Determination of fatty acids and volatile compounds in fruits of rosehip (Rosa L.) species by HS-SPME/GC-MS and Im-SPME/GC-MS techniques

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Abstract: In this study, we aimed to compare fatty acid and volatile compound compositions of four rosehip species, namely Rosa pimpinellifolia, R. villosa, R. canina, and R. dumalis, by gas chromatography with flame ionization detector (GC/FID) and headspace and immersion solid-phase microextraction gas chromatography-mass spectrometry (HS-SPME/GC-MS and Im-SPME/GC-MS) techniques. The total lipid contents in fruits of the rosehip species varied from 5.83% (R. villosa) to 7.84% (R. dumalis). A total of 21 fatty acids were detected and quantified. In all species, except R. canina, polyunsaturated fatty acids (PUFAs) predominated over saturated fatty acids (SFAs) and monounsaturated fatty acids (MUFAs). Palmitic acid is the major SFA in R. villosa (5.50%), R. canina (8.27%), and R. dumalis (7.46%). Oleic acid is the most abundant MUFA, and linoleic and α-linolenic acids are the most abundant PUFAs. Sixty-two volatile compounds were detected by the HS-SPME/GC-MS technique, and 54 volatile compounds were determined by the Im-SPME/GC-MS technique. Fifty-three volatile components of rosehips have been detected for the first time in this study. While 19 acids, 9 aldehydes, 6 ketones, 18 alcohols, 5 esters, 2 terpenes, and 2 phenols were identified by HS-SPME/GC-MS, 20 acids, 5 aldehydes, 8 ketones, 13 alcohols, 5 esters, 1 terpene, and 2 phenols were identified by Im-SPME/GC-MS. The HS-SPME/GC-MS technique allowed identification of a larger number of volatile compounds and thus is more efficient than the Im-SPME/GC-MS technique.

Key words: Fatty acid, HS-SPME/GC-MS, Im-SPME/GC-MS, rosehip, volatiles

1. Introduction
Horticulture is concerned with plants that are used by people for food, either as edible products or for culinary ingredients, for medicinal use, or for ornamental and aesthetic purposes. They are a genetically very diverse group and play a major role in modern society’s end economy. They are important components of traditional food, but are also central to healthy diets of modern urban populations (Bajpai et al., 2014; Feng et al., 2014; Ruttanaprasert et al., 2014; Mlcek et al., 2015).

Rosehips are members of the genus Rosa, which contains about 200 species in the world, 25 of which are found in Turkey (Ku and Robertson, 2003). They are mostly grown in central and northeastern Anatolia in Turkey (Davis, 1972) and the fruits are an important source of vitamin C, antioxidants, phenolics, carotenoids, organic acids, fatty acids, and minerals (Uggla et al., 2003, 2005; Çınar and Çolakoğlu, 2005). They have economic value and are also consumed for medicinal purposes (Ercişi, 2005). Rosehips have laxative and diuretic properties, help regulate the menstrual cycle, and are used as a cure for flu, infections, inflammatory diseases, and chronic pain (Nojavan et al., 2008; Yildiz and Alpaslan, 2012). In addition, rosehip fruits are generally consumed in the form of tea, wine, jam, jellies, and marmalade (Guimarães et al., 2010).

Extensive fatty acid research has been carried out on seeds of rosehips, but only a few studies have been done on rosehips (Nowak, 2005; Ercişi, 2007; Barros et al., 2011). Rosehips contain both monounsaturated fatty acids (MUFAs) and polyunsaturated fatty acids (PUFAs). Unsaturated fatty acids are a nutritional requirement due to their health benefits. Consumption of MUFAs, such as oleic acid, has been shown to decrease plasma triacylglycerol and cholesterol concentrations (Kris-Etherton et al., 1999). Similarly, PUFAs, such as linoleic and linolenic acids, contribute to the prevention of atherosclerosis, cancer, heart disease, and diabetes (Ha et al., 1989; Houseknecht et al., 1998; Chahoud et al., 2004). Daily intake of fatty acids in fruit or vegetables may reduce the risk of cardiovascular disease by approximately 20% to 30% (Engelbert et al., 2010). Essential oils provide the specific smell to plants and they...
have cytotoxic and antioxidative properties (Aridogan et al., 2002; Haze et al., 2002). Essential fatty acids are required but cannot be synthesized by the human body (Cunnane and Anderson, 1997).

The aroma and flavor of fruit is a mixture of many low-molecular-weight volatile compounds, which vaporize at room temperature (Baldwin, 2002; Lara et al., 2003; Dunlevy et al., 2009). Aroma compounds are naturally present in all fruits. The mixture of flavor and aroma compounds in fruits is important for fruit quality. Volatile compounds are synthesized during fruit growth and may change both qualitatively and quantitatively (Amira et al., 2011). Volatile substances are strongly related to the species, agricultural conditions, environment, and stage of maturity (Vendramini and Trugo, 2000; Soares et al., 2007). A total of 52 volatile compounds have previously been identified in rosehip species. They include alcohols, aldehydes, ketones, monoterpenes, sesquiterpenes, total sesquiterpene esters, and other miscellaneous compounds (Demir et al., 2014).

Various tests have been developed for the determination of volatile compounds in different fruits, with the use of gas chromatography mass spectrometry (GC-MS) techniques (Lopez et al., 1998; Chen et al., 2004; Cheistophe and Celine, 2007; Zhang et al., 2007). Solid phase microextraction (SPME) was developed in the 1990s as an alternative technique for separation of volatiles from interfering nonvolatile matrix compounds. SPME is considered a fast, simple, affordable, sensitive, solvent-free, and easily automated technique, and it has been extensively used for the analysis of flavor compounds in fruits (Arthur and Pawliszyn, 1990; Kataoka et al., 2000; Jelen et al., 2012). SPME is based on the interaction with a fiber of the vapor phase of solid, liquid, and gaseous samples (Alver et al., 2012).

