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Effects of foliar iron spraying on Cabernet Sauvignon phenolic acids and proanthocyanidins

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Abstract

In order to explore the effect of different irons on the fruit quality of wine grapes, as well as the phenolic acids and proanthocyanidins of the peel, "Cabernet Sauvignon" was taken as the research object. Ferrous sulfate, EDTA-Fe, ferric citrate, ferric gluconate and ferric sugar alcohol were sprayed between the coloring periods, and the foliar sprayed water was used as the control. The results showed that foliar spraying of iron would increase the fruit sugar-acid ratio and 100-grain weight; iron spraying would up-regulate the content of phenolic acid monomers, among which EDTA-Fe and ferric citrate had significant up-regulating effects, but all iron treatments had a significant effect on the increase. The content of caffeic acid and chlorogenic acid was down-regulated; the content of proanthocyanidin monomer was up-regulated by iron spraying, and the content of proanthocyanidin monomer was significantly up-regulated by ferric citrate treatment. Foliar spraying of ferric citrate not only balanced the sugar-acid ratio of the fruit, but also increased the content of phenolic acid and proanthocyanidin in the grape peel, which further improved the quality of the grapes and helped to increase the flavor of the wine.

Keywords: iron fertilizer; cabernet sauvignon; phenolic acid; proanthocyanidins.

Practical Application: In this work, we evaluated the effects of different iron sources on proanthocyanidins and phenolic acids in Cabernet Sauvignon fruit by foliar spraying of iron. By chromatographic analysis, metabolite content was detected, and phenolic acids and procyanidins were clustered. The results obtained will improve the iron deficiency at the foot of Helan Mountain, have a positive effect on improving the fruit quality of Cabernet Sauvignon, and help increase the flavor of the wine.

1 Introduction

Iron is an essential micronutrient for the growth and development of wine grapes. The application of iron is to ensure the growth of the grapes and to enrich the flavor combination of the grapes (Tagliavini & Rombola, 2001; Bertamini & Nedunchezhian, 2005; Karimi et al., 2019). Foliar spraying of iron fertilizer can promote the secondary metabolism of grapes and improve the nutritional value of grapes and wine (Shi et al., 2018). The eastern foothills of Helan Mountain in China is a calcareous soil and lacks iron. Iron deficiency will reduce the nutritional value of grapes and the flavor of wine (Barton & Abadia, 2006). Under alkaline soil conditions, application of chelated iron can significantly increase the content of soluble sugar and phenolic acid in grape fruit (Karimi et al., 2019). Foliar application of iron, especially in a specific phenological period, can quickly supply iron through the pores of the cuticle of grape leaves to meet the needs of grape growth and development. Foliar application of iron has a very positive effect on grape yield and berry sugar content (Bacha et al., 1995; Shi et al., 2017). Iron spraying increased the soluble sugar and anthocyanin content of berries, and also had a certain effect on pH (Ahmed et al., 1997; Amiri & Fallahi, 2007). A moderate amount of iron will increase the concentration of reducing sugars and anthocyanins, and both iron deficiency and excess will lead to a decrease in the content of reducing sugars and anthocyanins (Shi et al., 2017).

Phenolic acids, including hydroxybenzoic acid and hydroxycinnamic acid, are important components in wine and affect its sensory quality (Somkuwar et al., 2018). Phenolic acid can reflect the pros and cons of terroir and guide the production of grapes (Lampíř et al., 2013). At the same time, phenolic acid can also distinguish the geographical origin of wine and grape variety (Sun et al., 2015). Gastón's findings suggest that seaweed extracts also have an effect on phenolic acid content (Gutierrez-Gamboa et al., 2020). Phenolic acids are involved in the pigmentation of wine as a cofactor, inducing the pigmentation reaction of anthocyanins and increasing the color of wine (Bimpilas et al., 2016). Grape dehydration before winemaking increases the content of four hydroxybenzoic acids (ethyl gallate, p-hydroxybenzoic acid, hexose gallate and gallic acid) and two hydroxycinnamic acids (caffeic acid and isovaleric acid). Contribute to the improvement of wine quality (Nievierowski et al., 2021).

