ISSN 1644-0692
www.acta.media.pl

ACTA *Acta Sci. Pol. Hortorum Cultus, 15(1) 2016, 41-54*

CHEMICAL COMPOSITION, VOLATILES, AND ANTIOXIDANT ACTIVITY OF *Rosa iberica* STEV. hips

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Abstract. Rosehip fruits have been known to contain significant amounts of bioactive compounds. These bioactive compounds positively affect human health due to their antioxidant activities. This study aimed to analyze the total phenolic content (TPC) and total anthocyanin content (TAC), organic acids, total soluble solids (TSS), sugars, total dry matter (TDM), L-ascorbic acid content (AAC), total antioxidant capacity and volatile components present in *R. iberica* Stev. hips using spectrophotometry, high performance liquid chromatography (HPLC) and Headspace and Immersion Solid Phase Micro Extraction gas chromatography-mass spectrometry (HS and Im-GC/MS). TSS, TDM, AAC, acidity, TAC and TPC were found to be 27, 44.6%, 503.26 mg·100 g^{-1} frozen weight (FW), 2%, 2.50 mg · 100 g^{-1} FW, 2832.3 mg · 100 g^{-1} FW, respectively. The major acids detected in *R. iberica* Stev. hips were citric acid (0.62 g · 100 g^{-1} FW) and malic acid (0.49 g · 100 g^{-1} FW) other detected acids included succinic acid (0.012 g · 100 g^{-1} FW) and fumaric acid (0.016 g · 100 g^{-1} FW). Total sugar content was 26.74 g · 100 g^{-1} FW, and glucose was the major sugar (9.35 g. · 100 g^{-1} FW), followed by fructose (8.58 g g · 100 g^{-1} FW), sorbitol (8.32 g · 100 g^{-1} FW), and very low quantities of sucrose (0.49 g · 100 g^{-1} FW). Twenty-five volatile components were identified using HS-GC/MS, and the major volatiles were 2,4-bis (1,1-dimethylethyl) phenol (20.35%), naphthalene (18.72%), ethanol (16.59%), nonanal (6.23%), acetic acid (4.39%), 2-propanone, 1-hydroxy (2.53%). Twenty-three volatile components of *Rosa* hips have been detected for the first time in this study. Twenty-eight components were identified by Im-GC/MS; however, fifteen of these components were determined to be different from those identified using HS-GC/MS. The FRAP value of hips was 38.55 mmol TE · g^{-1} FW and the ABTS value was 47.75 mmol TE · g^{-1} FW.

Key words: phenolic, sugars, organic acids, volatile, HS, Im-SPME/GC/MS

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INTRODUCTION

The genus *Rosa* contains over 100 species. Rosehips are naturally grown in almost all regions of Turkey. *Rosa pisiformis* and *Rosa dumalis* subsp. *antalyensis* are endemic to Turkey. *Rosa iberica* Stev., widespread in North and East Anatolia [Nilsson 1997], is a compact shrub that can grow up to 2 m in height. They usually grow at an altitude of 1200–2400 m [Ercişli 2005]. The petal color is white or light pink and they are used for making jam [Baytop 2001].

Rosehip fruits (especially *Rosa canina* hips) are seldom eaten fresh and mostly used to make tea, marmalade or wine [Uggla et al. 2005, Yildiz and Alpaslan 2012]. They have also been used for medicinal purposes [Grochowski 1990]. Rosehip fruits have been reported to contain significant amounts of bioactive components such as phenolics, sugars, ascorbic acid, minerals, lycopene, β-carotene, and flavonols, and have been used as a rich source of nutrients in many countries [Artik and Eksi 1988, Demir and Ozcan 2001, Hvattum 2002, Bohm et al. 2003, Ercişli 2007, Demir et al. 2014, Cunja et al. 2015]. These bioactive compounds have a positive effect on health due to their antioxidant activities [Hertog et al. 1995, Lai et al. 2013, Park et al. 2013]. Reactive oxygen species (ROS), such as O_2^-, OH^-, H_2O_2, produced in boyd [Dina et al. 2009], can cause oxidative stress, which is associated with the development of cancer, ageing and cardiovascular diseases [Bagchi et al. 2000]. Antioxidants are capable of overcoming the harmful effects of ROS and thus help in prevention of these diseases [Haruenkit et al. 2007, Seifried et al. 2007]. Rosehips have high antioxidant capacity and could inhibit cancer cell proliferation [Olsson et al. 2004]. Sources of natural antioxidants have high demand due to their health protective effects, especially for being able to boost the defense mechanisms against infection and common cold [Shnyakina and Mallygina 1975, Baytop 1984]. Rosehip fruits are used for the treatment of certain conditions caused by vitamin C deficiency, apart from diarrhea, gastrointestinal diseases, kidney, bladder and liver diseases [Strzelecka and Kowalski 2000, Pawlaczyk et al. 2009]. Most of the phytochemical and pharmacological studies have been conducted on *R. canina* hips, with very scarce reports on *R. iberica* hips.

