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Variation in volatile and fatty acid contents among Viburnum opulus L. Fruits growing different locations

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ABSTRACT

This study aimed to compare fatty acid and volatile compound compositions of *Viburnum opulus* fruits grown at various locations at different altitudes of Turkey (Ardahan/Center, Sivas/Gemerk, Kayseri/Develi, Gumushane/Kelkit). The total lipid contents in fruits varied from 9.34 % (Ardahan) to 12.35 % (Gümüşhane). A total of ten fatty acids (lauric acid (C12:0), myristic acid (C14:0), oleic acid (C 18:1), palmitic acid (C16:0), linoleic acid (C18:2), α-Linolenic acid(C18:3), arachidic acid (C20:0), gondoic acid (C20:1), behenic acid (C22:0), stearic acid (C18:0)) have been identified and quantified. The major fatty acids in all the samples were oleic acid, linoleic acid, and palmitic acid. The highest saturated fatty acid (SFA) content was found in Gümüşhane sample (18.14 %), while the lowest content was detected in Sivas (13.46 %). Unlike SFA, the highest unsaturated faty acid (UFA) content was determined in Sivas sample (87.01 %), while the lowest content was identified in Gümüşhane sample (82.26 %). We used headspace and immersion solid-phase microextraction gas chromatography-mass spectrometry (HS-SPME/GC–MS and Im-SPME/GC–MS) techniques to identify the volatiles. 23 and 35 compounds were identified by the HS-SPME/GC–MS technique at 28 and 40°C, however, 44 and 38 compounds were detected by the Im-SPME/GC–MS technique at 28 and 40°C. Thirty volatile components of *V.opulus* fruits have been detected for the first time in this study. 3-methylbutanoic acid in Ardahan, Kayseri, Sivas samples, ethyl acetate in Sivas sample, 2-octanol in Gümüşhane sample, phenol in Ardahan sample are the main volatile compounds. Im-SPME/GC–MS technique allowed identification of a larger number of volatile compounds and thus is more efficient than the HS-SPME/GC–MS technique.

1. Introduction

Viburnum is a genus of family Caprifoliaceae. The genus is represented by four species in Turkey; *Viburnum opulus* L., *V. lantana* L., *V. orientale* Pallas, and *V. tinus* L. (Davis et al., 1988). The majority of them being endemic. There are several names of *V.opulus*: cranberry bush, guelder rose, snowball tree, cramp bark, growing in Turkey is named gilaburu (Cesoniene et al., 2010; Velioglu et al., 2006). It's leaves, flowers and fruits have been used in Turkish folk medicine. *V.opulus* are preferred because of their use as decorative ornamental plants as well as benefits for human health and nutrition (Cesoniene et al., 2010). The fruits of *V.opulus* are consumed as jellies, marmalades, sauces, and beverages. The fruits contain organic acids, polyphenolics, flavonoids, and anthocyanins. Because *V.opulus* fruits have a high content of these natural compounds, they have been used to treat of stomach, kidney, lung and heart disease as well as tuberculosis, menstrual cramps and high blood pressure (Velioglu et al., 2006; Bae et al., 2010; Rop et al., 2010). Even the origin of the cramp bark name in English comes from its antispastic feature whereas cramping is a kind of spasm disease in which tissue is contracted and leading to sudden and severe pain and commonly occurs during sleep. At the same time, different studies suggested that its fruit possess antimicrobial properties against human-pathogenic bacteria (Sagdic et al., 2006).

The fatty acids, which may include saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), and polyunsaturated fatty acids (PUFA) are beneficial to human health (Mehmood et al., 2008) especially, polyunsaturated fatty (Laura et al., 2009). The volatile compounds, such as fatty acids, also affect the nutritional value of fruits. All fruits emit volatile compounds. However, the content and composition of these molecules vary with species, variety, location, the composition of soils, usage of fertilizer, climate, and temperature Maffei (2010). The aroma is a complex mixture of a large number of volatile compounds,

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Table 1
The lipid contents (%) and fatty acid compositions of the *V.opulus* fruits.

