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ORIGINAL ARTICLE

Effect of harvest time on physico-chemical properties and bioactive compounds of pulp and seeds of grape varieties

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Abstract In this study, physicochemical properties and bioactive compounds of three grape varieties (Cardinal, Müşküle and Razaki) harvested at the three different harvest times (on time, one and two weeks earlier) were investigated. The highest antioxidant activity, total phenolic and flavonoid contents were observed in Razaki pulp and these were 82.854%, 127.422 mg/100 g, 3.873 mg/g, respectively. The contents of bioactive compounds in grape seeds were found higher than those in pulps. Similarly, seed of Razaki had higher antioxidant activity (91.267%) and total phenolic content (477.500 mg/100 g) when compared to results of other varieties. The key phenolic compounds of all grape variety and seeds were gallic acid, 3,4-dihydroxybenzoic acid, (+)-catechin ve 1,2-dihydroxybenzene. The oil content of grape seeds ranged from 8.50% (Razaki harvested one week ago) to 19.024% (Müşküle harvested one week ago). The main fatty acids of grapeseed oils were linoleic, oleic and palmitic acids. In addition, the oil of Razaki seeds was rich in tocopherols when compared to the other varieties.

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Keywords Grape · Bioactive compounds · Antioxidant · Fatty acid composition · Harvest time

Introduction

Harvest at the most appropriate stage of ripening is crucial for optimum quality of grape with respect to some physicochemical and sensory properties, and maturity of grape begins at the moment of veraison and continues until the harvest (Piazzolla et al. 2015). Some changes such as accumulation of secondary metabolites occur in fruit during the ripening process. The optimum proportion of sugar-acid shows pulp maturity. Skin maturity is provided with the maximum level of some aroma components and phenolic compounds (Pena-Neira et al. 2004). Grapes (*Vitis vinifera* L.) are significant sources of natural antioxidants such as phenolic compounds. Environmental and geographical factors, and variety affect on the amounts of phenolics of grape fruits (Yang et al. 2009). In recent years, determination of natural antioxidants has been drawn attention because of free radical damage (Nawaz et al. 2006; Shaker, 2006; Yalcin et al. 2016). Grapes, contain a great quantity of phenolic substances in skins, pulp and seeds. Therefore, grapes have the importance for health protective effects (Yılmaz et al. 2014). The aim of present work was to determine and compare the effect of both variety and harvest time on several physicochemical properties (^{o}Brix, titratable acidity, maturation index, total dry matter, mineral content) and bioactive compounds (antioxidant activity, total phenolic and flavonoid contents, phenolic compounds, fatty acid composition and tocopherol content) of grape pulp and seeds.

Materials and methods

Material

The grape fruits used for the experiment were freshly harvested from vineyard garden of Viticulture Research Institute of Tekirdağ in Turkey. The experiment consisted of two factors like maturity stages and different postharvest treatments. The experiment was conducted in the laboratories of the Department of Food Engineering, Faculty of Agriculture, Selçuk University. Pulp and seeds of table grapes were obtained from Viticulture Research Institute of Tekirdağ in Turkey. 3 kg of random grape samples were harvested at three different harvest date. Grapes were brought to the laboratory in cool bag and cut from middle using knife. Pulp + skin (seedless parts) and seeds were separated manually. Cleaned grape seeds were dried in an oven at 40°C until constant weight. Seeds were stored at +4 °C; parts of pulp and skin were frozen at −80 °C until analysis.

Methods

Sample extraction

Phenolic compounds and antioxidants were extracted according to Gomez-Alonso et al. (2007) with some modifications. 2 g of ground samples were added to 15 ml mixture of methanol: water: formic acid (5:4.85:1.5, v/v). The mixture was homogenised using a blender for 2 min and kept in rinsing water-bath for 1 h, followed by centrifugation at 4500 rpm for 15 min. and then the supernatant was collected, and injected. Prior to injection, the extract was filtered through a 0.45 µm nylon filter. All analyses were carried out in triplicate.

Physico-chemical analysis

^{0}Brix, titratable acidity, maturation index and total dry matter were analysed according to Cemeroğlu (1992).Percent dry matter content of the grape pulp was calculated from the data obtained during moisture estimation using the following formula: % dry matter = 100 − % moisture content.

Total phenolic content

Total phenol contents of extracts were determined by using the Folin–Ciocalteu (FC) method as reported by Yoo et al. (2004). 1 ml of FC reagent was added and mixed for 5 min. Afterwards, 10 ml of Na_2CO_3 was added into mix, the final volume was completed to 25 ml with distilled water. After 1 h, sample was measured in 750 nm in spectrophotometer. The results were given as mg GAE/100 g.

Antioxidant activity

The antioxidant activity values of grape pulp and seed extracts were determined using DPPH (1,1-diphenyl-2-picrylhydrazyl) method according to Lee et al. (1998). The extract was mixed with 2 ml methanolic DPPH solution, and the mixture was shaken, and kept at room temperature for 30 min. The absorbance was measured at 517 nm by using a spectrophotometer. All determinations were performed in triplicate.

Determination of phenolic compounds

Phenolic compounds were determined by Shimadzu-HPLC equipped with PDA detector and Inertsil ODS-3 (5 µm; 4.6 × 250 mm) column. As mobile phases, 0.05% acetic acid in water (A) and acetonitrile (B) mixture were used. The flow rate of the mobile phase and the injection volume were 1 ml/min at 30 °C and 20 µl, respectively. The peak records were carried out at 280 and 330 nm. The total running time for each sample was 60 min. The analysis was carried out according to gradient elution program in order to determine the profile of phenolic substances.

HPLC Conditions are as shown below,

Colonm: ODS-3 (5 µm; 4.6 × 250 mm)
Flow rate: 1 ml/min.
Wave length: 278 nm
Control system: SCL-10A VP- SHIMADZU
Dedector: SPD-M10Avp diode arrray dedectör - SHIMADZU
Degazör: DGU-14A- SHIMADZU
Colonm oven: CTO-10 AVP-SHIMADZU
Program: Class-VP, 5.0 (Software)

Total flavonoid content

Total flavonoid content of samples was determined using colorimetric method (Hogan et al. 2009). Methanol extracts were properly diluted with distilled water. 5% $NaNO_2$ solution was added to each test tube; after 5 min, 10% $AlCl_3$ solution was added and then after 6 min 1.0 M NaOH was added. Finally total volume was filled up to 5 ml with water and the test tubes were mixed well. Absorbance of the resulting pink-colored solution was measured at 510 nm versus blank.

