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Six Different Vineyard Treatments to Improve Chemical Properties and Taste Sensory Profiles of ‘Syrah’ (*Vitis Vinifera* L.) Wines

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Abstract

Canopy management is a viticulture tool to improve berry and wine quality. Accordingly, the main purpose of this study is to evaluate the effects of cluster thinning at two different times (V: cluster thinning at the beginning of véraison and AV: cluster thinning at the end of véraison), leaf removal (LR), and combinations of cluster thinning–leaf removal (VLR: cluster thinning at the beginning of véraison and leaf removal before flowering, AVLR: cluster thinning at the end of véraison and leaf removal before flowering) on the quality of ‘Syrah’ wines. The highest pH, total phenolic compound, total anthocyanin, antioxidant capacity, colour parameters, phenolics and anthocyanin compound levels were obtained from VLR and AVLR wines. Total phenolic compound, total anthocyanin, *trans*-resveratrol, catechin and malvidin-3-glucoside levels of AVLR wines increased by 74%, 56%, 20%, 42%, and 10%, respectively, compared to the control group wines. According to the results of flavour sensory profile, AVLR wines had the highest scores in the parameters of intensity, dark fruit, liquorice, chocolate, dried fruit, and earthy. The wines obtained from combinations of leaf removal and cluster thinning (VLR and AVLR) had a higher score in body, harmony, and peppery parameters compared to the control wines. The characteristic rotundone aroma of ‘Syrah’ wines was also felt most in VLR and AVLR wines according to the sensory profile tastings. This research aims to provide data to viticulturists and oenologists on the use of sustainable alternative practices in viticulture of ‘Syrah’ variety, which is one of the most grown red wine grapes in Turkey. Based on the results, it may be concluded that the combination of cluster thinning at the end of véraison and leaf removal has a large impact on the organoleptic quality and antioxidant compounds in wines.

Keywords ‘Syrah’ · Anthocyanin · Antioxidant · Rotundone · Viticulture practice · Winegrape

Introduction

Wine production is a very challenging task that is affected by many factors such as grape variety, terroir, viticulture practices, winemaking techniques, and aging conditions (Anastasiadi et al. 2009; Van Leeuwen and Darriet 2016; Kupsa et al. 2017; Reynolds 2021). The main varieties that are cultivated in winegrape producing regions are characterized by the average climatic conditions of the region, and changes in these conditions result in differences among the wines produced from the harvest of that year. Viticulture practices are the second most significant factor that influences the quality of grapes. Vine canopies are managed more intensively than most horticultural plants. The applications of cluster thinning and leaf removal practices are widely used in winegrape growing to achieve the target quality (Rutan et al. 2018; Ivanišević et al. 2020).

High quality is often associated with low vine yields. Cluster thinning is a way to control the crop load of a vine by cutting away the clusters to obtain the desired yield. After cluster thinning, the produce that has decreased quantity is exposed to better photosynthesis. Therefore, the crop which is developed in a denser leaf area with less clusters is known to be affected positively. It is argued that the water-soluble dry matter and pH levels of ‘Cabernet Sauvignon’, ‘Merlot’, ‘Pinot Noir’, ‘Syrah’, and ‘Tempranillo’ grapes are elevated and that total soluble solid accumulation timing is influenced positively through the practice of cluster thinning, (Reynolds et al. 1994; Nuzzo and Matthews 2006; Petrie and Clingeleffer 2006; Valdes et al. 2009; King et al. 2012). In addition, yield management through cluster thinning can induce changes in the chemical composition of

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grapes (Keskin et al. 2013; Isci et al. 2015), thereby affecting wine aroma, taste, and mouthfeel (Rutan et al. 2018; Alba et al. 2022). Previous research on red wines states that there is a close relationship between a lower product load and an increase in phenolic composition, which is responsible for the colour of the wine and the sensation it leaves in the mouth (King et al. 2012; Gil-Munoz et al. 2016).

Another common practice just like cluster thinning is leaf removal, which is a widely applied method in grape canopy management (Korkutal et al. 2017, 2021, 2022; Köse et al. 2018) from flowering to harvest to enhance sunny microclimate due to improved air circulation and light penetration (Anić et al. 2021). Grapes that are well exposed to sunlight as a result of leaf removal have higher sugar, anthocyanin, and phenolic concentrations compared to grapes in shade. Photo-regulation of invertase and phenylalanine ammonia lyase enzymes is primarily thought to play a role in these responses to leaf removal (Dokoozlian and Kliewer 1996). Regardless of the timing and method (manual or mechanical) of leaf removal, it has been observed to cause the accumulation of phenolics and anthocyanins in ‘Tempranillo’ grapes (Diago et al. 2012). Early leaf removal is also stated to reduce inflorescence and yield but increase total phenolic, anthocyanin, and tannins concentrations in wines (Hickey et al. 2018). Non-flavonoid and flavonoid biosynthetic pathways are subjected to the action of light and temperature sensitive regulatory enzymes (Downey et al. 2003). Therefore, any changes in the microclimate which are caused by the removal of leaves may have a remarkable effect on the synthesis and accumulation of these compounds in grapes and consequently wine quality. In additional, early leaf removal (from flowering to the stages of fruit formation) reduce the size and number of fruits and increase the skin/pulp ratio, which lead to increased phenolic compound content in wine (Poni et al. 2005). Leaf removal results in higher sugar content in wine, increased phenolic content in fruit skin, and more stable anthocyanin in wine (Baiano et al. 2015). Selective leaf removal in a vine canopy with low photosynthetic photon flow is reported to increase the photosynthetic activity of the remaining leaves and can positively affect fruit composition (Smart et al. 1988). Among the biologically active metabolites that contribute to the defence against environmental negativity, phenolics play a particularly important role. In fact, phenolic compounds represent one of the main components of the antioxidative defence of cells. The antioxidative effect of this group of compounds is linked with their ability to inhibit or slow the spread of cell oxidation, which causes cell damage due to lipid peroxidation and enzyme inactivation (Olas 2018; Averilla et al. 2019; Saha et al. 2019).

