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Characterization of some bioactive compounds and physicochemical properties of grape varieties grown in Turkey: thermal degradation kinetics of anthocyanin

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Abstract: In the present study, five different grapes varieties grown in Turkey were comprehensively characterized in terms of physicochemical properties, total bioactive content, antiradical activity, and volatile sugar compounds. Thermal degradation kinetics of anthocyanin in the selected grape varieties were also analyzed. All the bioactive compounds and antiradical activity varied depending on variety and grape part (skin, pulp, or seed). Higher amounts of total phenolics, total flavonoids, anthocyanin, and antiradical capacity were obtained from seeds. Fifty-nine volatile compounds were observed in the grape varieties. Terpenoid compounds were determined to be the predominant aroma compounds, of which limonene and citral had the highest content, with values ranging from 46.269% to 77.209% and from 3.327% to 12.371%, respectively. The half-life period of anthocyanin degradation in grapes with a temperature range of 60 to 90 °C ranged from 3.51 to 34.65, 3.26 to 35.50, 2.76 to 40.77, and 3.02 to 43.31 for Antep Karası, Efes, Kara Dimrit, and Cardinal Red, respectively. Efes and Cardinal had the greatest amount of bioactive compounds among the grape varieties.

Key words: Grape, Antep Karası, Efes, Kara Dimrit, phenolic

1. Introduction

Since grape and its wastes are rich in nutritional compounds, such as glucose, fructose, several types of phenolics, and organic acids, they have been consumed in most parts of the world for many years. Turkey is one of the leading counties in the world in terms of grape production, with an estimated production of 3,650,000 Mt of grapes, including wine, table, and raisin varieties. In Turkey, grapes have been used for products such as wine, vinegar, grape juices, pekmez (traditional Turkish syrup), and raisins (Yemis et al., 2008).

Phenolics are one of the most abundant constituents affecting grape quality (Baiano and Terracone, 2011). A grape cultivar's phenolic compound profile varies according to several factors, such as ripening, climate, region, and soil type. Distribution of phenolics in grapes also differs according to skin, pulp, and seeds. The skin of red grapes is rich in anthocyanin, the pulp shows high amounts of hydroxycinnamic acids, and flavonols are mainly located in the seeds. Generally, the amount of phenolics in seeds is higher than in the skin and pulp (Yılmaz and Toledo, 2004).

Color is the main factor that determines consumer preferences. Anthocyanins are a group of phenolic compounds that are responsible for the red color of vegetables and fruits. Anthocyanins have a potential use as a natural colorant in food industry due to their bright red color and water solubility; additionally, they have been known to have beneficial effects on coronary heart disease and to reduce levels of serum triglyceride (Morais et al., 2002). However, anthocyanin pigments are affected by several factors, such as temperature, light, pH, metal ions, and oxygen. Heat treatment is considered the most important factor affecting anthocyanin stability (Wang and Xu, 2007). Grape and grape wastes, namely grape skin extract and grape color extract, are rich in anthocyanin content and are a good source of anthocyanin. However, grapes are subjected to heat treatment during some processes, such as jam and juice production, pasteurization, and drying. Therefore, thermal stability of anthocyanin should be taken into account during grape processing in order to estimate the final product's color retention.

Another important parameter affecting grape quality and customer acceptance is the aroma characteristics of

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several types of grapes. Volatile compounds of the grapes play a significant role in determining the aroma value of the grapes. Volatile compounds of the grapes vary according to grape variety, cultivation technique, harvest time, and several other factors (Vilanova et al., 2012). Terpenes, norisoprenoids, benzene compounds, and C6 alcohols are the main compounds that contribute to grape aroma (Noguerol-Pato et al., 2012). Therefore, analyzing specific aroma compounds and determining the phenolics in different parts of the grape is very helpful in grape identification.

These quality attributes are most likely related to grape variety. Selecting high-quality grape varieties is very important for achieving desired product quality. The aim of the present study was to create a comprehensive characterization of five grape varieties grown in Turkey (Efes, Kara Dimrit, Müsküle, Cardinal Red, and Antep Karası) by determining the total bioactive contents in different parts of the grapes, analyzing physicochemical properties and specific volatile compounds, and determining anthocyanin degradation kinetics at different temperature values.

2. Materials and methods

2.1. Materials

Efes, Kara Dimrit, Müsküle, Cardinal Red, and Antep Karası grape varieties (*Vitis vinifera* L.) were used in this study for the their characterization. Kara Dimrit and Antep Karası are red-purple raisin grapes and Efes, Cardinal, and Müsküle are used as table grapes. Müsküle was the only white grape in the study. Grapes were obtained from a grape producer in Denizli (Aegean Region) in Turkey in the same harvest year (2013). The grapes were washed thoroughly and transferred to the laboratory. Each analysis was conducted in triplicate. The different parts of the grapes were manually separated and kept at –18 (C until further analysis.

