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Research Article

Comparison of Some Biochemical Properties in the Seeds and Juice of Grapevine Cultivars (*Vitis vinifera* L.)

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Abstract: This study revealed some biochemical properties in the seeds and the fruit juice of twelve local grapevine cultivars- Karrod, Siyah gozane, Tayifi, Resealya, Heseni, Boga, Binetati, Beyaz sinciri, Askar, Emiri, Duvrevi, and Cicikenator. The colored and white grapes were categorized separately, and it was evaluated whether the skin color affected the biochemical content of the seed, and the compositions of the seeds were compared with the parallel samples taken from the juice. Total phenolic contents, proanthocyanidin contents, and total antioxidant capacities were also determined in the samples taken from the seeds and fruit juice for comparison purposes. The obtained results were mostly statistically significant [(P<0,01), (P<0,05)]. Considering the highest values detected in the seeds; the highest phenolic content was determined in cv. Binetati (87.30 GAE mg $100g^{-1}$); antioxidant capacity was in cv. Gozane (1344.86 mg g^{-1}) and Proanthocyanidin value was in cv. Cicikenator (34.19 mg CE g^{-1}).

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1. Introduction

Grapevine, which is known to have been cultivated in Anatolian lands for at least 8 thousand years, is among the most important cultural plants for all civilizations that have existed in these lands. In addition to being consumed as fresh and dried grapes, it can be converted into many products such as wine, vinegar, molasses, fruit pulp, and several other sweets (kofter, sucuk, bastik, etc.) obtained by processing the must (Gazioglu Sensoy and Tutus, 2017; Unal, 2022). Around 4.2 million tons of grape production, which is 91 million tons worldwide, is made in Türkiye. Among the world countries, Türkiye ranks 5th with its vineyard area of 405 439 ha and 6th in terms of production amount. It has been reported that a total of 4.2 million tons of grapes are produced in the country, 2.2 million tons of which are table grapes, 1.5 million tons for dried, and about 0,5 million tons of wine (Anonymous, 2020).

Although studies on grapevines are generally concentrated in fruit juice, few studies have shown that the nutrient content in the seed is approximately four times higher than in fruit juice (Pantelić et al., 2016; Kamaladdin et al., 2020). Because most of the total grape production in the world is processed into wine, approximately 10 million tons of grape pulp is produced in the world in a few weeks of the harvest campaign. This pulp remaining from wine and grape juice production contains significant levels of bioactive compounds (Demirtas et al., 2013; Barba et al., 2016; Gazioglu Sensoy, 2019). Grape seeds constitute an important part of this pulp, 38-52% by dry weight. While many wineries did not consider grape pulp as recyclable waste until recent years, these pulps, which have a very high nutritional value, have started to be sold as raw materials for factories producing grape seed oil or for sectors producing cosmetics and pharmaceuticals due to their high antioxidant content (Teixeira et al., 2014; Rombaut et al., 2015; Machado and Perles, R. 2017; Sevindik and Selli, 2020). It has been reported that the annual average amount of grape seed production in Türkiye is 25 000- 30 000 tons (Anonymous, 2014).

The most significant byproducts from the wine and grape juice industries are grape seeds, and proteins (6.3-11%), fiber (40%), oil (11.6-16.5%), complex carbohydrates (29.2%), proanthocyanidin, phenolic compounds, fatty acids, minerals, tocopherols, and other vitamins are all present in large amounts in grape seeds (Molva and Baysal 2015; Tangolar et al. 2019).

A survey study conducted in the province of Siirt, where the plant material is supplied, states that although the region has a very high potential in the field of viticulture, this potential is not used sufficiently, especially in terms of the amount of product obtained from the unit area (Gazioglu Sensoy et al, 2020). The present study aimed to provide a better understanding of the importance and value of both grape seeds and grape juice in these genetic sources. Revealing the valuable compositions of the seeds might help to prevent the seed leftovers from the production of foods made from molasses and grape juice, which are parts of this ancient culture, as waste, and to bring these valuable wastes into production. It is thought the present study might constitute an important reference for studies on the determination of chemical properties of other grapevine cultivars. The data within the scope of the study were categorized based on the white and colored grapevines to determine the effect of grape skin color on the studied traits.