Mineral content

Grape pulp and seed samples were dried at 70 °C in a drying cabinet with air-circulation until they reached constant weight. Later, about 0.5 g dried and ground sample was digested by using 5 ml of 65% HNO_3 and 2 ml of 35% H_2O_2 in a closed microwave system (Cem-MARS Xpress) at 200 °C. The volumes of the digested samples were completed to 20 ml with ultra-deionized water and mineral concentrations were determined by inductively coupled plasma-optical emission spectroscopy (ICP-AES; (Varian-Vista, Australia). The heavy metal contents of the samples were quantified against standard solutions of known concentrations which were analysed concurrently (Skujins 1998).

Working conditions of ICP-AES Instrument is ICP-AES (Varian-Vista), and its RF Power is 0.7–1.5 kw (1.2–1.3 kw for axial). Plasma and Auxilary gas flow rates (Ar) are 10.5–15 l/min. (radial) 15 "(axial) and 1.5", respectively. Viewing height is 5–12 mm. Reading and Copy times are 1–5 s (max. 60 s) and 3 s (max. 100 s), respectively.

Oil content

Oil contents of grape seed samples were determined according to AOAC (1990) method. Total oil content of grape seed was extracted with petroleum benzine in Soxhlet Apparatus for 5 h and the solvent was removed with a rotary vacuum evaporator at 50 °C.

Fatty acid composition

Fatty acid methyl esters of Grape seed oil esterificated according to ISO-5509 (ISO 1978) method were analysed using gas chromatography (Shimadzu GC-2010) equipped with flame-ionization detector (FID) andcapillarycolumn (Tecnocroma TR-CN100, 60 m × 0.25 mm, film thickness: 0.20 μm). The temperature of injection block and detector was 260 °C. Mobile phase was nitrogen with 1.51 ml/min flow rate. Total flow rate was 80 ml/min and split rate was also 1/40. Column temperature was programmed 120 °C for 5 min and increased 240 °C at 4 °C/min and held 25 min at 240 °C. Commercial mixtures of fatty acid methyl esters were used as reference data for the relative retention times (AOAC 1990).

Tocopherol content

Tocopherol content of grape seed oil was performed according to Spika et al. (2015). 0.1 g of oil was dissolved in 10 ml of *n*-hexane and filtered through a 0.45 μm nylon fitler. HPLC analyses of tocopherols were determined using Shimadzu-HPLC equipped with PDA detector and LiChroCART Silica 60 (4.6 × 250 mm, 5μ; Merck, Darmstadt, Germany) column. Tocopherols were separated by isocratic chromatography using a mobile phase of 0.7% propan-2-ol in *n*-hexane. The flow rate of the mobile phase was 0.9 ml/min, and the injection volume was 20 μl. The peaks were recorded at 295 and 330 nm with PDA detector. The total running time per sample was 30 min. Standard solutions of tocopherols (α, β, γ and δ-tocopherol) were constructed in the concentrations of 0–100 mg/l (Balz et al. 1992).

Statistical analyses

A complete randomized split plot block design was used. Analysis of variance (ANOVA) test was performed using JMP software, version 9.0 (SAS Inst. Inc., Cary, N.C.U.S.A). The results are mean ± standard deviation (MSTAT C) of three independent grape samples (Püskülcü and İkiz 1989).

Results and discussion

Physico-chemical properties (^{0}Brix of pulp, total dry matter of seed, titratable acidity, maturation index and harvest date) of grape varieties are given in Table 1. The highest ^{0}Brix content was found in Razaki (19.70%). ^{0}Brix of samples, harvested early, was lower than samples harvested on time. The results of titratable acidity ranged from 4.10 to 7.80 g/l. The highest titratable acidity was determined for Razaki (harvested two weeks ago, while the minimum value was found in Müşküle (harvested on time). The titratable acidity, which was higher in samples harvested early, showed a decrease as the harvest time approached. Maturation index of grape varieties in harvest time varied from 18.10 (in Cardinal) to 44.40 (in Müşküle). Maturation indexs of Cardinal, Müşküle and Razaki varieties which harvested early were 24.30, 30.60 and 25.10 (harvested one week earlier); 18.10, 24.80 ve 19.20 (harvested two weeks earlier), respectively. While the highest dry matter is found in Razaki (66.18%), the lowest dry matter was determined in Cardinal (46.84%) variety. A decrease was observed in total dry matter contents of grape seeds with early harvest, similar to ^{0}Brix content of grape varieties. There were statistically significant differences between ^{0}Brix values of grape varieties depending on harvesting time. While the titrable acidity of the samples increased, the ripening index and the total dry matter content decreased and statistically significant differences were detected between variety and harvesting time ($p < 0.05$).

Antioxidant activity, total phenol and flavonoid contents of grape pulp and seed samples are presented in Table 2. Antioxidant activity of samples varied between 38.658 and 82.854%. According to harvest time, the highest antioxidant activity was observed in Razaki when harvested one week earlier (82.854%), followed by Müşküle (harvested two weeks earlier) (70.554%) and Cardinal (harvested one week ago) (61.342%). According to results of total phenolic contents of grape samples, Razaki variety, harvested one week earlier, had the highest total phenolic content (127.422 mg GAE/100 g), followed by Müşküle, harvested two weeks ago (93.516 mg GAE/100 g). The results revealed that early harvest caused a change in total phenolic contents of samples. The changes were similar to antioxidant activity of grape samples. Total flavonoid contents of grape varieties ranged from 0.854 to 3.873 mg/g. The increase and decrease in flavonoid contents were closed each other and in accordance with total phenolic