Fatty acid	Ardahan	Sivas	Kayseri	Gumushane	LSD
Total lipid	9.34 ± 0.18 c	9.97 ± 0.23 b	12.08 ± 0.09 a	12.35 ± 0.33 a	1.602**
UFAs					
Oleic acid	62.96 ± 0.62	67.09 ± 1.11	66.39 ± 2.30	61.21 ± 2.12	–
Linoleic acid	18.53 ± 1.66	17.62 ± 1.62	16.29 ± 0.56	18.79 ± 5.84	–
Arachidic acid	0.85 ± 0.12	0.57 ± 0.07	0.62 ± 0.06	0.72 ± 0.01	–
Gondoic acid	0.89 ± 0.01	0.91 ± 0.137	1.04 ± 0.07	0.81 ± 0.25	–
α-Linolenic acid	1.14 ± 0.02 a	0.82 ± 0.05 b	0.93 ± 0.09 bc	0.73 ± 0.00 c	0.154**
SFAs					
Palmitic acid	11.77 ± 0.80	11.17 ± 0.48	11.36 ± 0.75	11.32 ± 1.05	–
Lauric acid	0.33 ± 0.02	0.24 ± 0.01	0.32 ± 0.01	0.31 ± 0.06	–
Myristic acid	0.27 ± 0.12	0.37 ± 0.01	0.41 ± 0.03	0.46 ± 0.04	–
Behenic acid	0.60 ± 0.013	0.55 ± 0.11	0.51 ± 0.05	0.69 ± 0.04	–
Stearic acid	0.53 ± 0.06	0.51 ± 0.01	0.55 ± 0.08	0.48 ± 0.05	–
Others	2.65 ± 0.11	0.62 ± 0.27	1.85 ± 0.36	4.88 ± 1.38	–

*LSD. Least Significant Difference (LSD).

Table 2
The aroma compounds (%) in *V.opulus* fruits by HS/SPME/GC/MS technique at 28°C.

R.T*		Ardahan	Kayseri	Sivas	Gümüşhane
11.1	Nonanal	15.64 ± 1.88	0.83 ± 0.15	0.00 ± 0.00	0.30 ± 0.15
16.3	2,5-dimethyl-benzaldehayde	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.39 ± 0.09
	Total aldehydes	**15.64**	**0.83**	**0.00**	**0.69**
1.8	Trans-2,3-Dimethoxycinnamic acid	0.00 ± 0.00	3.53 ± 0.05	0.00 ± 0.00	0.24 ± 0.03
16.8	Pentanoic acid	0.00 ± 0.00	1.52 ± 0.15	0.00 ± 0.00	0.00 ± 0.00
17.6	Hexanoic acid	0.00 ± 0.00	0.39 ± 0.59	0.00 ± 0.00	0.17 ± 0.07
17.6	2-ethyl-Hexanoic acid	1.80 ± 0.90	0.00 ± 0.00	0.00 ± 0.00	0.27 ± 0.02
18.6	Octanoic acid	2.49 ± 0.49	2.30 ± 0.62	0.00 ± 0.00	0.79 ± 0.26
19.6	Nonanoic acid	0.00 ± 0.00	8.39 ± 1.90	0.00 ± 0.00	5.22 ± 1.81
20.6	n-decanoic acid	0.00 ± 0.00	1.10 ± 0.73	2.86 ± 0.05	1.74 ± 0.33
22.9	1.2-benzenedicarboxylic acid	0.00 ± 0.00	2.05 ± 0.86	4.38 ± 0.99	2.32 ± 0.76
14.0	3-methyl-butanoic acid	36.13 ± 3.33	38.10 ± 2.47	34.00 ± 2.09	12.86 ± 0.94
	Total acids	**40.42**	**57.38**	**41.25**	**23.61**
2.2	Ethyl acetat	3.47 ± 0.47	14.75 ± 0.34	42.93 ± 4.40	8.58 ± 0.95
5.1	2-methyl-butanoic acid,ethyl ester	0.00 ± 0.00	2.78 ± 0.96	0.33 ± 0.17	0.74 ± 0.19
6.6	3-methyl-1-butanol,acetate	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.18 ± 0.03
	Total esters	**3.47**	**17.53**	**43.26**	**9.50**
3.3	Ethanol	0.00 ± 0.00	0.41 ± 0.12	0.00 ± 0.00	0.00 ± 0.00
12.0	2-octanol	1.54 ± 0.64	0.00 ± 0.00	0.00 ± 0.00	36.01 ± 2.64
13.4	2-nonanol	0.00 ± 0.00	15.40 ± 0.88	0.00 ± 0.00	0.00 ± 0.00
18.4	1,2-decanediol	0.00 ± 0.00	0.53 ± 0.15	0.00 ± 0.00	0.30 ± 0.03
	Total alcohol	**1.54**	**16.34**	**0.00**	**36.31**
7.6	2(3 H)furanone	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.35 ± 0.01
7.8	2-heptanone	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.53 ± 0.05
9.5	2-octanone	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	11.42 ± 1.08
10.3	6-methyl-5-hepten-2-one	0.00 ± 0.00	0.32 ± 0.05	1.84 ± 0.47	0.49 ± 0.12
	Total ketons	**0.000**	**0.320**	**1.840**	**12.790**
21.0	Phenol	38.9 ± 1.9	7.32 ± 0.67	13.62 ± 0.92	0.43 ± 0.13
	Others	**0.03**	**0.28**	**0.03**	**16.67**

* R.T.: Retention time.

whose composition is specific to species and often to the variety of fruit (Sanz et al., 1997; Schwab (2008).