2. Material and Methods

2.1. Plant materials and sampled vineyards

In the present study, twelve local grape cultivars are grown in the Siirt province of Türkiye colored grapes (Karrod, Siyah Gozane, Emiri, Tayifi, Resealya, and Boga) and white grapes (Askar, Duvrevi, Binetati Cicikenator, Haseni, and Sinciri) were studied as the plant materials. All of the cultivars were not grafted and grown on their roots. They all have produced similar conditions; in rainfed conditions with no fertilization. Goble applications are traditional training systems for 10-15 years old vineyards.

2.2. Methods

2.2.1. Sample preparation

The width, length, and weight measurements of the seeds and the number of seeds were determined in the samples taken from the local cultivars chosen from the vineyards with similar cultivation conditions. The above-mentioned measurements, counts, and weighing were carried out in 3 replications for each cultivar and 10 berry samples (taken as mixed from the middle parts of the clusters) per replication (using two clusters randomly taken from 5 different vines). Grape berries were harvested at full maturity in the 2020 production season and stored at -20 °C until analysis, and fresh grape seeds were used in the analysis. (Duran, 2014; Demiray, 2019). Total phenolic compounds, total antioxidant capacity, and proanthocyanidin in the seeds and grape juice of the cultivars were studied.

2.2.2. Total phenolic content

Total phenolic content was determined by spectrophotometer by modifying the Folin-Ciocaltaeu calorimetric method (Swain and Hillis, 1959). About 50 g of grape berry flesh was fragmented and 1 ml of grape juice from each sample was transferred to centrifuge tubes. About 5 g of grape seeds were fragmented and 1 g from each sample was transferred to centrifuge tubes. Then, 5 ml of methanol was added and centrifuged at 10 000 rpm for 10 minutes, and the supernatant remaining on top was taken. 150 µl of supernatant is taken from the part, 2400 µl of distilled water, 150 µl of Folin cioucelta (1:10 solution) are added, 3-4 seconds vortex is made, 300 µl of 20% sodium carbonate is added, and it is kept in the dark at room temperature for 60 minutes, then the absorbance of the resulting solution was read spectrophotometrically at 725 nm wavelength and the total amount of phenolic substance was expressed as gallic acid equivalent (GAE) mg 100 g^{-1} fresh weight (FW). The analyses were carried out in 3 replications for each cultivar.

2.2.3. Total antioxidant capacity

About 50 g of grape berry flesh was fragmented and 1 ml of grape juice from each sample was transferred to centrifuge tubes. About 5 g of grape seeds were fragmented and 1 g from each sample was transferred to centrifuge tubes. Then, 5 ml of methanol was added and centrifuged at 10 000 rpm for 10 minutes, and the supernatant remaining on top was taken. The FRAP (Ferric Reducing Antioxidant Power) reagent was prepared with a 300 mmol l^{-1} acetate buffer (pH 3.6), 20 mmol/L ferric chloride ($FeCl_3.6H_2O$), and 10 mmol/L TPTZ (2,4,6-tripyridyl-s-triazine in 40 mmol/L hydrochloric acid) at a ratio of 10:1:1. The mixture prepared for ABTS analysis with 2850 µl of FRAP reagent for samples was diluted 50 times with ethanol, then 150 µl of the sample was mixed and left at room temperature for 30 minutes. The resulting ferrous tripyridyl triazine complex was measured at 593 nm in the spectrophotometer and the results were reported as µmol Trolox equivalent (TE) g^{-1} FW (Lutz et al., 2011). Trolox concentration range has been studied as 0-500 ppm.