2.2. Methods

2.2.1. Physicochemical properties of grape varieties

Surface color of the fresh grapes was measured with a chroma meter (CR-400, Konica Minolta, Japan). The color values were recorded as L^*, a^*, and b^*. L^* values represent the level of black to white (0–100), a^* values represent red to green (+ = red and − = green), and b^* values represent yellow to blue (+ = yellow and − = blue).

The pH level was measured with a pH meter (WTW-Inolab, Germany) at 25 °C. pH measurement was conducted on grape paste (after maceration) before the extraction process. The Brix value was obtained using an automatic refractometer (AR 700; Reichert, USA) at 25 °C and dry matter content was determined by the conventional drying method described by AOAC (AOAC, 2000).

2.2.2. Determination of sugar composition

Sugar composition of the grape varieties was determined according to method described by Ozturk et al. (2014). A high performance liquid chromatography refractive index detector (1100 series; Agilent, USA) equipped with a manual injection quaternary pump (USA) and Zorbax carbohydrate column (4.6 × 250 mm, 5 (m particle size) was used for chromatographic analysis. Samples of 1 g were extracted with 10 mL of distilled water at room temperature. After the extraction process, extracts were centrifuged (Universal 320; Hettich, Germany) at 550 × *g* for 5 min and the obtained supernatant was filtered with a 0.45 µm micro filter. Then 20 L of the filtrate was injected into the column, and the mobile phase (80:20 acetonitrile:water) flow rate was adjusted to 1.4 mL/min. Sugar composition was analyzed by comparing their retention time with those of standard, while amounts were calculated by the calibration curve of each sugar. Analyses were carried out in triplicate.

2.2.3. Determination of bioactive compounds

2.2.3.1. Extraction procedure of the bioactive compounds

Fifty grams of the grapes were mixed in 20 mL of methanol:water (80:20). The mixture was homogenized by ULTRA-TURAX (HG-15D; Daihan, South Korea) at 10,000 rpm for 2 min and held for 2 h at room temperature. After the incubation period, the extract was centrifuged (Universal 320R, Hettich) at 3500 × *g* for 10 min, and the supernatants were filtered using a 0.45 µm filter.

2.2.3.2. Determination of the total phenolic content

Total phenolic content (TPC) of different grape varieties was determined according to the modified method described by Singleton and Rossi (1965). Briefly, 0.2 N 2.5 mL of Folin Ciocelteau's phenol reagent (Merck, USA) (10-fold diluted) was mixed with 0.5 mL of extracted samples and 2 mL of 7.5% Na_2CO_3. The obtained mixture was held for 30 min at room temperature and in a dark place. At the end of the incubation, the absorbance was recorded at 760 nm using a UV-Vis spectrophotometer (UV-1800; Shimadzu, Japan) (Li et al., 2006). Results were expressed as milligrams of gallic acid per kilogram of sample (mg GA/1000 g sample).

2.2.3.3. Total flavonoid compound analysis

Total flavonoid content (TFC) was determined according to the method described by Zhishen et al. (1999). TFC was calculated in catechin equivalent. The grape extracts were transferred into a 10-mL volumetric glass and mixed with distilled water to reach up to 5 mL, after which 0.3 mL of $NaNO_2$ (5%) was added to the glass. After 5 min, 0.3 mL of $AlCl_3$ (10%) was added and the total volume of the solution was brought to 10 mL with 2 mL of 1 M NaOH and 2.4 mL of pure water. The obtained solution was thoroughly mixed and the absorbance was recorded at 510 nm with a

UV-Vis spectrophotometer (UV-1800, Shimadzu). Results were expressed as milligrams of catechin per kilogram of sample.

2.2.3.4. Total anthocyanin compound analysis

The total anthocyanin content of the grapes was obtained according to the pH differential method (Giusti and Wrolstad, 2001). The extracts were mixed buffers of pH 1 and pH 4.5 and held at room temperature and in a dark place for 30 min. The absorbance of the samples was recorded at 510 and 700 nm using a UV-Vis spectrophotometer (UV-1800, Shimadzu). The total anthocyanin content was determined in milligrams of cyanidin-3-glucoside per kilogram of fresh sample.

2.2.3.5. Antioxidant capacity

Antioxidant capacity (AC) analysis was performed by determining the free radical scavenging capacities of samples. DPPH scavenging capacities were determined according to the method reported by Blois (1958). A 0.1-mL aliquot of each extract was mixed with 4.9 mL of DPPH solution (0.1 mM in ethanol) and thoroughly mixed by vortex for 1 min. After 30 min of incubation at room temperature, the absorbance at 517 nm was recorded. Radical scavenging capacity was described as percentage of scavenging effect according to the following formula:

$$DPPH\ Scavenging\ Capacity\ (\%) = \left(\frac{Ac - As}{Ac}\right) x100\,, \qquad (1)$$

where A_C shows the absorbance of the blank and A_S represents the absorbance of the sample solution.

