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ORIGINAL PAPER

Polyphenols, organic acids, and their relationships in red grapes of *Vitis vinifera* and Isabella *(Vitis labrusca)* under arid conditions

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Abstract

Grape is one of the most valuable sources of polyphenols that act as radical scavengers and stress suppressors. This study discussed the polyphenolic and the organic acid composition regarding ecology and secondary metabolism of red grapes of two *Vitis vinifera* varieties (Sülün Kara and Tombak Kara) and a *Vitis labrusca* cultivar (Isabella) grown under arid conditions. Isabella, a grape adapted to high humidity, had notably higher flavonoids, particularly catechin. *Vitis vinifera* varieties contained higher phenolic acids than Isabella, except for syringic, *p*-coumaric, and gallic acids. Organic acids were divergent among the varieties and Isabella. Correlation analysis suggested some noteworthy relations among organic acids, such as the positive linear relationships of malic, tartaric, and ascorbic acids. Oxalic acid was negatively correlated to other organic acids except for succinic acid. High correlations among flavonoids suggested an enhanced stress defense metabolism caused by rain scarcity during the growing season. This study will be a helpful example of alterations in grape biochemical composition and relationships of secondary metabolites. The results also suggest that Isabella is an excellent genetic source of biochemically fortified berries under arid conditions.

Keywords Grape · Phenolic acids · Flavonoids · Tartaric acid · Correlations

Introduction

Grapes are one of the most produced crops in the world. In addition to its high production, its processed products also have a significant place in agriculture-based trade [1]. Wine is the most exported product (10.6 million t), followed by fresh grapes (4.8 million t). The import value roughly coincides with the export value. There are approximately 39 billion dollars in wine, 10 billion dollars in fresh grapes, and about 2 billion dollars in raisin trade (export and import values are close to each other) in the sector [2].

The Eurasian grape species are widely cultivated and processed to diverse by-products thanks to their superior characteristics such as fruitfulness and quality, diverse usage opportunity, and lime tolerance compared to the American species [3]. *Vitis vinifera* (*V. vinifera)* is the most commonly grown species in the vine-growing latitudinal ranges. Although *V. vinifera* has some considerable superiorities, poor disease tolerance arises as a massive drawback in cultivating the species in a humid ecology. On the contrary, North American grapes are mainly spread close to water sources such as rivers, springs, or streams with good disease and phylloxera resistance [4].

Vitis labrusca L. (*V. labrusca*) is commercially grown in the USA and Brazil to produce juice, jam, jelly, and wine among American grapes [5]. This species is easily discriminated by the 'foxy flavor' that makes it popular in the US but strange to Europe [6]. In this species, Isabella is widely spread to humid ecologies such as tropical and coastal regions by taking advantage of fungal disease resistance [7]. The coastal territories of the Black Sea Region, Turkey, have severe precipitation and humidity that hamper the cultivation of *V. vinifera* commercially. However, Isabella was introduced to the region and well received by the native people thanks to its unique flavor and resistance to common grapevine diseases, making it the sole cultivar in the area [8].

Polyphenols are oxidative stress-preventive moieties naturally found in fruits and vegetables. Grapes are a significant source of polyphenolic compounds that ensure a high antioxidant power [9]. Phenolics differentiate according

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to the authenticity of the cultivar and geographical origin [10]. Besides these vine-based factors, the environmental biotic and abiotic determinants and human interference significantly impact the grape's chemical composition [11]. The effects of factors such as altitude, solar radiation, water deficit, harvest time, and plant growth regulators on secondary metabolites of grapes were individually or interactively studied [12][12]. However, there is no comprehensive study explaining compositional changes of bioactive compounds considering their relationships to the best of our knowledge.

In this regard, the biochemical composition of three varieties of two *Vitis* species, two varieties of *V. vinifera* and a *V. labrusca*, was determined in an arid ecology, and comprehensive evaluations were performed on associations of some prominent polyphenols and organic acids.