Table 1 Some properties of grape varieties

Grape varieties	Harvest date	Brix (pulp, %)	Titratable acidity (g/l)	Maturation index	Total dry matter (seed, %)
Cardinal*	17.08.15	15.20 ± 0.56****a	5.30 ± 0.45c	29.00 ± 1.28a	51.55 ± 1.17a
Cardinal**	10.08.15	14.20 ± 0.98b*****	5.90 ± 0.87b	24.30 ± 1.33b	49.03 ± 0.98b
Cardinal***	03.08.15	13.20 ± 1.13c	7.30 ± 0.58a	18.10 ± 1.56c	46.84 ± 0.75c
Müşküle*	29.09.15	18.30 ± 1.21a	4.10 ± 0.64c	44.40 ± 2.45a	64.83 ± 0.58a
Müşküle**	21.09.15	16.50 ± 0.67b	5.40 ± 0.71b	30.60 ± 3.69b	63.38 ± 0.73b
Müşküle***	14.09.15	15.60 ± 0.93c	6.30 ± 0.83a	24.80 ± 2.17c	61.25 ± 0.84c
Razaki*	01.09.15	19.70 ± 0.69a	5.90 ± 0.88c	33.70 ± 1.18a	66.18 ± 0.58a
Razaki**	24.08.15	17.60 ± 0.71b	7.00 ± 0.61b	25.10 ± 1.23b	59.48 ± 0.47b
Razaki***	17.08.15	15.00 ± 0.88c	7.80 ± 0.92a	19.20 ± 1.56c	54.21 ± 0.65c

* Harvest; ** harvested one week ago; *** harvested two weeks ago; **** each value is expressed as mean ± standard deviation; ***** values in each column with different letters are significantly different ($p < 0.05$)

Table 2 Antioxidant activity, total phenolic and total flavonoid contents of grape pulp and seeds

Grape varieties (pulp)	Antioxidant activity (%)	Total phenolic content (mg/100 g)	Total flavonoid content (mg/g)
Razaki*	60.011 ± 0.015****c	80.313 ± 0.015b	1.723 ± 0.002b
Razaki**	82.854 ± 0.004a*****	127.422 ± 0.014a	3.873 ± 0.003a
Razaki***	63.525 ± 0.002b	79.766 ± 0.005c	1.798 ± 0.002b
Müşküle*	68.850 ± 0.006b	89.375 ± 0.017b	2.235 ± 0.002a
Müşküle**	48.190 ± 0.002c	59.844 ± 0.027c	1.148 ± 0.001b
Müşküle***	70.554 ± 0.003a	93.516 ± 0.027a	2.454 ± 0.002a
Cardinal*	38.658 ± 0.009c	50.000 ± 0.018c	0.854 ± 0.001c
Cardinal**	61.342 ± 0.005a	80.156 ± 0.022a	2.248 ± 0.002a
Cardinal***	53.727 ± 0.006b	72.266 ± 0.017b	1.666 ± 0.003b

Grape seed varieties	Antioxidant activity (%)	Total phenolic content (mg/100 g)	Total flavonoid content (mg/g)	Oil content (%)
Razaki*	89.830 ± 0.0000c	474.063 ± 0.037b	155.873 ± 0.020b	10.800 ± 0.200b
Razaki**	91.267 ± 0.001a	477.500 ± 0.026a	152.123 ± 0.004c	8.500 ± 0.100c
Razaki***	90.522 ± 0.002b	456.563 ± 0.036c	161.706 ± 0.001a	11.100 ± 0.500a
Müşküle*	85.836 ± 0.004b	470.000 ± 0.034b	91.984 ± 0.002c	18.970 ± 0.830b
Müşküle**	88.019 ± 0.001a	475.300 ± 0.022a	96.984 ± 0.002b	19.024 ± 0.024a
Müşküle***	84.878 ± 0.003c	460.313 ± 0.024c	99.761 ± 0.009a	17.719 ± 0.119c
Cardinal*	90.948 ± 0.000b	464.063 ± 0.029b	155.956 ± 0.014a	14.784 ± 0.584b
Cardinal**	90.149 ± 0.000b	473.750 ± 0.012a	138.095 ± 0.006c	15.347 ± 0.747a
Cardinal***	91.054 ± 0.001a	461.563 ± 0.021c	147.539 ± 0.003b	14.762 ± 0.362b

* Harvest; ** harvested one week ago; *** harvested two weeks ago; **** each value is expressed as mean ± standard deviation; ***** values in each column with different letters are significantly different ($p < 0.05$)

content and antioxidant contents of grape samples. In addition to pulp of grapes, antioxidant activity, total phenolic and total flavonoid contents of grape seeds were determined and are shown in Table 2. Antioxidant activities of seeds were determined between 84.878 and 91.267%, and these values were found higher than results of grape pulp. Razaki (harvested one week ago) and Cardinal (harvested two weeks ago) varieties had the greatest amount of antioxidant activities, with the proportion of 91.267 and 91.054%, respectively. Total phenolic contents of grape seeds ranged from 456.563 to 477.500 mg GAE/100 g and were higher than 400 mg GAE/100 g in all of seed varieties. Total flavonoid contents of grape seeds were considerably high compared the pulp of grapes and found between 91.984 and 161.706 mg/g. Razaki and Cardinal were significant source of flavonoids with maximum contents. Therefore, grape seeds had rich bioactive substance and were good for health. Antioxidant activity, total phenol and flavonoid (except seed) values of grape pulp were found to be statistically significant differences depending on harvesting time. Statistically significant differences were found between naringenin and kaempferol contents of rape pulp harvested one and second week ago ($p < 0.06$). In the experiments reported by Obreque-Slier et al. (2010), total phenolic contents of Carmenere and Cabernet Sauvignon grape skins ranged from 110 to 290 mg GAE/100 g; from 80 to 180 mg GAE/100 g, respectively. Total phenolic contents of grape seeds varied from 1000 to 2250 mg GAE/100 g; from 850 to 2040 mg GAE/100 g, respectively. Total phenolic content increased with early harvest. According to study of Anjelkovic et al. (2013), the maximum radical scavenging activity was determined in seed (from 77.73 to 82.22%), followed by skin (from 49.04 to 68.12%) and pulp (from 21.96 to 36.24%). Antioxidant activity of seeds and pulp increased during ripening period and the highest radical scavenging activity was observed at 40th day after veraison. In addition, total phenolic content of grape seed and pulp showed increase during grape maturity and also reduced relatively from 40th day after veraison. According to the oil contents of grape seeds, the highest oil content was determined in Müşküle variety (17.719–19.024%), while seeds of Razaki variety (8.500–11.100%) had the lowest oil content. Oil content was effected from harvest time as other results. The maximum oil contents of Müşküle and Cardinal varieties were observed in samples harvested one week earlier. In Razaki variety, oil content was higher in samples harvested two weeks earlier.

