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Study of Primary and Secondary Metabolites of Stenospermocarpic, Parthenocarpic and Seeded Raisin Varieties

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Abstract: (1) Background: Stenospermocarpic (Sultani Çekirdeksiz and Black Kishmish), parthenocarpic (Black Corinth), and seeded varieties (Ekşi Kara and Gök Üzüm) are used for raisin production. To our knowledge, there is little available information about the biochemical characteristics of raisins produced from these varieties. (2) Methods: Some metabolites, such as hormones, sugars, vitamins, minerals, and amino acids, including enzymatic activity, were determined in different raisin varieties. (3) Results: Seedless raisin varieties presented higher content of several hormones, vitamins, and minerals, as antioxidant capacity than the raisins produced from seeded varieties. Contrary to this, seeded raisin varieties presented higher contents of most measured sugars and amino acids than the raisins produced from seedless varieties. (4) Conclusions: Biological mechanisms of pollination and fertilization induced modifications in the primary and secondary metabolism of grapes, considerably affecting biochemical compounds and the antioxidant capacity of raisins.

Keywords: amino acids; grape; hormones; minerals; raisins; sugars; vitamins

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1. Introduction

Retention of the ovary under the pollination stimulus is usually known as setting fruit or fruit set [1]. Parthenocarpy trait is essential for crop plants, whose commercial product is their fruit, as in the case of grape production [2]. The success of fruit sets depends on pollination and fertilization, while fruit growth and cell expansion are induced by the presence of seeds and their implication on hormone biosynthesis [2]. The absence of fertilization and pollination causes ovary abscission, which results in the cessation of cell division [3]. Despite this, the ovary can be developed without fertilization, giving the place the presence of seedless berries [4]. Parthenocarpy and stenospermocarpy phenomena have been reported in seedless grapevine varieties [5]. Seedless berries are produced in parthenocarpic varieties, whereas in the stenospermocarpic ones, ovule fertilization takes place. Still, embryo and/or endosperm abort as the ovule integuments continue to grow before stopping, leading to small and rudimental seed traces in the mature berry [4]. Black Corinth or Black Currant are considered parthenocarpic varieties, and their berries lack seeds, which are very small and spherical [4,6,7]. Parthenocarpic grapevine varieties are attractive to raisin producers since they solve environmental problems related to pollination and fertilization and provide small-sized fruits best suited for raisin production [8]. Sultanina (syn. Thompson Seedless) is a variety considered stenospermocarpic and has

been used as the primary source of seedlessness in table grape breeding programs [4,9,10]. This variety is known in Turkey as Sultani Çekirdeksiz. Berries from stenospermocarpic varieties contain partially developed seeds or seed traces, and they are generally considered seedless for commercial purposes [4], in which, in some cases, berry size is improved by hormone applications [11]. Stenospermocarpic grapevine varieties are more popular in producing seedless table grape varieties [12].

Grapes are cultivated for different purposes in Turkey, such as table grapes, wine grapes, grape juice, concentrated must, and other local products, such as vinegar, kofter, sausage, and pekmez. Turkey is the third most crucial producer of fresh table grapes behind China and India and over Uzbekistan, Brazil, Egypt, the United States, and Chile. In Turkey, a third of the grape production is dried for raisin production, whereas the rest is mainly destined for fresh grape production. Most Turkey-produced raisins are obtained from Sultani Çekirdeksiz grapes, followed by different varieties, such as Black Kishmish, Ekşi Kara, Gök Üzüm, and Black Corinth grapes, or some other local grape varieties. Raisins are popular dried fruit since they contain easily digestible fibers and a wide range of phenolic compounds, vitamins, minerals, and sugars, that provides high health and nutritional values [13]. Some recent studies have investigated raisins' nutritional and biochemical compounds [13–17]. However, to our knowledge, there are available information about hormones, sugars, minerals, vitamins, enzyme activity, and amino acids of raisins varieties cultivated in Turkey. In addition, few investigations have been published regarding the differences in biochemical components depending on variety fertilization (i.e., parthenocarpic and stenospermocarpic varieties).

Therefore, this research aimed to study the differences in hormones, sugars, minerals, vitamins, enzymes, and amino acids of five Turkish raisin varieties: one parthenocarpic variety (Black Corinth); two stenospermocarpic varieties (Sultani Çekirdeksiz and Black Kishmish) and two seeded varieties (Ekşi Kara and Gök Üzüm).

2. Materials and Methods

2.1. Plant Material and Study Site

The research trial was conducted on two stenospermocarpy varieties, *Vitis vinifera* L. cv; Sultani Çekirdeksiz; Prime name; Sultanina, Variety number VIVC; 12051 and Black Kishmish; Prime name; Kishmish Chernyi, Variety number VIVC; 6256); one parthenocarpic variety (*Vitis vinifera* L. cv; Black Corinth) and two seeded varieties (*Vitis vinifera* L. cv; Ekşi Kara, Prime name; Ekşi Kara, Variety number VIVC; 3852 and Gök Üzüm, Prime name; Goek Uezuem, Variety number VIVC; 4847) during the 2020 season. Sultani Çekirdeksiz, Black Kishmish, and Black Corinth grapes were obtained from a vineyard established in the Manisa Viticulture Research Institute in Manisa (38°37′57.14″ NL and 27°23′57.26″ EL). In contrast, Ekşi Kara and Gök Üzüm grapes were obtained from a vineyard located at the Selçuk University in Konya (38°1′12.33″ NL and 32°30′52.23″ EL). The chosen vines in this trial were 8–12 years old and were spaced at 2.0 m within a row and 3.0 m between rows, accounting for an approximately plant density of 1600 vines.

The selected vineyards were subjected to similar viticultural practices regarding fertilization, irrigation, vine disease, and pruning management. Briefly, vine pests and diseases were controlled, and agricultural chemicals were applied, considering the maximum residual levels and recommended preharvest interval values. Fertilization in the vineyards was used according to soil analysis, and tillage was performed four times in each vineyard soil. Information about the climate conditions of each experimental site was obtained from an automatic wheatear station located at each studied site (Table 1).

