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Effect of Vine Age, Dry Farming and Supplemental Irrigation on Color and Phenolic Extraction of cv. Zinfandel Wines from California

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Abstract: A dry-farmed vineyard block with vines of varying ages including young vines (5 to 12 years old), control vines (2:1 ratio of old to young vines), and old vines (40 to 60 years old) was either submitted to irrigation or dry-farmed. The experimental design yielded six treatments, namely, Irrigated Control, Irrigated Young, Irrigated Old, Dry-farmed Control, Dry-farmed Young, and Dry-farmed Old. Irrigated Young wines were lower in alcohol, anthocyanins, and tannins, as well as higher in pH and hue angle values (H*), than the remaining treatments. Dry-farmed Young wines were higher in anthocyanins and small polymeric pigments, and showed higher color saturation and red hue. However, the magnitude of these differences was small. At pressing, the anthocyanin composition of these Zinfandel wines was largely dominated by malvidin-3-glucoside (60 to 65%), but after 15 months of bottle aging their anthocyanin profile shifted to 60% of anthocyanin derivatives, with small polymeric pigments accounting for more than 70% of the total polymeric pigment content of the wines. Irrigated Old wines and Dry-farmed Old wines did not differ to any significant extent in their basic chemistry, phenolic chemistry (including detailed anthocyanin composition), and chromatic composition.

Keywords: old vine; irrigation; dry farming; vine age; Zinfandel; phenolic composition; wine color

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1. Introduction

The grape cultivar (cv.) Zinfandel (syn. Primitivo) is currently the fourth most planted varietal in California, but between 1975 and 1998, it was the most planted winegrape in the state [1]. With 15,600 hectares in California today, it is just behind in planted acreage to Cabernet Sauvignon, Chardonnay and Pinot noir [2]. Zinfandel grapes and wines epitomize the patrimony of California viticulture, having been introduced to the state during the Gold Rush, with Zinfandel plantings recorded in the Sierra Foothills as early as 1854 [1]. Because some of these heritage vineyards still subsist today, Old vine Zinfandel is highly well-regarded by producers and consumers alike, almost representing a soft brand in itself. Zinfandel is effectively a Mediterranean variety whose genetic origin can be traced to the Dalmatian Coast of Croatia [3]. Because of this, Zinfandel can be typically dry farmed (i.e., farmed without supplementary irrigation applied during the growing season), under the predominant Mediterranean conditions of the Central Coast of California.

The effect of vine age on wine chemical and sensory composition has been previously assessed. A study looking at the effect of vine age (4 to 45 years old) on Chenin blanc from South Africa reported that although sensory judges agreed on the sensory descriptors associated with the concept of a typical old vine Chenin blanc character ("complex", "balance", "rich", and "mouthfeel"), no correlation was found between the vine age and the preferred occurrence of these sensory features [4]. Further, the use of the term "old vine" on back labels of Chenin blanc was found to positively contribute to the wine price [5]. Another study reported the effect of vine age, ranging from 4 to 168 years old, on Shiraz grapes from the Barossa valley in Australia. Results showed that older vines produced higher yields than young vines, but no wine or winemaking data were reported [6].

However, the first scientific studies looking at the effect of vine age on California Zinfandel's agronomical and winemaking performance have just only been recently published [7,8]. In them, Young vines (5 to 12 years old), Control (representative proportion of young to old vines in the block), and Old vines (40 to 60 years old) were compared for their agronomic and winemaking performances. Over two consecutive seasons, it was found that sugar accumulation during berry ripening occurred faster in Young vines, leading to an earlier harvest date relative to old vines [8]. In addition, yields were higher in Old vines (up to 104.83%) relative to Young vines. After winemaking, it was concluded that wines from Old vines were characterized by a wider array and intensity of a more complex set of aromas relative to Young vine wines [7].

The reported effects of dry farming on grape and wine composition are somewhat inconclusive and tenuous at times, most likely due to the confounding effect of various combinations of climate, soil, variety/cultivar (cv.), and rootstock. For example, a study on cv. Bobal grown in deep clay loam soils reported that supplemental irrigation to a dry-farmed vineyard resulted in wines with a lower concentration of anthocyanins, total phenolics and a different wine color, which was related to a larger berry size in irrigated vines [9]. Conversely, cv. Tempranillo grapes grown in the same soils and enhanced with supplemental irrigation produced wines with comparable anthocyanin and phenolic contents and color than dry-farmed wines [10], a difference attributable to the varietal.