Proanthocyanidins are secondary metabolites in the synthesis of flavonoids that play an important role in wine, contributing to taste and color stability (Bogs et al., 2005). During the grape growing process, the content of proanthocyanidins first increased and then decreased, and tended to be stable at the harvest period. Appropriate light and temperature will promote

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the synthesis of anthocyanins and procyanidins, and increase the phenolic maturity of grapes (Mota et al., 2021; Zhang et al., 2021). Application of exogenous abscisic acid can increase the content of proanthocyanidins in wine grapes and enhance the oxidative capacity of wine (Xi et al., 2013). Higher levels of proanthocyanidins in less oxidized, high-quality red wine (Longo et al., 2019).

There are many studies on phenolic acids and proanthocyanidins, but few studies on the effect of different irons on phenolic acids and proanthocyanidins in wine grapes. This study investigated the effects of different irons on the berry quality, peel phenolic acids and proanthocyanidins of Cabernet Sauvignon grapes with the aim of enhancing the flavor of wine grapes. The obtained results will help to clarify the influence of exogenous iron types on grape quality, and provide a basis for the improved cultivation of wine grapes on the alkaline soil at the eastern foot of Helan Mountain.

2 Materials and methods

2.1 Test design

The test was carried out in Lilan Winery, the wine grape producing area at the foot of Helan Mountain from April to October 2020(105°58′20″ E, 38°16′38″ N), soil type is gravelly calcareous soil. The 8-year-old Cabernet Sauvignon was selected as the experimental material, the tree shape was "plant", the rows were north-south, the row spacing was 0.6 m × 3.5 m, and sheep manure organic fertilizer was used as the base fertilizer, and the trench was opened once in early May. Sexual application 10500 kg/hm^2. Except for foliar application of iron fertilizer, no chemical fertilizer was applied during the whole experiment period, and the cultivation management methods such as irrigation (drip irrigation) and pruning of branches were the same for all treatments.

This experiment adopts a randomized block design, with 6 treatments, each treatment with 3 replicates, a total of 18 plots, and each plot area is 10.5 m^2. The iron fertilizer was sprayed in three times (July 12, July 27, and August 11) during the grape enlargement period and the color-changing period, and was sprayed with an electric sprayer. Each treatment was sprayed with 5 L of solution. Table 1 shows the total amount of nutrients after 3 applications for all treatments. All treatments except the application of iron fertilizer, the rest of the management measures are the same as the vineyard.

2.2 Determination of Cabernet Sauvignon fruit quality

The content of soluble solids was determined by hand-held sugar meter; the content of reducing sugar was determined by 3,5-dinitrosalicylic acid method; the content of titratable acid was determined by standard 0.1 mol/L NaOH (end point pH 8.2) (Jin et al., 2016; Ma et al., 2019; Wang et al., 2019).

2.3 Extraction of phenolic acids and proanthocyanidins from Cabernet sauvignon peel

The biological samples were placed in a lyophilizer (Scientz-100F) for vacuum drying and freezing for 24 h, and then ground (30 Hz, 1.5 min) with a grinder (MM 400, Retsch) to a powdery state, and the peel was extracted with 70% methanol solution (1.2 mL). powder (100 mg), then shake on a vortex shaker for 30 seconds every 30 minutes, a total of six times, let stand at 4 °C overnight, centrifuge the homogenate at 12,000 rpm for 10 minutes, aspirate the supernatant, and finally filter it with a microporous membrane (0.22 μm pore size) filtered samples for UPLC-MS/MS analysis. Three independent extractions were performed for each treatment.

2.4 Chromatographic analysis of phenolic acids and procyanidins in Cabernet Sauvignon peel

Sample extracts were analyzed using a UPLC-ESI-MS/MS system (UPLC, SHIMADZU Nexera X2, www.shimadzu.com.cn/; MS, Applied Biosystems 4500 Q TRAP, www.appliedbiosystems.com.cn/). The analytical conditions were as follows, UPLC: column, Agilent SB-C18 (1.8 µm, 2.1 mm*100 mm); mobile phase consisted of solvent A: pure water with 0.1% formic acid and solvent B: acetonitrile with 0.1% formic acid. Sample measurements were performed using a gradient program that used starting conditions of 95% A, 5% B; phase B increased linearly to 95% in 9 min and maintained at 95% for 1 min, 10-11.1 min, The proportion of phase B was reduced to 5% and equilibrated at 5% to 14 min; the flow rate was set to 0.35 mL/min; the oven temperature was set to 40 °C; the injection volume was 4 μL.