Table 1. Climatic information of the Manisa Viticulture Research Institute (Manisa) and Selçuk University (Konya) in the 2020 season.

	Manisa	Konya
Growing-season (April–September)		
Precipitations (mm)	223.89	180.21
ET_o (mm)	924.04	952.04
Minimum temperature (°C)	0.88	−1.01
Average temperature (°C)	23.45	20.53
Maximum temperature (°C)	37.14	31.2
RH (%)	63.1	55.23
Accumulated radiation (MJ m^{-2})	3683	3878
Warmest month (July)		
Average radiation (MJ m^{-2})	21.78	22.86
ET_o (mm)	175.42	178.12
Annual		
Precipitations (mm)	627.4	386.25
ET_o (mm)	1490	1540

Abbreviations: RH, relative humidity. ET_o, reference evapotranspiration.

2.2. Drying Process

Grapes under the study were harvested at similar technological maturity when the soluble solids content reached close to 22 °Brix. Around 12 kg of fresh grapes were harvested at optimum maturity for each grapevine variety, and three replications of 4 kg of grapes were defined. The drying process of grapes was similar to those reported by different authors and followed commercial issues [13,18]. Grape drying was carried out in the Manisa Viticulture Research Institute (Manisa, Turkey) to ensure that all raisins were produced in the same process as the commercial raisins. Black Kishmish, Black Corinth, and Gök Üzüm grapes were directly dried in the sun without applying pretreatments. Sultani Çekirdeksiz grapes were dipped in a potassium carbonate solution and dried in the sun. Ekşi Kara grapes were dipped in wood ash solution and dried in shade conditions [13,18]. Grapes used in the trial were dried until they reach a moisture content of 13–15%. After this, 500 g of each raisin by variety and replication were placed in polyethylene bags and stored at −20 °C.

2.3. Analysis of Hormones in the Raisins Varieties

Analysis for indole-3-acetic acid (IAA) and abscisic acid (ABA) analysis was performed according to the procedure of Kojima et al. [19]. Briefly, raisins tissues were homogenized and filtered three times into a solution containing 80% ethanol (1 g fresh weight). After this, 200 pmol of $^{13}C_6$-IAA and d_6-ABA were added as internal standards into the solution. The solution was then concentrated using a rotary evaporator, adjusted at a pH of 2.8 with dilute hydrochloric acid, and filtered with a 0.22 µm membrane filter. Partition extraction was performed with diethyl ether, which was also concentrated and filtered with a 0.22 µm membrane filter.

The extracts were fractionated with Agilent 1200 Series HPLC (Agilent, CA, USA) equipped with an ultraviolet detector. The HPLC column (Zorbax Eclipse-AAA C-18 column, Agilent, CA, USA) was isocratically eluted with a solution of 40% ethanol and 0.1% of acetic acid. The eluates are corresponding to the retention times of IAA and ABA that were collected separately. IAA and ABA fractions were dried under reduced pressure. After fractionation, the obtained fractions were further purified with the same HPLC system. The HPLC column was isocratically eluted, as was mentioned above. Fractions of IAA and ABA were injected, collected, and dried under reduced pressure. Chromatographic conditions to identify and quantify plant hormones are described by Kojima et al. [19].

Analysis of gibberellin (GA_3) was performed according to the methodology exposed by Kojima et al. [19]. To a solution containing 80% of ethanol (9 g fresh weight), 200 pmol of d_2-GA_3 was added. The solution was then concentrated to 20 mL, adjusted to pH 3.5 with

dilute hydrochloric acid, and filtered with a 0.22 µm membrane filter. Partition extraction was performed using ethyl acetate according to the exposure by Kojima et al. [20].

Anhydrous sodium sulfate at 1 g 10 mL^{-1} was added to the ethyl acetate layer for dehydration and allowed to stand overnight. The ethyl acetate layer was decanted, concentrated, dissolved in 1 mL of ethanol, and filtered with a 0.22 µm membrane filter.

Extracts from the ethyl acetate layer were fractionated using the HPLC system according to Kojima et al. [19,20]. In addition, extraction, separation, and purification of GA were performed according to the methodologies exposed by Kojima et al. [19,20].

Salicylic acid (SA) was analyzed based on the method described by Kim et al. [21] with some modifications. Raisins were ground to a fine powder using a mortar and pestle in liquid nitrogen, and 100 mg of the sample was mixed with the extraction solvents. SA was separated and quantified using an Agilent 1200 Series HPLC (Agilent, CA, USA) equipped with a photodiode array detector (Model YL9160). A 5 µL sample was injected into the HPLC system a Zorbax Eclipse-AAA C-18 column (5 µm, 4.6 × 250 mm, Agilent, CA, USA) that was set to 25 °C. The mobile phases were 0.3% phosphoric acid in water (v/v, solvent A) and 100% methanol (solvent B). The flow rate was 0.8 mL $min^{-1,}$ and the solvent system was programmed as follows: 0% isocratic of solvent B for 5 min, a subsequent gradient of solvent B from 0% to 100% over 40 min, and maintenance at 100% B for 5 min. Data were acquired and analyzed using the YL-clarity 4.0 software. SA contents were calculated using an external standard.

2.4. Analysis of Sugars in the Raisins Varieties

Chemicals for sugars (rhamnose, glucose, galactose, xylose, maltose, fructose, and sucrose) in the raisins were purchased from Sigma (Steinheim, Germany). Sugar extraction was conducted as described by Nikolidaki et al. [22]. A weighted quantity of mechanically homogenized raisins (2 g) was extracted with aqueous ethanol (20 mL, 80% v/v). Sonication and overnight agitation of samples for 2.5 h was applied. For the analysis of sugars in raisins, an HPLC system (Agilent Technologies, 1100 series, USA) combined with a refractive index detector (RID, 1260 series) and equipped with an auto-sampler, an isocratic pump, and a data analysis software was used. Isocratic elution was performed using water/acetonitrile (30:70) on a Purospher® star NH2 (250 × 4.6 mm, 5 µm) (Merck-Millipore, Darmstadt, Germany) column at a flow rate of 1 mL min^{-1}. The injection volume was 10 µL, and RID and oven were maintained at 40 °C. Sample determination was performed using calibration standards of HPLC grade (Sigma-Aldrich, Shanghai, China) sugars.