Until now, few studies of rosehip fruit have focused on its bioactive components, such as phenolics, minerals, ascorbic acid, and flavonoids, as well as on its antioxidant properties. Only one study reported the volatile compounds identified by headspace (HS)/GC-MS in Rosa canina, R. dumalis, R. gallica, R. dumalis subsp. boissieri, and R. hirtissima (Demir et al., 2014). As far as we know, this is the first comparative study of the volatile compound profiles of major rosehip species grown in Turkey using immersion solid-phase microextraction gas chromatography-mass spectrometry (Im-SPME/GC-MS). We also aimed to compare the lipid contents (%) and fatty acid compositions of the species.

2. Materials and methods
2.1. Plant material
Ripe fruits of the R. pimpinellifolia, R. villosa, R. canina, and R. dumalis species were harvested from Ardahan Province of Turkey in September 2014. Those species are the main rosehip species found in Turkey (Ercisli, 2005). Rosehip species were identified by morphological key characteristics described by Davis (Davis, 1972). The harvested fruits were immediately transferred to the laboratory in polyethylene bags and stored at −20 °C until analysis. The analyses were carried out in triplicate. In total, 75 fruits were used for each species and each replicate consisted of 25 fruits. The rosehip fruits were homogenized using a blender, and the homogenates were used for the identification of fatty acids and volatile components.

2.2. Oil extraction
Oil extraction was performed according to Bligh and Dyer (1959). A sample of 20 g of fruits was extracted using diethyl ether as a solvent for 1 h using automatic Soxhlet equipment (Gerhardt Soxtherm). The residue was placed in a drier and weighed up to a constant value. Boron trifluoride/methanol was used for the preparation of fatty acid methyl esters (FAMEs) (AOAC, 1990).

2.3. GC with flame ionization detector (GC/FID) analysis
Fatty acids were analyzed using a Clarus 500 gas chromatograph with an autosampler (PerkinElmer, Shelton, CT, USA) equipped with a flame ionization detector and a fused-silica capillary SGE column (30 m × 0.32 mm, ID 0.25 µm, BP20 0.25 UM; PerkinElmer, Austin, TX, USA). The oven temperature was held at 140 °C for 5 min and then raised to 200 °C at a rate of 4 °C min⁻¹ and to 220 °C at a rate of 1 °C min⁻¹, while the injector and the detector temperatures were set at 220 and 280 °C, respectively. The sample volume was 1 µL, and the carrier gas was controlled at 16 psi. The split ratio was 1:100. Fatty acids were detected by comparing the retention indices of the FAMEs with a standard 37-component FAME mixture (Supelco, Bellefonte, PA, USA). Triplicate GC analyses were performed and the results were expressed as a mean GC area (%) value ± standard deviation. The results were analyzed in a completely randomized design using analysis of variance (ANOVA). Means were separated by LSD multiple range test at 0.05 levels.

2.4. Extraction and identification of volatile compounds
The automatic HS-SPME/GC-MS (purge/trap) and Im-SPME/GC-MS techniques were used for extraction of volatile compounds in rosehips (Kafkas and Paydaş, 2007). For HS- and Im-SPME techniques, a Supelco fiber holder and a 100-µm polydimethylsiloxane (PDMS)-coated fused-silica fiber were used, being the most suitable fiber for adsorbing volatile compounds from the rosehip fruits. Prior to the first extraction, the fiber was equilibrated in the GC injector port at 250 °C for 1 h according to the manufacturer’s recommendation. The samples were homogenized with saturated sodium chloride (1 g) and 5 mL for HS-SPME of sample for each extraction was placed into a 100-mL glass vial. For Im- and HS-SPME analysis,
the PDMS fiber was inserted into the headspace of the glass vial and PDMS fiber was immersed into the sample for 30 min at 30 °C. During this time, experimental samples were stirred with a magnetic stirrer. After equilibration the fiber was removed from the sample and the analytes were thermally desorbed in the injector port of the GC-MS instrument for analysis. Thermal desorption was conducted in the injector glass liner at 250 °C for 10 min. The analyses were carried out in triplicate.

2.5. GC-MS analysis
Aroma compounds in the samples were analyzed by GC-MS. A PerkinElmer Clarus 500 instrument equipped with a CPSil5CB (25 m × 0.25 mm ID, 0.4 µm film thickness) fused-silica capillary column was used. The flow rate of helium as a carrier gas was 1 mL/min. The injector temperature was set at 250 °C for splitless injection. The column temperature was 6 °C/5 °C/min/260 °C (20 min). Mass spectra were taken at 70 eV. The mass range was between m/z 30 and 425. A library search was carried out using the Wiley GC-MS Library and the Flavor Library of Essential Oil Constituents. The mass spectra were also compared with those of reference compounds and confirmed based on retention indices from published sources. Relative percentage amounts of the separated compounds were calculated from total ion chromatograms by a computerized integrator.

2.6. Statistical analyses
A sample of 25 fruits was randomly selected for evaluating each species. Three replicates were carried out for each species. The results were analyzed in a completely randomized design using ANOVA. Means were separated by LSD multiple range test at 0.05 levels. Triplicate GC analyses were performed and the results were expressed in GC area % as a mean value ± standard deviation.

3. Results and discussion
The lipid contents (%) and fatty acid compositions of the rosehip species are given in Table 1. As seen from the