Materials and methods

Vineyard site and climate

This study was carried out at a farmer's vineyard located in the city center of Seben district, Bolu, in 2019. The vineyard is at 40°24′37.4"N and 31°34′39.7"E geographical location and 630 m above sea level. The long-term monthly average temperature varies between 10.7℃ and 22.6℃ in the growing season (April–November). In the region, April, May, and June have higher precipitation than the other months of the season. The average relative humidity is similar to monthly rainfall in terms of monthly distribution and varies between 54.3% (August) and 66.9% (May). Figure 1 demonstrates the long-term climate data of the region.

In 2019, monthly temperatures were almost the same with long-term distributions with very few deviations (± 1 ℃). However, the rainfall regime was considerably lower than the long-term trend, while the average relative humidity was similar. May was the rainiest month (30.7 mm), and almost no rainfall occurred in September (0.6 mm). The climate data belonging to 2019 are shown in Fig. 2.

Vineyard management

The vineyard was established in the south-to-north orientation in 2012. Two own-rooted *V. vinifera* varieties (Sülün Kara and Tombak Kara) and an own-rooted *V. labrusca* (Isabella) were planted 3 × 2 m between and within row spacings. The vines were trained in the goblet system. The vineyard was not irrigated. Weed control was performed by hand hoeing, and no external chemical applications were implied to control pests and diseases.

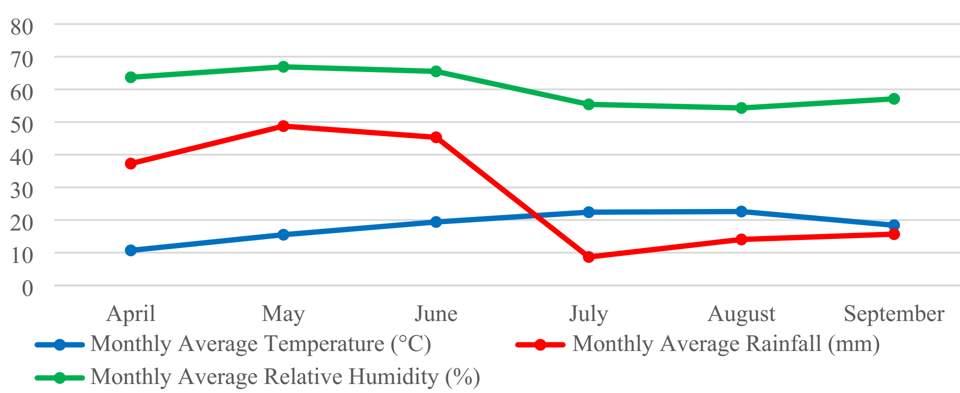

Fig. 1 Average climate data of Seben district in the growing seasons from 2000 to 2018

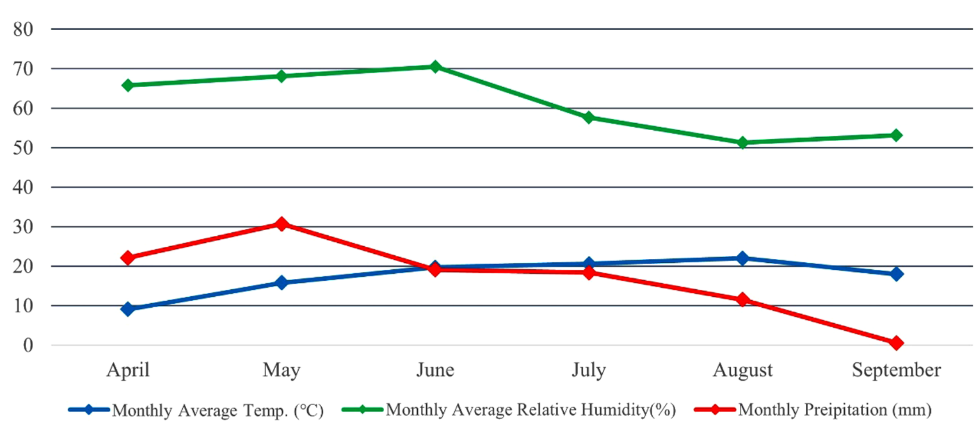

Fig. 2 The climate data of Seben in the 2019 growing season

Fruit sampling

Sampling was performed as three biological replications. Clusters from three vines of each variety were randomly harvested when total soluble contents reached 19%. After harvesting, clusters were put into plastic cooler bags and taken to the laboratory without losing time. Approximately 100 g berries were split by randomly selecting from the cluster's tip, middle, and base for each replication and stored at -20 ℃ until analysis.