Phenolic compounds of grape pulp and seed are shown in Table 3. Generally, dominant phenolic compounds of all varieties harvested on time were gallic acid, 3,4-dihydroxybenzoic acid, (+)-catechin and 1,2-dihydroxybenzene. Early harvest of Razaki, Müşküle and Cardinal varieties caused some changes in phenolic compounds. The results demonsrated that early harvest (one week) in Razaki variety provided an increase in (+)-catechin content, but caused a decrease in 1,2-dihydroxybenzene content. There was an increase in gallic acid, (+)-catechin and ferullic acid contents when samples were harvested two weeks earlier. In Müşküle variety, early harvest (one week) was significantly decreased the dominant phenolics. In Cardinal variety, an increase in gallic acid, (+)-catechin and 1,2-dihydroxybenzene contents was observed, while a decrease in content of 3,4-dihydroxybenzoic acid is found with early harvest.

Phenolic compounds of grape seeds were determined as significantly high in comparison with pulp of grapes. The highest gallic acid (40.496 mg/100 g) and (+)-catechin (768.751 mg/100 g) contents of Razaki seeds were found when harvested two weeks earlier, while gallic acid (59.336 mg/100 g) and (+)-catechin (85.457 mg/100 g) contents were determined the maximum in Müşküle seeds when harvested on time. In all grape varieties, Cardinal (harvested two weeks earlier) had the greatest gallic acid (216.165 mg/100 g) and trans-ferulic acid (426.080 mg/100 g) contents. Additionally, harvesting one week earlier significantly increased the amount of 1,2-dihydroxybenzene (848.063 mg/100 g). There were no statistically significant differences in trans-cinnamic acid and kaempferol contents of Cardinal grape seed harvested one and two weeks earlier. Phenolic compounds were considerably impressed from harvest time. Dominant phenolics of Carmenere and Cabernet Sauvignon grape varieties skins were gallic acid (2.1–3.4; 1.5–3.5 mg/kg), (+)-catechin (1.3–3.1; 0.5–5.1 mg/kg), syringic acid (1.0–3.1; 0.7–1.8 mg/kg) during ripening (Obreque-Slier et al. 2010). Gallic acid contents of grape seeds during ripening varied between 37.7 and 220 mg/kg; 36.9 and 113.2 mg/kg, respectively (Obreque-Slier et al. 2010).

Fatty acid compositions of grape seed oil samples are shown in Table 4, and dominant fatty acids were linoleic, oleic, palmitic and stearic acids. It could be concluded that grape seeds are good source of essential fatty acids especially linoleic acid (64.532–73.571%). Oleic acid content ranged from 13.959 to 19.366%. The content of palmitic and stearic acids of grape seed oil changed between 6.233 and 9.797%; 3.558 and 5.435%, respectively. Besides, linolenic acid content of seed oil was determined below 1%. Fatty acid profile of Müşküle variety was not significantly affected by early harvest. However, early harvest (one week) caused a minor decrease in linoleic acid content and increase in oleic acid content of Razaki variety. Contrary to this, in Cardinal variety, it was found that linoleic acid content was higher and oleic acid content was also lower when samples were harvested early. There was no statistically significant difference between linoleic acid

Table 3 Phenolic compounds of grape pulp

Phenolic compounds of pulp (mg/100 g)	Razaki*	Razaki**	Razaki***	Müşküle*	Müşküle**
Gallic Acid	38.828 ± 0.295****b	37.715 ± 0.627c	48.951 ± 1.020a	43.352 ± 1.115b	12.554 ± 0.324c
3.4-Dihydroxybenzoic acid	45.806 ± 0.102b*****	54.681 ± 0.066a	35.830 ± 0.747c	47.454 ± 0.840b	5.741 ± 0.479c
(+)-Catechin	56.056 ± 1.430c	76.081 ± 0.588a	61.075 ± 1.466b	63.767 ± 0.150a	3.535 ± 0.330c
1.2-Dihydroxybenzene	58.547 ± 2.116a	32.918 ± 0.592c	53.921 ± 0.143b	47.227 ± 0.704a	3.878 ± 0.215c
Syringic acid	15.726 ± 0.092c	17.307 ± 0.861b	18.399 ± 0.381a	17.426 ± 0.151a	0.914 ± 0.081b
Caffeic acid	12.712 ± 0.049b	10.125 ± 0.082c	13.173 ± 0.049a	16.278 ± 0.115a	1.855 ± 0.218b
Rutin trihidrate	16.926 ± 0.034a	14.521 ± 0.227b	16.636 ± 0.488a	9.638 ± 0.420a	0.967 ± 0.090c
p-Coumaric acid	1.323 ± 0.021c	1.874 ± 0.091b	1.906 ± 0.073a	1.234 ± 0.085a	0.205 ± 0.011b
trans-Ferulic acid	9.724 ± 0.256b	6.324 ± 0.143c	20.304 ± 0.349a	6.854 ± 0.410a	1.160 ± 0.063c
Apigenin 7 glukozid	9.573 ± 0.317c	11.904 ± 0.158b	12.223 ± 0.086a	13.561 ± 0.214a	0.706 ± 0.045c
Resveratrol	3.973 ± 0.152a	3.975 ± 0.084a	3.840 ± 0.122b	2.885 ± 0.191a	1.180 ± 0.018b
Quercetin	12.765 ± 0.045b	11.787 ± 0.412c	13.137 ± 0.033a	10.247 ± 0.683a	6.963 ± 0.064b
trans-Sinnamic acid	2.618 ± 0.165a	2.175 ± 0.060c	2.481 ± 0.150b	2.118 ± 0.167c	2.365 ± 0.042b
Naringenin	3.871 ± 0.000a	2.774 ± 0.237b	2.158 ± 0.000b	0.922 ± 0.000c	10.997 ± 0.222a
Kaempferol	12.149 ± 0.035a	6.703 ± 0.026b	6.682 ± 0.096b	5.882 ± 0.500a	5.867 ± 0.000a
Isorhamnetin	25.293 ± 0.236a	21.629 ± 0.582c	23.579 ± 0.347b	9.336 ± 0.107a	5.906 ± 0.101c