2.5. Analysis of Enzymes in the Raisins Varieties

Analysis of enzymes was performed according to the methodology exposed by Keskin et al. [13]. Samples were washed three times with 50 mM Tris-HCl + 0.1 M Na_2SO_4 (pH 8.0) and homogenized using liquid nitrogen. Subsequently, samples were transferred to 10 mM NaN_3 + 100 mM PVP + 0.1 M Na_2SO_4 (pH 8.0) + 50 mM Tris-HCl buffer. Samples were then centrifuged at 15,000 rpm for 60 min at 4 °C. Afterward, the glutathione (GSH) activity of samples was determined based on the method described by Minucci et al. [23]. Additionally, the activities of glutathione S-transferase (GST-EC 2.5.1.18) and glutathione reductase (GR-EC 1.8.1.7) were assayed according to the method published by Chikezie et al. [24]. Enzymatic activities in reactions initiated by the addition of enzyme solution were detected spectrophotometrically at 25 °C using a spectrophotometer (Shimadzu 1208 UV, Kyoto, Japan). Superoxide dismutase (SOD-EC: 1.15.1.1), catalase (CAT-EC: 1.11.1.6), and peroxidase (POD-EC: 1.11.1.7) activities of raisin samples were determined based on the methods described by Abedi and Pakniyat [25] and Angelini et al. [26].

2.6. Analysis of Vitamins in the Raisins Varieties

Vitamins were analyzed according to the method published by Keskin et al. [13]. Samples of raisins were sliced and then frozen with liquid nitrogen and stored at −80 °C until the vitamin C analysis. Samples were weighed and then mixed with 2.5 mL of an

extraction solution containing 0.1% oxalic acid, 3% MPA and 8% acetic acid. The sample mixture was then titrated with indophenol solution (25% 2,6-dichloroindophenol and 21 % $NaHCO_3$ in water) until turn to a distinct rose-pink color. Vitamin E analysis was performed in 0.5 g of raisin immersed in 20 mL of ethanol for 30 min in a water bath at 85 °C. The mixture solution was cooled, filtered, and added into a separatory funnel, and then heptane (10 mL) was added, and the mixture was shaken for 5 min. Subsequently, 20 mL of sodium sulfate (1.25%) was added to the solution and shaken again for 2 min to separate layers. Vitamin E was detected by a reaction with cupric ions and their complexation with 2,2′-biquinoline based on the methodology described by Kumar et al. [27]. Samples were then transferred to a conical flask in which 25 mL of the extraction solution was added and sonicated for 40 min at 70 °C. Then, the samples were cooled and finally filtered and mixed with the extraction solution, obtaining 50 mL of the mixture. The extraction solution was again filtered with 0.45 µm filters, and 20 µL injected into the HPLC using an auto-sampler. Separation of B complex vitamins was carried out using an analytical reversed-phase C-18 column (STR ODS-M, 150 mm × 4.6 mm I.D., 5 µm, Shimadzu Corporation, Japan). The mobile phase consisted of a mixture of 100 mM sodium phosphate buffer (pH 2.2) containing 0.8 mM sodium-1-octane sulfonate and acetonitrile (9:1% *v*/*v*) at 40 °C. The flow rate was kept at 0.8 mL min^{-1}. Detection was performed using a PDA at 270 nm. Vitamins B was semi calculated from the standard method described by Mozumder et al. [28].

2.7. Analysis of Minerals in the Raisins Varieties

Samples were oven-dried at 60 °C for 48 h. The Kjeldahl method and a Vapodest 10 Rapid Kjeldahl Distillation Unit (Gerhardt, Königswinter, Germany) were used to detect total N in samples [29]. Macroelements (K, P, Mg, Ca, and Na) and microelements (Zn, Fe, Cl, S, Cu, Mn, and B) were determined using an inductively coupled plasma spectrophotometer (Optima 2100 DV, PerkinElmer, Shelton, CT, USA) as exposed by Mertens [30].

2.8. Analysis of Amino Acids in the Raisins Varieties

Amino acid analysis in raisin varieties was performed using an Agilent HPLC (HP1100 system, Agilent Technologies Inc.) equipped with a diode array detector (DAD). A Zorbax Eclipse AAA analytical (4.6 mm × 150 mm, 5 µm Agilent Technologies Inc.) column was used for amino acid determination in raisin varieties. An autosampler (G1313A, Agilent Technologies Inc.) was utilized for the inline-derivatization by 9-fluorenylmethyl chloroformate (FMOC) and o-phthalaldehyde (OPA) immediately prior to injection onto the columns, as described in detail by Henderson et al. [31]. Chromatographic conditions were followed according to the methods described by some authors [31–33]. Briefly, OPA-derivatized amino acids were recorded at 338 nm, whereas FMOC-derivatized amino acids were registered at 262 nm. Purchased standards of each individual amino acid (Sigma Chemical Co.) were used for quantification and identification (standard external method). Two internal standards were used: sarcosine for FMOC-derivatized amino acids and norvaline for OPA-derivatized amino acids. Individual free amino acid values were expressed as g 100 g^{-1} of berries dry weight.

2.9. Statistical Analysis

Studied variables were performed in triplicate, and the reported results correspond to the means with their standard deviations. Data were subjected to an analysis of variance (ANOVA), and mean separation was conducted using Tukey's test at p-value ≤ 0.05. Statistical analysis was performed using the SPSS program version 13.0 (SPSS Inc., Chicago, IL, USA).

3. Results and Discussion

3.1. Hormone Contents in Raisin

Gibberellic acid (GA), salicylic acid (SA), indol-3-acetic acid (IAA), and abscisic acid (ABA) were identified and quantified in the different studied raisins varieties (Table 2).