The extent of sensory effects on wine appears to depend on various factors such as the variety and timing of removal applications (cluster or leaf). Ivanišević et al. (2020) states that cluster thinning and leaf removal affect grape quality and leaf composition of ‘Cabernet Sauvignon’ and ‘Probus’ (*Vitis vinifera* L.) and that the most effective practice for both species is early leaf removal. However, the timing of leaf removal and cluster thinning applications and the combinations of these applications as well as the grape variety produce different results.

The phenolic structure of a wine plays an important role in the perception of desirability and quality and is the primary important factor when considering the typicality of a region’s wine style. ‘Syrah’ (*Vitis vinifera L.*) is an international red variety which is considered as one of the noble black grape varieties due to its ability to produce high quality wines with heavy, aromatic, and dark colours. ‘Syrah’ (*Vitis vinifera* L.) is one of the most commonly cultivated grapes in Turkish winemaking. It is the dominant red grape variety in the Güney district of Denizli province, where most vineyards in Turkey are located.

The effect of cluster thinning on ‘Syrah’ wine composition has been studied by different authors (Silva et al. 2009; Gil et al. 2013). However, there is a limited number of studies in literature that compare the wine which is produced as a result of cluster thinning applied at two different times and the combination of leaf removal applications with the wine which is made with grapes produced from untreated vines and with only leaf removal applications. In the present study cluster thinning at the beginning of véraison (V), cluster thinning at the end of véraison (AV), leaf removal before flowering (LR), cluster thinning at the beginning of véraison and leaf removal before flowering (VLR), cluster thinning at the end of véraison and leaf removal before flowering (AVLR) applications were done. Syrah grapes obtained as a result of applications were processed as wine and the changes in their phenolic composition, anthocyanin, levels and sensory profiles based on tasting were examined. Accordingly, the present study aimed to reveal the changes after cluster thinning practices at different times, leaf removal, and the combinations of these applications in wine quality in terms of both organoleptic and phytochemical aspects.

Materials and Methods

Vineyard and Experimental Design

The experiment was carried out in 2021 with ‘Syrah’ (*Vitis vinifera* L.) grape variety in a vineyard on 41 B rootstock in Güney, Denizli, Turkey (38°09′45.29″ N, 29°07′14.46″ E), 795 m above sea level. The vines were spaced 2 m × 3 m with the Guyot system without irrigation. Each treatment had 15 vines with a total of 90 vines in the present study.

With the winter pruning in March 2021, the vines were pruned by leaving two renewal (two buds for each) and two cane (six buds for each) in the form of the Guyot system. Six different applications were carried out: no cluster thinning or leaf removal (UNT), cluster thinning at the beginning of véraison (V), cluster thinning at the end of véraison (AV), leaf removal before flowering (LR), cluster thinning at the beginning of véraison and leaf removal before flowering (VLR), and cluster thinning at the end of véraison and leaf removal before flowering (AVLR). Cluster thinning treatments were conducted with one cluster per shoot (approximately 50% of clusters were removed), and leaf removal treatments were conducted by manual removal of five basal leaves per shoot during the vegetation period. V treatment was conducted on 3 July 2021, AV was conducted on 20 July 2021, LR was conducted on 1 June 2021, VLR was carried out on 3 July 2021, and AVLR on 20 July 2021. A randomized complete block design was performed with three replicates for each treatment. Harvest was carried out manually on 26–29 August 2021 for each application when the grapes reached approximately 24 °Brix, with regular Brix and pH analyses performed twice weekly until harvest.

Microvinifications

On the harvest day, 45 kg of grapes were harvested for each application and treated with 60 g/tonne potassium metabisulfite ($K_2S_2O_2$) and taken into 20 L vessels after destemming and crushing ($n=3$). Alcohol fermentation was started by adding 200 g/ton of commercial *Saccharomyces cerevisiae* yeast (Laffort FX10, France) and 300 g/tonne of yeast nutrient (Laffort Dynastart, France). Fermentations were conducted in 50 L glass fermentors and the caps were mixed and wetted twice daily. After 8 days of maceration at approximately 20 ± 1 °C, wine was pressed with a basket press. The pressed wines were taken into glass demijohns and malolactic fermentation was started by adding 250 g/hL of commercial *Oenococcus oeni* bacteria (Laffort 450 Preac, France). Malolactic fermentation (MLF) was carried out at 24 ± 1 °C, and at the end of the MLF (42 days) the wines were racked and sulphurised at the rate of 60 g/ton. At 5 months after the end of fermentation samples were taken for the chemical and sensory analyses.

Physical and Chemical Grape Analyses

Yield (kg/vine), pH, total acidity (mg/g), °Brix of grape juices, skin weight of berry (g), and cluster weight (g) were measured on the day of harvest (OIV 2009).

Chemical Analyses of Wines

In samples, pH, total acidity (mg/mL), alcohol (%), total extract (g/L), and malic acid (mg/mL) measurements were performed in treatment wines (OIV 2009). In addition, the wines were filtered via 45 µm PVDF filters and the changes in total phenolic compounds, total anthocyanin, and antioxidant capacity levels according to the applications were examined by UV-VIS spectrophotometer (Shimadzu UV VIS 1208, Japan).