	Müşküle***	Cardinal*	Cardinal**	Cardinal***
Gallic Acid	56.747 ± 1.323a	24.670 ± 1.066c	35.029 ± 3.657b	53.524 ± 0.150a
3.4-Dihydroxybenzoic acid	49.656 ± 0.929a	80.693 ± 0.216a	38.052 ± 2.375b	26.254 ± 0.884c
(+)-Catechin	13.669 ± 0.844b	3.139 ± 0.212c	23.553 ± 2.123a	18.733 ± 1.012b
1.2-Dihydroxybenzene	12.098 ± 0.892b	2.860 ± 0.012c	15.009 ± 1.125a	12.033 ± 0.208b
syringic acid	0.899 ± 0.038c	1.860 ± 0.020b	2.409 ± 0.006a	0.603 ± 0.023c
Caffeic acid	1.045 ± 0.021c	1.212 ± 0.089b	5.822 ± 0.880a	0.772 ± 0.039c
Rutin trihidrate	2.710 ± 0.389b	1.511 ± 0.081b	4.027 ± 0.624a	0.946 ± 0.071c
p-Coumaric acid	0.234 ± 0.022b	1.341 ± 0.210b	1.829 ± 0.284a	0.275 ± 0.012c
trans-Ferulic acid	1.242 ± 0.080b	6.759 ± 1.161a	6.295 ± 0.974b	0.869 ± 0.062c
Apigenin 7 glukozid	0.800 ± 0.066b	0.539 ± 0.028c	9.382 ± 1.346a	0.900 ± 0.058b
Resveratrol	1.114 ± 0.034c	3.706 ± 0.453a	2.874 ± 0.362b	1.343 ± 0.043c
Quercetin	3.565 ± 0.130c	5.805 ± 0.169c	6.766 ± 0.403a	6.432 ± 0.175b
trans-Sinnamic acid	2.738 ± 0.049a	3.496 ± 0.106a	3.505 ± 0.121a	2.730 ± 0.025b
Naringenin	8.673 ± 0.056b	9.008 ± 0.005b	8.981 ± 0.221c	9.227 ± 0.044a
Kaempferol	–#	–		–
Isorhamnetin	8.368 ± 0.159b	9.603 ± 0.252a	6.970 ± 0.090c	7.475 ± 0.016b

Phenolic compounds of seeds (mg/100 g)	Razaki*	Razaki**	Razaki***	Müşküle*	Müşküle**
Gallic acid	29.096 ± 1.505b	22.337 ± 0.478c	40.496 ± 0.899a	59.336 ± 2.384a	47.703 ± 2.734b
3.4-Dihydroxybenzoic acid	147.250 ± 0.430b	186.374 ± 0.735a	159.431 ± 2.434c	130.701 ± 0.366a	79.841 ± 0.162b
(+)-Catechin	761.568 ± 4.363b	243.382 ± 2.720c	768.751 ± 21.390a	85.457 ± 3.324a	71.663 ± 0.710b
1.2-Dihydroxybenzene	210.097 ± 0.961b	848.063 ± 1.512a	97.099 ± 6.327c	61.700 ± 0.669b	28.832 ± 0.085c
Syringic acid	38.321 ± 0.914c	56.325 ± 1.232a	45.453 ± 1.503b	27.295 ± 0.480c	31.177 ± 2.031
Caffeic acid	73.704 ± 1.493a	70.977 ± 0.984b	35.660 ± 1.145c	22.202 ± 0.762c	41.465 ± 1.973b
Rutin trihidrate	53.521 ± 0.458c	140.033 ± 0.309b	156.788 ± 0.324a	28.787 ± 0.648b	25.049 ± 0.291c
p-Coumaric acid	11.549 ± 0.026a	9.644 ± 0.393c	10.205 ± 0.361b	5.124 ± 0.038c	5.542 ± 0.169b
trans-Ferulic acid	54.140 ± 0.875c	111.639 ± 2.260a	69.097 ± 1.652b	47.425 ± 0.096a	41.073 ± 0.518b
Apigenin 7 glukozid	76.992 ± 3.330c	105.296 ± 2.579a	78.459 ± 1.668b	64.526 ± 2.015a	32.223 ± 0.814c
Resveratrol	12.245 ± 0.208b	9.866 ± 0.289c	14.422 ± 0.510a	10.918 ± 0.084a	10.661 ± 0.790a

Table 3 continued

Phenolic compounds of seeds (mg/100 g)	Razaki*	Razaki**	Razaki***	Müşküle*	Müşküle**
Quercetin	9.951 ± 0.481c	25.410 ± 0.539b	28.349 ± 0.111a	23.693 ± 0.605b	45.030 ± 0.400a
trans-Sinnamic acid	1.347 ± 0.163c	4.345 ± 0.161a	2.902 ± 0.155b	3.372 ± 0.114b	2.230 ± 0.117c
Naringenin	4.884 ± 0.840c	10.931 ± 0.539a	10.085 ± 0.113b	9.204 ± 0.172a	7.991 ± 0.501c
Kaempferol	1.847 ± 0.027c	21.540 ± 0.407a	13.603 ± 0.526b	10.973 ± 0.533b	9.644 ± 0.661c
Isorhamnetin	1.842 ± 0.028c	19.753 ± 0.245a	16.551 ± 1.147b	11.508 ± 0.436b	7.707 ± 0.715c