LIT and triple quadrupole (QQQ) scans were acquired on a triple quadrupole linear ion trap mass spectrometer (Q TRAP), AB4500 Q TRAP UPLC/MS/MS system equipped with an ESI Turbo Ion-Spray in29 interface, both positive and negative ion modes exist and are controlled by Analyst 1.6.3 software (AB Sciex). Instrument tuning and mass calibration were performed

Table 1. Type and dosage of iron source.

Indexes	Type of iron fertilizer	Solution concentration	Iron fertilizer application rate	Iron dosage
		%	kg/hm^2	
Control	-	-	-	-
FB1	Ferrous sulfate	0.09	4.44	0.89
FB2	EDTA-Fe	0.15	7.14	0.89
FB3	Ferric citrate	0.08	3.99	0.89
FB4	Ferric Gluconate	0.16	7.76	0.89
FB5	Iron sugar alcohol	0.19	8.93	0.89

Note: ferrous sulfate (Fe 20.10%); EDTA-Fe (Fe 12.50%); ferric citrate (Fe 22.40%); ferric gluconate (Fe 11.50%); ferric sugar alcohol (Fe 100 g/L).

in QQQ and LIT modes using 10 and 100 μmol/L polypropylene glycol solutions, respectively. QQQ scans were acquired by MRM experiments with the collision gas (nitrogen) set to medium. With further DP and CE optimization, DP and CE for a single MRM transition are completed. A specific set of MRM transitions was monitored in each epoch based on the metabolites eluted in each epoch. By comparing the ion current intensity and retention time and comparing with the self-built database MWDB (metware database), qualitative and quantitative analysis of substances was carried out according to the secondary spectrum information, and the content of different metabolites was analyzed according to the metabolite detection multi-peak map.

2.5 Statistical analysis

The data were processed and analyzed by Microsoft Excel 2010 and SPSS 21.0 software, and R-4.0.3 was used for graphing, and the significance level was ($p < 0.05$, $n = 5$).

3 Results

3.1 Effects of different iron on the quality of Cabernet Sauvignon berries

The results in Table 2 show that the content of soluble solids and reducing sugar in Cabernet Sauvignon berries increased after iron spraying, and the sugar-acid ratio and 100-grain weight increased. The content of soluble solids increased by 0.2% - 4.5%, and the increase was the most after FB3 treatment. The content of reducing sugar increased by 0.1% - 12.4%, and the increase was the highest under FB3 treatment, and the content of reducing sugar in berries increased significantly. Except for FB3, the content of titratable acid (TAC) in berries was decreased under other treatments, and the content of titratable acid (TAC) in berries treated with FB4 was the lowest, which decreased by 16.67%. Spraying with different irons all increased the ratio of buconic acid (TSS/TAC) by 14.63%, 8.12%, 4.47%, 20.28% and 16.04%, respectively, with the most significant increase in FB4. FB1 significantly increased berry 100-kernel weight; FB3 significantly increased berry soluble solids, reducing sugar and 100-kernel weight; FB4 significantly increased the ratio of berry to acid; FB5 significantly increased berry reducing sugar.