Total phenolic compound (TPC) determination was performed according to Singleton and Rossi (1965) and results were expressed as mg gallic acid equivalent/L for each wine. The pH differential method of Giusti and Wrolstad (2001) was used to determine the total amounts of anthocyanin (TA) in treatment wines. The total amount of anthocyanin was expressed as malvidin-3-monoglicoside, mg/L. Antioxidant capacity (AC) levels were determined by three different methods: the 2,2′-azinobis (3-ethyl-benzothiazoline-6-sulfonic acid) (ABTS) method, the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method, and the ferric reducing antioxidant power (FRAP) method. The ABTS method was performed according to Re et al. (1999), the DPPH method was performed according to Katalinić et al. (2004), and the FRAP method was performed according to Benzie and Strain (1996). The results are expressed as trolox equivalents (µmol trolox/mL) to facilitate comparability with each other.

Colour Analyses of Wines

In order to prevent the effect of SO_2 in the wines, 20 µL of 10% (v/v) acetaldehyde was added to 2 mL of wine and left for 20 min and the CIELAB coordinates lightness (L*), chroma (C*), hue (h*), red–greenness (a*), and yellow–blueness (b*) values were carried out according to Ayala et al. (1997), while colour intensity and colour hue values were carried out according to Cliff et al. (2007) with a UV-VIS spectrophotometer (Shimadzu, Japan). The total colour difference (ΔEab*) between two samples was obtained using the expression: $\Delta Eab^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ (Pérez-Magariño and González-Sanjose 2003).

HPLC-DAD Analyses of Anthocyanin and Phenolic Compounds of Wines

The effects of applications on *trans*-resveratrol, *cis*-resveratrol, (+)-catechin, (–)-epicatechin, rutin, quercetin delphinidin-3-glucoside, cyanidin-3-glucoside, petunidin-3-glucoside, peonidin-3-glucoside and malvidin-3-glucoside amounts in wines were investigated (Downey and Rochfort 2008). For this purpose, the wines that have completed their fermentation are racked and filtered through 0.45 µm pore

Table 1 Physical and chemical grape parameters at harvest

Parameters	UNT	V	AV	LR	VLR	AVLR	LSD (0.05)
pH	3.11 d	3.41 b	3.22 c	3.40 b	3.24 c	3.49 a	0.038
Total acidity (mg/g)[a]	7.53 a	7.23 b	7.10 bc	7.07 bc	6.97 c	6.97 c	0.250
°Brix	24.00 c	24.37 b	25.17 a	24.80 b	24.93 ab	25.10 a	0.263
Vine yield (kg)	3.21 a	1.63 d	1.91 b	3.20 a	1.70 c	1.95 b	0.063
Berry weight (g)	1.66 c	2.00 a	2.01 a	1.75 c	1.89 b	1.97 ab	0.092
Skin weight (g)	0.26 e	0.51 a	0.29 d	0.39 c	0.46 b	0.30 d	0.025
Cluster weight (g)	250.00 d	290.00 a	255.00 c	250.33 d	261.00 b	259.67 b	3.587

Means followed by different letters on the lines indicate significant differences after the treatments ($P < 0.05$)

UNT Untreated, *V* Cluster thinning at the véraison, *AV* Cluster thinning after véraison, *LR* Leaf removal before flowering, *VLR* Cluster thinning at véraison and leaf removal, *AVLR* Cluster thinning after véraison and leaf removal, *LSD* least significant difference

[a] In terms of tartaric acid

sizes PVDF membrane filters to analyses with Shimadzu HPLC-DAD (Japan) device. The column was a Gemini Phenomenex C18 (Calif., U.S.A.): 4.6 mm × 260 mm protected by a guard column of the same material. Identification of the compounds was performed using the retention times and their visible spectrum of the standard substances used. Since there is no commercial standard for determining *cis*-resveratrol, the prepared *trans*-resveratrol standards were converted to the *cis* form by exposing them to 254 nm UV-C light for 30 min. Standard curves were prepared by setting the standards at 1–50 ppm concentrations and these curves were used to determine the phenolic compound amounts of the samples. Formic acid 10% in water (solvent A) and formic acid 10% in a methanol (solvent B) were used as mobile phase. Flow elution was set at 1.0 mL/min according to the following gradient: (v/v): 0 min 18% B, 14 min 29% B, 16 min 32% B, 18 min 41% B, 18.1 min 30% B, 29 min 41% B, 32 min 50% B, 34.5 min 100% B and 35–38 min 18% B. Anthocyanins and phenolics were quantified by determining the peak area of the absorbance between at 210–600 nm. Results are expressed in mg/L.

Sensory Profiles of Wines

The sensory differences of the application wines were determined according to Jackson (2002). A total of 20 highly experienced panellists (10 males, 10 females, 25–45 years old) tested each wine by blind tasting. Wines stored at 16 °C were served at room temperature. They evaluated each descriptor on a horizontally prepared 10 cm scale to rate aroma and test intensity of each descriptor (0 = descriptor not perceptible, 10 = descriptor strongly perceptible). Wine samples were presented in a completely random order. The results of the panellists were collected after the analysis of variance and presented by transferring to the radar plots.

Data Analyses

Statistical analyses were performed using JMP software (SAS Institute, Cary, NC, USA). The data were presented as arithmetic means of three replications. For each parameter, the LSD (the least significant difference) was used to determine the level of significant differences for all applications. Differences at $p < 0.05$ were considered significant.