As far as we know there are no previously published papers comparing guelder rose berries naturally grown at various altitudes. The aim of this study was to compare the fatty acids and volatile compounds of *V. opulus* fruits grown in different ecological conditions of Turkey to assess important agronomical traits and select the most valuable genotypes as sources of health-promoting componds.

2. Material and methods

2.1. Fruit material

Viburnum opulus fruits were harvested from four different altitudes [Gumushane/Kelkit town (altitude 1700 m), Kayseri/Develi town (altitude 1330 m), Ardahan/Central district (altitude 1900 m) and Sivas/Gemerek town (altitude 1200 m)] and used as study material. Fruits from all locations were harvested in October 2013 at the same time. Plants were identified by morphological key characteristics described by Davis and Davis (1972). Fruits immediately were treated by liquid N and were kept in −80 °C until analyses. The analysis was done in 5 replicates and each replicate consisted of 500 g of fruit.

Sivas has a dry-summer continental climate with warm and dry summers and cold and snowy winters. The driest months are July and August and the wettest months are April and May. But Gümüşhane has a humid continental climate with cold and snowy winters and warm summers. Ardahan has a warm summer humid continental climate, and a cool summer continental climate with warm and brief summers with cool nights and very cold winters. Winters are very snowy with snow cover lasting from late October to mid-April. Kayseri has a cold semi-arid climate, with cold, snowy winters and hot, dry summers with cool nights due to Kayseri's high elevation. Rainfall occurs mostly during the

Table 3
The aroma compounds (%) in *V.opulus* fruits by HS/SPME/GC/MS technique at 40°C.

R.T*		Ardahan	Kayseri	Sivas	Gümüşhane
11.1	Nonanal	1.30 ± 0.09	1.85 ± 0.09	0.26 ± 0.07	0.29 ± 0.06
12.5	Decanal	0.09 ± 0.02	0.26 ± 0.16	0.00 ± 0.00	0.33 ± 0.15
16.3	2,5-dimethyl-benzaldehayde	0.00 ± 0.00	1.52 ± 0.31	3.76 ± 0.37	0.82 ± 0.17
	Total aldehydes	**1.39**	**3.63**	**4.02**	**1.44**
1.8	Trans-2,3-Dimethoxycinnamic acid	0.00 ± 0.00	0.74 ± 0.17	0.00 ± 0.00	0.08 ± 0.04
3.3	Formic acid	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	5.00 ± 0.94
11.9	Acetic acid	0.14 ± 0.02	0.82 ± 0.17	1.14 ± 0.61	0.00 ± 0.00
14.0	3-methyl-butanoic acid	49.97 ± 2.16	33.74 ± 1.01	28.73 ± 2.45	18.01 ± 2.42
15.9	3-methyl-pentanoic acid	0.00 ± 0.00	0.00 ± 0.00	0.46 ± 0.15	0.17 ± 0.04
16.8	Pentanoic acid	0.00 ± 0.00	3.11 ± 0.4	0.00 ± 0.00	0.12 ± 0.17
17.6	Hexanoic acid	0.00 ± 0.00	0.00 ± 0.00	0.63 ± 0.89	0.00 ± 0.00
18.6	Octanoic acid	0.00 ± 0.00	1.92 ± 0.43	0.65 ± 0.92	0.80 ± 0.22
19.6	Nonanoic acid	6.21 ± 0.23	7.52 ± 0.43	14.9 ± 2.21	3.05 ± 0.54
20.6	n-decanoic acid	1.70 ± 0.26	3.11 ± 0.48	2.83 ± 0.73	1.17 ± 0.24
22.9	1.2-benzenedicarboxylic acid	10.58 ± 1.34	6.67 ± 0.71	0.57 ± 0.01	2.88 ± 0.30
	Total acids	**68.60**	**57.63**	**49.91**	**31.28**
2.2	Ethyl acetate	3.00 ± 0.5	1.41 ± 0.99	7.61 ± 1.53	1.93 ± 0.31
5.5	3-methyl-butanoic acid,ethyl ester	0.00 ± 0.00	0.25 ± 0.06	0.00 ± 0.00	0.20 ± 0.06
6.6	3-methyl-1-butanol,acetate	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.08 ± 0.02
	Total esters	**3.00**	**1.66**	**7.61**	**2.21**
3.3	Ethanol	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	5.43 ± 0.68
8.4	2-hexanol	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	9.97 ± 1.10
10.0	Carveol	1.95 ± 0.14	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
11.2	4-methyl-1-Heptanol	0.00 ± 0.00	7.34 ± 1.38	0.00 ± 0.00	0.24 ± 0.04
12.0	2-octanol	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	31.97 ± 4.32
13.1	Linalool	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.3 ± 0.42
13.4	2-nonanol	0.00 ± 0.00	2.36 ± 0.81	0.00 ± 0.00	0.56 ± 0.19
14.9	A-terpineol	6.68 ± 1.46	0.25 ± 0.06	3.06 ± 0.70	0.70 ± 0.14
18.4	1,2-decanediol	3.1 ± 0.52	5.31 ± 0.46	3.97 ± 0.21	2.68 ± 0.77
20.2	1-butanol	0.77 ± 1.09	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
	Total alcohol	**12.50**	**15.26**	**7.03**	**51.85**
7.6	2(3 H)furanone	0.00 ± 0.00	1.97 ± 0.79	0.00 ± 0.00	0.00 ± 0.00
9.5	2-octanone	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	6.98 ± 1.92
10.3	6-methyl-5-hepten-2-one	0.00 ± 0.00	0.22 ± 0.31	0.00 ± 0.00	0.00 ± 0.00
12.8	Ionone	1.85 ± 0.16	2.87 ± 0.98	4.23 ± 0.61	1.02 ± 0.50
16.6	Dihydropseudionone	3.92 ± 0.30	4.64 ± 1.14	2.04 ± 0.4	0.41 ± 0.31
	Total ketons	**5.77**	**9.70**	**6.27**	**8.41**
21.0	Phenol	4.2 ± 0.51	5.5 ± 0.22	8.35 ± 1.53	4.04 ± 0.51
9.2	O-Cymene	0.09 ± 0.12	0.55 ± 0.78	0.00 ± 0.00	0.00 ± 0.00
	Others	**4.45**	**6.07**	**16.81**	**0.77**