2.2.4. Thermal degradation kinetics of anthocyanin in grapes

In order to determine the heat stability of grape anthocyanins, extracts of the grapes were subjected to different temperatures for different lengths of time according to the method described by Wanh and Xu (2007). A water bath (WSB-30, Daihan) was used to hold the extracts at 60 °C, 70 °C, 80 °C, and 90 °C. For this aim, grape extracts were transferred to a glass tube (2 cm diameter, 20 mL) with a screw cap already equilibrated in a thermostatic water bath at the specified temperature (±0.1 °C) for 8 h at each temperature. An exponential model was used to determine the first order kinetics behavior of the grape anthocyanins:

$$C = C_0 \exp(-kt) \qquad (2)$$

Here C_0 is the initial content of anthocyanin, C is the anthocyanin concentration after heating at a given temperature, and k is the constant for the first-order kinetic model. Half time ($t_{1/2}$) and decimal reduction time (D) were calculated by Eqs. (3) and (4), respectively:

$$t_{1/2} = \frac{\ln(0.5)}{k} \qquad (3)$$

$$D = \frac{2.303}{k} \qquad (4)$$

The temperature dependency parameters of anthocyanin degradation were determined by the following equation:

$$k = A \exp\left(\frac{E_a}{RT}\right) \qquad (5)$$

Here A is the frequency factor, E_a is the activation energy (J/mol), R is the universal gas constant (J/mol K), and T is the absolute temperature (K).

2.2.5. Volatile profile of grapes

Volatile compounds of the grapes were analyzed with gas chromatography–mass spectrometry (GC–MS) (7890A GC system, Agilent) using a mass selective detector (Agilent) and a DB-WAX column (60 × 0.2501 m inner diameter, 0.25 mm film thickness). The oven temperature was adjusted to 40 °C for 10 min, then heated to 110 °C at a rate of 3 °C/min, from 110 °C to 150 °C at 4 °C/min, then from 150 °C to 210 °C at 10 °C/min, and then increased to 210 °C/min for 15 min. As a carrier gas, the flow rate of helium was set to 1.0 mL/min. The electron ionization detector voltage was 70 eV. Adsorption of the compounds was done by fibers at 40 °C for 1 h and were desorbed from the injection port for 15 min at 50 °C in the splitless mode. GC–MS libraries (Flavor 2, NIST 05, and Wiley 7n) were used to identify the aroma compounds by comparing their retention indices and matching their spectra with reference compounds in the data system. The peak areas were used to determine the volatile composition of the samples as a percentage by dividing the area of each peak by the total area under all of the peaks.

2.2.6. Statistical analysis

SPSS (SPSS Statistics 17.0, USA) was used to perform statistical evaluation. ANOVA was carried out to determine the differences among the samples. Duncan's multiple comparison test was used to determine the differences between the parameters at the probability level of 0.05. Nonlinear regression analysis was performed with the Statistica 8.0 (StatSoft Inc., USA) software package based on the Levenberg–Marquardt algorithm. The coefficient of determination (R^2) was the main criterion for determining the model acceptability to describe anthocyanin degradation kinetics of different grape varieties.

3. Results and discussion

3.1. Physical and chemical properties of grapes

The physicochemical properties of grape varieties are shown in Table 1. Lengths and diameters of the grapes differed significantly ($P < 0.05$). Lengths of the grapes varied between 1.52 and 2.45 cm and diameters ranged from 1.66 to 2.66 cm. Kara Dimrit had the lowest diameter, whereas Antep Karası and Cardinal Red had the greatest diameter and length, respectively. Cardinal Red also had the highest weight value. L^*, a^*, and b^* values of the grapes varied significantly ($P < 0.05$) and were found to be 21.71–31.81, 0.46–6.67, and 0.97–3.89, respectively. As expected, the highest L^* value was obtained from Müsküle, which is the white grape variety, and the highest a^* value was found in Cardinal Red. The pH values of the samples varied from 3.32 to 3.87 ($P < 0.5$) and the highest and lowest pH values were obtained from Antep Karası and Kara Dimrit, respectively. The highest Brix and dry matter values of the samples were found to be 23.85% (Antep Karası) and 26.11% (Cardinal Red), respectively.

3.2. Sugar profile

Sugar profiles of the grapes are shown in Table 1. Glucose and fructose were the major sugars in the grape varieties. Fructose and glucose contents ranged from 5.8% to 9.66% and from 6.77% to 10.77%, respectively (wet basis) and a significant difference was observed ($P < 0.05$). With the exception of Kara Dimrit, glucose content was greater than fructose content in all the varieties. Table 2 shows the percentage weight ratio of the parts of the grapes to whole grapes. According to Table 2, Antep Karası had the highest pulp percentage and Kara Dimrit had the highest seed and skin percentage and the lowest pulp percentage.

Table 1. Physicochemical properties of grape varieties.