Results and Discussion

Effects of Treatments on the Physical and Chemical Characteristics of Grapes

Table 1 shows the effects of six applications on physical and chemical grape parameters at harvest. Thinning is the main factor that significantly reduced the number of clusters per vine and undoubtedly contributed to the reduction in yield and crop load (Kaya 2019). Compared to UNT vines, vine yield decreased because of applications ($p < 0.05$). The application that effected the decrease in yield most was V application (49% decrease) and the least effective application was LR application (0.3% decrease). Despite the decrease in yield, there was an increase in berry weight, skin weight, and cluster weight values ($p < 0.05$). Berry and cluster weight were less effected by the applications: maximum increase in berry weight was 20% with V, while minimum increase was 5% with LR; maximum increase in cluster weight was 16% with V, and 0.1% with LR. On the other hand, the increases in skin weight were impressive: 96% increase was achieved as a result of V application compared to UNT grapes, which is a desirable increase since the skin weight will also determine the amount of anthocyanins that provide colour transition in vinification. pH and °Brix values increased, and total acidity decreased as a result of the applications (Table 1). It may be concluded that grape thinning applications accelerate maturation. Especially in cool ecologies, AV at the end of véraison may be recommended for rapid ripening to prevent the harvest from shifting to rainy seasons. Additionally, the level of °Brix increased as a result of LR application, which often results from increased exposure of vine to sunlight resulting from early leaf removal (Bubola et al. 2019), denser young leaves, better maturation and higher dry matter formation (Poni et al. 2006). While the results of pH, total acidity, °Brix, vine yield, and berry and cluster weights are in the same trend in the present study as reported by Condurso et al. (2016), Gil-Muñoz et al. (2009) detected an upward trend in grape and cluster weights as a result of cluster thinning and concluded that there may be a natural compensatory increase in the rest of the clusters when yield decreases. Nicolosi et al. (2012) showed that leaf removal created a downward trend in skin weight in 'Syrah', 'Frappato', 'Cabernet Sauvignon', and 'Nero d'Avola' grapes, contrary to the present research. Ivanišević et al. (2020) highlighted that skin weight increases as a result of leaf removal.

Effects of Treatments on Chemical Characteristics of Wines

The results of the basic wine composition are given in Table 2. pH, total acidity, and alcohol levels are parallel with pH, total acidity, and Brix levels of grapes. According to UNT control group, the highest pH result was 3.65 in AVLR, the highest total acidity was 8.13 in UNT, and the highest alcohol level was 13.44% in AV ($p < 0.05$). Although there are no significant differences among the concentrations of MLF, malic acid is not particularly preferred in red wines and decreased as a result of the applications compared to UNT wines. The highest total extract value was detected in VLR wines (45.30 g/L) and was detected lowest in UNT wines (33.97 g/L). In the studies where only cluster thinning and only leaf removal were performed, there was an increase in the aforementioned parameters (pH, total acidity, and Brix) compared to the control group. However, there are also some studies which do not report an effect on pH and acidity levels of wines after cluster thinning applications (Bubola et al. 2019). It is concluded in the present research that a higher rate of increase was achieved thanks to the combined applications.

TPC, TA, and AC results are given in Table 2. TPC content in 'Syrah' wines increased by 34, 33, 20, 73, and 74%, respectively, as a result of V, AV, LR, VLR, and AVLR applications compared to the control group UNT ($p < 0.05$). TPC level in the UNT wine, which was 1737 mg GAE/L, showed the highest increase after VLR and AVLR applications, and AVLR resulted in the highest level (3014 mg GAE/L). It can be stated that the combinations of leaf removal and cluster thinning (VLR, AVLR) are the most effective applications. All the performed applications were effective on TPC levels of wines compared to the UNT, but only leaf removal (LR) has a lower effect than others. The increments in TPC levels suggest that the applications had a significant impact on phenolic maturity. The lowest TA content was in UNT wine at 447 mg/L, while the highest was in AVLR at 699 mg/L. The proportional variations of TA levels in wines after V, AV, LR, VLR, and AVLR applications with respect to the control group were 34, 34, 0.9, 52, and 56%, respectively. The amount of TA in LR wines showed no significant increase compared to the control group. Therefore, it was only the leaf removal process which did not alter the TA level. Gil et al. (2013) achieved a 24% increase in TA levels of wines as a result of cluster thinning process performed in the middle of véraison in 'Syrah' grapes compared to the control group, which sup-

Table 2 Chemical parameters of wines at the end of fermentation

Parameters	UNT	V	AV	LR	VLR	AVLR	LSD (0.05)
pH	3.30 d	3.58 b	3.47 c	3.60 b	3.42 c	3.65 a	0.100
Total acidity (mg/mL)[a]	8.13 a	7.20 c	6.90 c	7.67 b	7.03 c	6.87 d	0.389
Alcohol (% v/v)	12.41 c	13.28 ab	13.44 a	13.10 b	13.12 b	13.27 ab	0.306
Total extract (g/L)	33.97 c	42.13 b	43.13 ab	43.47 ab	45.30 a	42.96 b	2.228
Malic acid (mg/mL)	0.06	0.04	0.01	0.05	0.03	0.01	NS
TPC (mg GAE/L)	1737 d	2330 b	2301 b	2080 c	3006 a	3014 a	81.483
TA (mg/L)	447 c	597 b	599 b	451 c	681 a	699 a	31.550
ABTS (μmol trolox/mL)	25.23 c	25.74 b	26.06 b	25.85 b	29.44 a	30.29 a	1.046
DPPH (μmol trolox/mL)	15.82 c	17.39 b	16.03 c	17.87 b	19.41 a	19.48 a	0.654
FRAP (μmol trolox/mL)	6.41 e	8.39 bc	8.15 c	7.34 d	8.74 ab	9.04 a	0.508

Means followed by different letters on the lines indicate significant differences after the treatments ($P<0.05$)

UNT Untreated, *V* Cluster thinning at the véraison, *AV* Cluster thinning after véraison, *LR* Leaf remove, *VLR* Cluster thinning at véraison and leaf remove, *AVLR* Cluster thinning after véraison and leaf remove, *TPC* Total phenolic compound, *TA* Total anthocyanin, *ABTS* Antioxidant capacity with 2,2′-azinobis (3-ethyl-benzothiazoline-6-sulfonic acid) method, *DPPH* Antioxidant capacity with 2,2-diphenyl-1-picrylhydrazyl method, *FRAP* Antioxidant capacity with ferric reducing antioxidant power method, *LSD* least significant difference