The detailed phenolic composition of Zinfandel wines also remains relatively unexplored, especially with regard to vine age. Zinfandel is typically dry farmed in the Central Coast of California [7], and thus the effect of supplemental irrigation on its phenolic composition is currently unknown. Phenolic compounds, including anthocyanins, tannins and their reaction products formed during winemaking (e.g., polymeric pigments), are key determinants of wine sensory features [11]. Overall, anthocyanins are lower in Zinfandel wines relative to other varietals such as Merlot and Cabernet Sauvignon [12], but its tannin concentration is comparable with Cabernet Sauvignon and reportedly higher than Merlot, Syrah and Pinot noir [13]. An early study on Zinfandel anthocyanins reported both a lower concentration and a faster rate of degradation of acylated anthocyanins relative to Cabernet Sauvignon wines [14]. However, levels of polymeric pigments were up to three times higher in Zinfandel than in Pinot noir wines from the Central Coast of California [15], suggesting that this varietal does have a certain aging potential. With regard to winemaking techniques, the use of enzymatic preparations to enhance phenolic extraction in Crljenak kaštelanski (syn. Zinfandel, Primitivo, Tribidrag) did not result in enhanced phenolic extraction, and additionally, catechin, epicatechin and gallic acid derivatives were major determinants of the wines' antioxidant capacity [16]. Extended maceration for a 6-month period applied to Zinfandel wines uncovered anthocyanin losses of 64% relative to a control wine without extended maceration, which was primarily attributed to pigment degradation during prolonged contact time with Zinfandel fermentation solids [15].

Climate change may reportedly impose increasingly warm and dry conditions on vineyards [17]. This effect may be compounded in Mediterranean regions such as the Central Coast of California, where appropriate recharging of the soil water holding capacity may not be achieved due to insufficient winter rainfall [18]. Thus, the irrigation of traditionally dry-farmed vineyards has been proposed as an option to sustain yields and quality [17]. However, the effect of supplemental irrigation in a traditionally dry-farmed varietal such as Zinfandel in California remains unreported. Thus, the objective of the present study was to document the effect of supplemental irrigation on a traditionally dry-farmed vineyard, with emphasis on the chemical and detailed phenolic and chromatic composition of the resulting wines. The effect of vine age was also considered, and thus wines were produced from Young and Old vines under dry-farmed and irrigated conditions, together with a Control treatment.

2. Materials and Methods

2.1. Viticulture Experiment

Details related to the growing season and the full experimental design in the vineyard are published elsewhere [19]. Briefly, cv. Zinfandel grapes from a dry-farmed vineyard with interplanted vines of varying ages, located in the Templeton Gap District of the Paso Robles AVA (American Viticultural Area) of California's Central Coast, were evaluated during the 2021 growing season. Treatments included Young vines (5 to 12 years old), Control vines (2:1 ratio of old to young vines representative of the vineyard), and Old vines (40 to 60 years old). For each vine age treatment (i.e., Control, Young, and Old vines), two irrigation modalities were applied: dry farming (i.e., no irrigation during the growing season) and supplemental irrigation (Figure S1). Supplemental irrigation was manually and equally applied to the irrigated treatment vines at véraison and véraison + 4 weeks and was calculated on the basis of age-specific ETc and to replenish 95% of crop evapotranspiration (ETc) [19]. The following 6 treatments were established in triplicate (n = 3), namely Irrigated Control, Irrigated Young, Irrigated Old, Dry-farmed Control, Dry-farmed Young, and Dry-farmed Old. These vineyard triplicates directly translated into winemaking triplicates. Due to the differences in maturity progression and sugar accumulation within vine age and irrigation treatments [19], fruit from each treatment had varying harvest dates to meet the Brix target, which was established at 23 $\pm$ 0.5 Brix in all cases. Therefore, harvest occurred on 13 September for Irrigated Young, on 24 September for Irrigated Control and Dry-farmed Young, on 28 September for Dry-farmed Control, and on 7 October for Irrigated Old and Dry-farmed Old.