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>R. dumalis</th>
<th>R. canina</th>
<th>R. pimpinellifolia</th>
<th>R. villosa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capric acid</td>
<td>C10:0</td>
<td>nd</td>
<td>0.09&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.04&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>C12:0</td>
<td>0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.60&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.56&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>C14:0</td>
<td>0.10&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.32&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.67&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>C16:0</td>
<td>0.26&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.33&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pentadecanoic acid</td>
<td>C15:0</td>
<td>0.06&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.07&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.14&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Margaric acid</td>
<td>C17:0</td>
<td>0.23&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.24&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.14&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Lignoceric acid</td>
<td>C18:0</td>
<td>0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.08&lt;sup&gt;a&lt;/sup&gt;</td>
<td>nd</td>
</tr>
<tr>
<td>Nonadecylic acid</td>
<td>C19:0</td>
<td>nd</td>
<td>0.02</td>
<td>nd</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>C20:0</td>
<td>1.90&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.67&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.78&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Oxoheicosylic acid</td>
<td>C21:0</td>
<td>nd</td>
<td>0.07</td>
<td>nd</td>
</tr>
<tr>
<td>Cerotic acid</td>
<td>C22:0</td>
<td>0.26</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Behenic acid</td>
<td>C22:0</td>
<td>0.60&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.76&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>C18:0</td>
<td>0.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.81&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Oxirane octanoic acid</td>
<td>C19:0</td>
<td>0.44&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.70&lt;sup&gt;a&lt;/sup&gt;</td>
<td>nd</td>
</tr>
<tr>
<td>∑SFA</td>
<td></td>
<td>11.51&lt;sup&gt;b&lt;/sup&gt;</td>
<td>13.42&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>C18:1</td>
<td>40.98&lt;sup&gt;a&lt;/sup&gt;</td>
<td>44.63&lt;sup&gt;a&lt;/sup&gt;</td>
<td>26.75&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>C16:1</td>
<td>0.22&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.62&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.90&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gondoic acid</td>
<td>C20:1</td>
<td>1.31&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.31&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.83&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>∑MUFA</td>
<td></td>
<td>42.51&lt;sup&gt;a&lt;/sup&gt;</td>
<td>46.56&lt;sup&gt;a&lt;/sup&gt;</td>
<td>28.48&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>C18:2</td>
<td>33.71&lt;sup&gt;b&lt;/sup&gt;</td>
<td>27.97&lt;sup&gt;c&lt;/sup&gt;</td>
<td>41.21&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>α-Linolenic acid</td>
<td>C18:3</td>
<td>11.88&lt;sup&gt;b&lt;/sup&gt;</td>
<td>11.48&lt;sup&gt;b&lt;/sup&gt;</td>
<td>10.08&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Eicosadienoic acid</td>
<td>C20:2</td>
<td>0.39&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.02&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>∑PUFA</td>
<td></td>
<td>45.98&lt;sup&gt;a&lt;/sup&gt;</td>
<td>40.02&lt;sup&gt;a&lt;/sup&gt;</td>
<td>52.31&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total lipid %</td>
<td></td>
<td>7.84&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.92&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.38&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Different letters (a–d) in the same line show statistically significantly differences among sampling dates by Duncan’s multiple range test at P < 0.05. nd: not detected.
It is known that a diet rich in saturated fatty acids (SFAs) increases the risk of hypercholesterolemia, diabetes, and atherosclerosis, whereas PUFAs and MUFAs have several beneficial health-related effects (Simopoulos, 1999). In fruits, PUFAs were shown to predominate over SFAs and MUFAs (Bastos et al., 2015). As shown in Table 1, all of the rose species, except *R. canina*, contained PUFAs > MUFAs > SFAs. The highest SFA content was found in *R. pimpinellifolia* (19.2%), while the lowest content was detected in *R. villosa* (9.03%). Palmitic acid was found to be the major SFA, and its levels varied from 5.50% (*R. villosa*) to 8.27% (*R. canina*). Palmitic acid is considered as an atherogenic compound when consumed in high amounts (Lai et al., 2015). The second most abundant SFA was determined to be arachidic acid, and its levels varied from 0.78% (*R. pimpinellifolia*) to 1.90% (*R. dumalis*). Nonadecylic acid was found to be the least abundant SFA.

The highest MUFA content was found in *R. canina* (46.56%), while the lowest content was found in *R. pimpinellifolia* (28.48%). Oleic acid was the most abundant MUFA, and its levels varied from 26.75% (*R. pimpinellifolia*) to 44.63% (*R. canina*). Gondoic acid was the second most abundant MUFA after oleic acid, and its content was 1.72% in *R. villosa*. PUFAs represented a considerable part of the fatty acids. The highest PUFA amount was found in *R. pimpinellifolia* (52.31%), while the lowest amount was found in *R. canina* (40.02%). Linoleic acid was determined to be the most abundant PUFA, and its levels varied from 27.97% (*R. canina*) to 44.12% (*R. pimpinellifolia*). Linoleic acid is an important component of the cell membranes and is a precursor of other substances involved in many physiological responses (Lai et al., 2015). Eicosadienoic acid was the least abundant PUFA detected in all species. The most abundant fatty acids reported for berries (bilberry, cranberry, rosehips, strawberry, elderberry, and black currant) in the literature are also linoleic, linolenic, and oleic acids (Helbig et al., 2008). Similar to our results, Barros et al. (2011) found that *R. canina* had 23 fatty acids, with linoleic and α-linolenic acids being the major fatty acids, and the total lipid content was 0.67%. α-Linolenic and linoleic acids are known as essential fatty acids, but they are not synthesize by the human body (Guney et al., 2015). In addition, it was reported that the total lipid content was 1.52% in *R. villosa*, 1.78% in *R. canina*, and 1.85% in *R. dumalis* subsp. *boissieri*, and the main fatty acids in these species were α-linolenic, palmitic, and linoleic acids (Ercislî, 2007). The differences may be due to different extraction methods, the ripening stage of the rosehips, environmental conditions, or plant genotypes. It was reported that palmitic and palmitoleic acids are the main fatty acids in sea buckthorn fruits (Cakir, 2003). The dominant fatty acids in rosehip seeds are linoleic and α-linolenic acids (Szenthihalyi et al., 2002). Oleic, linoleic, and linolenic acids are important cell components (Berti and Johnson, 2008). Sánchez-Salcedo et al. (2016) identified and quantified 14 fatty acids in mulberry fruits. They determined that the most abundant fatty acids are linoleic, palmitic, oleic, and stearic acids in *M. alba* and *M. nigra*.