Analysis of phenolic compounds by U-HPLC

Phenolic compounds were determined by [14] method with some modifications. Briefly, a 50 g fruit sample was diluted 1:1 with distilled water and centrifuged at 15,000 rpm for 15 min. The supernatant was filtered through a 0.45 µm Millipore filter and injected into HPLC. Chromatographic separation was performed on an Agilent 1100 (Agilent) HPLC device using a DAD (diode-array detector) (Agilent, USA) and a 250*4.6 mm, four µm ODS column (HiChrom, USA). Solvent A: Methanol–acetic acid–water (10:2:88), Solvent B: Methanol–acetic acid–water (90:2:8) was used as mobile phase. Separation was performed at 254 and 280 nm with a 1 mL/min flow rate and a 20 µL injection volume.

Analysis of organic acids by U-HPLC

The method reported by [15] was modified and used to extract and analyze organic acids. 50 g grape samples were placed in centrifuge tubes and homogenized with 20 ml of 0.009 N H2SO4. Afterward, it was centrifuged at 15,000 rpm for 15 min after mixing for 1 h in a shaker (Heidolph Unimax 1010, Germany). The supernatant was first passed through coarse filter paper, then a 0.45 µm membrane filter (Millipore Millex–HV Hydrophilic PVDF, Millipore, USA) twice, and finally through a SEP–PAK C18 cartridge. Organic acids were analyzed in a U-HPLC device (Agilent HPLC 1100 series G 1322 A, Germany). Aminex HPX–87 H, 300 mm × 7.8 mm column (Bio-Rad Laboratories, Richmond, CA, USA) was used in the HPLC system, and the device was controlled by a computer with the 'Agilent' package program. The DAD detector in the system (Agilent, USA) was set to 214 and 280 nm wavelengths.

Analysis of ascorbic acid (vitamin C) by U-HPLC

Ascorbic acid content was determined following the modified HPLC (isocratic program) (Agilent 1100 series HPLC G 1322 A, Germany) analytical procedure outlined by [16]. 5 g of sample was transferred to a 50 ml volumetric flask, including 10 ml 6% (w/v) metaphosphoric acid (Sigma, M6285, 33.5%). The sample was then homogenized at 24,000 rpm for 15 s and centrifuged at 14,000 rpm for 10 min at 1℃. 5 ml of the supernatant was filtered through 0.45 µm PTFE syringe filters (Phenomenex, UK) and placed in an amber-colored vial (AIM, Screw vial, SV-15A). The ascorbic acid was quantified by a standard external method using an L-ascorbic acid Standard (Sigma A5960).

Data analysis and statistical evaluations

The study was carried out as three biological replicates in randomized parcels trial pattern. Statistical differences among the means of the studied varieties were determined by the Student's *t* test. The relationships of biochemical moieties were determined by the hierarchical clustering and correlation analyzes according to Pearson's pairwise analysis performed by the 'corrplot' package of the R Studio [17].

Results

Phenolic acid contents

The quantities of studied phenolic acids are presented in Table 1. Gallic acid was the most abundant phenolic acid, being constituted the highest in Isabella (5.32 mg/L), followed by Tombak Kara (3.90 mg/L) and Sülün Kara (1.45 mg/L), respectively (Fig. 3). The second most abundant phenolic acid was chlorogenic, and *V. vinifera* cultivars were higher in terms of this substance. The amounts of caffeic, vanillic, and *o*-coumaric acids were in line with chlorogenic acid content with the same abundance order in varieties. On the other hand, syringic and *p*-coumaric acids were considerably high in Isabella, followed by Sülün Kara and Tombak Kara. Sülün Kara constituted the highest ferulic acid content and statistically separated from the other varieties.