	Müşküle***	Cardinal*	Cardinal**	Cardinal***
Gallic acid	8.471 ± 0.545c	119.081 ± 1.451b	216.165 ± 0.551a	79.915 ± 4.628c
3.4-Dihydroxybenzoic acid	45.000 ± 0.320c	34.613 ± 3.713b	83.080 ± 0.124a	13.210 ± 0.807c
(+)-Catechin	66.348 ± 2.556c	48.445 ± 1.845c	67.826 ± 0.000b	154.031 ± 0.290a
1.2-Dihydroxybenzene	66.198 ± 0.720a	121.094 ± 3.467b	121.385 ± 0.000b	966.396 ± 7.258a
Syringic acid	85.365 ± 3.124a	15.076 ± 1.378c	188.310 ± 1.717a	55.719 ± 2.376b
Caffeic acid	123.506 ± 1.446a	37.710 ± 2.588c	41.353 ± 1.188b	200.934 ± 2.204a
Rutin trihidrate	33.070 ± 0.349a	38.999 ± 0.845c	51.107 ± 2.342a	44.646 ± 2.644b
p-Coumaric acid	7.379 ± 0.337a	13.640 ± 0.020a	9.985 ± 0.617c	11.534 ± 0.192b
trans-Ferulic acid	40.007 ± 1.548a	46.328 ± 0.780c	52.901 ± 0.106b	426.080 ± 1.803a
Apigenin 7 glukozid	48.219 ± 0.864b	164.161 ± 2.939a	113.338 ± 0.016b	97.803 ± 1.591c
Resveratrol	8.708 ± 0.427b	24.440 ± 0.394c	46.122 ± 1.253a	40.889 ± 0.424b
Quercetin	13.233 ± 0.140c	61.682 ± 1.604a	49.072 ± 0.423c	57.299 ± 1.526b
trans-Sinnamic acid	3.944 ± 0.072a	5.579 ± 0.205a	4.841 ± 0.155b	4.419 ± 0.188b
Naringenin	8.265 ± 0.104b	11.067 ± 0.570c	14.999 ± 0.261a	12.807 ± 0.072b
Kaempferol	14.627 ± 0.124a	17.371 ± 0.472a	13.687 ± 0.617b	13.807 ± 0.018b
Isorhamnetin	12.701 ± 0.127a	14.736 ± 1.031a	9.175 ± 0.279b	5.626 ± 0.199c

Not detected; * harvest; ** harvested one week ago; *** harvested two weeks ago; **** each value is expressed as mean ± standard deviation; **** values in each row with different letters are significantly different ($p < 0.05$)

contents of Cardinal grape seed oil harvested one and two weeks earlier. In general, statistically significant differences were found between fatty acid composition of grape seed oil depending on the harvest time and variety.According to Yoo et al. (1984), grape seed oil was mainly composed of palmitic (6.7–9.1%), oleic (13.4–20.7%) and linoleic (68.1–78.1) acids. In previous study, Riccardo and Muratore (1993) found 65.9–62.2% linoleic, 18.6–16.9% oleic, 11.6–10.7% palmitic, 3.8–3.4% stearic and 3.5–2.8% myristic acid in seed oils of red and white Italian grapes, respectively. Won Young et al. (2000) reported that linoleic, oleic, palmitic and stearic acids were main components of grape seed oil, respectively. Uslu and Dardeniz (2009) reported that grape seed cultivars contained 8.40–6.51% palmitic, 16.1–11.62% oleic, 77.59–72.50% linoleic, 3.86–3.07% stearic acids. Özcan et al. (2010) determined 4.1% palmitic, 10.4% stearic, 16.4% oleic and 69.3% linoleic acids in grape seed oil. Results related to grape seed oils were quite similar to those in literature. There is some variation, among cultivars, in terms if their fatty acid composition. Also, grape seeds can be used as a source of edible vegetable oil. It is concluded that the seeds as a by-product of grape processing industries in Turkey could be benefited for mainly edible oil and the other functional components.

The tocopherol compositions of seed oils are illustrated in Table 4. α- Tocopherol contents of seed oils ranged from 0.138 (Müşküle) to 0.213 mg/g (Razaki). The amounts of β- and γ- tocopherol were 0.116–0.191 mg/g; 0.107–0.123 mg/g, respectively. δ- tocopherol was not detected in Müşküle variety. Additionaly, Razaki variety exhibited the highest total tocopherol content, followed by Cardinal variety. Tocopherol contents of grape seed oils were found statistically significant depending on the variety and time ($p < 0.05$).

Table 5 shows the mineral content of pulp of grape varieties. The major minerals were potassium (K, 1584.038–2824.760 mg/kg), calcium (Ca, 174.465–329.947 mg/kg), phosphorus (P, 143.932–233.307 mg/kg), sulfur (S, 146.826–179.140 mg/kg), magnesium (Mg,

Table 4 Fatty acid and tocopherol compositions of grape seeds

Fatty acids (%)	Razaki*	Razaki**	Razaki***	Müşküle*	Müşküle**	Müşküle***	Cardinal*	Cardinal**	Cardinal***
Palmitic	8.965 ± 0.180****b	9.797 ± 0.028a	8.668 ± 0.072b	6.234 ± 0.082b	6.233 ± 0.078b	6.284 ± 0.007a	8.084 ± 0.035a	7.458 ± 0.010b	7.608 ± 0.048b
Stearic	4.754 ± 0.055c*****	4.757 ± 0.018b	4.787 ± 0.013a	5.435 ± 0.018a	5.253 ± 0.002a	4.995 ± 0.014b	3.832 ± 0.006a	3.626 ± 0.008b	3.558 ± 0.003c
Oleic	17.414 ± 0.206b	19.366 ± 0.009a	17.208 ± 0.015b	18.112 ± 0.028b	18.129 ± 0.019b	18.336 ± 0.023a	16.118 ± 0.018a	14.112 ± 0.013b	13.959 ± 0.002c
Linoleic	67.511 ± 0.118a	64.532 ± 0.065b	67.969 ± 0.037a	69.094 ± 0.033c	69.242 ± 0.051a	69.148 ± 0.040b	70.618 ± 0.053b	73.483 ± 0.008a	73.571 ± 0.038a
Arachidic	0.171 ± 0.008b	0.183 ± 0.003a	0.171 ± 0.002b	0.188 ± 0.002a	0.184 ± 0.001b	0.181 ± 0.000c	0.147 ± 0.000a	0.134 ± 0.001c	0.137 ± 0.001b
Linolenic	0.281 ± 0.137a	0.122 ± 0.008c	0.145 ± 0.009b	0.121 ± 0.001a	0.120 ± 0.003b	0.120 ± 0.001b	0.129 ± 0.003a	0.121 ± 0.000c	0.123 ± 0.003b
Tocopherols (mg/g)	Razaki*	Razaki**	Razaki***	Müşküle*	Müşküle**	Müşküle***	Cardinal*	Cardinal**	Cardinal***
α-Tocopherol	–#	–	0.213 ± 0.574	0.176 ± 0.068a	0.138 ± 0.028c	0.148 ± 0.029b	0.140 ± 0.002c	0.150 ± 0.047b	0.179 ± 0.997a
β-Tocopherol	0.125 ± 0.042b	0.130 ± 0.102c	0.146 ± 0.667a	–	0.119 ± 0.001b	0.145 ± 0.077a	0.191 ± 0.113b	0.116 ± 0.029b	0.157 ± 0.570a
γ-Tocopherol	0.110 ± 0.091b	0.107 ± 0.079c	0.121 ± 0.156a	–	0.107 ± 0.035b	0.112 ± 0.165a	0.123 ± 0.066a	0.107 ± 0.058c	0.111 ± 0.030b
δ-Tocopherol	0.253 ± 0.311c	0.358 ± 0.099b	0.425 ± 0.811a	–	–	–	0.288 ± 0.048b	0.409 ± 0.091a	–