2.2. Winemaking

As stated, each treatment had differing phenological progression throughout the season. Therefore, treatments were harvested based on different harvest dates to target soluble solids (Brix) of 23 $\pm$ 0.5, indicated by a composite sample of sample vines from each respective treatment. The total yield from all irrigated vines was 297.4 kg, which included 67.7 kg from Irrigated Young vines, 117.2 kg from Irrigated Old vines, and 112.5 kg from Irrigated Control vines; in comparison, there was 245.5 kg of total yield from Dry-farmed treatments, which included 69.1 kg from Dry-farmed Young vines, 75.9 kg from Dry-farmed Old vines, and 100.5 kg from Dry-farmed Control vines. Each treatment was crushed and destemmed using a crusher/de-stemmer (Bucher Vaslin, Niderweningen, Switzerland) separately and fermented individually in triplicate for each treatment (n = 3), using 30 L food-grade fermenters. After crushing and destemming, 50 ppm SO_2 were added, and musts were inoculated with a commercial yeast strain (*Saccharomyces cerevisiae*, strain EC-118, Lallemand, Montreal, QC, Canada) at a rate of 30 g/hL. Diammonium phosphate (DAP) at a rate of 200 mg/L (Fermaid K, Scott Laboratories, Petaluma, CA, USA) was added on day two of alcoholic fermentation to all fermenters. After 48 h post-crushing and destemming, commercial malolactic bacteria (*Oenococcus oeni*; MLB VP-41, Lallemand, Montreal, QC, Canada) was added. Cap management consisted of three punch downs for the first three days of post-crushing/destemming: the first at 8 am, the second at 1 pm, and the third at 6 pm, with each punch down lasting exactly 1 min and 30 s at a gentle pace. After the first three days, only two punch downs a day were made, at approximately 8 am and 5 pm, for 1 min each. Total soluble solids (°Brix), and daily temperature were monitored via a densitometer (Anton Paar DMA 35 Basic, Graz, Austria) during the 12-day maceration period, after which the fermentation solids of the wines were drained off. Only free-run wines were considered for this study. Malolactic fermentation was monitored via the enzymatic analysis of malic acid and lactic acid (Admeo Y15, Angwin, CA, USA), using commercial enzymatic analysis kits (Biosystems, Barcelona, Spain). Cold stabilization occurred at 10 °C for 40 days, after which all wines were racked and adjusted to

30 mg/L SO_2. Wines were readjusted to 30 mg/L SO_2, and bottled on 20 April 2022. DIAM 5 (44 × 23.5 mm) micro-agglomerated cork closures (G3 Enterprises, Modesto, CA, USA) were used and the wines were stored at a controlled temperature (~14 °C), until analysis.

2.3. Wine Basic Analysis

Analysis of the basic chemistry of the wines and their replicates was performed at bottling, including the pH (Thermoscientific Orion Star A211 Benchtop pH meter, Waltham, MA, USA), titratable acidity (TA) by automatic titration, end-point at pH 8.2 (Hanna HI901W-TA Wine Titrator, Woonsocket, RI, USA), and ethanol content using an alcoholyzer (Anton Paar Alcolyzer Wine M/ME Wine Analysis Meter, Graz, Austria). Acetic acid, glucose/fructose, lactic acid, and malic acid were analyzed using an Admeo Y15 analyzer (Admeo, Angwin, CA, USA) and enzymatic analysis kits (Biosystems, Barcelona, Spain).

2.4. Wine Spectrophotometric Analysis

Spectrophotometric measurements consisted of analysis of phenolic compounds and chromatic parameters (CIELab tristimulus colorimetry), carried out throughout the winemaking process and up to 15 months of bottle aging. Sampling points were as follows: day 14 (pressing); post-malolactic fermentation (post-MLF); bottling; and 9 and 15 months of bottle aging. Anthocyanins and total polymeric pigments (TPP) (hereafter defined as the sum of small polymeric pigments (SPP) and large polymeric pigments (LPP)) were measured as previously reported [20]. Tannins were analyzed using protein precipitation [21]. CIELab coordinates including L* (lightness), H* (hue angle), a* (green/red component) and b* (blue/yellow component) were calculated using the Cary WinUV color software (version 6.0, Startek Technology, Boronia, VIC, Australia) under a D65 illuminant [22]. Spectrophotometric measurements were made with an 18-sample cell auto-sampler Cary 60 UV-Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA), and recorded in a 1 mm path-length quartz cuvette.