Table 1 Phenolic acids content of the studied varieties (mg/L)

Variety	Isabella	Sülün Kara	Tombak Kara
Species	*V. labrusca*	*V. vinifera*	*V. vinifera*
Gallic acid	5.32 ± 0.27 a	1.45 ± 0.07 c	3.90 ± 0.20 b
Chlorogenic acid	1.97 ± 0.10 c	3.64 ± 0.18 a	2.80 ± 0.14 b
Caffeic acid	1.10 ± 0.06 c	1.78 ± 0.09 a	1.52 ± 0.08 b
Vanillic acid	0.81 ± 0.04 c	1.07 ± 0.05 a	0.91 ± 0.05 b
Syringic acid	1.20 ± 0.06 a	0.89 ± 0.04 b	0.33 ± 0.02 c
p-Coumaric acid	0.63 ± 0.03 a	0.35 ± 0.02 b	0.16 ± 0.01 c
Ferulic acid	0.93 ± 0.05 b	1.22 ± 0.06 a	0.88 ± 0.04 b
o-Coumaric acid	0.85 ± 0.04 c	1.54 ± 0.08 a	1.06 ± 0.05 b

Different letters in the same row indicate significant difference at $p \leq 0.05$

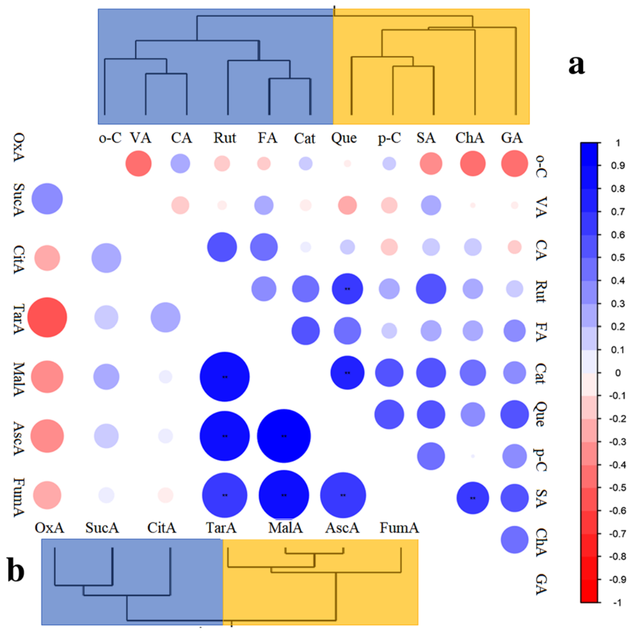

Fig. 3 Correlations among phenolic compounds (**a**) and organic acids (**b**) in *V. vinifera*. Self-correlations excluded. The size of the circles demonstrates the redundance of correlations. ** indicates significance at $p<0.01$. *o-C* o-Coumaric acid, *VA* Vanillic acid, *CA* Caffeic acid, *Rut* Rutin, *FA* Ferulic acid, *Cat* Catechin, *p–C* p-Coumaric acid, *SA* Syringic acid, *ChA* Chlorogenic acid, *GA* Gallic acid, *OxA* Oxalic acid, *SucA* Succinic acid, *CitA* Citric acid, *TarA* Tartaric acid, *MalA* Malic acid, *AscA* Ascorbic acid, *FumA* Fumaric acid

Flavonoid contents

In this study, three different flavonoid contents of grape varieties were determined. Rutin was not statistically different, while quercetin significantly diverged according to varieties, being the highest in Isabella (Table 2). The catechin was considerably higher than rutin and quercetin in all samples, possessing significant differences among the varieties. Isabella had the most quercetin, followed by Sülün Kara and Tombak Kara.