2.2.4. Proanthocyanidin content

About 50 g of grape berry flesh was fragmented and 1 ml of grape juice from each sample was transferred to centrifuge tubes. About 5 g of grape seeds were fragmented and 1 g from each sample was transferred to centrifuge tubes. After the samples were centrifuged, the supernatant remaining on top was removed, first passed through coarse filter paper and then through a 0.45 µm membrane filter twice. The obtained extraction was kept at -20°C until readings were taken. The total proanthocyanidin content of the must and seeds of the cultivars was determined using the dimethylaminocinnamaldehyde (DMACA) method. A 1% (w/v) DMACA solution in a cold mixture of methanol and HCl (4:1) was prepared just before analysis. It was diluted with methanol (1/10, v/v) and 1.5 mL of acidified DMACA solution was added to 30 µL of extraction. The mixture was allowed to react for 10 minutes at room temperature. The samples were read against a methanolic blank solution at 640 nm absorbance in the spectrophotometer. The amount of proanthocyanidin was standardized according to a catechin curve expressed as mg catechin (CE) equivalent/gram (mg (CE) g^{-1}) (Nayak et al., 2018). The amount of proanthocyanidin was standardized according to a catechin curve expressed as mg catechin (CE) equivalent g^{-1} (mg CE g^{-1}). The calibration curve was formed by diluting the stock solutions with methanol to give the standard concentration for catechin [(+) Catechin Sigma Aldrich] in the range of 1-250 mg l^{-1}. The analyses were carried out in 3 replications for each cultivar.

2.2.5. Statistical analysis

The measurement, weighing, and laboratory analysis results obtained in the study were subjected to a completely randomized design, and the differences among the grape cultivars were analyzed with the One-way ANOVA in the SPSS package program (IBM SPSS Statistics 21.0). Duncan's multiple comparison test was used to determine the differences between the means according to $P<0.01$ and $P<0.05$ levels. Significance levels, mean values, and ± standard error values are indicated in the tables (Eckstein, 2013).

3. Results

3.1. Seed traits

The difference in the number of seeds of the cultivars was statistically significant ($P<0.01$), and the maximum number of seeds per berry was 3.00 in cv. Emiri with black skin color and the least seed per berry was 1.47 in cv. Heseni with white skin color. It was seen that the number of seeds of the colored cultivars was higher and the average number of seeds according to the colors was also significant ($P<0.01$). (Table 1). There were significant ($P<0.01$) differences for each grape color. Accordingly, the highest value was found to be 0.12 g in cv. Cicikenator and the lowest value was 0.06 g in cv Karrod, cv. Boga and cv. Askar. Seed weights were not statistically different between the two grape skin colors (Table 1). The seed widths of each cultivar were statistically significant ($P<0.01$), but the difference between grape skin colors was insignificant. The highest value was determined as 4.83 mm in cv. Siyah Gozane and the lowest value was found as 3.20 mm in cv. Beyaz Heseni (Table 1). There was a significant (P<0.01) difference, and the highest value was 9.77 mm in the white cv. Cicikenator and the lowest value was 4.60 mm in black cv. Emiri (Table 1). The seed size was also found to be significantly different (P<0.01), with the highest value being 44.18 mm in white cv. Cicikenator variety and the lowest 14.63 mm in the black cv. Emiri variety (Table 1).

Table 1. Some seed traits in the studied grape cultivars

Grape skin color	Grape cultivars	Seed number	Seed weight (g)	Seed width (mm)	Seed length (mm)	Seed size (width x length)
White	Askar	1.60±0.12B-D**	0.06±0.00 C**	3.90±0.06 B**	7.33±0.09BC**	28.61±0.77 C**
	Binetati	2.73 ±0.07 A	0.07± 0.00 B	3.70±0.15 B	7.70±0.21 B	28.55±1.92 C
	Sinciri	1.73 ±0.18 BC	0.11± 0.01 A	4.43±0.15 A	7.90±0.23 B	34.96±0.15 B
	Heseni	1.47 ±0.07CD	0.08± 0.00 B	3.20±0.06 C	6.33±0.03 D	20.27±0.46 D
	Cicikenator	1.20± 0.12 D	0.12± 0.01 A	4.53±0.19 A	9.77±0.62 A	44.18±2.56 A
	Duvrevi	2.00 0.20 B	0.09± 0.00 B	3.80±0.12 B	6.47±0.17 CD	24.57±0.96 CD
	Mean	**1.79±0.13 B****	**0.09±0.01 ^{ns}**	**3.93±0.12 ^{ns}**	**7.58±0.29 A****	**30.19±1.92 ^{ns}**
Colored	Boga	2.80±0.12AB**	0.06±0.00C**	4.50±0.00 AB**	7.27±0.19 ^{ns}	32.70±0.84 A**
	Karrod	1.60±0.23 C	0.06±0.01 B	3.37±0.17 C	6.50±0.12	21.85±0.75 BC
	Tayifi	1.67±0.24 C	0.09±0.00 A	3.83±0.19 BC	7.13±0.19	27.31±1.11 AB
	Siyah gozane	2.93±0.24 AB	0.10±0.01 B	4.83±0.38 A	6.97±0.12	33.76±3.28 A
	Emiri	3.00±0.12 A	0.09±0.00 A	3.33±0.23 C	4.60±1.95	14.63±6.11 C
	Resealya	2.33±0.13 B	0.10±0.00 B	3.73±0.18 C	6.60±0.15	24.66±1.45 AB
	Mean	**2.39±0.15 A**	**0.08±0.00**	**3.93±0.16**	**6.51±0.35 B**	**25.82±1.88**
	General mean	**2.0889±0.11**	**0.09±0.00**	**3.93±0.10**	**7.05±0.00**	**28.00±1.38**