3.2 Effects of different iron on Cabernet Sauvignon peel phenolic acid

Figure 1. shows the effect of different irons on the phenolic acid content of pericarp. UPLC-MS analysis showed that there were 118 phenolic acids in grape peel, mainly caffeic acid, vanillic acid and gallic acid. The most representative 9 groups of phenolic acids were selected for analysis. The results showed that the content of total phenolic acids increased significantly after FB3 treatment, and the contents of vanillic acid, gentisic

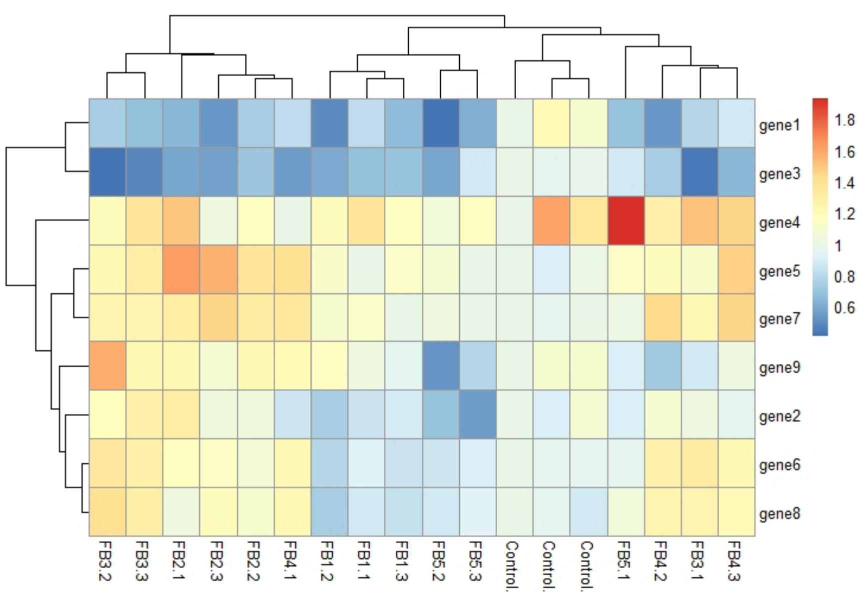

Figure 1. Cluster analysis of phenolic acids in Cabernet Sauvignon peel.

Table 2. Effects of different iron on the quality of Cabernet Sauvignon berries.

indexes	Control	FB1	FB2	FB3	FB4	FB5
TSS	26.87 ± 0.05e	27.87 ± 0.06ab	27.67 ± 0.05bc	28.07 ± 0.10a	26.93 ± 0.09d	27.47 ± 0.02c
RS	17.84 ± 0.08c	17.86 ± 0.06c	18.70 ± 0.07b	20.06 ± 0.08a	18.91 ± 0.14b	19.82 ± 0.05a
TAC	0.84 ± 0.01a	0.76 ± 0.01bc	0.80 ± 0.01ab	0.84 ± 0.01a	0.70 ± 0.02d	0.74 ± 0.01cd
TSS/TAC	31.97 ± 0.21d	36.64 ± 0.12b	34.56 ± 0.14c	33.39 ± 0.11cd	38.45 ± 0.09a	37.09 ± 0.13ab
WB	94.78 ± 0.36c	115.42 ± 1.04a	110.66 ± 0.92b	117.05 ± 1.16a	113.63 ± 1.88ab	111.48 ± 0.98b

TSS: total soluble solids (%), RS: Reducing Sugar (expressed in gram equivalent glucose L^{-1}), TAC: Titratable Acid Content (expressed in gram equivalent tartaric acid L^{-1}), WB: weight of 100 berrys (g). Different lowercase letters indicate significant differences between treatments as calculated by Tukey's HSD test ($p < 0.05$).