GA content in the raisin varieties ranged from 187.79 and 285.49 ng μL^{-1} (Ekşi Kara and Black Corinth, respectively). SA content ranged from 76.33 and 106.94 ng μL^{-1} (Black Corinth and Black Kishmish, respectively). IAA content ranged from 0.19 to 1.29 ng μL^{-1} (Ekşi Kara and Black Kishmish, respectively). ABA content ranged from 0.17 to 7.78 (Black Kishmish and Ekşi Kara, respectively). The parthenocarpic variety (Black Corinth) showed the highest content of GA, whereas Ekşi Kara presented the lowest content of this hormone. Seeded varieties (Ekşi Kara and Gök Üzüm) showed a lower content of SA and IAA and considerably higher content of ABA than the seedlessness varieties.

Table 2. Hormone contents (ng μL^{-1}) of two stenospermocarpy varieties (Sultani Çekirdeksiz and Black Kishmish); one parthenocarpic variety (Black Corinth) and two seeded varieties (Ekşi Kara and Gök Üzüm) in 2020 season.

	Sultani Çekirdeksiz	Black Kishmish	Black Corinth	Ekşi Kara	Gök Üzüm
Gibberellic acid (GA)	243.60 ± 3.743 ^{b}	220.12 ± 2.122 ^{c}	285.49 ± 7.813 ^{a}	187.79 ± 9.208 ^{d}	212.71 ± 8.393 ^{c}
Salicylic acid (SA)	90.04 ± 1.227 ^{b}	106.94 ± 4.625 ^{a}	76.33 ± 4.422 ^{c}	51.31 ± 1.717 ^{d}	54.95 ± 1.381 ^{d}
Indole-3-acetic acid (IAA)	1.26 ± 0.057 ^{a}	1.29 ± 0.045 ^{a}	1.12 ± 0.031 ^{b}	0.19 ± 0.017 ^{c}	0.19 ± 0.012 ^{c}
Abscisic acid (ABA)	0.24 ± 0.015 ^{b}	0.17 ± 0.015 ^{b}	0.21 ± 0.015 ^{b}	7.78 ± 0.330 ^{a}	7.65 ± 0.521 ^{a}

Different lowercase letters indicate significant differences on hormone contents among raisin varieties by Tukey's test (p-value ≤ 0.05).

Seeds induce the hormone synthesis that controls fruit development in grapefruits [4]. Changes in endogenous hormonal levels are known to be related to embryo abortion in seedless grape varieties. In this way, gibberellin is considered an important component for seed development regulation, and its exogenous application has been reported to cause grape seedlessness [34]. This effect has been reported in seedless grape varieties, such as Ribier, Emperatriz, and Superior Seedless [35,36]. Some evidence has also shown that gibberellins and auxins may play an essential role in seedlessness and affect berry size development [37]. Black Corinth is known for its small berry size and, regarding Table 2 shows the highest GA levels. Based on the above mentioned, we can suggest that the smaller berry size in seedless grape varieties may be caused by high GA and IAA endogenous content. Meng et al. [38] reported that the main representative biochemical compound in raisins was salicylic acid. In this study, seeded varieties presented low levels of SA and widely high levels of ABA compared to the rest varieties (Table 2). Some studies have reported an increase of abscisic acid at the ripening onset [39,40]. Hormone accumulation in the seeded grape varieties is due to its synergies and antagonism effect among endogenous hormones. Based on this, the high ABA amount in seeded varieties is likely coming from the seeds. In addition, seeded grape varieties had lower IAA content than the rest of the studied varieties (Table 2). Indole-3-acetic acid is considered a negative regulator of maturation, which may represent an antagonism and synergies effect among the endogenous hormones. Despite this, there is little available information about the role of hormones in raisins, and more research is needed on this subject for future studies.

3.2. Sugar Contents in Raisins

Sucrose, glucose, fructose, rhamnose, galactose, xylose, and arabinose were identified and quantified in the different studied raisins varieties (Table 3). Sucrose content in raisins ranged from 35.76 and 75.93 g 100 g^{-1} (Ekşi Kara and Black Kishmish, respectively). Glucose content in raisins varied from 9.70 to 18.20 to g 100 g^{-1} (Gök Üzüm and Black Kishmish, respectively). Fructose content in raisins ranged from 7.81 to 24.53 g 100 g^{-1} (Black Kishmish and Gök Üzüm, respectively). Rhamnose content in raisins varied from 2.30 to 11.67 g 100 g^{-1} (Sultani Çekirdeksiz and Gök Üzüm, respectively). Galactose content in raisins ranged from 3.44 to 44.18 g 100 g^{-1} (Sultani Çekirdeksiz and Gök Üzüm, respectively). Xylose content in raisins varied from 2.45 to 60.19 g 100 g^{-1} (Black Kishmish and Gök Üzüm, respectively). Arabinose content in raisins ranged from 2.74 to 28.12 g 100 g^{-1} (Black Kishmish and Gök Üzüm, respectively). Seeded varieties (Ekşi Kara and Gök Üzüm)

showed significantly lower content of sucrose and considerably higher content of glucose, fructose, rhamnose, galactose, xylose, and arabinose than the seedlessness varieties (Sultani Çekirdeksiz, Black Kishmish, and Black Corinth). Generally, seedless varieties presented lower sugars than seeded varieties (Table 3).

Table 3. Sugar contents (g 100 g^{-1}) of two stenospermocarpy varieties (Sultani Çekirdeksiz and Black Kishmish); one parthenocarpic variety (Black Corinth), and two seeded varieties (Ekşi Kara and Gök Üzüm) in 2020 season.