** Values within the same column for white or colored grapevine cultivars not followed by the same letter indicate a significant difference (P<0.01); ns: non-significant.

3.2. Biochemical Content

3.2.1. Total phenolic content

It was found to be significantly varied (P<0.05) in varieties with white grapes- the lowest amount was in cv. Cicikenator, but insignificant in colored grapes. Moreover, there were significant differences in the total phenolic contents in the grape juices of both white and colored cultivars; the white cultivars Askar and Sinciri and black cv. Emiri stands out in terms of total phenolic content. It was determined that the amount in the seed was considerably higher (about twice) than the fruit juice (Table 2).

Table 2. Total phenolic matter contents

Grape skin color	Grape cultivars	Phenolic matter in the seed (GAE mg $100g^{-1}$)	Phenolic matter in the grape juice (GAE mg $100g^{-1}$)
White	Askar	86.19± 5.28 A*	59.99±15.87 A*
	Binetati	87.31± 2.44 A	28.37±7.54 AB
	Sinciri	85.64± 3.01 A	47.31±15.31 A
	Heseni	78.19 ±0.99 AB	10.41±0.52 B
	Cicikenator	72.77 ±0.32 B	27.95±4.89 AB
	Duvrevi	81.61 ±3.90 AB	42.26±9.54 AB
	Mean	**81.95± 1.65**	**36.05±5.27**
Colored	Boga	77.07 ±3.50 ns	34.76±5.44 B*
	Karrod	76.01 ±0.40	18.97±3.18 B
	Tayifi	77.68 ±1.00	33.65±12.69 B
	Siyah gozane	80.18 ±5.09	42.21±5.75 AB
	Emiri	83.56± 3.70	61.29±6.28 A
	Resealya	81.70 ±3.54	31.66±5.17 B
	Mean	**79.37 ±1.31**	**37.09±3.94**

* Values within the same column for white or colored grapevine cultivars not followed by the same letter indicate a significant difference (P<0.05); ns: non-significant.

3.2.2. Total antioxidant capacity

It is seen that the antioxidant capacity of the seed is much higher than the fruit juice. The difference between the cultivars in terms of total antioxidant capacity was significantly varied in both white (P<0.05) and colored cultivars (P<0.01) (Table 3). The white cultivars except for cv. Sinciri and black cultivars Siyah gozane and Resealya stand out in terms of total phenolic content in the seeds. Moreover, white cv. Duvrevi and black cv. Emiri had the highest total phenolic content in grape juice.

3.2.3. Proanthocyanidin contents

It is also seen that the proanthocyanidin content of the seed is much higher than the fruit juice. The difference between the cultivars in terms of total proanthocyanidin content was significantly varied in both white and colored cultivars (P<0.01) (Table 4). The white cv. Cicikenator and black cultivars Siyah gozane and Tayifi stand out in terms of proanthocyanidin content in the seeds. Moreover, white cv. Askar and black cv. Emiri and cv. Tayifi had the highest proanthocyanidin content in the grape juice.