The fruit aroma is formed by a mixture of chemical substances (e.g., aldehydes, alcohols, ketones, esters, lactones, and terpenes) (Riu-Aumatell et al., 2004). Most fruits produce significant numbers of volatile compounds as indicators of fruit ripening (Goff and Klee, 2006). Volatiles are biosynthesized from amino acids, membrane lipids, and carbohydrates (Sanz et al., 1997). Numerous studies have been published on volatile compounds from *Rosa* petals. More than 400 volatile compounds have been described in the floral flavor of various rose varieties (Dobson et al., 1987; Pavlov et al., 2005; Rusanov et al., 2011). As far as we know, volatile compounds in fruits of rosehip species were determined by HS-SPME/GC-MS in only one study (Demir et al., 2014), and no research has been previously performed by Im-SPME/GC-MS. In the present study, a total of 62 volatile compounds were identified by HS-SPME/GC-MS in the rosehip species. These compounds included 19 acids, 9 aldehydes, 6 ketones, 18 alcohols, 5 esters, 2 terpenes, and 2 phenols (Table 2). Of the compounds detected, 53 compounds have not been previously reported in the literature. The contents of 9 compounds (6-methyl-5-hepten-2-one, hexanal, 2-hexenal, nonanal, decanal, benzaldehyde, 1-pentanol, 2-ethyl-1-hexanol, and dodecanoic acid) were found to be similar to the results of previous studies (Nowak, 2005; Demir et al., 2014). Demir et al. (2014) detected 52 volatile compounds in rosehip species by HS-SPME/GC-MS. These compounds included 10 alcohols, 10 aldehydes, 2 ketones, 24 terpenoids, 2 esters, and 4 miscellaneous compounds. Although their contents varied depending on the species, acids (6.71%–49.9%) and alcohols (7.53%–67.53%) were found to be dominant volatile compounds. *R. pimpinellifolia* had the highest total acid content (49.9%). Acetic acid was the most abundant acid in *R. villosa* (7.93%), *R. dumalis* (3.40%), and *R. pimpinellifolia* (13.41%); butanoic acid was the most abundant acid in *R. canina* (25.68%). In the previous study, no aromatic acids could be detected in rosehip species (Demir et al., 2014). Kraujalyte et al. (2012) reported that 3-methyl- and 2-
Table 2. Volatile components of four rosehip species detected by HS-SPME/GC-MS (%).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R. dumalis</th>
<th>R. canina</th>
<th>R. pimpinellifolia</th>
<th>R. villosa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-Dimethoxycinnamic acid</td>
<td>nd</td>
<td>nd</td>
<td>2.75 ± 0.2</td>
<td>nd</td>
</tr>
<tr>
<td>Sinapic acid</td>
<td>nd</td>
<td>nd</td>
<td>6.65 ± 0.12</td>
<td>nd</td>
</tr>
<tr>
<td>Formic acid</td>
<td>nd</td>
<td>3.10 ± 0.38c</td>
<td>3.24 ± 0.2b</td>
<td>3.46 ± 0.26a</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>3.40 ± 0.85c</td>
<td>1.26 ± 0.28c</td>
<td>13.41 ± 0a</td>
<td>7.93 ± 1.21b</td>
</tr>
<tr>
<td>Ionone</td>
<td>nd</td>
<td>3.70 ± 0.06c</td>
<td>1.91 ± 0.02b</td>
<td>nd</td>
</tr>
<tr>
<td>3-Methylbutanoic acid</td>
<td>nd</td>
<td>0.42 ± 0.19c</td>
<td>1.66 ± 0a</td>
<td>1.35 ± 0.29b</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>1.37 ± 0.94b</td>
<td>25.68 ± 3.32a</td>
<td>nd</td>
<td>0.58 ± 0.22c</td>
</tr>
<tr>
<td>2-Methyl-2-propenoic acid</td>
<td>nd</td>
<td>0.29 ± 0.4</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>3-Methylpentanoic acid</td>
<td>1.71 ± 0.69</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>nd</td>
<td>0.41 ± 0.08b</td>
<td>2.04 ± 0.23a</td>
<td>0.54 ± 0.76b</td>
</tr>
<tr>
<td>Heptanoic acid</td>
<td>nd</td>
<td>0.94 ± 0.04</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>nd</td>
<td>0.30 ± 0.12b</td>
<td>1.29 ± 0.01a</td>
<td>0.19 ± 0.16c</td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>nd</td>
<td>0.71 ± 0.02b</td>
<td>9.04 ± 0.23a</td>
<td>nd</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>0.23 ± 0.03</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>n-Decanoic acid</td>
<td>nd</td>
<td>0.36 ± 0.05b</td>
<td>1.44 ± 0.06a</td>
<td>nd</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>nd</td>
<td>nd</td>
<td>3.74 ± 0.23a</td>
<td>0.73 ± 0.03b</td>
</tr>
<tr>
<td>Dodecanoic acid</td>
<td>nd</td>
<td>nd</td>
<td>1.67 ± 0</td>
<td>nd</td>
</tr>
<tr>
<td>1,2-Benzenedicarboxylic acid</td>
<td>nd</td>
<td>nd</td>
<td>1.06 ± 0b</td>
<td>2.51 ± 0.54c</td>
</tr>
<tr>
<td>Pentadecanoic acid</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td>Total 19 acids</td>
<td>6.71</td>
<td>37.17</td>
<td>49.9</td>
<td>17.45</td>
</tr>
<tr>
<td>Ketones</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>nd</td>
<td>nd</td>
<td>2.75 ± 0.1</td>
<td>nd</td>
</tr>
<tr>
<td>2(3H)-Furanone</td>
<td>4.01 ± 0.67c</td>
<td>0.65 ± 0.06c</td>
<td>nd</td>
<td>2.00 ± 0.83b</td>
</tr>
<tr>
<td>2-Heptanone</td>
<td>0.39 ± 0.55</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>6-Methyl-5-hepten-2-one</td>
<td>nd</td>
<td>0.25 ± 0.15b</td>
<td>0.93 ± 0a</td>
<td>0.80 ± 0.14b</td>
</tr>
<tr>
<td>1-hydroxy-2-propanone</td>
<td>0.42 ± 0.09c</td>
<td>nd</td>
<td>3.48 ± 0.96a</td>
<td>4.48 ± 1.23c</td>
</tr>
<tr>
<td>2H-Pyran-2,6(3H)-dione</td>
<td>nd</td>
<td>nd</td>
<td>0.94 ± 0.02</td>
<td>nd</td>
</tr>
<tr>
<td>Total 6 ketones</td>
<td>4.82</td>
<td>0.9</td>
<td>8.1</td>
<td>7.28</td>
</tr>
<tr>
<td>Aldehydes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexanal</td>
<td>0.91 ± 0.71c</td>
<td>0.11 ± 0.05b</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2-Hexenal</td>
<td>0.14 ± 0.19</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.91 ± 0.13c</td>
<td>0.44 ± 0.22b</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Nonanal</td>
<td>0.99 ± 0.14</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.97 ± 0.37c</td>
<td>nd</td>
<td>3.14 ± 0.23a</td>
<td>2.84 ± 0.02b</td>
</tr>
<tr>
<td>Decanal</td>
<td>1.89 ± 0.67</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>1.21 ± 0.17a</td>
<td>0.62 ± 0.88b</td>
<td>nd</td>
<td>0.52 ± 0.04c</td>
</tr>
<tr>
<td>Dodecanal</td>
<td>0.40 ± 0.17</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>3-caren-10-al</td>
<td>nd</td>
<td>nd</td>
<td>0.91 ± 0</td>
<td>nd</td>
</tr>
<tr>
<td>Total acetaldehyde</td>
<td>7.42</td>
<td>1.17</td>
<td>4.05</td>
<td>3.36</td>
</tr>
</tbody>
</table>