	Sultani Çekirdeksiz	Black Kishmish	Black Corinth	Ekşi Kara	Gök Üzüm
Sucrose	70.41 ± 1.79 [a]	75.93 ± 1.76 [a]	68.15 ± 1.38 [a]	35.76 ± 2.11 [b]	36.66 ± 4.26 [b]
Glucose	11.56 ± 0.49 [b]	9.70 ± 0.52 [b]	13.17 ± 0.27 [b]	17.72 ± 35.05 [a]	18.20 ± 55.44 [a]
Fructose	9.26 ± 0.56 [b]	7.81 ± 0.16 [b]	10.07 ± 0.18 [b]	22.31 ± 1.32 [a]	24.53 ± 1.42 [a]
Rhamnose	2.30 ± 0.15 [b]	2.89 ± 0.83 [b]	2.96 ± 0.36 [b]	10.69 ± 41.72 [a]	11.67 ± 89.71 [a]
Galactose	3.44 ± 0.34 [b]	3.74 ± 0.27 [b]	4.22 ± 0.11 [b]	42.87 ± 1.52 [a]	44.18 ± 1.80 [a]
Xylose	2.71 ± 0.23 [b]	2.45 ± 0.08 [b]	3.00 ± 0.11 [b]	54.76 ± 3.40 [a]	60.19 ± 7.34 [a]
Arabinose	3.62 ± 0.17 [b]	2.74 ± 0.04 [b]	3.13 ± 0.11 [b]	22.25 ± 2.28 [a]	28.12 ± 3.18 [a]

Different lowercase letters indicate significant differences on hormone contents among raisin varieties by Tukey's test (p-value ≤ 0.05).

Sucrose was the most abundant sugar in the seedless grape varieties, contrary to those exhibited in the literature, in which glucose and fructose are the most abundant sugars. However, it was possible to detect high sucrose content in some *Vitis rotundifolia* and hybrids between *V*. *labrusca* and *V*. *vinifera*. Sugars are first imported as sucrose in berries from the photosynthetic activity and then reduced to hexoses, namely glucose and fructose [41]. Glucose predominates over fructose early at berry development, and then, sugar accumulation increases during ripening, reaching similar concentrations at maturity [42]. Seedless grape varieties contain glucose and fructose, though in lower concentrations than sucrose (Table 3), similar to previous results exposed in raisins [43]. On the other hand, the most common sugars in *V*. *vinifera* species are glucose, followed by galactose, rhamnose, xylose, and arabinose [43]. Based on the exposed results, rhamnose was the second most dominant sugar in seeded grape varieties. The overall range of the rhamnose across the seeded raisin varieties is not consistent in the scientific literature, and more research deserves to develop to improve current knowledge.

3.3. Enzymatic Activity in Raisins

The activity of glutathione reductase (GR), glutathione (GSH), glutathione S-transferase (GST), catalase (CAT), peroxidase (POD), and superoxide dismutase (SOD) were quantified in the different raisin varieties studied (Table 4). GR activity in raisins varied from 39.05 to 2125.67 nmol g^{-1} (Ekşi Kara and Black Kishmish, respectively). GSH activity in raisins ranged from 262.41 to 2637.00 nmol g^{-1} (Ekşi Kara and Black Kishmish, respectively). GST activity in raisins varied from 1245.89 to 3856.00 nmol g^{-1} (Ekşi Kara and Black Kishmish, respectively). CAT activity in raisins ranged from 69.91 to 373.33 EU g $berry^{-1}$ (Ekşi Kara and Black Kishmish, respectively). POD activity in raisins varied from 4504.37 to 15,181.33 EU g $berry^{-1}$ (Ekşi Kara and Black Kishmish, respectively). SOD activity in raisins ranged from 112.11 to 551.33 g $berry^{-1}$ (Ekşi Kara and Black Corinth, respectively). Black Kishmish reached the highest activity of GR, GSH, GST, CAT, and POD, except SOD. Seeded raisin varieties (Ekşi Kara and Gök Üzüm) showed the lowest activity of all the studied enzymes.

Table 4. Antioxidant enzymes of two stenospermocarpy varieties (Sultani Çekirdeksiz and Black Kishmish); one parthenocarpic variety (Black Corinth), and two seeded varieties (Ekşi Kara and Gök Üzüm) in the 2020 season.

	Sultani Çekirdeksiz	Black Kishmish	Black Corinth	Ekşi Kara	Gök Üzüm
Glutathione reductase (nmol g^{-1})	1504.33 ± 44.99 ^{c}	2125.67 ± 110.18 ^{a}	1766.67 ± 45.00 ^{b}	39.05 ± 1.53 ^{d}	43.33 ± 2.11 ^{d}
Glutathione (nmol g^{-1})	1925.00 ± 56.32 ^{c}	2637.00 ± 83.80 ^{a}	2120.33 ± 89.67 ^{b}	262.41 ± 11.11 ^{d}	264.65 ± 22.05 ^{d}
Glutathione S-transferase (nmol g^{-1})	3396.33 ± 169.99 ^{b}	3856.00 ± 69.66 ^{a}	3551.67 ± 212.56 ^{b}	1245.89 ± 66.54 ^{c}	1271.32 ± 74.05 ^{c}
Catalase (EU g $berry^{-1}$)	244.00 ± 10.54 ^{c}	373.33 ± 27.10 ^{a}	312.33 ± 11.50 ^{b}	69.91 ± 4.08 ^{d}	75.99 ± 8.60 ^{d}
Peroxidase (EU g $berry^{-1}$)	12339.67 ± 210.60 ^{c}	15181.33 ± 280.45 ^{a}	13623.00 ± 171.29 ^{b}	4504.37 ± 172.71 ^{d}	4703.83 ± 93.14 ^{d}
Superoxide dismutase (EU g $berry^{-1}$)	457.67 ± 16.80 ^{b}	326.00 ± 16.37 ^{c}	551.33 ± 38.53 ^{a}	112.11 ± 2.99 ^{d}	112.94 ± 5.79 ^{d}

Different lowercase letters indicate significant differences in hormone contents among raisin varieties by Tukey's test (p-value ≤ 0.05).

Sério et al. [14] reported that the raisins produced from the white Sultana seedless grape variety showed a lower antioxidant capacity than the commercial raisin samples obtained from red and/or seed-containing berries. Costa et al. [44] reported that the seeds, rather than skins and pulps in different grape varieties, had the highest antioxidant capacity. Based on the exposed results, seeds in seeded varieties would negatively affect glutathione reductase, glutathione, glutathione S-transferase, catalase, and peroxidase. Despite this, the present study did not include the analysis of antioxidants in seeds of the seeded varieties. It is not possible to determine if the seed in raisins affects enzymatic activity. Besides, drying conditions in the seedless grape varieties may have affected enzymatic capacity by causing higher oxidative stress.