[a] In terms of tartaric acid

ports the 57% increase in the present study with AVLR. According to the results, it may be noted that cluster thinning which was performed in combination with LR at the end of véraison is more effective. Some of the previous studies observed an increase in anthocyanins as a result of LR (Hickey et al. 2018), higher anthocyanin accumulation in wines compared with cluster thinning (CT) application (Bubola et al. 2022), or no difference in anthocyanin content even as a result of CT (Mawdsley et al. 2018). However, the most striking result of this study is the remarkable increase in TA content of leaf removal and cluster thinning combinations. It is thought that this is the result of higher alcohol content in the vine compared to LR, due to higher sugar accumulation and the vine is thought to be under more intense stress.

The study aimed to increase both AC and organoleptic parameters of wines. The chemical variety of antioxidants makes them difficult to be distinguished from the matrix of grapes and wine and to determine their quantity. Therefore, a single antioxidant test is insufficient to study multifunctional antioxidants, and multiple methods should be used to provide sufficient information about the antioxidant properties of wines (Lutz et al. 2011). For this purpose, AC analysis was performed with three different methods and the results are given in Table 2. As a stable 2,2-diphenyl-1-picrylhydrazyl radical, DPPH can interact efficiently and quickly with free DPPH radicals of ethanolic extracts and, of course, wine, it is widely used to determine radical cleaning capacity (Mavi et al. 2004). The FRAP method is similar to the ABTS method but preferred over the DPPH method because it gives more reliable results (Danilewicz 2015). ABTS is performed in neutral pH, while FRAP is carried out under acidic conditions (pH 3.6) to ensure the solubility of iron (Büyüktuncel 2013). The ABTS method, on the other hand, is stable in a wide pH range of ABTS radical although it takes longer. It has a radical low redox potential and is highly suitable to evaluate the antioxidant capacity of phenolics due to their relatively lower redox potentials. The results of these methods indicate that significant levels of ABTS, DPPH, and FRAP in VLR and AVLR results in wines ($p < 0.05$). The highest values were found in AVLR wines with ABTS, DPPH, and FRAP ranking at 30.29 µmol trolox/mL, 19.48 µmol trolox/mL, and 9.04 µmol trolox/mL, respectively. Compared to UNT wine, ABTS level increased by 2%, 3%, 2%, 17%, and 20%; DPPH level increased by 10%, 1.3%, 13%, 23%, and 23%; and FRAP levels increased by 31%, 27%, 15%, 36%, and 41%, respectively after V, AV, LR, VLR, and AVLR applications. The highest increase in AVLR result is the increase in FRAP level from 6.41 µmol trolox/mL to 9.04 µmol trolox/mL. It corresponds to an increase of 41%. There are studies that reported increased antioxidant capacity in wines obtained by cluster thinning (Prajitna et al. 2007; Gatti et al. 2011) and leaf removal (Osrečak et al. 2016). The difference of the present study is that a higher rate of increase was achieved by combinations of the two applications at different times.

Effects of Treatments on Colour Parameters of Wines

The colour differences caused by the applications relative to the control wine (UNT) are given in Table 3. Although colour intensity (CI) increased with the effect of all applications, the highest intensities were observed in AVLR (25.9 AU) and VLR (25.6 AU). The main reason is that the total anthocyanin levels in these two applications are higher than the others, and the high ethanol concentration in these applications is thought to support the formation of polymeric pigments that lead to darker wines. Colour hue values are also in the same trend as colour intensity and were measured as ranging from 10.0 to 22.3. All the applications effected the other colour parameters of wines (Lightness values, Chroma values, Green-red component, Blue-yellow component, Saturation value), but the applications that created the highest effects were VLR and AVLR applications. It is much more important for winemakers to know whether the human eye can distinguish the colours of their wine than to have significant differences between these parameters. Therefore, the total colour differences between

Table 3 Colour parameters of wines

Parameters	UNT	V	AV	LR	VLR	AVLR	LSD (0.05)
CI	23.3 c	24.8 b	25.7 a	25.1 b	25.6 a	25.9 a	0.418
L	33.1 d	33.7 cd	36.4 c	33.5 cd	35.2 b	37.8 a	0.529
C	57.4 d	59.2 c	59.7 c	58.0 d	60.3 b	64.8 a	0.780
H	10.0 d	12.0 c	15.1 bc	16.0 bc	19.1 ab	22.3 a	0.103
a	60.2 e	70.2 c	72.3 c	65.9 d	82.8 b	86.9 a	2.023
b	22.1 e	29.2 d	34.3 c	34.0 c	40.2 b	43.5 a	1.290
SAT	3.32 f	4.21	4.55 d	4.49 c	5.01 b	5.27 a	0.087
ΔEab^*	Control	30.4 b	38.7 b	3.7 c	40.2 a	43.3 a	0.675

Means followed by different letters on the lines indicate significant differences after the treatments ($P < 0.05$)
CI Colour intensity of wines, *L* Lightness values, *C* Chroma values, *H* Hue values, *a* Green-red component, *b* Blue-yellow component, *SAT* Saturation value (expressed as the chroma to lightness ratio), ΔEab^* Total colour differences, *LSD* least significant difference

wines (ΔEab^*) were calculated to confirm whether the differences are large enough to be distinguished by the human eye. When $\Delta Eab^* \geq 1$, the human eye can usually distinguish two different colours (Pérez-Magariño and González-Sanjose 2003). However, it has been recognized that wine tasters are able to distinguish the colour differences of wine in glass when $\Delta Eab^* \geq 5$. Indeed, differences also depend on CI which the human eye can distinguish since the capacity to distinguish decreases when colour perception reaches saturation. Nevertheless, ΔEAb values were found to be ≥ 5 in all the applications except for LR compared to UNT wines. ΔEab value of LR wines was calculated as 3.7. It was calculated as ≥ 43.3 in the wine obtained as a result of AVLR application, where the CI value was the highest. The increase in b (Blue-yellow component) parameter after AVLR application is striking due to the dark colours of the wines. The results suggest that AVLR application is effective on the colour parameters of wines, which can also be distinguished by the naked eye.