Parameters	Grape varieties				
	Kara Dimrit	Antep Karası	Efes	Cardinal Red	Müsküle
Length (cm)	1.520 ± 0.14	1.645 ± 0.17	2.165 ± 0.23	2.450 ± 0.37	2.245 ± 0.20
Diameter (cm)	1.660 ± 0.15	2.660 ± 0.23	2.045 ± 0.25	2.215 ± 0.30	1.790 ± 0.13
Weight (g)	2.540 ± 0.50	5.312 ± 0.84	6.721 ± 1.64	9.461 ± 2.23	4.831 ± 1.18
L^*	26.46 ± 3.45	22.31 ± 1.08	21.71 ± 1.27	26.46 ± 3.46	31.81 ± 2.62
a^*	3.20 ± 0.59	1.55 ± 0.25	1.77 ± 0.16	6.67 ± 1.71	0.46 ± 0.34
b^*	1.79 ± 0.53	1.85 ± 0.41	1.42 ± 0.43	0.97 ± 1.00	3.89 ± 0.74
pH	3.320 ± 0.02	3.870 ± 0.01	3.545 ± 0.00	3.795 ± 0.10	3.620 ± 0.04
Brix (°B)	19.950 ± 0.07	23.850 ± 0.07	19.700 ± 0.28	18.733 ± 0.63	17.900 ± 0.27
Dry matter (%)	23.159 ± 0.24	25.439 ± 0.45	23.164 ± 0.73	26.112 ± 0.16	22.257 ± 0.11
Glucose (%)	8.278 ± 0.09	10.721 ± 0.01	9.043 ± 0.04	8.37 ± 0.04	6.77 ± 0.03
Fructose (%)	8.586 ± 0.06	9.66 ± 0.09	6.877 ± 0.02	8.31 ± 0.02	5.81 ± 0.12

*Means ± standard deviation.

Table 2. Percentage weight of different parts of grape varieties.

Grape varieties	Weight (%)		
	Pulp	Peel	Seed
Müsküle	81.93 ± 1.75	14.06 ± 0.75	4.01 ± 0.51
Cardinal Red	89.94 ± 3.25	7.8 ± 1.35	2.26 ± 0.30
Efes	87.88 ± 1.31	8.84 ± 1.05	3.28 ± 0.35
Antep Karası	81.83 ± 2.68	15.8 ± 2.26	2.37 ± 0.15
Kara Dimrit	72.68 ± 3.50	22.22 ± 1.61	5.1 ± 0.24

3.3. Total bioactive compounds and antioxidant capacity

Table 3 represents total phenolic, flavonoids, anthocyanin, and DPPH radical scavenging activity of the different grape varieties in pulp, skin, and seeds.

TPC differed significantly depending on the variety and grape part. TPC was found to range from 10.09 to 120.45, 207.12 to 1312.84, and 1931.98 to 3790.09 mg/L for pulp, skin, and seeds, respectively. The results show that the phenolic content of the seeds was higher than that of the pulp and skin. Concerning the amounts of phenolics in the pulp, Kara Dimrit grapes had the highest TPC, while Cardinal Red had the lowest. In terms of the skin, Efes had the highest phenolic content, whereas Müsküle exhibited the lowest phenolic content. With regard to seeds, Antep Karası was the richest in phenolics while Müsküle had the lowest phenolic content. As table grapes, Efes had considerable amounts of phenolic content in the skin compared to the other varieties, while as raisin varieties Kara Dimrit and Antep Karası grapes had higher phenolic content in their pulps, and the phenolic content in their skin and seeds was lower than those of the other varieties. Since all grape varieties had higher amounts of phenolics in their seeds than in their pulp and skin, consumption of the varieties with their seeds may be recommended due to potential health benefits. The data obtained from the present study are in accordance with other studies (Baiano et al., 2011; Lutz et al., 2011; Santos et al., 2011). Those studies also revealed that the phenolic content in grape seeds is higher than that in the skin and pulp.

Similar trends were observed for TFC analysis. The flavonoid content differed among the grape varieties and parts of fruit and ranged from 0.028 to 0.13, 0.095 to 0.428, and 0.836 to 1.47 mg/L for pulp, skin, and seeds, respectively. Müsküle had a higher flavonoid content in the pulp, while Kara Dimrit had lower flavonoids. Concerning skin and seeds, Efes exhibited the highest flavonoid content.

Antioxidant activity was determined according to DPPH radical-scavenging capacity. AC values ranged from 4.62% to 15.31%, 52.27% to 93.00%, and 86.25% to 94.47% for pulp, skin, and seeds respectively. AC of the grapes differed significantly depending on the varieties in a manner similar to TPC and TFC. The obtained results indicate that antioxidant activity in the seeds and skin was higher than in the pulp. These results might be due to the incorporation of considerable amounts of bioactive components in the seeds and skin. The highest antioxidant activity was in the pulp of the Kara Dimrit grapes. Concerning skin and seeds, Efes had higher antioxidant capacity than other varieties. A positive trend between the antioxidant activity and the total phenolic content in the grape pulps was observed. Although samples that had higher amounts of phenolics in the seeds and the skin showed higher antioxidant activity, there was no rational relation observed between the amount of phenolics and the antioxidant activity. For example, although there were significant differences ($P < 0.05$) among Müsküle, Cardinal Red, and Efes in terms of TPC in the skins, the antioxidant activity of the skin was not found to be significant ($P > 0.05$). Some authors (Xu et al., 2010; Mitic et al., 2011; Rockenbacha et al., 2011; Kelebek et al., 2013) reported a positive correlation between phenolic content and antioxidant activity in grapes while others (Hogan et al., 2009; Baiano et al., 2011; Lutz et al., 2011) stated that antioxidant activity was dependent on the phenolic profile as well as TPC. It is well known that phenolic antioxidant activity differs according to phenolic profile. Therefore, some varieties might have shown a higher antioxidant activity in spite of lower levels of phenolic content.