Not detected; * harvest; ** harvested one week ago; *** harvested two weeks ago; **** each value is expressed as mean ± standard deviation; ***** values in each rows with different letters are significantly different ($p < 0.05$)

76.106–164.734 mg/kg) ve sodium (Na, 54.195–166.228 mg/kg). Other minerals, e.g. Fe, Al, B, Cu, Cd, Mo, Zn, Mn and Pb were found at lower levels. The highest potassium content was observed in Müşküle variety (2824.760 mg/kg), followed by Cardinal (2194.259 mg/kg) when harvested on time. Cardinal, harvested on time, contained the highest Ca contents (329.947 mg/kg), while Razaki variety, harvested one week earlier, had the maximum Mg (164.734 mg/kg). Cd element shows toxic effect and was found below 1%, while Ni and Cr elements were not detected in all varieties.

Mineral contents of grape seeds are given Table 6. Macro elements such as K, Ca, P, Mg, S and Na varied between 3950.714 and 7575.742 mg/kg, 3813.456 and 6190.063 mg/kg, 1627.718 and 2113.753 mg/kg, 923.203 and 1396.977 mg/kg, 761.623 and 984.442 mg/kg, 73.255 and 300.260 mg/kg, respectively. Mineral content of grape seed was higher than pulp of grape. Mineral contents of Razaki, Müşküle and Cardinal varieties showed a change according to harvest time. Generally, early harvest decreased the mineral contents of Razaki and Müşküle seeds. In addition, grape seeds did not contain Ni and Cr and Cd mineral and these werepresent (<1%)in grape pulp. It was ascertained that grape seed was a significant source of mineral.Mineral contents of grape seed and pulp differed according to harvest time and these differences were statistically significant ($p < 0.05$). According to Fazlo et al. (1982) mean values of Na, K and Ca contents of grape seeds were 4660, 124,000 and 271,000 mg/kg, respectively. The range of concentrations of minerals in grape seed and pulp as reported here differed from previous reports. The variations observed between the results of this work could be probabaly due to differences in climatic conditions, soil structure, genetic factor, variety and environmental temperature during maturation of grape seeds.

Conclusion

Both grape pulp and seeds are source of important compounds for health, such as antioxidants, phenolics and flavonoids. Grape seeds had higher bioactive compounds in comparison with pulp. The results of analysis showed a change in all varieties according to harvest date. The highest antioxidant activity, total phenolic and flavonoid contents were observed in Razaki variety when harvested one week ago. Early harvest caused a minor changes in fatty acid compositions of seed oils, while there were significant differences in mineral contents of pulp. Moreover, the tocopherol contents of seed oils increased with early harvest.

Table 5 Mineral contents of grape samples (mg/kg)

Grape varieties (pulp)	Al	Mo	Ca	B	Cd	Cu	Fe	K
Razaki*	0.537 ± 0.016b****	–	257.360 ± 6.505c	7.132 ± 0.045c	0.263 ± 0.379a	1.006 ± 0.050a	5.337 ± 0.119a	1584.038 ± 10.530c
Razaki**	1.400 ± 0.020a*****	0.074 ± 0.008	286.343 ± 6.662a	7.182 ± 0.065b	0.037 ± 0.006b	0.742 ± 0.061b	4.171 ± 2.972b	2320.799 ± 8.008b
Razaki***	–******	–	235.200 ± 6.521b	7.334 ± 0.050a	0.022 ± 0.007c	0.751 ± 0.060b	3.336 ± 0.051c	2565.728 ± 7.113a
Müşküle*	0.992 ± 0.011c	–	230.707 ± 2.526a	7.272 ± 0.045a	0.039 ± 0.012b	0.684 ± 0.070b	6.728 ± 0.135c	2824.760 ± 6.516a
Müşküle**	2.133 ± 0.029b	–	174.465 ± 5.064c	4.909 ± 0.055c	0.034 ± 0.005c	0.652 ± 0.055c	10.765 ± 0.085b	1714.069 ± 7.001c
Müşküle***	4.793 ± 1.667a	–	206.518 ± 5.069b	5.556 ± 0.041b	0.054 ± 0.014a	0.783 ± 0.045a	14.034 ± 0.130a	2303.934 ± 7.564b
Cardinal*	*	0.076 ± 0.006b	329.947 ± 8.615a	3.024 ± 0.058b	0.062 ± 0.016a	0.832 ± 0.052b	8.499 ± 0.090a	2194.259 ± 8.013a
Cardinal**	1.148 ± 0.027b	0.339 ± 0.017a	215.820 ± 2.024b	3.318 ± 0.056b	0.014 ± 0.005b	0.878 ± 0.045a	5.126 ± 0.060b	2137.085 ± 9.194b
Cardinal***	1.323 ± 0.035a	0.012 ± 0.007c	191.166 ± 3.014c	4.123 ± 0.035a	0.052 ± 0.017a	0.370 ± 0.046c	5.855 ± 0.103b	2068.206 ± 7.009c

