. The data presented here unequivocally suggest that quality parameters and bioactive compounds in both yellow and red hawthorn at the beginning time were better than the end of drying process. The vitamin C, quercetin and catechin level decreased in all evaluated drying methods while the antioxidant capacity and total phenolic compounds increased.

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WPŁYW PROCESU SUSZENIA NA ZWIĄZKI BIOAKTYWNE GATUNKÓW GŁOGU

Streszczenie. Świeże owoce dwóch gatunków głogu *Crataegus azarolus* L. (o żółtych owocach) i *Crataegus orientalis* L. (o czerwonych owocach) poddano suszeniu pięcioma metodami (mikrofalowo, w suszarce w temp. 50 i 70°C, na słońcu, w cieniu) w celu określenia wpływu metody stabilizacji surowca na zdolność antyoksydacyjną i zawartości przeciwutleniaczy. Stwierdzono, że w tym samym czasie zdolność przeciwutleniająca ekstraktów wzrosła, zaś suma związków fenolowych zmniejszyła się wraz ze wzrostem temperatury w suszarce, podczas gdy w innych metodach suszenia (mikrofalowe, na słońcu i w cieniu) całkowita zawartość związków fenolowych wzrastała. Niezależnie od metody suszenia, we wszystkich analizowanych próbkach obserwowano zmniejszenie się zawartości witaminy C. Próbki owoców wysuszone mikrofalowo wykazywały najsilniejsze właściwości antyoksydacyjne. Suszenie mikrofalowe okazało się najlepszą metodą stabilizacji surowców w celu zachowania odpowiedniego poziomu bioaktywnych substancji obecnych w owocach analizowanych gatunków głogu.

Słowa kluczowe: zdolność przeciwutleniająca, związki flawonoidowe, metody suszenia, witamina C

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