Aroma is a mixture of a large number of volatile compounds [Sanz et al. 1997], and many fruits produce volatile compounds during fruit ripening [Golf and Klee 2006]. The most important aroma compounds are derivatives of amino acids, lipids and phenolics, and mono and sesquiterpenes [Schwab et al. 2008]. There are very few studies on the volatile components of rosehip fruits [Nowak 2005, Demir et al. 2014]. Therefore, in the present study, we aimed to define the pomological features, document the nutritional and chemical compositions and quantitate the total antioxidant capacity of *R. iberica* Stev. hips grown in Ardahan, Turkey. To the best of our knowledge, there is no previous literature on the phytochemical characteristics of *R. iberica* Stev. hips. This paper will provide important information on the chemical composition of *R. iberica* Stev. hips that would be useful for future research.

MATERIALS AND METHODS

Plant Material. Mature hips of *Rosa iberica* Stev. were harvested from Posof/Ardahan (altitude 1900 m) in September 2014, transferred to laboratory in polyethylene bags and stored at -20°C until analysis. Rosehip species were identified based on

fruit, flower and leaf of the collected samples as described by Davis [1972]. In total, 75 hips were used for analysis and each replicate consisted of 25 hips.

Fruit Weight, Brix˚, pH and Titratable Acidity. R. iberica Stev. hips were weighed in groups of ten hips on a digital scale with a sensitivity of 0.01 g (TX-4202L, Shimadzu, Japan). TSS was determined with a digital refractometer (Mettler Toledo 30P, USA) at 22°C, total dry matter (TDM) was estimated according to the AOAC reference method [1998]. Acidity was determined titrimetrically according to Cemeroğlu [1992] and expressed as percent citric acid (%).

Total Anthocyanin and Total Phenolic Content. Total anthocyanin content (TAC) was estimated by the pH differential method of Giusti and Wrolstad [2001] with slight modifications. Frozen *R. iberica* Stev. hip (5 g) without nuts was homogenized in 10 mL methanol containing 1% HCl for two minutes, kept overnight, and filtered using a Whatman No. 2 filter paper. Two extracts were prepared, one with potassium chloride buffer (pH 1.0) (1.86 g KCI in 1 L of distilled water), and the other with sodium acetate buffer (pH 4.5) (54.43 g $CH_3CO_2Na \cdot 3H_2O$ in 1 L of distilled water). Absorbance of the extracts was measured in 510 and 700 nm (SQ2800, Unico UV visible Spectrophotometer, USA) after 15 min of incubation at room temperature. The total anthocyanin content was determined from the molar absorptivity of cyanidin 3-glucoside and expressed as cyanidin 3-glucoside equivalent. The anthocyanin content of the hips was calculated using molar absorptivity coefficient (Total Anthocyanins (mg/100 g) = (A × MW × DF × 10000)/ε × l (A = Absorbance difference, MW = Molecular Weight (MW : 449.2), DF = Dilution Factor, ε = molar extinction coefficient (ε : 26900, l = pathlength (1 cm)).

Total phenolic content (TPC) was determined by the Folin-Ciocalteu method [Spanos and Wrolstad 1992]. After homogenizing (T18, IKA Homogeniser, Germany) 5 g frozen *R. iberica* Stev. hip without nuts with 25 mL ethanol, the sample was centrifuged at 3500 × g for 3 min. The supernatant was filtered through a filter paper. Two milliliters of 10% Folin-Ciocalteu reagent was added to 0.4 mL extract and then was left for 2–3 min. And then, 1.6 mL (7.5%) of Na_2CO_3 solution was added to mix and incubated for 1 h in the dark. It was measured at 765 nm in a spectrophotometer against blank solution (0.4 mL water + 2 mL Folin-Ciocalteu reagent + 1.6 mL Na_2CO_3). The total amount of phenolic compounds was calculated as a mg gallic acid equivalent (GAE).100 g^{-1} by using the gallic acid standard.