Table 2 Flavonoids contents of the varieties (mg/L)

Varieties	Species	Catechin	Rutin	Quercetin
Isabella	*V. labrusca*	14.93 ± 0.73 a	0.66 ± 0.13 a	0.50 ± 0.07 a
Sülün Kara	*V. vinifera*	3.65 ± 0.55 c	0.68 ± 0.09 a	0.39 ± 0.04 b
Tombak Kara	*V. vinifera*	5.81 ± 0.42 b	0.71 ± 0.15 a	0.29 ± 0.04 c

Different letters in the same column indicate significant difference at $p \leq 0.05$

Organic acid contents

Seven organic acids were determined in the studied grape varieties. Tartaric acid, also known as grape acid, was the most abundant organic acid in all varieties. There was a statistical difference among the varieties regarding tartaric acid content, and Sülün Kara had the highest tartaric acid content. Malic acid was the second most abundant, accounting for half the tartaric acid in every variety. Malic acid contents in varieties were statistically different, being the highest in Sülün Kara. Except for two primary organic acids, citric acid was more abundant than the other organic acids. Sülün Kara had notably high citric acid than the others. The oxalic, succinic, and ascorbic acids were also the highest in Sülün Kara. Tombak Kara owned the highest fumaric acid, while Sülün Kara had the lowest amount (Table 3).

Relationships among bioactive compounds

Both polyphenols and organic acids were divided into two main clusters in hierarchical clustering analysis. The associations between phenolics were mostly positive. However, there were significant relationships between quercetin and the other flavonoids, as well as syringic acid and chlorogenic acid ($p<0.01$). On the other hand, it was noteworthy that *o*-coumaric acid was negatively associated with most phenolic acids (Fig. 3a). Relationships between organic acids were much more robust than those between polyphenols. Oxalic acid was negatively correlated with all organic acids except succinic acid. Correlations between other organic acids were positive. However, oxalic, succinic, and citric acids were not significantly correlated with organic acids, whereas tartaric, malic, ascorbic, and fumaric acids were highly correlated (Fig. 3b).

The heatmap analysis revealed relationships between organic acids and phenolics. Even though positive correlations did not exceed $r=0.60$, a moderate correlation, organic

Table 3 Organic acid contents of varieties

Variety	Isabella	Sülün Kara	Tombak Kara
Species	*V. labrusca*	*V. vinifera*	*V. vinifera*
Tartaric acid (g/L)	22.09 ± 1.13 b	37.30 ± 5.45 a	18.68 ± 2.21 c
Malic acid (g/L)	11.21 ± 1.71 b	17.87 ± 2.66 a	12.40 ± 2.13 b
Citric acid (mg/L)	22.16 ± 2.89 b	55.03 ± 3.42 a	22.14 ± 1.59 b
Oxalic acid (mg/L)	0.36 ± 0.07 b	0.60 ± 0.11a	0.22 ± 0.05 c
Succinic acid (mg/L)	1.65 ± 0.21 b	3.08 ± 0.44 a	0.98 ± 0.23 c
Fumaric acid (mg/L)	1.02 ± 0.15b	0.71 ± 0.09 c	1.98 ± 0.32 a
Ascorbic acid (mg/100 g)	0.36 ± 0.07 b	0.60 ± 0.11 a	0.22 ± 0.05 c

Different letters in the same row indicate significant difference at $p \leq 0.05$

acids except oxalic acid were mainly positively correlated to phenolics. Oxalic acid had negative correlations with phenolics except for gallic acid. Another noteworthy tendency was the correlations of tartaric and malic acids' almost the same tendencies with the phenolics. Succinic acid displayed a moderate negative relationship with *o*-coumaric acid and negligible correlations to other phenolic compounds. Citric acid showed positive correlations with syringic, *p*-coumaric, gallic, and caffeic phenolic acids and flavonoids. The ascorbic acid positively correlated to vanillic acid (Fig. 4).

Polyphenols mainly displayed positive relationships with organic acids in Isabella. However, fumaric acid possessed negative correlations with phenolics except for rutin and gallic acid. Among the polyphenols, gallic acid and catechin elicited a close tendency regarding negative correlations to organic acids. Fumaric acid owned negative correlations to phenolics except for rutin and gallic acid (Fig. 5).