3.4. Vitamin Contents in Raisins

Vitamins B1, B2, B6, C, and E were determined and quantified in the seeded and seedless raisins (Table 5). Vitamin B1 content in raisins ranged from 12.27 to 19.49 mg 100 g^{-1} (Sultani Çekirdeksiz and Gök Üzüm, respectively). Vitamin B2 content in raisins varied from 0.47 to 19.64 mg 100 g^{-1} (Ekşi Kara and Black Kishmish, respectively). Vitamin B6 in raisins content ranged from 30.40 to 73.08 mg 100 g^{-1} (Ekşi Kara and Black Kishmish, respectively). Vitamin C content in raisins varied from 18.76 and 34.27 mg 100 g^{-1} (Gök Üzüm and Sultani Çekirdeksiz, respectively). Vitamin E content in raisins ranged from 20.15 to 61.78 mg 100 g^{-1} (Gök Üzüm and Black Kishmish, respectively). Raisins from seeded grape varieties showed the lowest content of vitamins B2, B6, C, and E, as well as the highest content of vitamin B1. Vitamin B6 and E showed lower contents in the stenospermocarpy varieties (Sultani Çekirdeksiz and Black Kishmish) than in the parthenocarpic variety (Black Corinth).

Table 5. Vitamin contents (mg 100 g^{-1} of dry weight) of two stenospermocarpy varieties (Sultani Çekirdeksiz and Black Kishmish); one parthenocarpic variety (Black Corinth) and two seeded varieties (Ekşi Kara and Gök Üzüm) in 2020 season.

	Sultani Çekirdeksiz	Black Kishmish	Black Corinth	Ekşi Kara	Gök Üzüm
Vitamin B1	12.27 ± 1.00 ^{c}	15.15 ± 0.29 ^{c}	13.74 ± 0.61 ^{c}	18.65 ± 50.78 ^{b}	19.49 ± 38.60 ^{a}
Vitamin B2	18.52 ± 0.76 ^{a}	19.64 ± 0.45 ^{a}	18.52 ± 0.97 ^{a}	0.47 ± 0.04 ^{b}	0.49 ± 0.04 ^{b}
Vitamin B6	66.93 ± 1.70 ^{b}	73.07 ± 3.37 ^{a}	65.30 ± 3.95 ^{b}	30.40 ± 2.14 ^{c}	32.31 ± 3.37 ^{c}
Vitamin C	34.27 ± 1.12 ^{a}	27.52 ± 1.91 ^{b}	29.18 ± 1.75 ^{b}	18.80 ± 1.12 ^{c}	18.76 ± 1.09 ^{c}
Vitamin E	50.93 ± 2.90 ^{b}	61.78 ± 3.94 ^{a}	55.01 ± 4.20 ^{b}	23.31 ± 1.26 ^{c}	20.15 ± 2.12 ^{c}

Different lowercase letters indicate significant differences in hormone contents among raisin varieties by Tukey's test (p-value ≤ 0.05).

The United States Department of Agriculture reported that 100 g of raisins contain 2.3 mg of vitamin B6, 0.12 mg of vitamin E, and 0.17 mg of vitamin C. Pakistani grapes showed a mean vitamin C content of 1.64 mg 100 g^{-1} of fresh weight [45]. Similarly, Nikniaz et al. [46] reported that the average vitamin C content of Iranian grapes was 14.85 mg 100 g^{-1} of fresh weight for white varieties and 16.83 mg 100 g^{-1} of fresh weight for red varieties. Keskin et al. [47] showed that the vitamin C in the Katıkara and Isabella grapes ranged from 6.38 to 12.83 mg 100 g^{-1} of fresh weight. Generally, the composition

and content of vitamins obtained from raisins constitute a less attribute studied to date. Keskin et al. [13] showed that the most abundant vitamin in Gök Üzüm raisins was vitamin B2 (95.17 and 135.54 mg 100 g^{-1} of dry weight), followed by vitamin B6 (83.88 and 107.30 mg 100 g^{-1} of dry weight), and the least was vitamin C (12.54 and 17.28 mg 100 g^{-1} of dry weight). Based on this study, the drying process could affect vitamin contents in raisins. In this way, it was shown that vitamin contents in Gök Üzüm raisins were strongly influenced by the application of dipping solution before grape drying [13]. These authors reported that vitamins A, B1, B2, B6, and C contents were lower in the raisins dipped in potassium carbonate than in wood ash solutions. Generally, it is admitted that the drying process induces a loss of vitamins in most of the dried grapes, especially vitamin C, which is strongly vulnerable to oxygen, light, and heat exposure [48].

3.5. Mineral Contents in Raisins

Mineral elements such as nitrogen (N), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), phosphorous (P), sulfur (S), manganese (Mn), copper (Cu), iron (Fe), zinc (Zn) and boron (B) were identified in this study (Table 6). N, Ca, K, Mg, Na, P, S, Cu, Fe, Zn, and B content were higher in the Black Kishmish when compared to the rest of the raisin varieties. Seeded raisin varieties (Ekşi Kara and Gök Üzüm) showed significantly lower content of N, Ca, K, Mg, Na, P, Mn, Cu, Fe, Zn, and B than the seedlessness varieties (Sultani Çekirdeksiz, Black Kishmish, and Black Corinth).

Table 6. Mineral contents (ppm) of two stenospermocarpy varieties (Sultani Çekirdeksiz and Black Kishmish); one parthenocarpic variety (Black Corinth), and two seeded varieties (Ekşi Kara and Gök Üzüm) in 2020 season.