Table 3. Total bioactive compounds of grape varieties.

Parameters	Part	Kara Dimrit	Antep Karası	Efes	Cardinal Red	Müsküle
Total phenolic (mg/L)	Pulp	602.25 ± 6.69^{a}	246.40 ± 6.05^{b}	218.24 ± 5.73^{c}	68.47 ± 2.87^{d}	57.45 ± 3.50^{e}
	Skin	2588.96 ± 12.30^{c}	1153.15 ± 11.15^{e}	6648.65 ± 4.78^{a}	3579.95 ± 15.93^{b}	2346.85 ± 14.33^{d}
	Seeds	9783.78 ± 5.73^{d}	9659.91 ± 3.82^{e}	18533.78 ± 6.37^{b}	18950.45 ± 1.64^{a}	10549.55 ± 17.20^{c}
Total flavonoid (mg/L)	Pulp	95.914 ± 4.28^{a}	43.612 ± 3.21^{b}	45.50 ± 1.61^{b}	22.09 ± 0.53^{c}	18.59 ± 1.07^{d}
	Skin	128.129 ± 3.75^{c}	69.005 ± 2.68^{d}	321.79 ± 2.65^{a}	165.27 ± 3.75^{b}	141.77 ±11.25^{c}
	Seeds	679.574 ± 9.64^{c}	631.062 ± 6.43^{d}	1111.634 ± 8.75^{a}	1016.12 ± 5.78^{b}	676.16 ± 4.82^{c}
DPPH (%)	Pulp	15.31 ± 0.43^{a}	9.38 ± 1.37^{b}	5.92 ± 1.22^{c}	4.62 ± 0.21^{c}	5.02 ± 0.17^{c}
	Skin	76.67 ± 1.41^{b}	52.26 ± 0.64^{c}	92.20 ± 2.60	92.99 ± 1.20^{a}	90.03 ± 2.91^{a}
	Seeds	86.25 ± 1.38^{c}	91.35 ± 1.21^{b}	95.80 ± 1.54^{a}	93.73 ± 0.24^{a}	93.62 ± 0.25^{a}
Anthocyanin (mg/L)	Skin	47.07 ± 1.55^{b}	30.02 ± 0.25^{d}	82.74 ± 2.38^{a}	32.59 ± 0.17^{c}	nd

*nd: not determined

Different superscript letters on the same line indicate significant statistical differences.

3.4. Thermal degradation kinetics of grapes anthocyanin

As anthocyanin degradation is an important factor affecting the color and nutritional quality of the fruit, it should be taken into consideration in food processing, especially thermal treatment. In the present study, the effect of temperature on anthocyanin stability of the four red grape varieties was studied. The Figure shows the effect of temperature on anthocyanin content depending on four different temperature values. Anthocyanin degradation increased with increasing temperature and treatment time. It can be understood from the Figure that similar degradation kinetics were observed for anthocyanin in all four varieties. An approximately 20% reduction in anthocyanin content was observed for all varieties after an 8-h heat treatment at 60 °C, while an approximately 85% reduction in anthocyanin content was determined in the same amount of time at 90 °C. In the current study, first-order thermal degradation kinetics of grapes' anthocyanin were observed. Table 4 lists the temperature dependency and kinetic parameters of grape anthocyanins. The half-life period of the grapes between 60 °C and 90 °C was determined to be 3.51–34.65, 3.26–35.50, 2.76–40.77, and 3.02–43.31 h for Antep Karası, Efes, Kara Dimrit, and Cardinal Red, respectively (Table 4). E_a values were calculated by Eq. (5) in order to determine the temperature dependence of different grape anthocyanin content. E_a values of all of the varieties ranged from 44.207 to 45.051 kJ/mol for temperatures ranging from 60 °C to 90 °C (Table 4). As expected, no significant differences were observed among E_a values ($P < 0.05$). This might be due to the similar specific anthocyanin profiles of grape varieties. E_a values of anthocyanin degradation for different fruits were reported as 52.39 to 54.50 kJ/mol for pomegranate arils (Karaaslan et al., 2013), 58.95 kJ/mol for blackberry (Wang and Xu, 2007), and 45.47 kJ/mol for mahlap fruit (Ozturk et al., 2014). Lower E_a values indicate a higher stability of anthocyanin against temperature increase. Variations in E_a values of anthocyanin degradation for different fruits might have resulted from different anthocyanin profiles of fruits. k values increased and $t_{1/2}$ and D values decreased with increased temperature, indicating that an increase in temperature had significant effects on degradation of anthocyanin contents. It can be concluded that any temperature higher than 60 °C and long-term heat treatments may reduce the anthocyanin content in grapes. Therefore, parameters (especially temperature and time) should be optimized during thermal processes, such as drying (Sabarez and Henry, 2014). Some studies have indicated a considerable reduction in the anthocyanin content of some fruits occurs during different heating processes (Cisse et al., 2009; Bener et al., 2013; Ozturk et al., 2014).