Table 3. Total antioxidant capacity

Grape skin color	Cultivar	Antioxidant capacity in the seed (µmol (TE) g^{-1})	Antioxidant capacity in the grape juice (µmol (TE) g^{-1})
White	Askar	750.57± 165.79 A*	1.22±0.14 B**
	Binetati	786.29± 154.21 A	1.28±0.66 B
	Sinciri	296.29± 86.15 B	1.02±0.23 BC
	Heseni	749.14± 138.23 A	0.07±0.01 C
	Cicikenator	957.71± 121.78 A	0.81±0.19 CD
	Duvrevi	516.29± 129.58 AB	4.48±0.19 A
	Mean	**676.05± 69.379**	**1.48±0.36**
Colored	Boga	609.14± 124.47 B**	2.67±0.63 B**
	Karrod	419.43± 95.74 B	0.87±0.24 C
	Tayifi	689.14± 95.86 B	2.89±0.27 B
	Siyah gozane	1344.86 ±161.33 A	2.86±0.00 B
	Emiri	607.71 ±128.74 B	4.29±0.15 A
	Resealya	1193.43± 262.26 A	2.61±0.51 B
	Mean	**810.62± 97.617**	**2.70±0.27**

Values within the same column for white or colored grapevine cultivars not followed by the same letter indicate a significant difference **(P<0.01); *(P<0.05).

Table 4. Proanthocyanidin contents

Grape skin color	Cultivar	Proanthocyanidin in the seed (mg CE g^{-1})	Proanthocyanidin in the grape juice (mg CE g^{-1})
White	Askar	25.55±6.05 B**	0.28±0.06 A**
	Binetati	14.84±1.99 CD	0.04±0.02 BC
	Sinciri	7.31±0.64 D	0.05±0.01 BC
	Heseni	12.77±0.73 CD	0.01±0.01 C
	Cicikenator	34.19±1.23 A	0.03±0.00 C
	Duvrevi	17.52±0.36 BC	0.13±0.03 B
	Mean	**18.69±2.33**	**0.09±0.02**
Colored	Boga	16.38±1.54 B**	0.09±0.01 B**
	Karrod	13.02±1.41 B	0.01±0.00 C
	Tayifi	25.52±1.50 A	0.17±0.01 A
	Siyah gozane	22.65±2.04 A	0.09±0.02 B
	Emiri	12.89±2.04 B	0.15±0.03 A
	Resealya	17.58±0.91 B	0.07±0.02 B
	Mean	**18.01±1.27**	**0.09±0.01**

** Values within the same column for white or colored grapevine cultivars not followed by the same letter indicate a significant difference (P<0.01).

4. Discussion

4.1. Seed traits

Approximately 20% of the grapes consist of seeds. In the wine and fruit juice industry, grape seed emerges as a secondary product. It is known that approximately 15-25% of grapes are produced after processing the grapes. It has been determined that grape pomace is composed of approximately 33-45% of seeds (Yu & Ahmedna, 2013; Dwyer, 2014). Kupe et al. (2021) studied different clones of the Turkish grape cultivar 'Karaerik' and the seed traits given for common cultivars used in both studies show parallelism. In the present study, the highest and the lowest seed number values were determined between 1 to 4. In a study examining the sizes of 12 grape varieties grown in Southeastern Anatolia, seed properties ranged in: length, 5 - 8.5 mm; width, 2.5 - 5.5 mm; and thickness, 2 - 4.7 mm (Levent and Demir, 2020). In a study comparing the morphological features and chemical components of the seeds of 6 table grape varieties, the number of seeds per berry was 2-5; the average weight of the seeds was 82-315 mg; the weight of the seeds was 17-73 mg; the length of the seed was 1.4 - 9.3 mm; and the seed width was 1.9-5.8 mm (Elagamey, 2013). Dogan and Uyak (2022), in their study on some table grape varieties, found that the total antioxidant capacity of varieties with red-black skin color varied between 6.45-8.21 µmol TE g^{-1}; and they reported that the total antioxidant capacity of cultivars with green-yellow peel color varied between 4.27-6.20 µmol TE g^{-1} during the harvest period. Aydın (2015) reported the lowest total antioxidant capacity as 2.06 µmol TE ml^{-1} for cv. Sari kokulu and 9.33 µmol TE ml-1 for cv. Civek. In the present study, the seed samples of 12 local grape varieties grown in Siirt province in terms of various seed traits were as: the number of seeds ranges from 1.20 to 3.00; seed weight varied from 0.07- 0.12 g; seed width ranged from 3.20 to 4.83 mm; and seed length varied as 6.47-9.77. The white varieties were significant in all traits ($P<0.01$); and colored cultivars were significant ($P<0.01$), except for the seed size value. When evaluated according to the color of the seed, it was seen that the average number of seeds was higher in colored varieties, and the seed weight and seed length were higher in white varieties.