Different letters (a–d) in the same line show statistically significantly differences among sampling dates by Duncan's multiple range test at P < 0.05. nd: not detected.
Table 2. (Continued).

<table>
<thead>
<tr>
<th>Compound</th>
<th><em>R. dumalis</em></th>
<th><em>R. canina</em></th>
<th><em>R. pimpinellifolia</em></th>
<th><em>R. villosa</em></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Esters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>nd</td>
<td>0.95 ± 0.34</td>
<td>nd</td>
<td>0.67 ± 0.05</td>
</tr>
<tr>
<td>3-Methyl-butanoic acid, 3-methylbutyl ester</td>
<td>3.81 ± 0.27</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Acetic acid, methyl ester</td>
<td>nd</td>
<td>0.58 ± 0.01</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Hexanoic acid, butyl ester</td>
<td>1.58 ± 0.23</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Hexanoic acid, hexyl ester</td>
<td>1.57 ± 0.29</td>
<td>0.30 ± 0.42</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td><strong>Total esters</strong></td>
<td>6.96</td>
<td>1.83</td>
<td>0</td>
<td>0.67</td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Propanediol</td>
<td>2.28 ± 0.22</td>
<td>22.52 ± 5.51</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Ethanol</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>28.72 ± 4.61</td>
</tr>
<tr>
<td>1-Penten-3-ol</td>
<td>10.37 ± 3.54</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2-Methyl-1-propanol</td>
<td>8.72 ± 1.33</td>
<td>1.10 ± 0.55</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>3-Methyl-1-butanol</td>
<td>14.24 ± 20.14</td>
<td>2.16 ± 3.05</td>
<td>nd</td>
<td>11.62 ± 1.43</td>
</tr>
<tr>
<td>1-pentanol</td>
<td>0.89 ± 0.12</td>
<td>0.73 ± 0.03</td>
<td>nd</td>
<td>7.64 ± 0.6</td>
</tr>
<tr>
<td>4-Methyl-1-heptanol</td>
<td>nd</td>
<td>0.35 ± 0.01</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2-Nonen-1-ol</td>
<td>4.05 ± 0.04</td>
<td>nd</td>
<td>nd</td>
<td>5.65 ± 1.23</td>
</tr>
<tr>
<td>4-Hexen-1-ol</td>
<td>2.01 ± 0.84</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2-Furanmethanol</td>
<td>3.29 ± 0.65</td>
<td>3.00 ± 0.54</td>
<td>1.88 ± 0.04</td>
<td>3.72 ± 0.47</td>
</tr>
<tr>
<td>3,7-Dimethyl-1,6-octadien-3-ol</td>
<td>3.77 ± 0.36</td>
<td>0.55 ± 0.04</td>
<td>nd</td>
<td>0.21 ± 0.03</td>
</tr>
<tr>
<td>2-Ethyl-1-hexanol</td>
<td>6.42 ± 0.69</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Dodecanol</td>
<td>2.01 ± 0.08</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>a,a,4-Trimethyl-3-cyclohexene-1-methanol</td>
<td>2.36 ± 0.49</td>
<td>1.01 ± 0.29</td>
<td>nd</td>
<td>2.93 ± 0.14</td>
</tr>
<tr>
<td>Phenylethyl alcohol</td>
<td>1.27 ± 0.09</td>
<td>5.36 ± 1.77</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>1-Hexadecanol</td>
<td>nd</td>
<td>0.29 ± 0.41</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>5.85 ± 0.27</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td><strong>Total alcohols</strong></td>
<td>67.53</td>
<td>37.07</td>
<td>7.53</td>
<td>54.84</td>
</tr>
<tr>
<td><strong>Terpenes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-Caryophyllene</td>
<td>nd</td>
<td>8.28 ± 0.27</td>
<td>nd</td>
<td>6.06 ± 0.13</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.22 ± 0.01</td>
<td>6.63 ± 0.09</td>
<td>26.65 ± 0.25</td>
<td>6.02 ± 0.51</td>
</tr>
<tr>
<td><strong>Total terpenes</strong></td>
<td>0.22</td>
<td>14.91</td>
<td>26.65</td>
<td>12.08</td>
</tr>
<tr>
<td>Phenol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-bis (1,1-dimethylethyl) phenol</td>
<td>4.29 ± 0.78</td>
<td>5.94 ± 0.64</td>
<td>1.83 ± 0.01</td>
<td>0.45 ± 0.04</td>
</tr>
<tr>
<td>Phenol</td>
<td>1.97 ± 0.47</td>
<td>0.44 ± 0.27</td>
<td>1.94 ± 0.32</td>
<td>3.83 ± 0.42</td>
</tr>
<tr>
<td><strong>Total phenol</strong></td>
<td>6.26</td>
<td>6.38</td>
<td>3.77</td>
<td>4.28</td>
</tr>
<tr>
<td><strong>Other compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Dimethylbenzene</td>
<td>0.14 ± 0.02</td>
<td>0.13 ± 0.08</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

Different letters (a–d) in the same line show statistically significantly differences among sampling dates by Duncan’s multiple range test at P < 0.05. nd: not detected.
methyl-butanoic acids were the major aroma constituents of **Viburnum opulus** fruits.

