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Evaluation of volatiles, phenolic compounds and antioxidant activities of rose hip (*Rosa* L.) fruits in Turkey

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ABSTRACT

Five different rose hip (*Rosa* L.) species including *Rosa canina, Rosa dumalis, Rosa gallica, Rosa dumalis* subsp.*boissieri* and *Rosa hirtissima* grown in Turkey are studied. Phenolic compounds, organic acids, sugar and volatile compounds of five different species of rose hips are studied. Total phenolic contents of the rose hip fruits were significantly influenced by species and the levels of total flavonoid and tartaric esters were almost identical in the samples. Antioxidant activities and antiradical scavenging capacities of the extracts were high levels in all rose hip species. It is noticeable that organic acid and sugar contents of the fruits were highly dependence of species and the high levels of ascorbic acid were characteristic. In total, eighteen different phenolic compounds were identified in rose hip species by RP-HPLC-DAD method and, in particular, *R. dumalis* subsp. *boissieri*contained different phenolic compounds. Gallic acid, catechin, procyanidin-B2 and hydroxycinnamic acid derivatives (chlorogenic, *t*-caffeic, *p*-coumaric, ferrulic and sinapic acids) were principal for all rose hip species. A total of 52 volatile compounds were identified in rose hip species by SPME/GC-MS and it was characterized by abundance of alcohols and aldehydes with also some monoterpenes and sesquiterpenes.

1. Introduction

Recently, functional foods or food supplements which can protect humans from oxidative stress and several diseases have attracted worldwide interest (Losso, 2003). Rose hips are fruits of Rosa genus in the Rosaceae family, these are known as rich in phenolic compounds and valuable sources of vitamin C (Chrubasik, Roufogalis, Müller-Ladner, & Chrubasik, 2008). Therefore, rose hips may act as natural antioxidants due to their high content of phenolic substances. Rose hips are remarkable fruits for their pharmacological features as in grapes and wines (Olsson, Andersson, Werlemark, Uggla, & Gustavsson, 2005).

Rose hips are used for a large variety of purposes such as the protection of health and therapy in flu, infections, inflammatory diseases and chronic pains. Moreover, they have beneficial implications for skin care and antiulcer treatments (Guimaraes, Barros, Carvalho, & Ferreira, 2010). Rose hips have also been used in food and drink such as tea, marmalades, jellies and jams (Yıldız & Alpaslan, 2012); however, it has recently been utilized as an ingredient in probiotic drinks, yoghurts and soups as health supplements. Small scale industrial production has been made in the middle region of Turkey and dispatched to hypermarkets in big cities.

Anatolia is one of the major genetic diversity areas of rose hip species. The eastern and middle regions of Turkey are very rich in native rose hip population. It was reported that a total of 27 types of *Rosa* L. varieties have been identified in Turkey (Davis, 1972). From these varieties, some species have been grown in Northern Turkey, particularly in Gümüşhane and its neighboring cities. Furthermore, the medicinal functions of Rosaceae fruits may be partly attributed to their abundance of phenolics. Total antioxidant capacity of rose hips is higher than that of several fruits and berries including sour cherry, blackberry, strawberry, raspberry (Halvorsen et al., 2002).

It is significant to point out that only a few studies has been conducted on the Rosaceae family including blackberry, raspberry and strawberry (Ibáñez, López-Sebastián, Ramos, & Reglero, 1998); however, as we are aware, no studies have been made on rose hip. In previous studies, phenolic compounds were detected and characterized in rose fruits by determining the phenolic acids, flavanols, flavanones, proanthocyanidin aglycones and glycosides from some *Rosa* species (Fecka, 2009; Hvattum, 2002; Nowak, 2006; Salminen et al., 2005). In these studies, no attempts were made on their volatile characterization which is directly associated with sensorial properties. Hence, there are information gaps in the volatile profile

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of the fruit and it would be very beneficial to carry out a study on this particular topic.

The sampling of volatiles is made by certain techniques in fruits. The pre-concentration of volatile compounds by solid-phase microextraction (SPME) is a simple, rapid, good repeatability, reliable and solvent free method that does not have to undergo any modifications due to solvent effect or temperature (Kataoka, Lord, & Pawliszyn, 2000).

Nowak (2005), compared essential oils of 9 taxa of rose hips (*Rosa rugosa*, *Rosa canina*, *Rosa vosagiaca*, *Rosa coliifolia*, *Rosa subcanina*, *Rosa rubiginosa*, *Rosa villosa* and *Rosa tomentosa*) that were obtained by hydrodistillation with *m*-xylene. The author has detected a total of 97 components and predominant compounds which were vitispiran, α-*E*-acaridial, dodecanoic acid, hexadecanoic acid, docosane, β-ionone, 6-methyl-5-hepten-2-one, 2-heptanone, heptanal, myristic acid and linolic acid in the essential oil fraction.

In the past, researches have focused primarily on the chemical composition and Pomological properties of rose species; however, to the authors' knowledge, no study has been made on volatile components in rose hips using any technique in the literature. In Turkey, *R. canina, Rosa dumalis, Rosa gallica, R. dumalis* subsp. *boissieri* and *Rosa hirtissima* species have been grown and such species have increasingly been commercialized due to the use in pharmaceutical and food industry. The aim of this study is to characterize the volatile compounds of rose hips which were firstly determined in the literature by SPME-GC/MS. Also, it was determined that the organic acids, sugars, phenolic compounds by liquid chromatographic and spectrometric methods. Total andioxidant properties of rose species were determined by FRAP (ferric reducing antioxidant power) (FRAP), ABTS (2,2-azino-di-(3-ethylbenzothialozine-sulphonic acid)) and DPPH (2,2-diphenyl-1-picrylhydrazyl) assays. Therefore, the paper will encourage further researches as medicinal, harvest time or developments in its manufacturing regime associated with volatiles and other properties.