Discussion

Phenolic acids are plant polyphenols found in various forms in plants and exhibit high antioxidant activity [18]. They are primarily present in conjugated or bound forms attaching cell walls and comprise 1/3 of phenolic compounds [19]. Phenolic acids divide into two main classifications, hydroxybenzoic and hydroxycinnamic acids, by their distinctive carbon skeleton [20]. Hydroxybenzoic acids can easily be digested/absorbed gastrointestinally, and gallic, vanillic, and syringic acids are among the prominent hydroxybenzoic acids [21], while chlorogenic, caffeic, *p*-coumaric, *o*-coumaric, and ferulic acids are hydroxycinnamic acid derivates [22].

Due to their high health-promoting nature, phenolic acids are of great interest in berries, including grapes. Several studies have been conducted to determine these beneficial moieties in various parts of grapes, such as seed, skin, and pulp. This study used whole fruit to quantify bioactive compounds, and a significant variation was observed between varieties. Similar phenolic acid fluctuations based on variety were recorded by various researchers [23][23] [25][25].

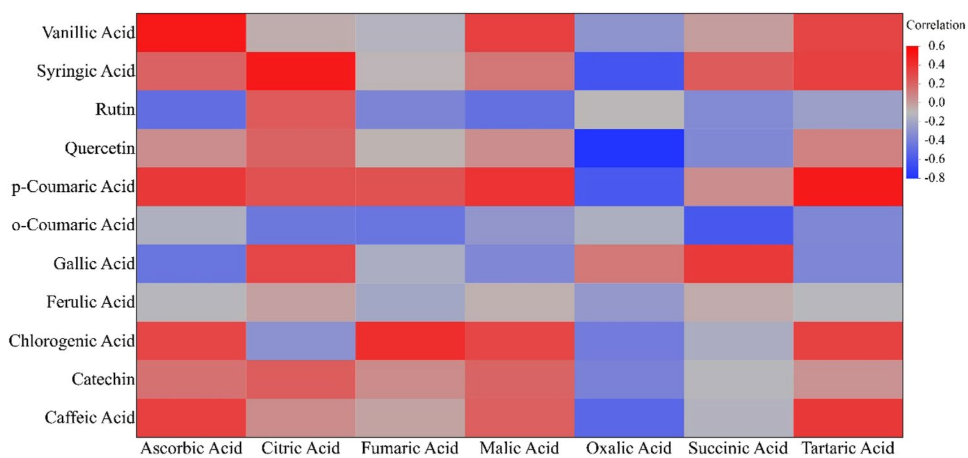

Fig. 4 Heatmap analysis illustrating correlations between polyphenols and organic acids in *V. vinifera*

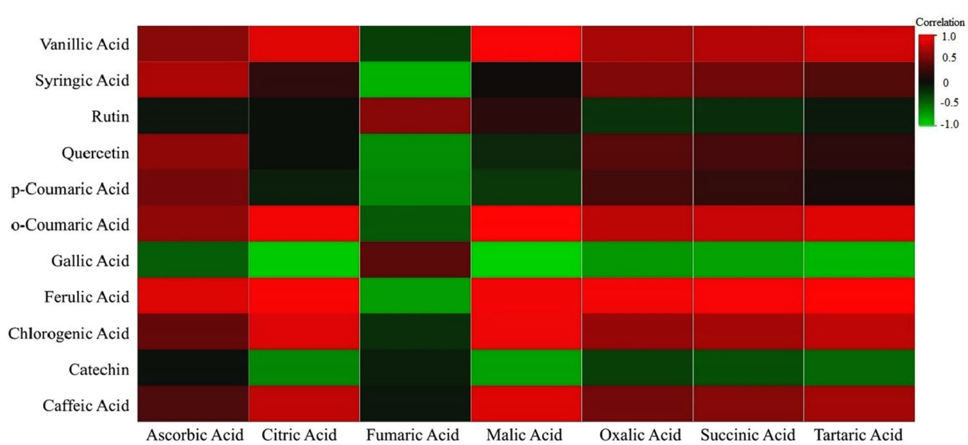

Fig. 5 Heatmap analysis showing the correlations among organic acids and polyphenolic compounds in Isabella