Sugar and Organic Acid Content. The sugar content (glucose, fructose, sorbitol and total sugar) in *R. iberica* Stev. was analyzed according to Miron and Schaffer [1991] by HPLC (HP 1100 series) on a Shim-Pack HRC NH_2 column (300 × 7.8 mm, 5 m) with a RID (Refractive Index) detector. Briefly, 1 g of frozen sample without nuts was weighed and powdered with liquid nitrogen in a mortar and transferred to Eppendorf tube, and 20 mL of aqueous ethanol (80%, v/v) was added. The mixture was placed in an ultrasonic bath, sonicated for 15 min at 80°C, then filtered (the procedure was repeated three times). All of the filtered extracts were pooled and evaporated till completely dried on the boiling water bath. The residue was dissolved in 2 mL of distilled water and filtered before HPLC analysis. The sugar content in samples was calculated from the calibration curves drawn using external standards, including fructose, glucose, sucrose and sorbitol.

The organic acid content (malic acid, citric acid, tartaric acid, succinic acid and fumaric acid) was measured by HPLC (HP 1100 series) using an HPX 87H (300 × 7.8 mm, 5 µm) column and a UV detector (at 210 and 242 nm wavelengths). The frozen sample (1 g) without nuts was weighed and powdered with liquid nitrogen in a mortar and mixed with 20 mL of aqueous meta-phosphoric acid (3%) at room temperature for 30 min using a shaker for the carboxylic acids and L-ascorbic acid detections. Acidic extract was filtered and made up to 25 mL with the same solvent, then used for HPLC analysis. External standards were used to identify and calculate organic acid content from the retention indices and the calibration curve of the external standard [Bozan et al. 1997].

Analysis of Volatile Components. The frozen hips without nuts were homogenized in a food processor (Braun FP 5150, Germany) and 5 g of the homogenate was weighed and subjected to HS and Im-SPME sampling. SPME fiber (Supelco), precoated with a 100 µm layer of polydimethylsiloxane blue fiber (85 µm CAR/ PDMS), was used, and the fiber was inserted into a vial and kept for 30 min at 30°C with stirring. The SPME syringe was then introduced into the injector port of the GC/MS instrument for analysis [Kafkas and Paydaş 2007].

Volatile compounds were analyzed on a Perkin Elmer apparatus equipped with a CP Sil 5CB (25 m × 0.25 mm i.d.) fused-silica capillary column. Helium (1 mL · min^{-1}) was used as the carrier gas. The injector temperature was set at 250°C for splitless injection. Column temperature settings were 60°C at the rate of 5°C · min^{-1} to 260°C for 20 min. The energy of ionization was 70 eV. Mass range was from m/z 30 to 425 Da. The mass spectra were also compared with those of reference compounds and confirmed with the aid of retention indices from published sources. Relative percentages of the separated compounds were calculated from total-ion chromatograms through a computerized integrator.

Total Antioxidant Capacity. Total antioxidant capacity was detected using the ferric reducing antioxidant power (FRAP) and 2,2'-azino-bis3-ethylbenzothiazoline-6-sulphonic acid (ABTS) [Benzie and Strain 1996, van den Berg et al. 1999, Kim et al. 2003]. For extraction, 1 g frozen hip without nuts was placed with 50 mL 80% methanol solution into flask that was wrapped with aluminum foil. The flasks were placed in an incubator shaker at temperature 30°C and 150 rpm for 24 h. The samples were centrifuged at 3200 rpm for 20 min and supernatant was collected.

For FRAP method, 100 µL extract was mixed with 2.9 mL FRAP reagent (30 mM acetate buffer, pH 3.6, 10 mM 2,4,6-tripyridyl-s-triazine (TPTZ) in 40 µM HCl, and 20 mM $FeCl_3$ at 10:1:1 (v/v/v)) and vortexed. The samples were incubated in water bath (ST30, Nüve, Turkey) for 30 min at 37°C and the absorbance was recorded determined at 593 nm. The values were expressed as millimole TE · g^{-1} of ferrous equivalent Fe (II) per gram of frozen sample.