The alcohol contents were the highest at 67.53% (**R. dumalis** and 54.84% (**R. villosa**), and the lowest alcohol content was found in **R. pimpinellifolia** (7.53%). **R. canina** had the highest 1,2-propanediol content (22.52%), **R. dumalis** had the highest 3-methyl-1-butanol content (14.24%), and **R. villosa** had the highest ethanol content (28.72%). 1,2-Propanediol has been reported to be a flavor precursor in strawberries (Zabetakis and Gramshaw, 1998). Methyl butanoate, ethyl butanoate, 3-methyl-1-butanol, and 1-butanol have been found to be the major components in papaya fruits (Pino et al., 2003). 4-Methyl-1-heptanol and 1-hexadecanol were found at very low levels of 0.35% and 0.29% (**R. canina**). Demir et al. (2014) revealed that aldehydes and alcohols are the major volatile compounds in rosehips and, differently from our results, 2-hexen-1-ol and 1-hexanol could be identified as the most abundant alcohols. This could be due to variation between species, differences in methods, maturation period, ecologic conditions, or the altitude at which the rosehips were grown.

Aldehydes and ketones are important flavor and fragrance volatiles in many fruits (Paull et al., 2008). Regarding the aldehyde group, 9 different volatile compounds (hexanal, 2-hexenal, acetaldehyde, nonanal, furfural, decanal, benzaldehyde, dodecanal, and 3-carene-10-al) were detected. The aldehyde contents varied from 1.17% in **R. canina** to 7.42% in **R. dumalis**. Among those, furfural was the most abundant aldehyde in **R. pimpinellifolia** (3.14%) and **R. villosa** (2.84%), while decanal and benzaldehyde were the most abundant aldehydes in **R. dumalis** and **R. canina**, respectively. Some volatiles may be common to many fruits, such as 2-hexenal. In a previous study, 2-hexenal, hexanal, and 2-heptanal were identified as the major aldehydes in **R. canina**, **R. dumalis**, **R. gallica**, and **R. hirtissima** (Demir et al., 2014). Ren et al. (2015) reported decanal and 2-hexenal as important compounds contributing to orange aroma. Similarly, it was reported that 2-hexenal is the most abundant volatile compound in Riesling and Cabernet Sauvignon grapes (Kalua and Boss, 2010).

Volatile esters contribute to the characteristic aroma of many fruits (Macku and Jennings, 1987). Esters are formed by combining alcohols with acyl-CoA derivatives of fatty acids by the action of alcohol acyltransferase (Park et al., 2006). In this study, 6 ketones and 5 esters were found in the rosehips. The highest ketone content was found in **R. villosa** (7.28%), and the most abundant ketone was 1-hydroxy-2-propanone (4.48%), whereas the lowest ketone content was determined in **R. canina** (0.9%). The highest ester content was found in **R. dumalis** (7.42%). Only 2 terpenes and 2 phenols could be detected in the rosehips. **R. pimpinellifolia** had the highest naphthalene content (26.65%), and **R. canina** had the highest phenol content (6.38%). Demir et al. (2014) reported that 4-ocetyl-3-one and 6-methyl-5-hepten-2-one are the most abundant ketones and there are only 2 esters (methyl benzoate, salicylic acid methyl ester). The quality and quantity of all volatile compounds may be influenced by factors such as the species, region, climate, soil, altitude, and harvest time.

Volatile compounds in rosehips have not been studied by the Im-SPME/GC-MS technique until now. This study is the first time that 54 compounds were detected by this technique. These compounds include 20 acids, 5 aldehydes, 8 ketones, 13 alcohols, 5 esters, 1 terpene, and 2 phenols. Similar to the HS/GC-MS results shown in Table 3, acids and alcohols were found to be the major volatile compounds (19.09%–48.13% and 8.16%–40.74%, respectively). **R. pimpinellifolia** had the highest acid content (48.13% of the total amount of volatile compounds). Similar to the HS-SPME/GC-MS results, acetic acid was determined to be the most abundant acid in the rosehip species. **R. dumalis** had the highest alcohol content (40.74%), while the lowest content was found in **R. villosa**. 1-Pentanol and 3-methyl-1-butanol were the most abundant compounds in **R. dumalis** (10.51% and 12.93%, respectively). Five aldehydes were found in the rosehips, and **R. villosa** had the highest aldehyde content. The maximum furfural content was detected in **R. dumalis** (4.67%) and **R. canina** (5.45%), and the maximum 2-furancarboxaldehyde level was found in **R. villosa** (9.28%) and **R. pimpinellifolia** (9.09%). Eight ketones were also detected by this method. The highest ketone content was detected in **R. villosa** (15.08%), and the most abundant ketone was 1-hydroxy-2-propanone (8.94%). At the same time, **R. villosa** was found to have the highest ester content (19.24%). Only 1 terpene and 2 phenols were detected in the rosehips. Unlike the HS-SPME/GC-MS results, **R. canina** had the highest naphthalene content (40.7%) and **R. dumalis** had the highest phenol content (22.7%).