Grape varieties (pulp)	Mg	Mn	Na	P	Pb	S	Zn
Razaki*	107.888 ± 3.169c	0.072 ± 0.017b	55.886 ± 3.172b	173.640 ± 5.039c	–	179.140 ± 6.005b	9.960 ± 0.223a
Razaki**	164.734 ± 4.405a	0.217 ± 0.047a	54.195 ± 4.265c	233.307 ± 7.780a	0.282 ± 0.035a	183.720 ± 5.024a	1.938 ± 0.140b
Razaki***	118.059 ± 2.912b	–	67.257 ± 3.525a	184.987 ± 6.000b	0.028 ± 0.011b	151.750 ± 6.628c	1.114 ± 0.065b
Müşküle*	108.653 ± 7.505a	0.130 ± 0.036b	83.584 ± 5.502b	186.601 ± 5.503a	–	155.064 ± 6.001c	1.431 ± 0.056c
Müşküle**	76.106 ± 4.552c	–	68.349 ± 4.508c	143.932 ± 6.574c	0.358 ± 0.056a	162.095 ± 6.201a	3.130 ± 0.072a
Müşküle***	93.918 ± 3.003b	0.190 ± 0.030a	105.575 ± 3.176a	173.283 ± 5.513b	0.287 ± 0.045b	161.550 ± 4.501b	2.461 ± 0.095b
Cardinal*	97.076 ± 4.609b	0.137 ± 0.031c	143.670 ± 4.510b	178.885 ± 6.003b	–	174.972 ± 5.575a	3.659 ± 0.097a
Cardinal**	101.041 ± 5.557a	0.196 ± 0.031a	166.228 ± 5.520a	186.806 ± 4.531a	0.135 ± 0.031b	146.826 ± 5.009c	2.267 ± 0.055b
Cardinal***	83.380 ± 5.504c	0.189 ± 0.030b	107.368 ± 5.505c	162.994 ± 6.556c	0.211 ± 0.045a	160.973 ± 6.564b	1.856 ± 0.070c

* Harvest; ** harvested one week ago; *** harvested two weeks ago; **** each value is expressed as mean ± standard deviation; ***** values in each column with different letters are significantly different ($p < 0.05$); ****** nondetected

Table 6 Mineral contents of grape seeds (mg/kg)

Grape seeds	Al	Mo	Ca	B	Cd	Cu	Fe	K
Razaki*	6.729 ± 0.112****b	0.222 ± 0.013a	4009.903 ± 9.039b	10.539 ± 0.044a	0.045 ± 0.005a	7.271 ± 0.026a	19.033 ± 0.152b	6008.179 ± 5.812a
Razaki**	3.169 ± 0.059c*****	0.182 ± 0.003b	4151.900 ± 1.853a	10.330 ± 0.043a	0.040 ± 0.010b	6.576 ± 0.068b	20.713 ± 0.030a	5313.065 ± 6.194b
Razaki***	55.601 ± 0.102a	–	3813.456 ± 13.438c	7.684 ± 0.104b	0.020 ± 0.001c	6.406 ± 0.109b	14.604 ± 0.350c	4796.281 ± 35.067c
Müşküle*	0.915 ± 0.014b	0.123 ± 0.015c	5145.905 ± 44.001a	11.351 ± 0.150a	0.021 ± 0.001b	7.715 ± 0.360a	21.473 ± 0.237b	4516.803 ± 10.229a
Müşküle**	0.401 ± 0.010c	0.138 ± 0.017b	4676.667 ± 7.638b	11.627 ± 0.142a	0.046 ± 0.005a	7.259 ± 0.151c	17.667 ± 0.551c	3950.714 ± 19.547b
Müşküle***	1.449 ± 0.026a	0.142 ± 0.028a	3884.985 ± 5.000c	10.705 ± 0.208	0.018 ± 0.007c	7.599 ± 0.100b	28.911 ± 0.183a	3981.599 ± 6.502b
Cardinal*	1.885 ± 0.079c	–	6190.063 ± 35.041a	9.544 ± 0.310a	0.046 ± 0.005b	8.421 ± 0.071b	26.220 ± 0.106c	6217.672 ± 24.110c
Cardinal**	3.228 ± 0.111b	0.523 ± 0.107a	6087.766 ± 2.657b	7.532 ± 0.207b	0.043 ± 0.006c	8.621 ± 0.071b	44.159 ± 0.122b	7123.793 ± 6.520b
Cardinal***	28.038 ± 0.707a	0.193 ± 0.003b	6147.987 ± 107.636a	9.632 ± 0.767a	0.051 ± 0.002a	9.000 ± 0.315a	49.532 ± 0.759a	7575.742 ± 156.657a

Grape seeds	Mg	Mn	Na	P	Pb	S	Zn
Razaki*	1089.706 ± 4.792a	8.093 ± 0.022a	129.828 ± 2.355c	1888.840 ± 10.618a	0.056 ± 0.006	958.034 ± 5.614a	11.252 ± 0.184b
Razaki**	1049.303 ± 1.478a	7.231 ± 0.114b	219.056 ± 3.676a	1749.547 ± 4.338b	–	862.990 ± 4.341b	12.094 ± 0.092a
Razaki***	923.203 ± 11.643b	5.164 ± 0.055c	133.117 ± 2.010b	1627.718 ± 10.753c	–	761.623 ± 7.083c	8.672 ± 0.403c
Müşküle*	1357.151 ± 28.506a	9.815 ± 0.110a	130.542 ± 0.505c	2113.753 ± 7.120a	0.031 ± 0.002	984.442 ± 4.073a	7.055 ± 0.250a
Müşküle**	1250.040 ± 9.000b	9.153 ± 0.068b	175.854 ± 7.525a	1943.932 ± 4.606b	–	900.973 ± 4.000b	7.636 ± 0.351a
Müşküle***	1200.371 ± 11.019c	9.101 ± 0.100b	157.161 ± 2.019b	1752.920 ± 9.528c	–	868.122 ± 16.737c	6.362 ± 0.251b
Cardinal*	1311.977 ± 12.533c	10.724 ± 0.120c	73.255 ± 2.536c	1836.637 ± 11.055c	0.404 ± 0.045b	944.436 ± 10.075a	11.827 ± 0.651a
Cardinal**	1330.758 ± 5.018b	12.185 ± 0.165b	300.260 ± 3.740a	1897.818 ± 15.06a7	–	916.420 ± 28.108b	10.166 ± 0.209b
Cardinal***	1396.977 ± 31.837a	13.521 ± 0.410a	171.876 ± 1.736b	1882.020 ± 22.025b	0.428 ± 0.002a	946.590 ± 23.743a	9.616 ± 0.252c

* Harvest; ** harvested one week ago; *** harvested two weeks ago; **** each value is expressed as mean ± standard deviation; ***** values in each column with different letters are significantly different ($p < 0.05$)

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