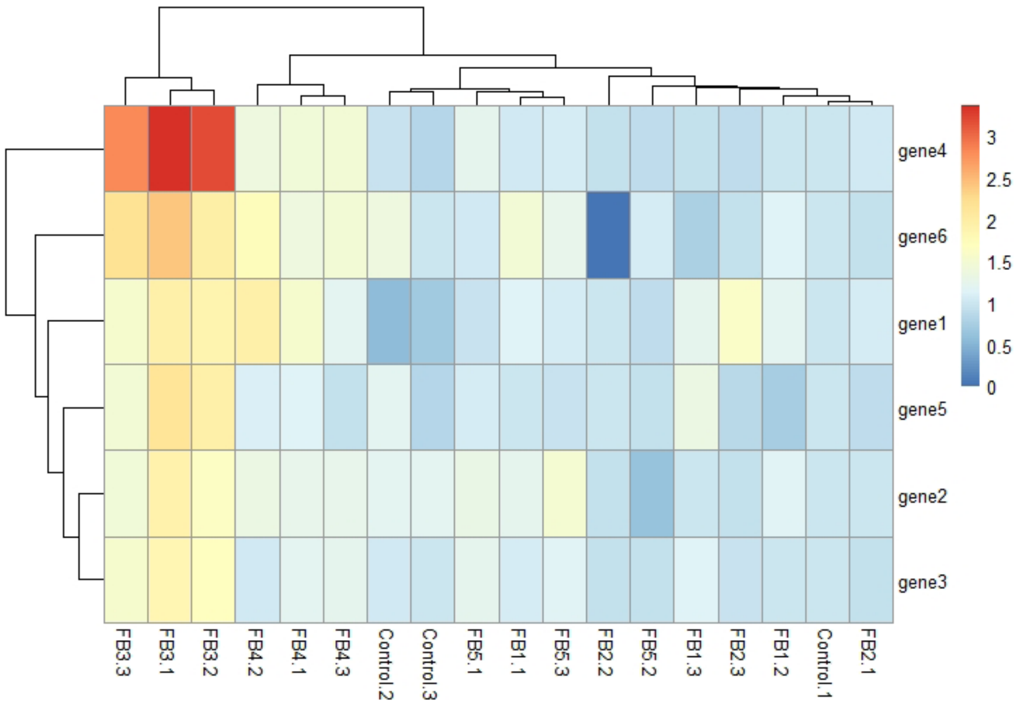

Figure 2. Cluster analysis of proanthocyanidins in Cabernet Sauvignon peel.

acid and p-hydroxybenzoic acid increased the most, increasing by 16%, 38.9% and 15.1%, respectively; under FB2 treatment, the content of syringic acid It was significantly higher than other treatments, 56.7% higher than Control; under FB4 treatment, the content of gallic acid increased significantly, 43.4% higher than Control; under FB5 treatment, the content of salicylic acid increased the most, with an increase of 4.5%. The relative contents of caffeic acid and chlorogenic acid decreased under all iron source treatments, and the content of caffeic acid decreased by 32.4%-48.1%, and the content of caffeic acid decreased most obviously under the FB5 treatment; the content of chlorogenic acid decreased by 21.1%-54.9%, the chlorogenic acid content decreased most obviously under the FB3 treatment.

3.3 Effects of different iron on proanthocyanidins in Cabernet Sauvignon peel

Figure 2 shows the effect of different irons on the proanthocyanidin content of peels. The results showed that FB3 had the most obvious effect on proanthocyanidins, and the contents of 6 proanthocyanidins increased the most, which were 136.4%, 46.9%, 66%, 237.1%, 83%, and 94.3% higher than Control, among which the content of procyanidin B2 increased. most notably. After FB4 treatment, the relative content of total proanthocyanidins also increased to a certain extent, among which the content of theaflavins, procyanidin B2 and procyanidin C1 were also significantly increased, which were increased by 32%, 45% and 35.4% respectively compared with Control; after FB1 and FB5 treatment, There was no obvious effect on the content of procyanidins; the content of total procyanidins decreased after FB2 treatment.

3.4 Principal component analysis of Cabernet Sauvignon peel phenolic acids and proanthocyanidins

In Figure 3, principal component 1 explains 70.6% of the variance. Principal component 2 explained 10.1% of the variance. Principal component 1 and principal component 2 explained a total of 80.7% of the variance, so two principal components were selected for principal component analysis of Cabernet Sauvignon peel. Principal component 1 was positively correlated with FB3, and principal component 2 was positively correlated with FB1 and FB5. In Figure 4, FB3 can distinguish well from other groups, and FB3 significantly outperforms other treatments in principal component 1. The metabolite accumulation of FB1, FB5 and Control were similar, and the overall score of FB2 was the lowest.