Effects of Treatments on Individual Phenolic and Anthocyanin Contents of Wines

The phenolic compound and anthocyanin levels of wines which were obtained from the grapes under the influence of the applications are given in Table 4. The wines with the highest levels of both phenolics and anthocyanins were VLR and AVLR wines. *Trans*-resveratrol, which has proven health benefits (Haunschild and Marx 2022), had increased at rates of 7.5%, 9.2%, 14.2%, 18.4%, and 19.6, respectively, in V, AVLR, LR, VLR, and AVLR wines compared to UNT ($p < 0.05$). Individual phenolic compound content increased after V and AV applications with cluster thinning only and VLR and AVLR applications combined with leaf removal all of which were conducted at the end of véraison. The least effective application on the amount of *trans*-resveratrol was V, which generated an increase of 7.5%. Nevertheless, the increase at this rate is also an undeniable rise. *Cis*-isomer is produced by UV irradiation of *trans*-isomer (Moreno et al. 2008). Very little is detectable in grapes (Careri et al. 2004), but both isomers are found in varying amounts in wines (Tahmaz and Söylemezoğlu 2017). Although there is no agreement on this subject, it is thought that *cis*-resveratrol is derived from *trans*-isomer during vinification (Jeandet et al. 1995). *Cis*-resveratrol is stated to have less health benefits compared to *trans*-resveratrol, including its anti-inflammatory power (Orallo 2005). In a study which describes its physiological activity, *cis*-resveratrol has been shown to have potential anticancer and antiplatelet activity, as *trans*-isomers, by inhibiting kinase activity which is a cancer-related factor (Bertelli et al. 1996; Morris et al. 2015). While the amount of *cis*-resveratrol was found to be 0.23 mg/L in UNT, the highest amounts were found at 0.29 mg/L and 0.32 mg/L in VLR and AVLR, respectively. The amount of *cis*-resveratrol at 0.28 mg/L in LR was only higher than those of V and AV because sun exposure is more intense in panicle area where leaf removal is applied.

Similarly to previous studies, catechin is found to be the one with the highest amount in wines among the phenolic compounds (Saucier and Waterhouse 1999). Catechin affects molecular mechanisms related to angiogenesis, extracellular matrix disruption, regulation of cell death, and multiple drug resistance in cancer and related disorders (Zanwar et al. 2014), and it is one of the most important phenolics in wines due to its antioxidant effect. The highest increase was measured as 41% in VLR and AVLR applications compared to UNT. There was a 3.5% increase in V and 4.7% in AV as a result of inflorescence alone, while 23.1% of catechin increase was observed as a result of LR. Along with catechins, epicatechins are associated with certain properties of wine, such as bitterness, body, and astringency (Pas-

Table 4 Phenolics and anthocyanins of wines

Parameters (mg/L)	UNT	V	AV	LR	VLR	AVLR	LSD (0.05)
Trans-resveratrol	4.24 d	4.56 c	4.63 c	4.84 b	5.02 a	5.07 a	0.090
Cis-resveratrol	0.23 c	0.23 c	0.21 c	0.28 b	0.29 ab	0.32 a	0.032
Catechin	57.13 d	59.11 c	59.81 c	70.33 b	80.66 a	80.97 a	0.540
Epicatechin	31.10 e	33.95 d	34.75 c	36.24 b	38.67 a	38.96 a	0.704
Rutin	12.38 c	13.04 b	13.04 b	14.10 b	14.73 a	15.03 a	0.343
Quercetin	6.83 c	7.49 b	7.50 b	7.70 b	8.15 a	8.23 a	0.315
Delphinidin-3-glucoside	69.30 c	74.06 a	70.61 bc	73.43 ab	74.66 a	74.90 a	3.097
Cyanidin-3-glucoside	46.75 d	49.84 abc	49.29 c	49.37 bc	50.85 a	50.78 ab	1.431
Petunidin-3-glucoside	9.16 c	10.23 b	9.43 bc	9.85 bc	11.57 a	9.61 bc	0.797
Peonidin-3-glucoside	17.31 c	18.18 b	18.01 bc	18.24 b	20.16 a	20.48 a	0.809
Malvidin-3-glucoside	722.67 c	761.67 b	771.67 b	765.33 b	790.00 a	793.33 a	12.723

Means followed by different letters on the lines indicate significant differences after the treatments ($P < 0.05$)

UNT Untreated, *V* Cluster thinning at the véraison, *AV* Cluster thinning after véraison, *LR* Leaf removal, *VLR* Cluster thinning at véraison and leaf remove, *AVLR* Cluster thinning after véraison and leaf removal, *LSD* least significant difference cual et al. 2016). Among other phenolics, epicatechin also increased as a result of the applications, and the highest increase was observed as from 31.10 mg/L to 38.96 mg/L in UNT and AVLR.