4.2. Phenolic matter content

In the present study, the distribution of the total phenolic contents of the seeds based on white cultivars varied from 72.77 to 87.31 mg GAE $100g^{-1}$; and it was found in the range of 76.01 to 83.56 mg GAE $100g^{-1}$ in colored cultivars. Moreover, the distribution of the total phenolic contents of the grape juice based on white cultivars varied from 10.41 to 59.99 mg GAE 100 g^{-1}, while the values of colored cultivars ranged from 18.97 to 61.29 mg GAE $100g^{-1}$. The phenolic contents of the seeds of the white cultivars were higher than the seeds of the colored cultivars. Grape juice total phenolic content values were found to be quite close to each other in white and colored cultivars. As a result of the study, it was observed that the ratio of total phenolic content in the seed was quite high compared to fruit juice.

Kupe et al. (2021) studied 9 different clones of the Karaerik grape cultivars and found that the highest FRAP values were expressed from seeds. The seed extract from FRAP values between are varied 52460 µmol Trolox 100 g^{-1} FW and 39880 µmol Trolox 100 g^{-1} FW. In fruit pulp, this value was found between 128 µmol Trolox 100 g^{-1} FW and 77 µmol Trolox 100 g^{-1} FW. In a study by Pantelić et al., (2016), the total phenolic concentration in grape seed samples ranged between 102.98 and 38.02 mg GAE g^{-1}, and grape juice samples ranged between 0,20-0,07 mg GAE g^{-1}, respectively. In a study of fresh grapes, the total phenolic content was 3.35 GAE mg g^{-1} in cv. Gros noir, 1.21 mg GAE g^{-1} in cv. Cardinal, 3.04 mg GAE g^{-1} in cv. Muscat noir, 1.82 mg GAE g^{-1} in cv. Victoria, and 1.58 mg GAE g^{-1} in cv. Muscat blanc (Derradji et al., 2014). In another study, in which the total phenolic content of 33 different grapevines was determined, the average phenolic contents of black, green, and red grapes were expressed as 77.00, 44.56, and 31.42 mg GAE $100g^{-1}$ (Chen et al., 2014). In a study evaluating the effects of whole grape pomace flour, seedless pomace flour, and seed flour on the quality of cookies, it was determined that the total phenol and antioxidant activities of cookies containing 10% seed flour were found to be higher than other additives, thus increasing the nutritional value the most (Acun and Gul, 2014). Gül et al. (2013), in their study on Narince and Okuzgozu cultivars, determined the total phenolic content of seed samples to be 563.27 g GAE kg^{-1} and 552.10 g GAE kg^{-1}, respectively. In another study in which phenolic compounds were determined in the seeds of *Vitis labrusca* B., the mean value was determined as 2.41 mg GAE l^{-1} (Ghafoor et al., 2012). In a study in which 7 standard cultivars and 5 wild vine genotypes were examined, the total phenolic content of grape seed extracts was determined as between 1694 and 1136 mg GAE 100 g FW^{-1} (Yegin and Uzun, 2018). Karateke et al., (2022), stated that the total phenolic content in grapes taken from control vines was 254.80 mg GAE $100g^{-1}$. In a study by Doshi et al. (2015), the total phenolic content of the Pusa navarang variety was determined as 95.8 mg ml^{-1}. The results of the present study do not fully agree with the studies mentioned in this paragraph; it is thought that the difference is due to different effects such as varietal traits, ecological differences, phenological periods from which the samples were taken, growing conditions, as well as the difference in the method used. On the other hand, Çakır et al. (2021) stated that some quality criteria may vary from year to year as well as the grape variety used, the way the grape is evaluated, climate, rootstock used, soil, aspect, cultural processes and altitude groups. In the study conducted by Gazioglu Sensoy et al. (2018), the average phenolic content was 73.60 mg GAE $100g^{-1}$ in the seed; 58.73 mg GAE $100g^{-1}$ in the skin, and 40.52 mg GAE $100g^{-1}$ in the fleshy part of the grape. The results expressed by the literature are generally compatible with the present study.