Gallic acid, one of the abundant phenolic acids in the grape berry, was stated to be relatively lower compared to other prominent phenolics such as syringic, p-coumaric, and vanillic acids in berries of both *V. vinifera* and *V. labrusca* [27] [8]. However, this study determined gallic acid the most abundant phenolic acid, except for the Sülün Kara variety, probably due to the seed/berry ratio. While phenolic substances are concentrated in the peel and seeds of grapes, gallic acid is the most abundant phenolic in grape seeds [26]. Sülün Kara is the largest berried variety (data are not shown) with the largest pulp, while Isabella is known for its high peel thickness and small berries. Gallic acid concentration in grape seeds also increases during the berry maturation [28], meaning that the time from flowering to harvest could be longer in the Sülün Kara. A study conducted in a high rainfall territory [8] reported significantly higher syringic acid, *p*-coumaric acid, and gallic acid contents in Isabella than in a *V. vinifera* cultivar, Kalınkara. In this study, the mentioned moieties were also higher in the Isabella than in the other two *V. vinifera* cultivars, indicating that these phenolic acids are species-specific regardless of the environmental effects. Likewise, vanillic acid showed a similarity that can be considered species-specific by being lower in Isabella in the previous and this study.

Chlorogenic acid has significant biological actions beneficial to glucose regulation and the development of type-2 diabetes by inhibiting Na^+-related glucose absorption and insulin secretion [29]. This polyphenol is also associated with inflammatory and oxidative stress reduction [30]. Although chlorogenic acid is this critical, very few studies evaluated the presence of this polyphenol in grape berries. However, this study and [25] showed that chlorogenic acid is one of the predominant polyphenolic acids in grapes. In this study, it was the second most abundant phenolic acid in Isabella and Tombak Kara and the highest in Sülün Kara. This moiety was mainly considered coffee acid and disregarded in grapes, most probably due to easily breaking down the carbon–carbon bonds by heat during the maceration process in winemaking, the high-value by-product of grapes extensively studied in terms of bioactive compounds. [31] reported a more than a six-fold reduction in chlorogenic acid content in roasted green coffee beans supporting this supposition.

Flavonoids play critical roles in plants, including pigmentation, auxin transport induction, pollen fertilization, protection against ultraviolet radiation, and pests and pathogens resistance [32]. Flavonoids like catechin and epicatechin can form hydrolyzable or condensed tannins by polymerizing [33]. Hydrolyzable tannins transform into gallotannins and ellagitannins, whose final products are gallic and ellagic acids, respectively, when hydrolyzed [34]. The condensed tannins, namely proanthocyanidins, of which catechin is the basic structural unit, are present in various parts of plants and contribute to biotic and abiotic stress defense. Their astringency protects the plants from pathogens and predators [33]. The literature and this study's results enlighten Isabella's natural resistance to grape pests and diseases by having significantly higher proanthocyanidins and metabolic by-products of their pathway. The sour flavor and notably thicker peels compared to European grapes might also be linked to the abundance of these polyphenols. Moreover, Isabella's high gallic acid content indicates excellent potential in hydrolyzable tannins, making it a tremendous health-promoting fruit.

The abundance and variation of organic acids influence the organoleptic properties of the fruits, thus the marketing of table and wine grapes. Among the grape's organic acids, tartaric and malic constitute almost 90% of total organic acids [35]. However, acidity and acid composition are altered by several factors, including environmental effectors such as light quantity and quality, high and low temperatures, daylight and season duration, slope, and soil properties [36]. Also, several biotic factors like pests and diseases, age, and varietal differences influence the organic acid composition in grapes. Moreover, berry maturity at harvest is another main factor, thanks to malic acid degradation to sugars during maturity progression, a well-known phenomenon in maturity physiology.