4 Discussion

Fruit sugar to acid ratio is usually a measure of fruit ripeness. In the present study, iron spraying increased the content of soluble solids and reducing sugars and decreased the titratable acid content in berries, which resulted in an increase in the sugar-to-acid ratio, which was consistent with the conclusion obtained by Shi et al. (2017). There were also significant differences in the contents of glucose fructose and acid under different iron treatments, and the contents of soluble solids and reducing sugars were higher under the treatments of EDTA-Fe, ferric citrate, ferric gluconate, and ferric sugar alcohol. It was found that all treatments except ferric citrate reduced the content of titratable acid in the fruit. This may be due to the fact that iron spraying promotes the accumulation of fruit sugar, which accelerates the ripening of the fruit, resulting in a decrease in the content of malic acid in the berries (Karimi et al., 2019).

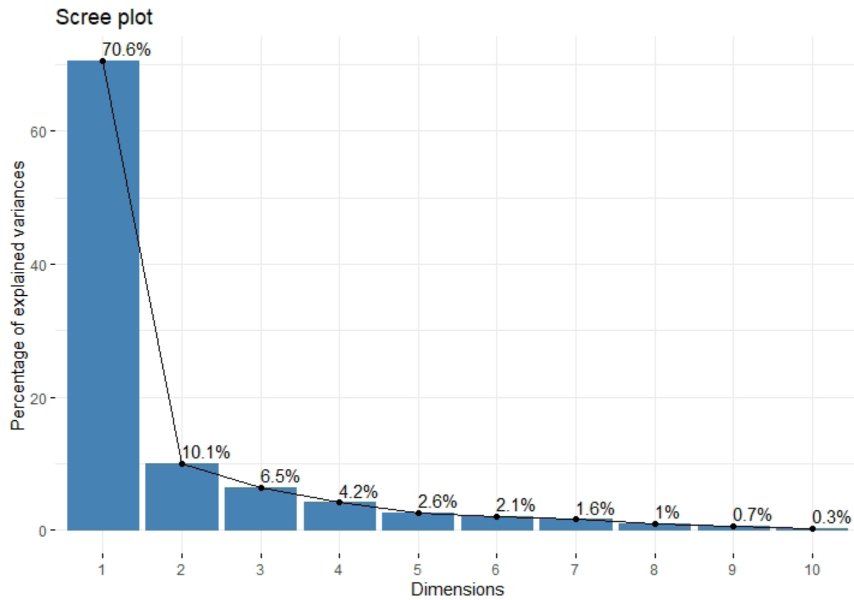

Figure 3. Principal component gravel inspection.

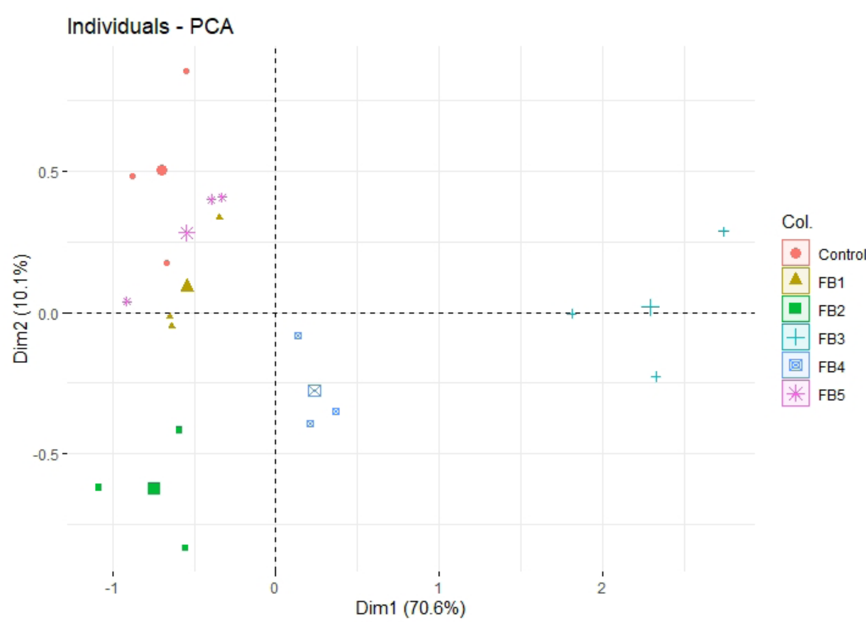

Figure 4. Principal Component Analysis of the Influence of Different Iron on the Phenolic Acids and Procyanidins of Cabernet Sauvignon Peel.