* R.T.: Retention time.

spring, early summer and late autumn.

2.2. Oil extraction

Thirty grams of dried fruits were used for oil extraction 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. 2 N Pottasium hydroxide in methanol was used for the preparation of fatty acid methyl esters (FAMEs). The fatty acid profile was detected by gas chromatography equipped with an FID detector (David et al., 2005).

2.3. Extraction and identification of volatile compounds

Volatile compounds were extracted in 5 M calcium chloride solution at 28 °C and 40 °C for 20 min using two HS-SPME/GC–MS and Im-SPME/GC–MS techniques with SPME fiber assembly Carboxen/Polydimethylsiloxane (CAR/PDMS). The analyses were done on an HS/GC/ MS apparatus equipped with an HP-5 MS (30 m × 0.25 mm × 0.25 µm) fused-silica capillary column. The carrier gas was Helium (0.6 ml/min). The temperature of the injector and interface were set 280 °C, and 300 °C, respectively. The initial column heating program was 40 °C for 2 min thereafter increased to 250 °C at the rate of 5 °C/minute and remained at this temperature for 20 min for column purge.

2.4. Statistical analyses

Statistical analyses were done using JMP statistical software from SAS (Version 7). Differences among the mean values were detected by the least significant differences (LSD) test at an alpha value of 0.05.

3. Results and discussion

The lipid contents (%) and fatty acid composition of the *V.opulus* fruits are given in Table 1. The lipid contents varied from 9.34 % (Ardahan) to 12.35 % (Gümüşhane). It was determined that the total lipid content changed according to the locations and differences among the locations were found to be statistically significant ($p < 0.01$). Eriksson and Ehrlén (1991) found the lipid concentration to be 1.3 % for *V.opulus*. Debussche and Isenmann (1987) identified that the lipid concentrations for *V.lantana* were 2 %. Snow and Snow (1988) revealed that the lipid concentrations were higher in *V. opulus* than in *V.lantana* in Spain. Maikhuri et al. (2012) reported that lipid content in the berry of *V. mullaha* was 184 mg/g.

As evident from the table, ten fatty acids (lauric acid (C12:0), myristic acid (C14:0), oleic acid (C 18:1), palmitic acid (C16:0), linoleic acid (C18:2), α-Linolenic acid(C18:3), arachidic acid (C20:0), gondoic acid (C20:1), behenic acid (C22:0), stearic acid (C18:0)) have been identified and quantified. The major fatty acids in all the samples were oleic acid, linoleic acid, and palmitic acid. To the best of our knowledge, there were no identified fatty acids in *V.opulus* fruits. Yilmaz et al.

Table 4
The aroma compounds (%) in *V.opulus* fruits by Im/SPME/GC/MS technique at 28°C.