In this study, tartaric and malic were also predominant organic acids and comprised 18.68 g/L to 37.30 g/L and 11.21 g/L to 17.87 g/L, respectively. However, the amount of these acids in all three varieties was considerably high compared to previously reported tartaric and malic acid contents in grapes. The ranges of tartaric and malic acids in eleven different table varieties were reported as 4.07–4.92 g/L and 1.36–3.47 g/L, respectively [37]. [38] noted relatively lower tartaric and malic acids in three Turkish grape varieties ranging from 2.96 g/kg to 4.83 g/kg for tartaric and 1.28 g/kg to 2.10 g/kg for malic acid, respectively. [39] and [40] stated relatively higher contents of malic and tartaric acids, however, not exceeding 7.8 mg/L. [35] showed a decrease in malic acid in the period from veraison to maturity. The researchers reported a decrease for tartaric and malic acids from 7.45 g/L to 1.28 g/L and 29.92 g/L to 0.39 g/L, respectively, diverging depending on the variety. In mentioned studies and [41], the tartaric/malic ratio was similar to that obtained in this study, suggesting that the berries were ripened, and the differences may be occurred due to genetics or environment. However, the study of [40] includes a synonym of Isabella, which has 5.26 g/L tartaric and 2.12 g/L malic acids, eliminating the possible effect of genetic divergence, because grapes are propagated mainly from canes, and this much variation unlikely occurs. Therefore, ecology, particularly the temperature and precipitation, should be the main reason. [42] demonstrated the metabolic effects of elevated temperature on the malate pathway. They suggested that malate regulatory mechanisms alter according to developmental stages and between day and night cycles, with a higher sensitivity to increasing day temperature than rising night temperatures during ripening. Water deficit is another crucial factor influencing berry biochemical composition via phenylpropanoid, ABA, isoprenoid, carotenoid, amino acid, and fatty acid metabolic pathways, particularly upregulating ABA [43]. ABA was proven to modulate grape berry ripening [44]. This study was carried out in a region with precipitation of about 100 mm during the growing season, which is at least six times lower than the seasonal requirement to avoid water stress. When considered all together, high levels of phenolic acids and flavonoids were supported by the phenomena of water deficit, while malic acid content contradicts this. Triggering of berry ripening by low water access is expected to cause a decrease in malic acid degrading to sugars, as stated by [35].

The majority of the organic acid composition of grapes consists of malic and tartaric acids, those highly positively correlated in this study. [45] reported a significant positive relationship between these organic acids and stated that the malic/tartaric ratio significantly fluctuates depending on the variety. [46] studied a mix of 45 grape varieties belonging to *V. vinifera*, *V. vinifera* x *V. labrusca*, and *V. vinifera* x *V. amurensis* and noted almost zero correlation between malic and tartaric acids, probably due to genetic variance. Moreover, [47] suggested that the malic/tartaric acid relation is sensitive to ecology, especially to high seasonal rainfall that lowered both acids.

In the TCA (Krebs) cycle, the malate, fumarate, and succinate two-way metabolize to each other, meaning an increase in one upregulates the others. On the other hand, oxalic acid is a final product derived from oxaloacetate, which is directly produced from pyruvic acid or malic acid metabolized in the TCA cycle [48]. In this study, oxalic acid exhibited negative correlations to other organic acids, ultimately supporting the TCA cycle phenomena.

Ascorbic acid, also known as vitamin C, is a six-carbon sugar acid synthesized via the conversion of D-hexose into L-ascorbic acid derivates [49]. Sugar accumulation in grape berries accompanies ultimate malic acid catabolism, while the tartaric acid decrease is limited. Regarding this well-known metabolism, ascorbic acid was expected to correlate with malic acid negatively. Tartaric and malic acids were drastically decreased, while sugars were not statistically changed by the extensive water supplementation [47]. However, ascorbic acid exhibited significant positive correlations with malic, tartaric, and fumaric acids suggesting up-regulation of the antioxidant/resistance system via secondary metabolites in an arid year (see Fig. 2).

Conclusion

This study discussed the composition of organic acids and polyphenols in certain varieties of *V. vinifera* and Isabella grapes in the context of physiological approaches to drought and secondary metabolism. The results suggest a considerable enhancement in the grape's secondary metabolites, particularly in flavonoids, under rain scarcity. Moreover, Isabella deserves more interest regarding cultivation under arid conditions to obtain biochemically fortified berries.

Data availability The manuscript includes all relevant data.

Declarations

Conflict of interest The author declares no known individual or financial conflict of interest.

Compliance with Ethics requirements This article does not contain any studies with human or animal subjects.

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