	Sultani Çekirdeksiz	Black Kishmish	Black Corinth	Ekşi Kara	Gök Üzüm
Nitrogen (%)	2.40 ± 0.05 ^{c}	3.11 ± 0.12 ^{a}	2.76 ± 0.08 ^{b}	0.73 ± 0.04 ^{d}	0.84 ± 0.03 ^{d}
Calcium	17,521.67 ± 717.12 ^{c}	23,982.48 ± 760.06 ^{a}	19,606.00 ± 709.54 ^{b}	3962.67 ± 140.09 ^{d}	4178.67 ± 51.64 ^{d}
Potassium	9040.00 ± 179.64 ^{c}	14,055.00 ± 1398.16 ^{a}	10,111.00 ± 192.57 ^{c}	4784.00 ± 61.02 ^{b}	4885.33 ± 92.72 ^{b}
Magnesium	2511.33 ± 153.30 ^{c}	4179.43 ± 160.69 ^{a}	3037.33 ± 65.77 ^{b}	153.00 ± 9.00 ^{d}	180.67 ± 8.50 ^{d}
Sodium	411.67 ± 23.50 ^{b}	585.43 ± 85.25 ^{a}	373.33 ± 41.79 ^{b}	148.67 ± 6.11 ^{c}	132.00 ± 5.29 ^{c}
Phosphorous	3229.33 ± 109.74 ^{c}	3925.33 ± 55.22 ^{a}	3521.00 ± 167.69 ^{b}	713.00 ± 9.54 ^{d}	734.00 ± 8.00 ^{d}
Sulphur	1226.00 ± 21.63 ^{b}	1454.00 ± 22.52 ^{a}	1100.00 ± 79.05 ^{c}	1300.33 ± 50.52 ^{b}	1433.67 ± 21.50 ^{a}
Manganese	24.33 ± 0.89 ^{b}	28.62 ± 0.78 ^{a}	29.00 ± 1.28 ^{a}	3.99 ± 0.21 ^{c}	4.39 ± 0.21 ^{c}
Cupper	11.45 ± 0.80 ^{c}	14.58 ± 0.38 ^{a}	13.15 ± 0.27 ^{b}	3.37 ± 0.33 ^{d}	3.70 ± 0.33 ^{d}
Iron	120.71 ± 2.29 ^{c}	140.52 ± 4.49 ^{a}	129.16 ± 3.90 ^{b}	23.15 ± 1.05 ^{d}	28.50 ± 1.65 ^{d}
Zinc	15.31 ± 0.89 ^{c}	21.78 ± 1.28 ^{a}	16.89 ± 1.08 ^{b}	2.84 ± 0.11 ^{d}	2.71 ± 0.25 ^{d}
Boron	11.04 ± 0.79 ^{c}	14.32 ± 1.00 ^{a}	12.22 ± 0.40 ^{b}	1.22 ± 0.04 ^{d}	1.37 ± 0.07 ^{d}

Different lowercase letters indicate significant differences in hormone contents among raisin varieties by Tukey's test (p-value ≤ 0.05).

Mineral concentrations measured in this study were similar to those observed in raisins by different authors [49,50]. Table 6 showed that the raisins obtained from seeded varieties had the lowest amount of several minerals compared to the other seedless varieties. Small berry size in seedless grape varieties for raisin production may probably resulted in high mineral content compared to seeded varieties. Indeed, it has been reported that seeded berries induced changes in berry size and skin to pulp ratio compared to seedless grape varieties [51]. Based on this, mesocarp cell size is responsible for the cell composition and morphology of seedless grapes, possibly affecting the mineral content of raisins. Grape varieties show differences in the morphology of exocarp and mesocarp cells and the number of cell layers [52]. Despite that, in this study, it was not determined the cell size of the mesocarp of grapes was before drying; it is possible that the cells in the seedless grape varieties were smaller than the seeded grape varieties, which could affect raisin mineral content.

3.6. Amino Acid Contents in Raisins

Amino acids, such as asparagine (Asn), glutamate (Glu), aspartic acid (Asp), serine (Ser), glutamine (Gln), histidine (His), glycine (Gly), threonine (Thr), arginine (Arg), alanine (Ala), tyrosine (Tyr), cystine (Cys), valine (Val), methionine (Met), tryptophan (Trp), phenylalanine (Phe), isoleucine (Ile), leucine (Leu), lysine (Lys), hydroxyproline (HoPro), and proline (Pro) were identified and quantified (Table 7). The most abundant amino acids found in raisins were Asp, Arg, Ala, Ser, and Gln, whereas the least quantified were Met, Trp, Phe, HoPro, and Cys. Seeded raisin varieties (Ekşi Kara and Gök Üzüm) showed significantly higher contents of Asn, Glu, Asp, Ser, Gln, His, Gly, Thr, Arg, Ala, Cys, Met, Trp, Phe, Ile, Lys, HoPro and Pro than the seedlessness raisin varieties (Sultani Çekirdeksiz, Black Kishmish, and Black Corinth). The parthenocarpic variety (Black Corinth) showed lower content of Asn, Glu, Asp, Ser, Gln, His, Gly, Thr, Arg, Tyr, Cys, Val, Met, Trp, Phe, Ile, Leu, Lys, HoPro and Pro than the stenospermocarpy raisin varieties (Sultani Çekirdeksiz and Black Kishmish).

Table 7. Amino acid contents (mg 100g $^{-1}$) of two stenospermocarpy varieties (Sultani Çekirdeksiz and Black Kishmish); one parthenocarpic variety (Black Corinth) and two seeded varieties (Ekşi Kara and Gök Üzüm) in 2020 season.