As other phenolic compounds known to have health benefits (Pace-Asciak et al. 1995; Iriti et al. 2017; Patel and Patel 2019), the quantities of rutin and quercetin also increased with the applications compared to UNT. The quantities of both compounds increased at a similar rate in V and AV (rutin V: 5.3%, quercetin V: 9.7%; rutin AV: 5.3%, quercetin AV: 9.8%), and the highest amounts were observed in AVLR (rutin: 15.03 mg/L, quercetin: 8.23 mg/L) and VLR (rutin: 14.73 mg/L, quercetin: 8.15 mg/L). Higher amounts of rutin and quercetin were determined in LR compared to the cluster thinning performed without leaf removal.

In addition to having antioxidant activity, anthocyanins (Kharadze et al. 2018) are among the most important compounds responsible for the colour of wine. As noted in previous studies, 84% of the total anthocyanins in the present study is malvidin-3-glucoside (Torres et al. 2021). Its level of 722.67 mg/L in UNT increased to 761.67, 771.67, 765.33, 790, and 793.33 mg/L in V, AVLR, LR, VLR, and AVLR, respectively ($p < 0.05$). Increases have been observed in malvidin-3-glucoside, the main colour compound of wine, as well as other anthocyanin compounds. However, there are also studies in literature where the level of anthocyanin with canopy management is not affected (Torres et al. 2021) or increased (Yu et al. 2021). In the present study, delphinidin-3-glucoside, cyanidin-3-glucoside, and petunidin-3-glucoside levels were the highest in VLR, while peonidin-3-glucoside and malvidin-3-glucoside levels were the highest in VLR and AVLR, which are combinations of leaf removal and cluster thinning.

Vineyard applications certainly affect the quality of wines (Tardáguila et al. 2010; Reynolds 2022). In the study, that the increase in phenolics and anthocyanins in VLR and AVLR was at a higher rate than in other applications is likely to be attributed to the increased exposure of clusters to sunlight as a result of LR and the concentration of phenolic compounds in fewer products as a result of cluster thinning. In general, although VLR and AVLR yielded phenolic and anthocyanin results close to each other, they were found at higher levels in AVLR wines. This means that LR combination grape thinning at the end of véraison is the most effective application on these compounds. At the end of the véraison, the temperature also increases as the clusters are exposed to more sun as a result of LR, and phenolic concentrations also increase (Poni et al. 2006). Phenolic concentrations increased as product levels decreased by cluster thinning. The result is not expected, similar to the studies in which the composition of ‘Syrah’ wines are developed only by cluster thinning (Gil-Muñoz et al. 2009; Gil et al. 2013; Cañón et al. 2014; Wang et al. 2022) or in which the improvement in composition is achieved by leaf removal in other wine varieties (Guidoni et al. 2008; Gatti et al. 2012; Vander Weide et al. 2021; Artem et al. 2022), but the consistency of trends is quite remarkable. The important difference of this study compared to the others is that AVLR application at the end of véraison (cluster thinning at the end of véraison + leaf removal before flowering) created significantly more important effects on wine quality compared to only LR or only V and AV.

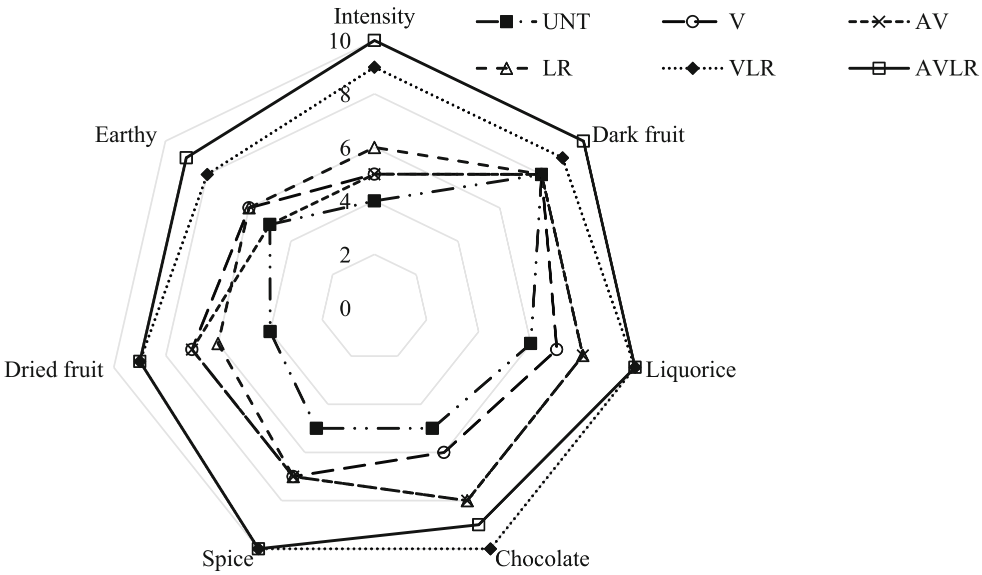

Fig. 1 Flavour sensory profile of ‘Syrah’ in control and treatment wines. (Radar plots of attributes found different at $p < 0.05$ in the wines of UNT and treatments ‘Syrah’ wines. *UNT* Untreated, *V* Cluster thinning at véraison, *AV* Cluster thinning after véraison, *LR* Leaf removal, *VLR* Cluster thinning at véraison and leaf removal, *AVLR* Cluster thinning after véraison and leaf removal)

Effects of Treatments on Flavour and Mouthfeel Sensory Profiles of Wines

Tasting scores of 'Syrah' wines after V, AV, LR, VLR, and AVLR applications were transferred to radar plots, and their flavour and mouthfeel sensory profiles are given in Figs. 1 and 2, respectively. Flavour sensory profile parameters in Fig. 1 are intensity, dark fruit, liquorice, chocolate, spice, dried fruit, and earthy flavours. Based on tasting results, the wines with AVLR treatment scored 10 points for four of seven flavour criteria (intensity, dark fruit, liquorice, and spice) and 9 points for three of them (chocolate, dried fruit, and earthy). Consequently, AVLR has become the application with the highest score. VLR is the second highest rated application and received a score of 10 from liquorice, chocolate, and spice criteria; 9 from intensity, dark fruit, and dried fruit criteria; and 8 from earthy criteria. LR scored higher on intensity, liquorice, chocolate, and dried fruit criteria compared to V. When AV and LR are compared, LR stands out in intensity and earthy while AV stands out in dried fruit criteria. UNT wines are rated equal to V, AV, and LR wines only in dark fruit criterion. In conclusion, dark fruit flavour criterion differed only as a result of VLR and AVLR combinations.