R.T*		Ardahan	Kayseri	Sivas	Gümüşhane
11.1	Nonanal	2.36 ± 0.95	0.88 ± 0.07	1.68 ± 0.47	1.43 ± 0.18
12.1	Furfural	3.04 ± 0.35	4.28 ± 1.30	6.34 ± 0.71	0.60 ± 0.05
13.5	5-methyl-2-furancarboxaldehyde	0.17 ± 0.03	0.16 ± 0.06	0.55 ± 0.04	0.00 ± 0.00
16.3	2,5-dimethyl-benzaldehayde	0.31 ± 0.05	0.58 ± 0.01	0.70 ± 0.21	0.00 ± 0.00
23.0	Hydroxymethylfurfural	6.88 ± 0.67	5.98 ± 1.12	7.53 ± 0.69	0.00 ± 0.00
24.3	Dodecanal	0.00 ± 0.00	0.00 ± 0.00	0.89 ± 0.12	0.00 ± 0.00
	Total aldehydes	**12.76**	**11.88**	**17.69**	**2.03**
2.0	Sinapic acid	0.20 ± 0.04	0.00 ± 0.00	0.14 ± 0.04	0.38 ± 0.03
3.3	Formic acid	2.77 ± 0.58	2.50 ± 0.55	2.64 ± 0.78	0.00 ± 0.00
9.8	3-amino-2-3-dihydrobenzoic acid	0.65 ± 0.13	0.41 ± 0.12	0.57 ± 0.13	0.00 ± 0.00
11.9	Acetic acid	19.25 ± 0.68	21.55 ± 3.73	16.00 ± 0. 66	3.02 ± 0.17
13.4	2-methyl-propanoic acid	0.33 ± 0.18	0.00 ± 0.00	0.61 ± 0.05	1.88 ± 0.19
14.0	3-methyl-butanoic acid	25.89 ± 0.72	18.56 ± 0.79	16.46 ± 1.09	11.72 ± 1.5
14.8	2-methyl-2-propenoic acid	1.82 ± 0.07	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
15.9	3-methyl-pentanoic acid	1.42 ± 0.34	2.40 ± 0.99	0.96 ± 0.05	0.09 ± 0.04
16.8	Pentanoic acid	0.00 ± 0.00	0.58 ± 0.02	0.00 ± 0.00	0.11 ± 0.10
17.6	Hexanoic acid	0.61 ± 0.06	0.42 ± 0.13	0.63 ± 0.18	0.32 ± 0.03
17.8	Heptanoic cid	0.00 ± 0.00	0.00 ± 0.00	0.54 ± 0.37	0.19 ± 0.08
18.6	Octanoic acid	2.89 ± 0.36	0.00 ± 0.00	1.34 ± 0.71	0.66 ± 0.17
19.6	Nonanoic acid	2.41 ± 0.23	0.88 ± 0.26	2.76 ± 0.85	5.70 ± 0.95
20.6	N-decanoic acid	0.57 ± 0.09	0.34 ± 0.10	1.89 ± 0.57	0.77 ± 0.14
22.4	Dodecanoic acid	0.00 ± 0.00	0.00 ± 0.00	0.95 ± 0.29	0.00 ± 0.00
22.9	1.2-benzenedicarboxylic acid	1.74 ± 0.94	0.36 ± 0.02	1.21 ± 0.60	0.85 ± 0.14
24.1	Tertradecanoic acid	1.65 ± 0.77	0.12 ± 0.02	2.96 ± 0.48	0.00 ± 0.00
	Total acids	**62.200**	**48.12**	**49.66**	**25.69**
2.2	Ethyl acetat	0.00 ± 0.00	2.99 ± 0.78	3.64 ± 0.36	0.00 ± 0.00
2.0	Ketogluconic acid methyl ester	0.00 ± 0.00	0.00 ± 0.00	1.38 ± 0.39	0.00 ± 0.00
24.9	Octyl 4-methoxycinnamate	0.47 ± 0.08	0.3 ± 0.07	2.25 ± 0.57	0.00 ± 0.00
	Total esters	**0.47**	**3.29**	**7.27**	**0**
3.7	Ethanol	3.06 ± 0.62	4.43 ± 0.34	2.60 ± 0.61	3.13 ± 0.21
8.7	3-methyl-1-butanol	0.00 ± 0.00	0.00 ± 0.00	1.10 ± 0.18	1.31 ± 0.77
10.5	2-heptanol	0.00 ± 0.00	0.00 ± 0.00	0.15 ± 0.06	0.12 ± 0.02
10.0	Carveol	0.00 ± 0.00	0.64 ± 0.12	0.00 ± 0.00	0.00 ± 0.00
11.8	2-furanmethanol	1.17 ± 0.03	0.34 ± 0.09	1.33 ± 0.45	0.12 ± 0.30
12.0	2-octanol	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	47.33 ± 3.02
13.1	Linalool	0.53 ± 0.09	0.00 ± 0.00	0.30 ± 0.05	0.00 ± 0.00
	Total alcohols	**4.76**	**5.41**	**5.48**	**52.01**
7.6	2(3 H)furanone	1.34 ± 0.28	1.37 ± 0.37	0.76 ± 0.38	0.13 ± 0.03
7.8	2-heptanone	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.37 ± 0.04
9.5	2-octanone	1.74 ± 0.6	0.00 ± 0.00	0.84 ± 0.14	16.68 ± 1.26
10.3	6-methyl-5-hepten-2-one	1.79 ± 0.83	1.06 ± 0.39	1.16 ± 0.05	0.18 ± 0.03
10.6	3-hydroxy-2-butanone	0.00 ± 0.00	1.25 ± 0.19	0.28 ± 0.09	0.00 ± 0.00
10.9	1-hydroxy-2-propanone	7.18 ± 0.39	12.5 ± 1.33	4.63 ± 1.07	0.23 ± 0.09
12.7	1-(2-furanyl)-ethanone	0.27 ± 0.05	1.18 ± 0.18	0.44 ± 0.08	0.00 ± 0.00
15.7	2(5)-furanone	0.87 ± 0.52	4.91 ± 0.81	0.37 ± 0.06	0.00 ± 0.00
23.6	Hydroquinone	0.00 ± 0.00	0.27 ± 0.03	0.00 ± 0.00	0.37 ± 0.11
18.5	Furyl hydroxymethyl ketone	4.39 ± 0.98	4.02 ± 0.56	3.54 ± 0.95	1.88 ± 0.33
	Total ketons	**17.58**	**26.56**	**12.02**	**19.84**
21.0	Phenol	0.8 ± 0.03	3.5 ± 0.62	1.89 ± 0.28	0.00 ± 0.00
	Others	**1.430**	**1.24**	**5.99**	**0.43**