For ABTS method, ABTS solution was prepared by mixing 7 mmol · L^{-1} ABTS and 2.45 mmol · L^{-1} potassium peroxydisulfate solutions (1:1 (v/v)). The mixture was incubated in the dark at room temperature for 16 h. The solution was diluted with 20 mM sodium acetate buffer to reach the absorbance 0.7 ±0.02 at 734 nm. 100 µL of diluted extract were added to 1900 µL of the ABTS solution and the decay in absorbance at 734 nm was followed on spectrophotometer. The decrease in absorption after 5 min of

the solution addition was used for calculation. The antioxidant activity of the extracts was calculated in terms of Trolox Equivalent Antioxidant Capacity. Standard curves for both assays were obtained and the antioxidant activity was expressed as millimole TE · g^{-1} of frozen weight of hips.

Statistical Analysis. All analyses were performed three times and data were analyzed using SPSS (ver. 15) statistical analysis package.

RESULT AND DISCUSSION

TDM, TSS, pH, acidity values of *R. iberica* Stev. hips are given in Table 1. TDM is made up of carbohydrate, like soluble sugars and insoluble forms such as starch and various structural carbohydrates [Suni et al. 2000, Gibson 2012]. Starch and structural carbohydrates are converted into sugars during fruit ripening making mature fruits sweeter than immature fruits [Palmer 2010]. TSS and TDM were 27 and 44.6%, respectively. Ercişli [2007] have reported a TSS content that varied from 29.42 to 37.33%, and a TDM content that ranged from 33.85 to 40.35% in various rosehip species. Further, Dogan and Kazankaya [2006] have reported a total dry matter content of 46.75% in *R. iberica* Stev. hips, with an acidity of 0.75% and a pH of 4.43, and the data reported here are comparable to the values available in literature.

Table 1. Some pomological and biochemical properties of *R. iberica* Stev. hips

		R. iberica
	fruit shape	long
	flesh colour	orange
	peel colour	red
	TSS (%)	27 ±1.2
	TDM (%)	44.6 ±1.8
	acidity (%)	1.00 ±0.05
	pH	3.91 ±0.03
	total anthocyanin (mg · 100 g^{-1})	2.50 ±0.01
Organic acids	total phenolic (mg · 100 g^{-1})	2832.32 ±11.6
	FRAP (mmol TE · g^{-1})	38.55 ±0.95
	ABTS (mmol TE · g^{-1})	47.75 ±0.36
	L ascorbic acid (mg · 100 g^{-1})	503.26 ±18.8
	oxalic acid (g · 100 g^{-1})	0.26 ±0.01
	tartaric acid (g · 100 g^{-1})	0.42 ±0.07
	malic acid (g · 100 g^{-1})	0.49 ±0.05
	citric acid (g · 100 g^{-1})	0.62 ±0.06
	succinic acid (g · 100 g^{-1})	0.012 ±0.01
	fumaric acid (g · 100 g^{-1})	0.016 ±0
	sucrose (g · 100 g^{-1})	0.49 ±0
	glucose (g · 100 g^{-1})	9.35 ±0.05
Sugars	fructose (g · 100 g^{-1})	8.58 ±0
	sorbitol (g · 100 g^{-1})	8.32 ±0.07
	total sugar (g · 100 g^{-1})	26.74 ±0.12

All values are presented as means ±SD (n = 3)

Anthocyanins are water soluble pigments that are present in most fruits. They may appear red, purple or blue depending on the pH of the fruit [Holton and Cornish 1995] and have strong antioxidant activity [Wang et al. 1997]. The TPC of unripe fruits is higher than in ripe fruits [Tucker 1993]. The total anthocyanin content in *R. iberica* Stev. hips was measured to be 2.50 mg · 100 g^{-1} FW. Hvattum [2002] and Guimarães et al. [2013] have established that the major anthocyanin in rosehips is cyanidin-3-O-glucoside, which has the highest oxygen radical scavenging activity [Wang et al. 1997]. We show that the total phenolic content (TPC) in rosehips is 2832.3 mg · 100 g^{-1} FW, while previous studies have reported a TPC content that varied from 176 to 9.600 mg · 100 g^{-1} [Ercişli 2007, Su et al. 2007, Yoo et al. 2008, Egea et al. 2010, Fattahi et al. 2012, Roman et al. 2013]. Phenolic components are important because of their antioxidant activity [Bataglion et al. 2014].