3.5. Volatile compounds

Aroma is one of the key factors directly affecting consumer preferences, especially in table grapes, and the quality index of grape-derived products for different grape varieties. As seen in Table 5, specific aroma compounds

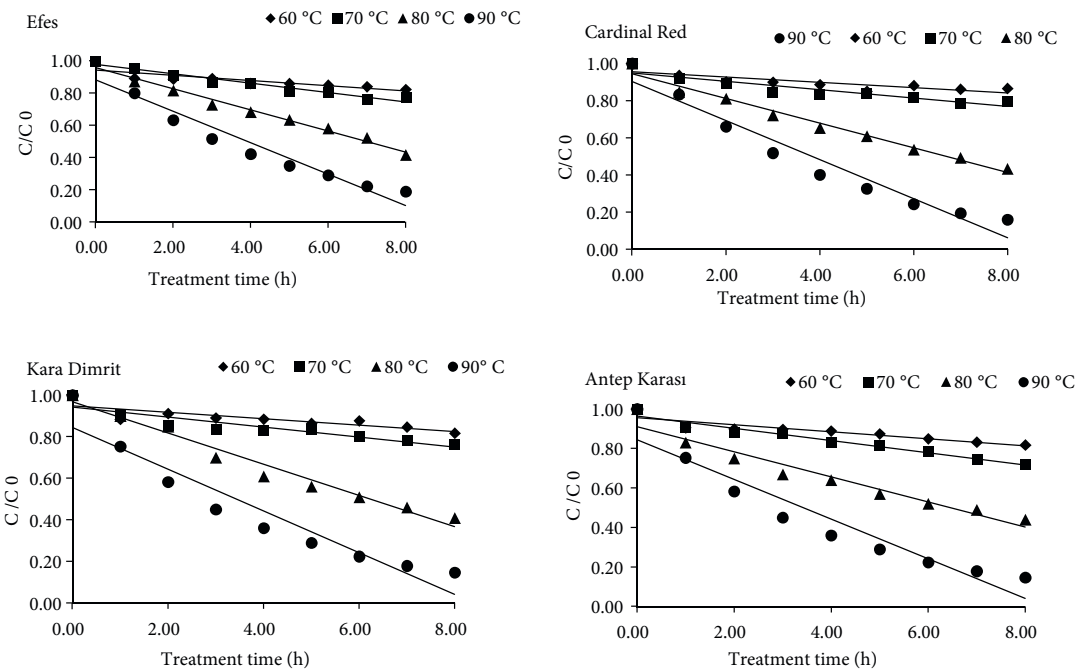

Figure. Thermal degradation kinetics of anthocyanins in grape varieties.

Table 4. Parameters of anthocyanin degradation kinetics.

	Temperature (C)	k	R^2	$t_{1/2}$ (h)	D value (h)	E_a (kJ/mol)
Efes	60	0.018 ± 0.004	0.9635	38.50 ± 0.001	127.94 ± 1.96	45.051 ± 0.11
	70	0.034 ± 0.002	0.9887	20.38 ± 0.001	67.73 ± 3.56	
	80	0.094 ± 0.004	0.9861	7.37 ± 0.001	24.5 ± 0.67	
	90	0.212 ± 0.020	0.9904	3.26 ± 0.001	18.86 ± 0.04	
Cardinal Red	60	0.016 ± 0.003	0.9572	43.31 ± 0.002	143.93 ± 3.14	44.371 ± 0.52
	70	0.026 ± 0.004	0.9546	26.65 ± 0.001	88.57 ± 14.94	
	80	0.099 ± 0.003	0.9777	7.00 ±0.001	23.26 ± 0.54	
	90	0.229 ± 0.004	0.9893	3.02 ± 0.001	10.05 ± 0.03	
Kara Dimrit	60	0.017 ± 0.004	0.9504	40.77 ± 0.001	135.47 ± 0.16	44.207 ± 0.11
	70	0.029 ± 0.004	0.9464	23.90 ±0.001	79.41 ± 0.55	
	80	0.114 ± 0.004	0.9996	6.07 ± 0.001	20.20 ± 0.35	
	90	0.251 ± 0.004	0.9832	2.76 ± 0.001	9.19 ± 0.11	
Antep Karası	60	0.020 ± 0.003	0.9585	34.65 ± 0.001	115.51 ± 1.21	44.335 ±0.83
	70	0.027 ± 0.002	0.9703	25.67 ± 0.001	85.29 ± 13.02	
	80	0.100 ± 0.005	0.9494	6.93 ± 0.000	23.03 ± 1.01	
	90	0.197 ± 0.004	0.9890	3.51 ± 0.000	11.69 ± 0.18	

*Means ± standard deviation.

Table 5. Aroma compounds of the grape varieties (% of peak area).