* R.T.: Retention time.

(2011) identified 21 fatty acids in *V.opulus* seeds. The highest fatty acids were oleic (51.74 %) and linoleic (31.33 %) acids in seeds. Yusunova et al. (1998) reported that *V. opulus* seeds contained 49.50 % of 18:2 linoleic acid.

In fruits, PUFAs were shown to predominate over SFAs and MUFAs (Bastos et al., 2015). As shown in Table 1, all tested fruits contained UFAs > SFAs. The highest SFA content was found in Gümüşhane sample (18.14 %), while the lowest content was detected in Sivas (13.46 %). Palmitic acid was the major SFA in fruits. Unlike SFA, the highest UFA content was determined in Sivas sample (87.01 %), while the lowest content was identified in Gümüşhane sample (82.26 %). Oleic acid was found to be the major UFA, and its levels varied from 61.21–67.09 %.

Information on the profiles of volatiles is limited to *V. opulus* fruit. We used HS and Im-SPMEGC/MS to identify the volatiles. The aroma compounds in *V. opulus* fruits growing in the cities of Gumüşhane, Kayseri, Ardahan and Sivas are shown in Table 2. We have identified 23 volatile compounds at 28°C in *V. opulus* fruits which included acids, alcohols, aldehydes, ketones, esters, fenols and terpenoids. Quantitatively, the major compound in the Ardahan sample was phenol (38.9 %), in the Kayseri sample, was 3-methyl-butanoic acid (38.1 %), in the Sivas sample was ethyl acetate (42.93 %) and in the Gümüşhane sample, was 2-octanol (36.01 %). No aldehydes and alcohols could be detected in the Sivas sample and ketones were not found in the Ardahan sample. 35 volatile compounds were identified in HP-SPME/GC/MS at 40°C. As shown in Table 2, the main volatile compound in Ardahan, Kayseri and Sivas samples were 3-methyl-butanoic acid (49.97, 33.74 and 28.73 %), in Gümüşhane sample was 2-octanol (31.97 %). Terpenoid was not found in Sivas and Gümüşhane samples.

We have identified 44 volatile compounds at 28°C in fruits. The major compounds in Ardahan Kayseri and Sivas samples were 3-methyl-butanoic acid (25.89 %, 18.56 %, 16.46 %) and acetic acid (19.25 %, 21.55 %, 16 %), in Gümüşhane sample was 2-octanol (47.33 %) and 2-octanone (16.68 %). No esters and phenol could be detected in Gümüşhane sample. 38 volatile compounds were identified at 40°C. Similar at 28°C, the main volatile compound in Ardahan, Kayseri and

Table 5
The aroma compounds (%) in *V.opulus* fruits by Im/SPME/GC/MS technique at 40°C.