HS-SPME/GC-MS and Im-SPME/GC-MS generally showed similar results with few minor differences. Sixty-two compounds were identified by HS-SPME/GC-MS, whereas 54 components were detected by Im-SPME/GC-MS. As seen in the tables, the compounds varied according to the rosehip species. In addition, the number of acids and ketones was found to be higher by Im-SPME technique compare to the HS-SPME technique, while esters, terpenes, and phenols were found to be similar. As for the aldehydes, the highest number was obtained from the HS-SPME technique.

Here we have shown that the rosehip species are a rich source of fatty acids and that there are important differences between the different species. In all species,
### Table 3. Volatile components of rosehip species detected by Im-SPME/GC-MS (%).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R. dumalis</th>
<th>R. canina</th>
<th>R. pimpinellifolia</th>
<th>R. villosa</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-Dimethoxycinnamic acid</td>
<td>nd</td>
<td>0.15 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.35 ± 0.19&lt;sup&gt;a&lt;/sup&gt;</td>
<td>nd</td>
</tr>
<tr>
<td>Sinapic acid</td>
<td>0.78 ± 0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>nd</td>
<td>8.14 ± 0.51&lt;sup&gt;a&lt;/sup&gt;</td>
<td>nd</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.73 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.60 ± 0.36&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.53 ± 0.07&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.90 ± 1.63&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>10.47 ± 1.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>11.35 ± 1.97&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.86 ± 2.63&lt;sup&gt;a&lt;/sup&gt;</td>
<td>16.86 ± 1.84&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
<tr>
<td>3-Methylbutanoic acid</td>
<td>3.00 ± 0.24&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.24 ± 0.26&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.55 ± 0.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.93 ± 0.14&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>1-Methyl-1H-pyrazole-4-carboxylic acid</td>
<td>1.17 ± 0.65&lt;sup&gt;c&lt;/sup&gt;</td>
<td>nd</td>
<td>nd</td>
<td>4.19 ± 0.93&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>2.21 ± 0.13&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.34 ± 0.08&lt;sup&gt;b&lt;/sup&gt;</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2-Methyl-2-propenoic acid</td>
<td>nd</td>
<td>nd</td>
<td>4.84 ± 0.22</td>
<td>nd</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>3.27 ± 0.66&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.05 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.67 ± 0.04&lt;sup&gt;b&lt;/sup&gt;</td>
<td>nd</td>
</tr>
<tr>
<td>Heptanoic acid</td>
<td>nd</td>
<td>nd</td>
<td>0.39 ± 0.05</td>
<td>nd</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>0.73 ± 0.06&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.05 ± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>3.44 ± 0.91&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.58 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.78 ± 0.01&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>1.98 ± 2.79&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>nd</td>
<td>nd</td>
<td>4.20 ± 0.34</td>
<td>nd</td>
</tr>
<tr>
<td>n-Decanoic acid</td>
<td>nd</td>
<td>nd</td>
<td>0.35 ± 0.09</td>
<td>nd</td>
</tr>
<tr>
<td>2-Decenoic acid</td>
<td>nd</td>
<td>nd</td>
<td>1.13 ± 0.59&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.44 ± 0.62&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>0.64 ± 0.09&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.07 ± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.36 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>nd</td>
</tr>
<tr>
<td>Dodecanoic acid</td>
<td>0.44 ± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>nd</td>
<td>nd</td>
<td>0.53 ± 0.74&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>1,2-Benzenedicarboxylic acid</td>
<td>nd</td>
<td>0.71 ± 0.02</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Tetradecanoic acid</td>
<td>2.36 ± 0.18&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.05 ± 0.03&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.96 ± 0.25&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.22 ± 0.17&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pentadecanoic acid</td>
<td>2.37 ± 0.34&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.05 ± 0.02&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.37 ± 0.02&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.69 ± 0.09&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total acids</td>
<td>31.61</td>
<td>19.09</td>
<td>48.13</td>
<td>34.74</td>
</tr>
<tr>
<td><strong>Ketones</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>nd</td>
<td>nd</td>
<td>2.50 ± 0.54</td>
<td>nd</td>
</tr>
<tr>
<td>2(3H)-Furanone</td>
<td>3.45 ± 0.92&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.80 ± 0.06&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.09 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.76 ± 0.07&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>6-Methyl-5-hepten-2-one</td>
<td>nd</td>
<td>0.90 ± 0.27</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>1-Hydroxy-2-propanone</td>
<td>5.63 ± 0.96&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.54 ± 0.2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.59 ± 0.38&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>8.94 ± 0.54&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethanone, 1-(2-furanyl)</td>
<td>0.45 ± 0.04&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.05 ± 0.03&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.76 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.38 ± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ionone</td>
<td>nd</td>
<td>nd</td>
<td>0.91 ± 0.28</td>
<td>nd</td>
</tr>
<tr>
<td>2H-Pyran-2,6(3H)-dione</td>
<td>nd</td>
<td>nd</td>
<td>1.44 ± 0.09</td>
<td>nd</td>
</tr>
<tr>
<td>Furfyl hydroxymethyl ketone</td>
<td>nd</td>
<td>0.20 ± 0.08&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.46 ± 0.07&lt;sup&gt;a&lt;/sup&gt;</td>
<td>nd</td>
</tr>
<tr>
<td>Total ketones</td>
<td>9.53</td>
<td>4.49</td>
<td>12.25</td>
<td>15.08</td>
</tr>
<tr>
<td><strong>Aldehydes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>nd</td>
<td>nd</td>
<td>0.84 ± 0.18&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.11 ± 0.57&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Nonanal</td>
<td>6.30 ± 0.34</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Furfural</td>
<td>4.67 ± 1.32&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>5.45 ± 0.54&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.11 ± 0.98&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.96 ± 0.25&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>1.93 ± 0.46&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.05 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.53 ± 0.04&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.51 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2-Furancarboxaldehyde</td>
<td>0.83 ± 0.17&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.47 ± 0.05&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.09 ± 0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.28 ± 2.54&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total aldehydes</td>
<td>13.73</td>
<td>9.97</td>
<td>11.73</td>
<td>17.75</td>
</tr>
</tbody>
</table>