Aroma compounds	Müsküle	Cardinal Red	Efes	Antep Karası	Kara Dimrit
M-Bis(m-phenoxyphenoxy) benzene	17.691	-	-	-	-
2-phenyl-2-tipyl-acenapthenone	0.841	-	-	-	-
8-methylisothiazolo	2.235	-	-	-	-
Trans-2 hexenal	0.083	0.527	0.976	0.101	1.082
Benzene, 1,2-dimethyl	0.292	-	-	0.308	-
Benzene, 1,3-dimethyl	0.362	-	-	-	-
3-phenyllactic acid	0.314	-	-	-	-
Myrcene	0.318	0.69	-	0.778	0.672
Limonene	46.269	73.945	71.219	64.467	77.209
Linalol	0.267	0.538	-	0.618	0.469
Nonanal	0.397	0.285	0.719	0.347	0.367
N-undecane	0.279	-	-	-	-
N-decane	0.288	-	-	-	-
P-hydroxypheny l-ethanediol 3tms	0.332	-	-	-	-
2-hydroxy-benzoic acid	0.662	-	-	-	-
Camphor	0.592	0.429	-	0.686	0.433
3-methyldecane	0.868	-	-	-	-

Table 5. (Continued).

Aroma compounds	Müsküle	Cardinal Red	Efes	Antep Karası	Kara Dimrit
N-dodecane	0.448	-	-	-	-
3-[N-(Phenylimino)]-Indole	0.845	-	-	-	-
Pentadecane	0.356	-	-	-	-
3-Octyne	0.533	-	-	-	-
N-decanal	0.266	0.169	0.422	0.283	-
2,6-octadienal, 3,7-dimethyl	0.338	-	-	-	-
Citral	3.327	10.852	5.683	12.371	6.917
Pentanoic Acid, 2,2,4-trimethy	0.574	-	-	-	-
Beta-pinene	-	0.837	-	0.699	0.235
2-Ethyl-1-hexanol	-	0.643	-	-	-
Gamma-terpinene	-	0.204	-	-	-
Isoborneol	-	2.395	0.72	0.718	0.663
Pulegone	-	1.445	-	-	-
Alpha-terpineol	-	0.483	-	-	-
3,5-Heptadienal, 2-Ethylidene-6-Methyl-	-	0.243	-	-	-
1-hexanol	-	-	0.579	-	-
P-cymene	-	-	1.191	1.678	-
3,5-Octadiene, (Z,Z)-	-	-	0.595	-	-
Phenethyl alcohol	-	-	-	-	0.781
2-Ethyl-1-hexanol	-	-	-	0.692	0.568
Phenylacetaldehyde	-	-	-	-	0.3
4-Carvomenthenol; terpinene-4-ol	-	-	-	-	0.4
Alpha-terpineol	-	-	-	-	0.275
Ethyl octanoate	-	-	-	-	0.897
Acetic acid	-	-	-	0.879	0.482
Ethyl decanoate	-	-	-	-	0.408

are given as a percentage of peak area and they differed according to grape varieties. Terpenoid compounds such as limonene, linalool, citral, and terpineol, which made up nearly 80% to 85% of the total aromatic compounds, were the main aromatic compounds. Limonene accounted for most of the aromatic compounds, regardless of variety. Limonene percentage varied from 46.269% to 77.209% among the varieties. Kara Dimrit exhibited the highest level of limonene, while Müsküle had the lowest. The second major aroma was citral, which varied from 3.327% to 12.371%. As a white variety, Müsküle grapes were also rich in m-bis benzene compounds (17.691%). Terpenoid compounds are considered responsible for the Muscat aroma, which has fruity and floral characteristics (Vilanova et al., 2012). Muscat aroma is desired in fresh grapes during consumption and wine production (Crespan and Milani, 2001). Other important factors affecting Muscat aroma are the amount of terpenoids and their interaction with other compounds (Ruiz-García et al., 2014). Müsküle variety had more specific aroma compounds than other varieties. All grape varieties contained considerable amounts of citral (terpenoids).

In conclusion, total bioactive compounds of the grape differed significantly based on variety and grape part. Since higher bioactive compounds and antioxidant capacity were found in seeds for all grape varieties, grapes should be consumed with their seed. This study also showed that these grapes are a potential source of natural bioactive compounds. A significant reduction in anthocyanin content was observed at high temperatures. Temperature should be optimized for maintaining anthocyanin content and assuring color quality. The results here provide important information in food science and technology. It can be concluded that selected grape varieties and their parts can be considered a good source of phenolics and antioxidants.

References

AOAC (2000). Official Methods of Analysis. 17th ed. Arlington, VA, USA: AOAC.

Baiano A, Terracone A (2011). Varietal differences among the phenolic profiles and antioxidant activities of seven tables grape cultivars grown in the south of Italy based on chemometrics. J Agric Food Chem 59: 9815–9826.

Bener M, Shen Y, Apak R, Finley JW, Xu Z (2013). Release and degradation of anthocyanins and phenolics from blueberry pomace during thermal acid hydrolysis and dry heating. J Agric Food Chem 61: 6643–6649.