Figure 2 shows the effects of the applications on mouthfeel sensory profiles of the wines. Regarding the evaluation results, the highlights are VLR and AVLR wines. The parameters of body, harmony, and peppery are given exactly the same scores to both wines by tasters. In addition, these wines received 9 points for bitterness and astringency aftertaste criteria and 8 for astringency criterion. The biggest difference between the two applications is acidity as VLR was felt to be more acidic on the palate compared to AVLR. The wines of the applications have higher tasting grades compared to UNT wines. Condurso et al. (2016) detected that cluster thinning has a positive effect on aroma compounds and that the wine which is made with diluted grapes tend to be rich in various flavours and possibly organic precursors that form fermentation aromas, while Tardáguila et al. (2008) stated that early leaf removal is more effective in changing the final wine composition and quality than late foliar removal. As a result of the panellists' scoring, the wines for which leaf removal and cluster thinning were carried out seem to stand out. The chemical composition of a wine is also reflected in its organoleptic assessment. An important result is that VLR and AVLR wines with the highest colour and chemical composition in the present study also stand out in their tasting profiles. Consumers have recently turned to healthy and tasty foods, and it is an important criterion that the sensory profiles of wine have the desired qualities. Rotundone is one of the most important aroma compounds that give 'Syrah' wines their characteristics. As an oxygenated sesquiterpene, it is the powerful aroma compound responsible for the "peppery" aroma in grapes and wine. Rotundone is quite unusual as it originates directly from grapes, has a low sensory threshold, and is relatively stable in wine (Herderich et al. 2012). VLR and AVLR are the wines in which rotundone was perceived as the highest in tasting results. It was concluded that pre-bloom defoliation and cluster thinning both at the beginning and the end of véraison strengthen the phenolic and organoleptic characteristics of the grapes.

Conclusion

The present study shows that different canopy applications have different effects on 'Syrah' wine quality. The two most

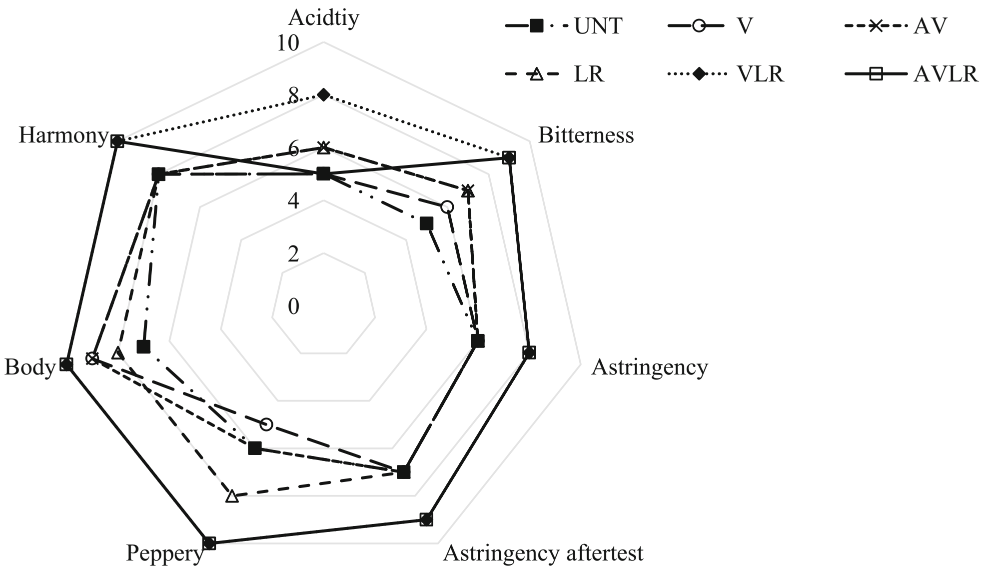

Fig. 2 Mouthfeel sensory profile of 'Syrah' in control and treatment wines. (Radar plots of attributes found different at $p < 0.05$ in the wines of UNT and treatments 'Syrah' wines. *UNT* Untreated, *V* Cluster thinning at véraison, *AV* Cluster thinning after véraison, *LR* Leaf removal, *VLR* Cluster thinning at véraison and leaf removal, *AVLR* Cluster thinning after véraison and leaf removal)

effective applications at TPC, TA, DPPH, and ABTS levels have been VLR and AVLR. Although both applications are effective in statistical terms, the increases that resulted from AVLR application are somewhat higher. Similarly, the parallel results were achieved in colour parameters and tasting results. Canopy managements of VLR and AVLR are also prominent in terms of the increases in individual phenolic compound and anthocyanin compounds. The best possible grape composition for a desired wine style can be achieved in the vineyard by promoting the optimal balance between vegetative growth and yield, which largely depends on the variety, region, season, and management. The results in the present study have highlighted pre-flowering leaf removal together with cluster thinning applications at the beginning and end of véraison carried out in 'Syrah' grape variety. While these findings demonstrate the significance of canopy management practices on the chemical and sensory properties of red wine, they also show that it is possible to obtain wine that contains more phenolic compounds which are beneficial to human health.

Conflict of interest H. Tahmaz declares that she has no competing interests.

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