2. Materials and methods

2.1. Material

All samples were at market maturity and reddish-orange in color. The species of rose hip fruits including *R. canina* (RC), *R. dumalis* (RD), *R. gallica* (RG), *R. dumalis* subsp. *boissieri* (RB) and *R. hirtissima* (RH) were harvested from Gümüşhane, Turkey, in September 2011. In practice, the fruits are processed to rose hip marmalade in some private factories and it is harvested at this stage, reddish-orange in color. The most common rose hip is RC in Turkey and other species have been cultivated in Gümüşhane province and around of the city. The harvested rose hip fruits were immediately transferred to laboratory and stored at −18 °C until analysis with exception of volatiles. All analyses were performed within three weeks. The volatiles were analyzed after harvesting without freezing at −18 °C. Before analyses, the seeds in the fruits were removed.

2.2. Total phenolics, total flavonols and tartaric esters assays

Total phenolic contents of rose hips were determined by the Folin–Ciocalteau procedure using gallic acid as standard with slight modifications (Yıldız, 2013). Briefly, various concentrations of gallic acid standard (1–10 mg/L) and samples (1 mg/mL) were diluted with 1.0 mL distilled water. 1.0 mL of Folin–Ciocalteu reagents was added, and the contents were vortexed. The content was mixed well and kept for 4 min at room temperature followed by addition of 1.0 mL of 10% aqueous sodium carbonate. The absorbance was measured at 760 nm after 120 min incubation period at 20 °C against blank. The concentration of total phenolic compounds was calculated as mg of gallic acid equivalents (GAE)/g dry weight, by using a standard graph. The standards including caffeic acid and rutin (Sigma–Aldrich, St. Louis, USA) were used for determination of tartaric esters and flavonols, respectively. Samples were diluted (1:10) with 10% (v/v) ethanol. A 0.25 mL of sample was mixed with 0.25 mL of 0.1% HCl (prepared in 95% ethanol) and 4.55 mL of 2% HCl (prepared in water). The solution was stirred and rested 15 min before measurement. The absorbance at 320 (A_{320}) nm was used to estimate tartaric esters and A_{360} nm was used to estimate flavonols (Mazza, Fucumoto, Delaquis, Girard, & Ewert, 1999). The concentration of each standard was ranged from 50 to 2000 mg/L for spectrophotometric analyses.

2.3. Determination of antioxidant capacity by $ABTS^{+\bullet}$ method

The $ABTS^{+\bullet}$ [2,2-azino-di-(3-ethylbenzothialozine-sulphonic acid) was assayed by the method described in Re et al. (1999). The ABTS solution (7 mmol) was prepared using 2.45 mmol potassium persulphate and the resultant solution was diluted with methanol to obtain absorbance of 0.70 ± 0.02 at 30 °C using UV–Vis spectrophotometer (Shimadzu model uv-1700, Shimadzu Corporation, Kyoto, Japan). The lyophilized hips were milled to a fine powder just before use and diluted with methanol at a level of 1.0 g/L (test sample). It was mixed with 0.1 mL of test sample and 3.9 mL of ABTS and measured ABTS at 734 nm. The absorbance of the samples was compared with the trolox standard and the results were expressed as μmol Trolox® equivalent/g dry weight antioxidant capacity (TEAC).

2.4. The ferric-reducing antioxidant power (FRAP) assay

Antioxidant activity of the samples were determined by ferric reducing/antioxidant power (FRAP). The FRAP assay is based on the measurement of the iron reducing capacities of the samples. Sample preparation in FRAP was the same with ABTS assay. The absorbance of the samples was read at 595 nm against a blank that was prepared using distilled water instead of sample. In order to make a comparison, Trolox was also tested under the same conditions as a standard antioxidant compound. FRAP values were expressed in dry weight of the samples as mM of ferrous equivalent Fe (II) per g of dry sample.

2.5. Evaluation of DPPH• radical scavenging activity

DPPH• radical scavenging activity was measured using spectrophotometric method at 517 nm as described in Chen, Mehta, Berenbaum, Zanger, and Engeseth (2000). Briefly, 0.75 mL of sample in methanolic extracts were mixed with 0.75 mL of a 0.1 mM of DPPH in methanol. Trolox standard solutions were prepared at a concentration ranging from 20 to 125 μg/ml and five different concentrations of samples were used to determine the scavenging concentration (SC_{50}). The values are expressed as SC_{50}, the concentration of the samples that cause 50% scavenging of DPPH radical.

2.6. Determination of phenolic compounds

The rose hip samples were lyophilized and 2 g of dry sample were mixed 100 mL of methanol/water/formic acid (50:48.5:1.5) solvent mixture and centrifuged at 3000× *g* (Hettich model 320 R, Tuttlingen, Germany) for 10 min at 4 °C. A 10 mL of supernatant was were subjected to twice 10 mL of ethyl acetate and 10 mL of