Cisse M, Vaillant F, Acosta O, Dhuique-Mayer C, Dornier M (2009). Thermal degradation kinetics of anthocyanins from blood orange, blackberry, and roselle using the arrhenius, eyring, and ball models. J Agric Food Chem 57: 6285–6291.

Crespan M, Milani N (2001). The Muscat: a molecular analysis of synonyms, homonyms and genetic relationships within a large family of grapevine cultivars. Vitis 40: 23–30.

Giusti M, Wrolstad RE (2001). Characterization and measurement of anthocyanins by UV-visible spectroscopy. Current Protocols in Food Analytical Chemistry. F:F1:F1.2.

Hogan S, Zhang L, Li J, Zoecklein B, Zhou Z (2009). Antioxidant properties and bioactive components of Norton (*Vitis aestivalis*) and Cabernet Franc (*Vitis vinifera*) wine grapes. LWT Food Sci Technol 42: 1269–1274.

Karaaslan M, Yilmaz FM, Cesur O, Vardin H, Ikinci A, Dalgic A C (2013). Drying kinetics and thermal degradation of phenolic compounds and anthocyanins in pomegranate arils dried under vacuum conditions. Int J Food Sci Technol 49: 595–605.

Kelebek H, Jourdes M, Selli S, Teissedreb PL (2013). Comparative evaluation of the phenolic content and antioxidant capacity of sun-dried raisins. J Sci Food Agric. 93: 2963–2972.

Li Y, Guo C, Yang J, Wei J, Xu J, Cheng S (2006). Evaluation of antioxidant properties of pomegranate peel extract in comparison with pomegranate pulp extract. Food Chem 96: 254–260.

Lutz M, Jorquera K, Cancino B, Ruby R, Henriquez C (2011). Phenolics and antioxidant capacity of table grape (*Vitis vinifera*) cultivars grown in Chile. Food Chem 76: 1088–1093.

Mitic MN, Obradovic MV, Grahovac ZB, Pavlovic AN (2010). Antioxidant capacities and phenolic levels of different varieties of Serbian white wines. Molecules 15: 2016–2027.

Morais H, Ramos C, Forgács E, Cserháti T, Oliviera J (2002). Influence of storage conditions on the stability of monomeric anthocyanins studied by reversed-phase high-performance liquid chromatography. J Chromatog B 770: 297–301.

Noguerol-Pato R, González-Barreiro C, Cancho-Grande B, Santiago JL, Martínez MC, Simal-Gándara J (2012). Aroma potential of Brancellao grapes from different cluster positions. Food Chem 132: 112–124.

Ozturk I, Karaman S, Baslar M, Cam M, Caliskan O, Sagdic O, Yalcin H (2014). Aroma, sugar and anthocyanin profile of fruit and seed of mahlap (*Prunus mahaleb*): optimization of bioactive compounds extraction by simplex lattice mixture design. Food Anal Method 7: 761–773.

Rockenbach II, Gonzaga LV, Rizelio VM, De Souza Schmidt Gonc-Alves AE, Genovese MI, Fett R (2011). Phenolic compounds and antioxidant activity of seed and skin extracts of red grape (*Vitis vinifera* and *Vitis labrusca*) pomace from Brazilian winemaking. Food Res Int 44: 897–901.

Ruiz-García L, Hellín P, Flores P, Fenoll J (2014). Prediction of Muscat aroma in table grape by analysis of rose oxide. Food Chem 154: 151–157.

Santos LP, Morais DR, Sauza NE, Cottica SM, Boroski M, Visentainer JV (2011). Phenolic compounds and fatty acids in different parts of *Vitis labrusca* and *V. vinifera* grapes. Food Res Int 44: 1414–1418.

Sabarez HT (2014). Mathematical modeling of the coupled transport phenomena and color development: finish drying of trellis-dried sultanas. Drying Technol 32: 578–589.

Singleton VL, Rossi JA (1965). Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. Am J Enol Vitic 16: 144–158.

Vilanova M, Genisheva Z, Bescansa L, Masa A, Oliveira JM (2012). Changes in free and bound parts of aroma compounds of four *Vitis vinifera* cultivars at the last ripening stages. Photochem 74: 196–205.

Wang WD, Xu SY (2007). Degradation kinetics of anthocyanins in blackberry juice and concentrate. J Food Eng 82: 271–275.

Xu C, Zhang Y, Cao L, Lu J (2010). Phenolic compounds and antioxidant properties of different grape cultivars grown in China. Food Chem 119: 1557–1565.

Yemis O, Bakkalbasi E, Artik N (2008). Antioxidative activities of grape (*Vitis vinifera*) seed extracts obtained from different varieties grown in Turkey. Int J Food Sci Technol 43: 154–159.

Yilmaz Y, Toledo RT (2004). Major flavonoids in grape seeds and skins: Antioxidants capacity of catechin, epicatechin, and gallic acid. J Agric Food Chem 52: 255–260.

Zhishen J, Mengcheng T, Jianming W (1999). The determination of flavonoid contents in mulberry and their scavenging effects on superoxide radicals. Food Chem 64: 555–559.