R.T*		Ardahan	Kayseri	Sivas	Gümüşhane
11.1	Nonanal	1.25 ± 0.51	0.33 ± 0.06	1.11 ± 0.17	4.24 ± 0.93
12.1	Furfural	2.35 ± 0.70	1.96 ± 0.51	4.06 ± 0.20	2.30 ± 0.72
16.3	2,5-dimethyl-benzaldehayde	0.00 ± 0.00	0.00 ± 0.00	0.68 ± 0.08	0.88 ± 0.52
18.0	2.5-furandicarboxaldehyde	1.41 ± 0.44	0.00 ± 0.00	0.24 ± 0.02	0.00 ± 0.00
23.0	Hydroxymethylfurfural	3.35 ± 0.46	1.61 ± 0.29	6.96 ± 1.10	0.98 ± 0.10
24.3	Dodecanal	1.91 ± 0.33	1.59 ± 0.65	2.50 ± 0.29	0.00 ± 0.00
	Total aldehydes	**10.27**	**5.49**	**15.55**	**8.40**
2.0	Sinapic acid	3.30 ± 0.91	0.00 ± 0.00	3.89 ± 0.38	1.97 ± 0.74
3.3	Formic acid	1.95 ± 1.73	3.30 ± 1.72	3.55 ± 0.63	0.45 ± 0.08
9.8	3-amino-2-3-dihydrobenzoic acid	1.16 ± 0.07	0.00 ± 0.00	0.52 ± 0.25	0.00 ± 0.00
11.9	Acetic acid	13.75 ± 1.02	13.57 ± 2.31	19.27 ± 1.15	7.59 ± 0.99
14.0	3-methyl-butanoic acid	32.91 ± 1.16	19.98 ± 2.22	20.82 ± 1.36	19.3 ± 1.7
14.8	2-methyl-2-propenoic acid	1.45 ± 0.61	1.29 ± 0.23	0.77 ± 0.34	0.00 ± 0.00
15.9	3-methyl-pentanoic acid	3.29 ± 1.08	2.33 ± 0.67	1.46 ± 0.49	0.16 ± 0.08
16.8	Pentanoic acid	0.00 ± 0.00	0.00 ± 0.00	0.43 ± 0.08	0.38 ± 0.07
17.6	Hexanoic acid	2.56 ± 0.03	0.80 ± 0.38	0.27 ± 0.47	0.72 ± 0.10
17.8	Heptanoic cid	0.18 ± 0.02	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
18.6	octanoic acid	0.65 ± 0.06	2.09 ± 0.84	0.94 ± 0.16	2.12 ± 0.38
19.6	Nonanoic acid	2.68 ± 0.74	2.58 ± 0.81	2.40 ± 0.78	10.4 ± 0.17
20.6	N-decanoic acid	1.18 ± 0.51	1.35 ± 0.16	1.50 ± 0.33	2.78 ± 0.91
22.4	Dodecanoic acid	0.33 ± 0.06	1.10 ± 0.25	1.16 ± 0.23	0.41 ± 0.04
22.9	1.2-benzenedicarboxylic acid	2.14 ± 0.25	1.29 ± 0.13	2.79 ± 0.59	0.45 ± 0.08
24.1	Tertradecanoic acid	1.15 ± 0.22	1.81 ± 0.62	1.21 ± 0.07	0.24 ± 0.02
	Total acids	**68.68**	**51.49**	**60.98**	**46.97**
2.2	Ethyl acetat	0.81 ± 0.41	0.00 ± 0.00	3.71 ± 0.46	2.53 ± 0.34
24.9	Octyl 4-methoxycinnamate	0.00 ± 0.00	1.66 ± 0.67	0.00 ± 0.00	0.18 ± 0.02
	Total esters	**0.81**	**1.66**	**3.71**	**2.71**
3.3	Ethanol	0.00 ± 0.00	3.85 ± 0.46	0.98 ± 0.18	1.68 ± 0.22
8.4	2-hexanol	0.00 ± 0.00	0.65 ± 0.13	0.00 ± 0.00	0.00 ± 0.00
8.7	3-methyl-1-butanol	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	1.46 ± 0.27
10.0	Carveol	0.50 ± 0.03	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
11.8	2-furanmethanol	0.93 ± 0.14	0.52 ± 0.10	0.88 ± 0.11	0.00 ± 0.00
12.0	2-octanol	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	24.1 ± 1.01
	Total alcohols	**1.43**	**5.02**	**1.86**	**27.24**
7.6	2(3 H)furanone	2.86 ± 0.27	1.67 ± 0.76	0.69 ± 0.07	0.48 ± 0.09
9.5	2-octanone	0.65 ± 0.13	0.00 ± 0.00	0.68 ± 0.17	7.01 ± 1.17
10.9	1-hydroxy-2-propanone	7.57 ± 0.60	10.1 ± 1.63	5.66 ± 0.98	0.00 ± 0.00
12.7	1-(2-furanyl)-ethanone	0.52 ± 0.10	0.25 ± 0.04	0.43 ± 0.04	0.16 ± 0.02
15.7	2(5)-furanone	1.44 ± 0.64	1.34 ± 0.32	0.00 ± 0.00	0.00 ± 0.00
18.5	Furyl hydroxymethyl ketone	4.85 ± 0.25	0.00 ± 0.00	4.81 ± 0.25	3.32 ± 1.29
23.6	Hydroquinone	0.00 ± 0.00	0.20 ± 0.05	0.00 ± 0.00	0.85 ± 0.15
	Total ketons	**18.05**	**13.56**	**12.27**	**11.82**
23.2	Phenol	0.47 ± 0.05	15.86 ± 0.84	4.71 ± 0.08	0.96 ± 0.05
	Others	**0.29**	**6.92**	**0.92**	**1.9**

* R.T.: Retention time.

Sivas samples 3-methyl-butanoic acid (32.91, 19.98, 20.82 %), in Gümüşhane sample was 2-octanol (24.1 %) (Table 3).