AAC was measured to be 503.26 mg · 100 g^{-1} FW. Roman et al. [2013] reported similar AAC that varied from 112.2 to 360.2 mg · 100 g^{-1} FW; and Barros [2010] reported an AAC of 68.04 mg · 100 g^{-1} dry weight (DW) in *R. canina* hips. It has been suggested that AAC increases during ripening, and AAC of ripe rosehip hips has been reported to be 417.5 mg. · 100 g^{-1} FW [Nojavan et al. 2008]. The AAC of *Rosa* hips in Turkey vary from 67.75 to 1032 mg. · 100 g^{-1} DW [Celik and Kazankaya 2009, Demir et al. 2014].

The acidity of *R. iberica* Stev. was found to be 2% with a pH of 3.91. Fruit acidity is due to the presence of several organic acids, whereas soluble sugars and aroma determine fruit taste and play an important role in determining fruit quality and its nutritive value. Citric acid is a natural preservative and used to give a sour taste to foods. Malic acid is a natural component of fruits that regulates metabolism and increases energy production [Ashoor and Knox 1982, Campeanu et al. 2009, Xie et al. 2011, Wu et al. 2012]. During ripening, acid content generally decreases as the organic acids are used up or converted to sugars [Gercekoglu et al. 2009]. The major acids in rosehips are determined to be citric acid (0.62 g · 100 g^{-1} FW) and malic acid (0.49g · 100 g^{-1} FW), while other acids that have been detected include succinic acid (0.012 g · 100 g^{-1} FW) and fumaric acid (0.016 g · 100 g^{-1} FW) (fig. 1). Our results are similar to the earlier reports. Citric acid has been found to be the main organic acid in rosehips [Kovacs et al. 2000, Zocca et al. 2011, Adamczak et al. 2012. Demir et al. 2014, Cunja et al. 2015]. According to Demir et al. [2014] citric acid content varies from 4.76 to 9.12 g · 100 g^{-1} DW, and malic acid content varies from 0.45 to 1.10 g · 100 g^{-1}. Adamczak et al. [2012] reported citric acid content of 4.34 g · 100 g^{-1} FW in *R. tomentosa* hips. However, we report lower values for organic acid content of *R. iberica* Stev., which may be due to variation between species, use of different estimation methods, differences of environmental conditions and altitude, or in fruit ripeness.

Sugars in fruits also affect taste. Fructose, glucose and sucrose have been identified as the major sugars in ripe rosehip fruits [Kovacs et al. 2000, Uggla et al. 2005, Barros et al. 2010, 2011, Cunja et al. 2015,], and the sucrose content varies according to the fruit species which in turn affects taste. Fructose is sweeter than sucrose,

and sucrose is sweeter than glucose [Gercekoglu et al. 2009]. The total sugar content of *R. iberica* Stev. hips was estimated to be 26.74 g · 100 g^{-1} FW, and glucose was the major sugar (9.35 g · 100 g^{-1}FW), followed by fructose (8.58 g · 100 g^{-1} FW), sorbitol (8.32 g · 100 g^{-1} FW), and very low quantities of sucrose (0.49 g · 100 g^{-1} FW) (fig. 1). Results from previous studies concord with our findings and a total sugar content of 12.05–20.46 g · 100 g^{-1}, a glucose content of 7.45–17.25 g · 100 g^{-1}, a fructose content of 7.96–18.84 g · 100 g^{-1}, and a sucrose content of 0.88–5.61 g. · 100 g^{-1} have been reported [Yoruk et al. 2008, Barros et al. 2011, Rosu et al. 2011, Özrenk et al. 2012, Demir et al. 2014].