Different letters (a–d) in the same line show statistically significantly differences among sampling dates by Duncan’s multiple range test at P < 0.05. nd: not detected.
except *R. canina*, PUFAs predominate over SFAs and MUFAs. Palmitic acid is the major SFA, while arachidic acid is the second most abundant SFA in *R. villosa*, *R. canina*, and *R. dumalis*. Stearic acid is the major SFA in *R. pimpinellifolia*. Oleic acid is the most abundant MUFA. Linoleic and α-linolenic acids are the most abundant PUFAs. α-Linolenic acid is the most important essential fatty acid in the human diet. Due to the high percentage of PUFAs and MUFAs, consumption of rosehip fruits is recommended. In the present study, 62 compounds were identified by the HS-SPME/GC-MS technique and 54 compounds were detected by the Im-SPME/GC-MS technique. Of the compounds detected, 53 compounds have not been previously reported in the literature. These compounds include acids, aldehydes, ketones, alcohols, esters, terpenes, and phenols. Alcohols and acids are the main volatile compounds found in rosehip species by both techniques. The application of both methods to the rosehip species showed that the HS-SPME/GC-MS method provides better results compare to the Im-SPME/GC-MS technique. In addition, it is clear that *R. pimpinellifolia* is quite different from the other species in terms of all examined parameters. That species has black fruits while the others have orange fruits.

**Table 3.** (Continued.)

<table>
<thead>
<tr>
<th>Compound</th>
<th><em>R. dumalis</em></th>
<th><em>R. canina</em></th>
<th><em>R. pimpinellifolia</em></th>
<th><em>R. villosa</em></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Esters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>nd</td>
<td>4.29 ± 0.33</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Acetic acid, 2-propenyl ester</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>14.99 ± 0.12</td>
</tr>
<tr>
<td>3-Methyl-butyric acid, 3-methylbutyl ester</td>
<td>nd</td>
<td>0.38 ± 0.03</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Acetic acid, methyl ester</td>
<td>nd</td>
<td>nd</td>
<td>6.49 ± 0.18</td>
<td>nd</td>
</tr>
<tr>
<td>2-Furancarboxylic acid, methyl ester</td>
<td>nd</td>
<td>nd</td>
<td>4.25 ± 0.74</td>
<td></td>
</tr>
<tr>
<td><strong>Total esters</strong></td>
<td>0</td>
<td>4.67</td>
<td>6.49</td>
<td>19.24</td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Propanediol</td>
<td>2.99 ± 0.22b</td>
<td>3.81 ± 1.39b</td>
<td>nd</td>
<td>0.73 ± 0.03b</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.72 ± 0.01b</td>
<td>nd</td>
<td>10.43 ± 0.23c</td>
<td>nd</td>
</tr>
<tr>
<td>1-Penten-3-ol</td>
<td>5.60 ± 1.09c</td>
<td>nd</td>
<td>0.51 ± 0.01c</td>
<td>1.70 ± 0.41c</td>
</tr>
<tr>
<td>2-Methyl-1-propanol</td>
<td>nd</td>
<td>7.03 ± 1.93</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>3-Methyl-1-butanol</td>
<td>12.93 ± 1.28b</td>
<td>4.80 ± 0.53b</td>
<td>nd</td>
<td>1.07 ± 0.51c</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>10.51 ± 1.29b</td>
<td>nd</td>
<td>nd</td>
<td>2.75 ± 0.89b</td>
</tr>
<tr>
<td>2-Nonen-1-ol</td>
<td>nd</td>
<td>nd</td>
<td>0.35 ± 0.09</td>
<td>nd</td>
</tr>
<tr>
<td>2-Furanmethanol</td>
<td>1.18 ± 0.59b</td>
<td>0.62 ± 0.08bc</td>
<td>0.38 ± 0.03b</td>
<td>0.99 ± 0.01b</td>
</tr>
<tr>
<td>3,7-Dimethyl-1,6-octadien-3-ol</td>
<td>0.68 ± 0.06b</td>
<td>nd</td>
<td>nd</td>
<td>0.92 ± 0.29b</td>
</tr>
<tr>
<td>a,a,4-Trimethyl-3-cyclohexene-1-methanol</td>
<td>nd</td>
<td>0.09 ± 0.02b</td>
<td>1.43 ± 0.02b</td>
<td>nd</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>3.74 ± 0.78</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Phenylethyl alcohol</td>
<td>1.39 ± 0.96b</td>
<td>2.85 ± 0.03b</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td><strong>Total alcohol</strong></td>
<td>40.74</td>
<td>19.2</td>
<td>13.1</td>
<td>8.16</td>
</tr>
<tr>
<td><strong>Terpenes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.08 ± 0.52c</td>
<td>40.7 ± 7.56c</td>
<td>1.19 ± 0.68c</td>
<td>3.24 ± 0.57c</td>
</tr>
<tr>
<td><strong>Total terpenes</strong></td>
<td>1.08</td>
<td>40.7</td>
<td>1.19</td>
<td>3.24</td>
</tr>
<tr>
<td><strong>Phenols</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-Bis(1,1-dimethylethyl) phenol</td>
<td>1.15 ± 0.62b</td>
<td>nd</td>
<td>2.15 ± 0.53c</td>
<td>nd</td>
</tr>
<tr>
<td>Phenol</td>
<td>2.27 ± 0.06c</td>
<td>0.06 ± 0.03c</td>
<td>0.81 ± 0.04b</td>
<td>0.75 ± 0.16c</td>
</tr>
<tr>
<td><strong>Total phenols</strong></td>
<td>2.27</td>
<td>0.06</td>
<td>0.81</td>
<td>0.75</td>
</tr>
<tr>
<td><strong>Other compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Dimethylbenzene</td>
<td>nd</td>
<td>1.72 ± 0.43c</td>
<td>0.56 ± 0.19b</td>
<td>nd</td>
</tr>
</tbody>
</table>

Different letters (a–d) in the same line show statistically significantly differences among sampling dates by Duncan’s multiple range test at P < 0.05. nd: not detected.
References