	Sultani Çekirdeksiz	Black Kishmish	Black Corinth	Ekşi Kara	Gök Üzüm
Asparagine	3133.52 ± 132.53 ^{b}	2762.80 ± 62.46 ^{c}	1666.21 ± 112.82 ^{d}	3766.33 ± 55.19 ^{a}	3702.67 ± 53.16 ^{a}
Glutamate	1235.33 ± 52.25 ^{b}	1100.03 ± 31.63 ^{c}	702.19 ± 86.51 ^{d}	1487.33 ± 38.55 ^{a}	1503.00 ± 51.47 ^{a}
Aspartic acid	10704.29 ± 517.01 ^{c}	9094.90 ± 228.38 ^{d}	5496.71 ± 369.93 ^{e}	13736.00 ± 141.74 ^{a}	12589.33 ± 341.80 ^{b}
Serine	3665.82 ± 155.04 ^{b}	3223.83 ± 73.84 ^{c}	1966.93 ± 132.66 ^{d}	5492.33 ± 165.96 ^{a}	5340.00 ± 60.00 ^{a}
Glutamine	3437.83 ± 145.40 ^{b}	2974.90 ± 116.54 ^{c}	1854.49 ± 127.89 ^{d}	4443.33 ± 113.43 ^{a}	4472.00 ± 161.45 ^{a}
Histidine	1245.37 ± 52.67 ^{c}	1142.27 ± 81.57 ^{c}	700.09 ± 75.92 ^{d}	2230.67 ± 45.17 ^{a}	2088.67 ± 86.00 ^{b}
Glycine	2320.01 ± 98.12 ^{b}	2028.90 ± 53.39 ^{c}	1236.44 ± 83.21 ^{d}	2667.33 ± 62.15 ^{a}	2773.67 ± 50.14 ^{a}
Threonine	2350.14 ± 99.40 ^{b}	2124.27 ± 103.61 ^{b}	1246.83 ± 85.21 ^{c}	3313.33 ± 171.35 ^{a}	2985.00 ± 498.99 ^{a}
Arginine	7462.20 ± 315.61 ^{c}	6575.70 ± 148.60 ^{c}	3946.99 ± 274.45 ^{d}	8437.67 ± 80.60 ^{a}	8251.67 ± 92.05 ^{a}
Alanine	5664.44 ± 239.57 ^{c}	4812.93 ± 329.05 ^{d}	3056.03 ± 210.93 ^{c}	7122.67 ± 37.87 ^{a}	6717.00 ± 116.86 ^{b}
Tyrosine	1044.51 ± 44.18 ^{a}	906.27 ± 32.12 ^{b}	575.63 ± 48.93 ^{c}	890.67 ± 16.80 ^{b}	932.33 ± 24.13 ^{b}
Cystine	652.82 ± 27.61 ^{b}	587.50 ± 24.88 ^{b}	377.27 ± 55.20 ^{c}	1096.33 ± 73.80 ^{a}	1115.67 ± 73.80 ^{a}
Valine	1235.33 ± 52.25 ^{a}	1103.03 ± 35.13 ^{b}	710.19 ± 98.67 ^{de}	697.00 ± 38.59 ^{e}	811.00 ± 35.76 ^{c}
Methionine	873.77 ± 36.96 ^{b}	852.12 ± 56.73 ^{b}	535.21 ± 34.68 ^{c}	1378.33 ± 90.03 ^{a}	1312.33 ± 95.66 ^{a}
Tryptophane	1064.59 ± 45.03 ^{c}	864.10 ± 102.86 ^{d}	582.77 ± 45.79 ^{e}	1641.67 ± 72.29 ^{b}	1772.33 ± 55.14 ^{a}
Phenylalanine	883.81 ± 37.38 ^{b}	880.47 ± 84.81 ^{b}	518.45 ± 86.99 ^{c}	1462.00 ± 61.02 ^{a}	1541.33 ± 99.03 ^{a}
Isoleucine	1185.11 ± 50.12 ^{c}	1056.30 ± 73.19 ^{c}	678.99 ± 91.07 ^{d}	1771.33 ± 96.46 ^{a}	1600.67 ± 31.21 ^{b}
Leucine	3464.95 ± 146.55 ^{a}	3042.83 ± 71.32 ^{b}	1858.47 ± 125.23 ^{d}	2077.00 ± 85.71 ^{c}	2003.00 ± 57.94 ^{cd}
Lysine	2129.19 ± 90.05 ^{c}	1843.80 ± 70.34 ^{d}	1168.55 ± 94.55 ^{e}	2730.00 ± 167.31 ^{b}	2939.00 ± 77.90 ^{a}
Hydroxyproline	832.19 ± 76.59 ^{b}	738.07 ± 75.21 ^{b}	425.20 ± 29.09 ^{c}	1138.00 ± 43.49 ^{a}	1126.00 ± 86.02 ^{a}
Proline	70.30 ± 2.97 ^{b}	60.63 ± 2.68 ^{c}	38.01 ± 2.66 ^{d}	81.00 ± 1.73 ^{a}	77.67 ± 5.69 ^{a}

Different lowercase letters indicate significant differences in hormone contents among raisin varieties by Tukey's test (p-value ≤ 0.05).

Some published reports showed that the amino acid contents in grapes vary according to grape variety, berry ripeness, viticultural practices, rootstock selection, pedoclimatic conditions, and other factors [53–55]. Generally, the most abundant amino acids in grapes are proline and arginine, a varietal characteristic [54,55]. Based on this, the drying process could alter the content of individual amino acids in raisins through degradation, denaturalization, and concentration effects. Seeded grape varieties had a higher free amino acid content than seedless grape varieties. Skins and seeds contain significant values of amino acids. In this way, approximately 36 to 65% of total nitrogen content is located in seeds and skins, whereas 7.8 to 8.5% of total amino acids are found in seeds [55]. To our knowledge, there are no similar studies regarding amino acid analysis in seeded and seedless raisin varieties. However, considering that the raisin samples were obtained from the most representative viticultural Turkish zones, characterized by different topography

and viticultural practices, it seems possible that seeded grape varieties are rich in amino acid content. Black Corinth showed lower content of several of the studied amino acids, which may indicate a low capacity that makes this variety for breeding programs in terms of nutritional values.

4. Conclusions

Several differences were found among the raisin varieties studied on primary and secondary metabolites. Generally, raisins produced from seedless varieties presented higher content of hormones, vitamins, minerals, and antioxidant capacity than the raisins produced from seeded varieties. Raisins produced from seeded varieties gave higher contents of most of the analyzed sugars and amino acids than the raisins produced from seedless varieties. Black Kishmish raisins showed a higher antioxidant capacity in most of the studied enzymes, as they have a higher content of several vitamins and minerals than the rest of the varieties. Black Corinth reached lower contents of several studied amino acids, except alanine. The results presented in this report could provide technical guidelines for raisin producers. Grape breeders could use them to develop new seedless varieties by embryo rescue techniques.

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