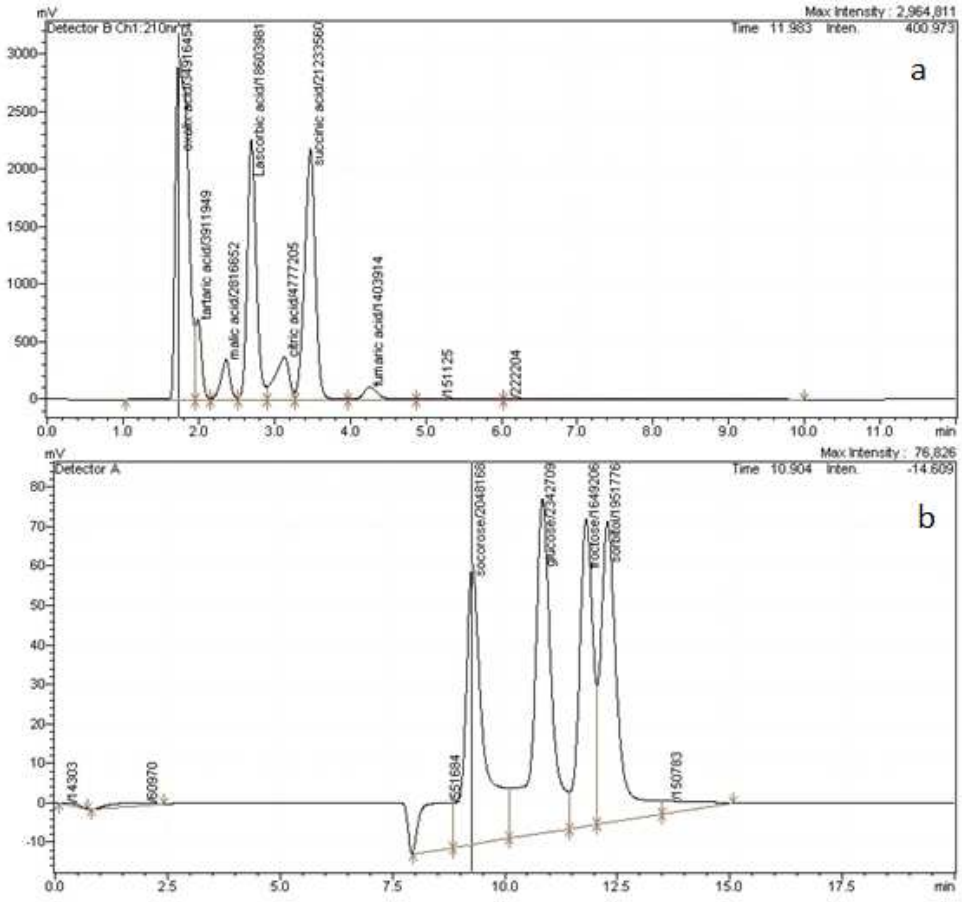

Fig. 1. A HPLC Chromatogram of organic acids (a) and sugars (a) for the *R. iberica*

Table 2. Volatile components of *R. iberica* Stev. hips detected by HS-GC/MS (%)

	R.T	Volatile	*R. iberica (%)*
Acids	2.1	sinapic acid	0.86 ±0.22
	12.4	acetic acid	4.39 ±0.04
	13.99	3-methyl-butanoic acid	3.92 ±0.69
	14.26	butanoic acid	1.36 ±0.93
	16.99	pentanoic acid	0.83 ±0.17
	17.75	heptanoic acid	0.90 ±0.27
	18.64	octanoic acid	0.36 ±0.51
	19.63	nonanoic acid	2.65 ±0.69
	22.38	dodecanoic acid	0.2 ±0.28
	Total 9 acids		15.47
Ketones	7.64	2(3H)furanone	1.99 ±1.03
	10.63	2-propanone, 1-hydroxy	2.53 ±1.24
	Total 2 ketones		4.52
Aldehydes	1.97	butanal	1.38 ±0.55
	11.09	nonanal	6.23 ±1.97
	12.49	decanal	0.32 ±0.15
	Total 3 acetaldehydes		7.93
Alcohols	3.3	1,2-Propanediol	4.17 ±1.10
	3.34	ethanol	16.59 ±2.46
	3.40	1-Penten-3-ol	0.26 ±0.17
	6.65	2-methyl-1-propanol	0.79 ±1.12
	8.68	3-methyl-1-butanol	7.12 ±4.88
	11.47	2-nonen-1-ol	0.79 ±0.12
	11.75	2-Furanmethanol	0.24 ±0.34
	14.46	dodecanol	1.11 ±0.56
	Total 8 alcohols		31.07
Terpene	14.80	Naphthalene	18.72 ±0.69
	Total 1 Terpene		18.72
Phenol	20.97	2,4-bis(1,1-dimethylethyl)Phenol	20.35 ±1.96
	23.2	phenol	1.94 ±0.65
	Total 2 phenol		22.29

All values are presented as means ± SD (n = 3)