When ferric citrate was sprayed, the content of soluble solids and reducing sugar in berries increased, while the content of titratable acid did not change compared with the control, probably because citric acid was consumed by berry respiration and the decomposition of malic acid was reduced. Therefore, lemon Ferric acid treatment has higher titratable acid content than other treatments (Smith et al., 2004; Schlegel et al., 2006). Berry weight is determined by berry size and density and is one of the important factors affecting grape quality. Under the iron treatment, the berry weight was significantly higher than that of the control, because the application of iron increased the photosynthesis of grapes and promoted the accumulation of dry matter (Bertamini & Nedunchezhian, 2005).

Iron application has a great effect on phenolic acids in Cabernet Sauvignon peel. The relative content of cinnamic acids, mainly caffeic acid and chlorogenic acid, was significantly reduced after iron application. It is speculated that the reason is that under the catalysis of iron, a part of cinnamic acid is converted into cinnamate (Gutierrez-Gamboa et al., 2020). However, the relative content of hydroxybenzoic acids, mainly salicylic acid, syringic acid and gallic acid, was significantly increased after iron application, which was similar to Karimi's research results (Karimi et al., 2019). The iron-reducing ability of phenolic acids increases with increasing concentration. Compared with -COOH, -CH=CHCOOH can enhance the antioxidant activity of phenolic acids (Gao et al., 2022). After treatment with EDTA-

Fe, ferric citrate and ferric gluconate, the contents of vanillic acid, protocatechuic acid, gentisic acid and p-hydroxybenzoic acid were all increased, similar to the results of Shi Pengbao's study (Shi et al., 2017). In wine grapes, hydroxybenzoic acid is necessary for the synthesis of other compounds related to the growth and development of grape berries, and iron spraying can significantly increase the content of hydroxybenzoic acid. Therefore, iron application plays an important role in the growth and development of Cabernet Sauvignon.

Procyanidins are polymers of flavanols, which are natural antioxidants. Proanthocyanidins play a central role in wine grapes because of their physiological and oenological significance (Li et al., 2021). In the analysis of proanthocyanidins, the relative content of proanthocyanidins in Cabernet Sauvignon peel was significantly increased after ferric citrate treatment, which may be that the oxidation of ferric citrate promotes the synthesis of Cabernet Sauvignon procyanidins (He et al., 2021). However, ferrous sulfate and ferric sugar alcohol have weak oxidizing properties, and the improvement of proanthocyanidins is not obvious. In this study, the content of cinnamic acid decreased after iron spraying, while the content of proanthocyanidins generally increased. Because cinnamic acid is one of the necessary substances in the synthesis pathway of proanthocyanidins (He et al., 2008), part of cinnamic acid is involved in the synthesis of proanthocyanidins.

5 Conclusion

Iron spraying had effects on Cabernet Sauvignon fruit quality and phenolic acid and proanthocyanidin content in peel. Foliar spraying of iron can increase the sugar-to-acid ratio and 100-grain weight of the fruit, and reduce the content of cinnamic acid (caffeic acid, chlorogenic acid) in the peel. The content of 2 kinds of phenolic acid monomers and 4 kinds of proanthocyanidin monomers increased by spraying ferrous sulfate; the content of 6 kinds of phenolic acid monomers and 2 kinds of procyanidin monomers increased by spraying EDTA-Fe; The contents of 4 kinds of phenolic acid monomers and 6 kinds of proanthocyanidin monomers were up-regulated; the content of 3 kinds of phenolic acid monomers and 4 kinds of proanthocyanidin monomers were up-regulated by spraying iron sugar alcohol; the contents of 7 kinds of phenolic acid monomers were up-regulated by spraying iron citrate The content of 6 kinds of proanthocyanidins monomers was significantly increased, and the content of total phenols in grape peel was increased significantly. Foliar spraying of ferric citrate not only balanced the ratio of sugar to acid, but also increased the content of phenolic acid and proanthocyanidin in grape peel, which further improved the quality of grapes and helped to increase the flavor of wine.

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