4.3. Total antioxidant capacity

Significant differences were observed among the values obtained for the antioxidant capacity in the seed parts of the studied cultivars; The highest value was measured with 1344.86 µmol TE g^{-1} in cv. Siyah gozane, which is a black variety, and the lowest value was measured in the variegated cv. Karrod with 242.00 µmol TE g^{-1}. In grape juice, the black cv. Duvrevi had the highest value with 4.48 µmol TE g^{-1} and cv. Heseni variety with white skin color had the lowest value with 0.07 µmol TE g^{-1}. The values were determined to be high in the seed and very low in the grape juice compared to the seed. In general, it was determined that the average values of the colored cultivars were higher than those of the white cultivars. It was seen that the rate was higher in colored varieties. Researchers stated that the antioxidant content of grapes is mostly in the skin and seeds. It was also reported that the antioxidant capacity of the extracts obtained from grape pomace was high. In the present study, it was determined that the antioxidant content in grape seeds was significantly higher when compared to grape juice. In the study conducted by Gazioglu Sensoy et al., (2018), the average antioxidant capacity was 1009.85 µmol TE g^{-1} in the seed; It was expressed as 310.92 µmol TE g^{-1} in the skin and 204.39 µmol TE g^{-1} in the pulp.

In a study conducted on grape juice, it was reported that the average antioxidant capacity of black grapes was 94.30 µmol TE 100 ml^{-1}, and that of white grapes was 31.10 µmol TE 100 ml^{-1} (Keskin-Šašić et al., 2012). In another study, the average antioxidant capacities of black, green, and red grapes were 3.34, 2.75, and 1.36 µmol TE g^{-1}, respectively (Chen et al., 2014). Pantelić et al., (2016) determined the total antioxidant content of the cultivars as 1039.92 and 481.69 µmol (TA) g^{-1}, respectively. Sochorova et al., (2020) determined that average antioxidant activity values using the FRAP method vary according to the cultivars in the years as it was 12,217 µg g^{-1} GAE in 2015; 13,724 µg g^{-1} GAE in 2016; and 14,807 µg g^{-1}GAE in 2017. Liu et al. (2018), in a study examining the FRAP values of 30 separately measured in grape pomace, stated that many researchers stated that the differences in antioxidant capacity in different grapes could be very large. Gazioglu Sensoy (2012) determined that the antioxidant activity values of the cultivars Kis kirmizisi, Okuzgozu, Agin beyazi, Ercis uzumu, and Silfoni; the highest antioxidant content was determined in cv. Kis kirmizisi as 5.74 mmol TE L^{-1}, and the lowest value was found in Ercis uzumu as 2.29 mmol TE L^{-1}. These values were largely similar except for a few varieties. The antioxidant capacity obtained by the FRAP method of several local grape varieties grown in Elazığ and Malatya provinces by Duran (2014) ranged from 2.64 mg TE L^{-1} to 31.47 mg TE L^{-1}. Sanyürek et al. (2018) conducted a study on several local cultivars grown in Tunceli province and determined the antioxidant capacity in the range from 32.30 µg TE ml^{-1} to 56.20 µg TE ml^{-1}. Tahmaz and Soylemezoglu (2019) studied the antioxidant contents of the grape skin and seeds separately by the HPLC method, and the antioxidant capacity of the seeds in all varieties was higher than the skins, and the highest content in the grape skin was measured in cv. Bogazkere as 544.3 µmol TE g^{-1} and the lowest in cv. Calkarası as 60.1 µmol TE g^{-1}. The highest antioxidant content in the seeds was measured in cv. Okuzgozu with 1133.00 µmol TE g^{-1}, and the lowest in cv. Bogazkere with 573.1 µmol TE g^{-1}. It was determined that the antioxidant content of the seeds compared with the fruit juice content was 99% higher than that of the grape juice. Most of the studies have found similar antioxidant values to the present study. Uyak et al. (2020) examined grape varieties that have similar ecology and maintenance conditions and observed statistical differences in terms of organic acid and phenolic compound contents;

therefore, it was reported that the variety was an effective factor in the chemical composition. Similarly, in the present study, it was determined that the results differed according to the cultivars.