The volatile components of *R. iberica* Stev. have not been identified so far. We used HS and Im-SPME GC/MS to identify these components, which are shown in Table 2 and 3. The volatile compounds provide the characteristic smell and taste to a fruit; they are present in very small amounts, and composed of esters, ketones, aldehydes, alcohols and acids [Tucker 1993]. These compounds are secondary metabolites that are formed during fruit ripening, and their concentration increases as the fruit matures [Perez-Cacho and Rouseff 2008]. We have identified 25 volatile components using HS-GC/MS in rosehips which include 9 acids, 3 aldehydes, 2 ketones, 8 alcohols, 1 terpene and 2 phenols. Quantitatively, the major volatiles were 2,4-bis (1,1-dimethylethyl) phenol (20.35%), naphthalene (18.72%), ethanol (16.59%), nonanal (6.23%), acetic acid (4.39%), and 2-propanone, 1-hydroxy (2.53%). Alcohols and phenols were the major compounds in rosehip volatiles, while only low quantities of ketones were found. Naphthalene was the only aromatic terpene detected in *R. iberica* Stev. A previous study, using an identical method, has reported the presence of 52 volatile components in rosehips, and 2-hexen-1-ol and 1-hexanol were the most abundant alcohols and the most

abundant aldehydes and ketones were 2-hexanal and 2-heptanal, 4-octen-3-one and 6-methyl-5-hepten-2-one, respectively. However, no acids could be detected [Demir et al. 2014]. Only two compounds that were detected in our study (nonanal, decanal) have been previously reported to be present in other rosehip species (*R. dumalis*, *R. canina*, *R. gallica*, *R. hirtissima*, *R. dumalis* subsp. *boissieri*), while the other twenty-three components have been detected and identified for the first time.

Table 3. Volatile components of *R. iberica* Stev. hips detected by Im-GC/MS (%)

	R.T	Volatile	*R. iberica (%)*
Acids	1.81	2,4-Dimethoxycinnamic acid	0.26 ±0.37
	2.01	sinapic acid	3.61 ±1.7
	3.33	formic acid	1.68 ±0.07
	11.89	acetic acid	11.35 ±1.65
	13.99	3-methyl-butanoic acid	0.96 ±0.24
	14.26	butanoic acid	0.94 ±0.08
	17.58	hexanoic acid	0.17 ±0.03
	17.75	heptanoic acid	0.28 ±0.09
	19.63	nonanoic acid	1.23 ±0.73
	19.94	oxalic acid	0.75 ±0.06
	21.98	benzoic acid	0.31 ±0.03
	23.99	tetradecanoic acid	0.40 ±0.08
	Total 12 acids		21.68
Alcohols	3.3	1,2-propanediol	16.45 ±23.26
	3.34	ethanol	10.66 ±15.07
	8.68	3-methyl-1-butanol	0.77 ±0.28
	Total 3 alcohol		27.88
Aldehydes	10.43	acetaldehyde	9.65 ±13.65
	12.14	furfural	5.50 ±0.92
	12.90	benzaldehyde	0.29 ±0.01
	23.08	2-furancarboxaldehyde	6.77 ±0.2
	Total 4 aldehydes		12.56
Ketones	7.64	2(3h)furanone	0.49 ±0.12
	10.63	2-propanone, 1-hydroxy	5.28 ±4.43
	12.63	ethanone,1-(2-furanyl)	0.65 ±0.07
	18.08	2h-pyran-2,6(3h)-dione	1.97 ±0.2
	Total 4 Ketones		8.39
Esters	2.19	ethyl acetate	2.36 ±0.02
	18.55	2-furancarboxylic acid, methyl ester	2.57 ±0.86
	Total 2 esters		4.93
Terpenes	14.26	a-caryophyllene	0.45 ±0.03
	14.81	naphthalene	13.32 ±1.91
	Total 2 terpenes		13.32
Phenols	23.20	phenol	0.40 ±0.06
	Total 1 phenols		0.40

All values are presented as means ± SD (n = 3)

A slightly different set of 28 compounds were identified using the Im-GC/MS method which included 12 acids, 3 alcohols, 4 aldehydes, 4 ketones, 2 esters, 2 terpenes and 1 phenol. As shown in Table 3, the most abundant volatiles were determined to be alcohols (27.88%) and acids (21.68%), while only a low amount of phenol (0.40%) was

found. 1,2-propanediol was found to be the major alcohol, and totally, only two terpenes, two esters and one phenol were detected in hips. Naphthalene was the most abundant terpene (13.32%). Finally, fifteen components were found to be different from those determined by the Im-GC/MS method and those determined using HS-GC/MS. This could be due to differences in the extraction methods.

We used FRAP and ABTS to determine total antioxidant activity in *R. iberica* Stev. hips. The FRAP value of hips was 38.55 mmol TE · g^{-1} FW and the ABTS value was 47.75 mmol TE · g^{-1} FW in our study, while Demir et al. [2014] reported that *R. dumalis* subsp. boissieri had an ABTS value of 194.36 mmol TE · g^{-1} DW while that of *R. canina* was 103.56 mmol TE · g^{-1} DW.