While 2 aldehydes, 3 esters, 9 acids, 4 alcohols, 4 ketones, and 1 phenol were identified by HS-SPME/GC–MS at 28°C, 6 aldehydes, 3 esters, 17 acids, 7 alcohols, 10 ketones and 1 phenol were identified by Im-SPME/GC–MS at 28°C. At 40°C, we identified 3 aldehydes, 3 esters, 11 acids, 11 alcohols, 6 ketones, 1 phenol and 1 terpenoid by HS-SPME/GC–MS, and 6 aldehydes, 2 esters, 16 acids, 6 alcohols, 7 ketones and 1 phenol by Im-SPME/GC–MS. The Im-SPME/GC–MS technique allowed the identification of a larger number of volatile compounds and thus is more efficient than the HS-SPME/GC–MS technique. As far as we know, volatile compounds in fruits of *V. opulus* were determined using HS-SPME/GC–MS in only one study (Kraujalyte et al., 2012) and no research has been previously performed by Im-SPME/GC–MS. The researchers found 41 volatile compounds in *V. opulus* fruits by HS-SPME/GC–MS. They identified 1 acid, 3 branched fatty acids, 13 alcohols, 4 aldehydes, 6 ketones, 4 esters and 10 terpenoids, and reported that the main volatile compounds present in samples were 3-methyl-butanoic acid, and 2- octanone (Tables 4 and 5). *V. opulus* fruits emit some displeasing odors. The odor of 3-methylbutanoic acid was described as smelling like “dirty socks” or “old cheese”. Unlike our findings, terpenoids identified in fruits consisted of a-terpinene, p-cymene, limonene, a-terpineol, 1,8-cineole, linalool, trans-linalool oxide and the bicyclic sesquiterpene beta-caryophyllene. Only 24 compounds identified in our study have been previously reported to be present in *V. opulus* fruits. The new 20 compounds (2,5-dimethyl-benzaldehayde, Decanal, Trans-2,3-Dimethoxycinnamic acid, Pentanoic acid, Hexanoic acid, 2-ethyl-Hexanoic acid, Octanoic acid, Formic acid, Nonanoic acid, n-decanoic acid, 1.2-benzenedicarboxylic acid, 2-nonanol, 1,2-decanediol, Carveol, 4-methyl-1-Heptanol, 1-butanol, Ionone, Dihydropseudionone, 2(3 H) furanone and Phenol) have been determined for the first time in *V. opulus* fruits. Of the compounds detected by Im-SPME/GC–MS, 30 compounds have not been previously reported in the literature. Yilmaz et al. (2008) discovered that the main volatile compounds in the essential oil of dried *V.opulus* were phytol, trans-b-damascenone, a-cadinal and c-cadinene. Yilmaztekin and Sislioglu (2015) examined volatile compounds of *V.opulus* fruits after traditional fermentation. The researchers identified 58 volatile compounds in fermented fruits. They included acids (10), alcohols (27), aldehydes (3), esters (3), ketones (12), and lactones (3). They also reported that 3-methyl-butanoic acid was the major compound and the total volatile components was increased in first month of fermentation and then decreased. The formation of compounds and their content in fruits depends on various factors, such as genotypic differences, environmental conditions (climate, temperature, soil) and cultivation practices (Yang et al., 2009).

4. Conclusion

In the present study, the fatty acid and volatile contents of *V.opulus* fruits were determined. Ardahan samples had the lowest lipid content, while Gümüşhane sample had the highest lipid content. Ten fatty acids have been identified and quantified. The major fatty acids were oleic, linoleic and palmitic acids, and all of the fruits contained UFAs > SFAs. We used HS and Im-SPMEGC/MS at different temperatures (28 and 40°C) to identify the volatiles even though there were some differences between the compounds identified using these two methods. 23 and 35 compounds which included acids, alcohols, aldehydes, ketones, esters, fenols and terpenoid were identified by the HS-SPME/GC–MS technique, and 44 and 38 compounds were detected by the Im-SPME/GC–MS technique at 28 and 40°C. Of the compounds detected, 30 have not been previously reported in the literature for *V.opulus* fruit. 3-methylbutanoic acid, ethyl acetate, 2-octanol and phenol were the main volatile compounds. Terpenoids were not found in the Sivas and Gümüşhane samples. The application of both fractionation methods to the *V.opulus* fruits showed that the Im-SPME/GC–MS method provided more chemical species when compares with compounds elucidated using HS-SPME/GC–MS. The differences between samples could be due to variation between environmental conditions and altitude. These results are important for further studies, especially those pertaining to breeding and cultivation.

CRediT authorship contribution statement

Mozhgan Zarifikhosroshahi: Conceptualization, Methodology, Software. **Zehra Tugba Murathan:** Data curation. **Ebru Kafkas:** Conceptualization, Methodology, Software. **Volkan Okatan:** Writing - review & editing.

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