4.4. Proanthocyanidin content

Proanthocyanidins, which are found in high amounts in grape seeds, regulate lipid homeostasis; and balance hyperlipidemia, one of the main causes of cardiovascular disease (Margalef, et al., 2014; Nunes et al., 2016). Numerous types of research utilizing both human and animal models have found that proanthocyanidins offer considerable health advantages. These have anti-protective effects against oncogenic events, metabolic diseases, and cardiovascular illnesses. Proanthocyanidins are therefore anticipated to be viable medicinal treatments for such discrepancies. (Nie and Stürzenbaum, 2019; Rauf et al, 2019). It has been stated that the grape seed is a very valuable product that cannot be seen as a waste, as it contains approximately 90% of proanthocyanidins and is rich in unsaturated fatty acids (Aktan and Kalkan, 2000). Mattivi et al. (2009) reported that proanthocyanidins in the structure of grape seeds vary according to the grape variety and ripening stages, but the largest amount of proanthocyanidins is localized in the seed. In the study in which the differences in the amount and structure of extractable skin and seed tannins between red grape varieties were revealed, the catechin equivalent value in the seed content was found to be the highest in cv. Pinot Noir with 232.9 mg (CA) kg^{-1} and the lowest was detected in cv. Syrah variety, 16.8 mg (CA) kg^{-1}. It is seen that the majority of the studies on proanthocyanidins are in the basic field of medicine. The amount of proanthocyanidin contained in the seed and fruit juice is proportionally quite different, and the proanthocyanidin content of the seed is much higher than the fruit juice. The difference between the cultivars in terms of total proanthocyanidin content was significantly varied in both white and colored cultivars. It was also seen that the proanthocyanidin content in the seed was quite high; in both, the proanthocyanidin content did not have a significant relationship with the grape skin color; It was determined that the color of the fruit skin did not make a difference in the proanthocyanidin content of the fruit juice, as in the seed. It is also seen that the majority of the studies on proanthocyanidin are in the basic field of medicine.

5. Conclusion

The present study is important in terms of determining some seed and grape juice traits of this grapevine germplasm, which is in danger of extinction. Considering the phenolic amounts, it was seen that the black varieties had higher amounts than the white varieties. It was also determined that the total antioxidant amounts were quite high in the seeds compared to the grape juice. It was determined that the total proanthocyanidin amounts were higher in the seed than in the grape juice. In the present study, it is seen that the biochemical properties of grapes are higher in the grape seeds than those of the grape juice and the skin, and this study is parallel when compared with other studies. The present study re-emphasized the fact that grape seeds could be used for both health and different evaluation forms increasing the value of this product.

There are not enough studies on grape seeds, and the total phenolic and antioxidant capacity are generally emphasized in the literature; It is seen that there are fewer studies dealing with proanthocyanidin content. Grape seed, both an important agricultural and industrial product, has bioactive components beneficial to human health. Its content has positive effects on human health supported by the literature in medicine, pharmacy, and food processing. In addition to the valuable phenolic substances, antioxidants, and proanthocyanidin contents were revealed in the present study. The present study has revealed again how valuable the grape seed is. Conscious consumption will be ensured thanks to the determination of the chemical compounds in the grape, especially in its seeds, and it has been determined that this important product can be used in many areas from cosmetics to the pharmaceutical industry, from the food industry to animal nutrition. By intensifying research on grape seed, this product, which is seen as a waste material, will be brought to different industries and new evaluation methods will be introduced. For this reason, researches on proanthocyanidin components, and phenolic and antioxidant contents of grape seeds provide important contributions to the reproduction and economy of this product, which is at risk of being lost without value.

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