CONCLUSION

In the present study total phenolic content, total anthocyanin content, organic acids, sugars, antioxidant capacity and volatile components of *R. iberica* Stev. hips were determined, and the results indicate that *R. iberica* Stev. hips are a rich source of phenolics and ascorbic acid with a high antioxidant capacity. Compared to previous reports, we show higher total sugar and citric acid content but lower malic acid content, this could be due to variation between species, differences in methods, environmental conditions and altitude at which the hips were grown. HS-GC/MS and Im-GC/MS analyses were successfully used to identify 23 new volatile components in *R. iberica* Stev. hips, even though there were some differences between the compounds identified using these two methods. These volatile components included acids, aldehydes, ketones, alcohols, esters, terpenes and phenols. Finally, this study provides important information on the composition of *R. iberica* Stev. hips for consumers, nutritionists and plant breeders.

ACKNOWLEDGEMENTS

This research was supported by a grant (2012/07) from Ardahan University.

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SKŁAD CHEMICZNY, ZWIĄZKI LOTNE ORAZ DZIAŁANIE ANTYOKSYDACYJNE OWOCÓW *Rosa iberica* STEV.

Streszczenie. Owoce dzikiej róży zawierają znaczne ilości związków bioaktywnych. Związki te pozytywnie wpływają na zdrowie człowieka ze względu na swe działanie antyoksydacyjne. Celem niniejszego badania była analiza całkowitej zawartości związków fenolowych (TPC) oraz całkowitej zawartości antocyjanów (TAC), kwasów organicznych, całkowitej zwartości rozpuszczalnych substancji stałych (TSS), cukrów, całkowitej suchej masy (TDM), zwartości kwasu askorbinowego (AAC), całkowitej

zdolności antyoksydacyjnej oraz składników lotnych obecnych w *R. iberica* Stev. przy użyciu spektrofotometrii, wysokosprawnej chromatografii cieczowej (HPLC) oraz chromatografii HS i Im-GC/MS. Stwierdzono, że TSS, TDM, AAC, kwasowość, TAC oraz TPC wynosiły odpowiednio 27,44.6%, 503,26 mg·100 g^{-1} masy zamrożonej (FW), 2%, 2,50 mg·100 g^{-1} FW, 2832,3 mg·100 g^{-1} FW. Główne kwasy wykryte w *R. iberica* Stev. to kwas cytrynowy (0,62 g·100 g^{-1} FW) i kwas jabłkowy (0,49 g·100 g^{-1} FW), natomiast inne wykryte kwasy to kwas bursztynowy (0,012 g·100 g^{-1} FW) i kwas fumarowy (0,016 g·100 g^{-1} FW). Całkowita zawartość cukrów wynosiła 26,74 g·100 g^{-1} FW. Glukoza była głównym cukrem (9,35 g·100 g^{-1} FW), następnie fruktoza (8,58 g·100 g^{-1} FW), sorbitol (8,32 g·100 g^{-1} FW) oraz bardzo niskie ilości sacharozy (0,49 g·100 g^{-1} FW). Zidentyfikowano 25 związków lotnych przy użyciu HS-GC/MS. Główne związki lotne to 2,4 (1,1-dimetyloetyl) fenol (20,35%), naftalen (18,72%), etanol (16,59%), nonanal (6,23%), kwas cytrynowy (4,39%), 1-hydroksy, 2-propanon (2,53%). Po raz pierwszy w niniejszym badaniu wykryto owocach dzikiej róży 23 związki lotne. 28 związków zidentyfikowano za pomocą Im-GC/MS. Jednak 15 z tych związków określono jako inne od tych, które zidentyfikowano za pomocą HS-GC/MS. Wartość FRAP owoców wynosiła 38,55 mmol TE·g^{-1} FW natomiast wartość ABTS 47,75 mmol TE·g^{-1} FW.

Słowa kluczowe: fenolowy, cukier, kwas organiczny, związki lotne, HS, Im-SPME/GC/MS

Accepted for print: 20.10.2015

For citation: Abaci, Z.T., Zarifikhosroshahi, M., Kafkas, E., Sevindik, E. (2016). Chemical composition, volatiles, and antioxidant activity of *Rosa iberica* Stev. hips. Acta Sci. Pol. Hortorum Cultus, 15(1), 41–54.