2.5. Anthocyanin Analysis using an HPLC-Diode Array Detector (DAD)–Mass Spectrometry (MS)

Monomeric anthocyanins and flavanols were quantified using HPLC-DAD, with peak identity confirmed by MS at bottling, and after 9 and 15 months of bottle aging. The wines were analyzed with an Agilent 1100 series HPLC-DAD system (Agilent Technologies, Santa Clara, CA, USA), as described [23], with minor modifications. Separation of anthocyanins occurred in a Zorbax SB-C18 column (4.6 mm × 150 mm, 3.5 µm particle size) thermostated at 40 °C and protected by a guard column of the same packing material. Peak identity was confirmed with a Waters Acquity I-Class ultra-performance LC system connected to an AB Sciex 4000 Q-Trap MS/MS (Waters, Milford, MA, USA). The column eluent, under the same modified conditions described above, was directed to the MS operating in positive ionization mode, and compounds were detected by multiple reaction monitoring, as reported [15]. Monomeric anthocyanins were quantified by DAD using malvidin-3-glucoside chloride as the standard (Extrasynthèse, Lyon, France) and a calibration curve (R^2 = 0.99).

2.6. Statistical Analysis

All the treatments and their respective wines were produced in triplicate fermentations (n = 3). The basic chemical, phenolic, color and sensory composition of the wines was analyzed using a one-way ANOVA. In all cases, Fisher's LSD test was used as a post hoc comparison of means with a 5% level for rejection of the null hypothesis. Data were analyzed with XLSTAT (Addinsoft, Paris, France), and all graphical representations were prepared with GraphPad Prism software version 10.0 (GraphPad Soft-ware, San Diego, CA, USA).

3. Results and Discussion

In the present study, grapes harvested from Zinfandel vines differing in age (Old, Young, and a Control), and either dry-farmed or supplemented with irrigation were made into wine and the wines followed during winemaking and up to 15 months of bottle aging. A factorial combination of vine age and irrigation treatment yielded the following treatments: Irrigated Control; Irrigated Young; Irrigated Old; Dry-farmed Control; Dry-farmed Young; and Dry-farmed Old. Results pertaining to vine performance, phenology, and fruit chemistry have been reported elsewhere [19].

3.1. Alcoholic Fermentation and Sugar Consumption

Figure 1 shows the evolution of sugar consumption during alcoholic fermentation (measured as Brix depletion, Figure 1A) and temperature (Figure 1B). At the time of pressing, all treatments except for one were considered dry from a winemaking perspective, showing negative Brix values. The only exception was the Irrigated Young wines, which fermented considerably slower and with more variation than the other treatments. This occurred even though Irrigated Young wines fermented at a slightly warmer temperature than the remaining treatments (Figure 1B). However, in the present experiment, fermentation temperatures were relatively colder, and ranged from 16 °C to 21 °C, which is below the 24 °C to 27 °C range of fermentation temperatures normally applied during red wine making [24]. The lower alcoholic fermentation rate in the Irrigated Young wines cannot be explained by differences in Brix at harvest, nor in yeast assimilable nitrogen (YAN), as wines from Young vines generally displayed higher YAN values than Control and Old vine wines [19]. Upon close inspection into the replicates of the Irrigated Young wines, it was observed that two fermenters stalled at around 10 Brix between days 9 and 11. However, the cause of the sluggish fermentation remains unknown.

3.2. Basic Chemistry of the Wines

The basic chemical composition of the wines, separated as a function of irrigation and vine age via a two-way ANOVA, is shown in Table 1. Ethanol levels ranged from 14.2% in Irrigated Young wines to 17.8% ABV in Dry-farmed Old wines, being generally higher in the wines made from dry-farmed grapes. These ethanol levels do not coincide with the reported target Brix of 23 $\pm$ 0.5 Brix set for this experiment. This discrepancy between the target Brix at harvest and final ethanol levels in the finished wines is a common feature of Zinfandel winemaking in California. Zinfandel is well known to produce raisined berries even at relatively low levels of sugar maturity. The proportion of raisins in Zinfandel can account for as much as 9.6% of the total berry size distribution [25]. These raisins do not immediately release their sugar content into the must but rather do so slowly. Thus, during sampling prior to harvest, only the non-raisined berries release their contents, as raisins require soaking in aqueous solution to release their content [7]. Although the proportion of raisins was not measured in the present study, the slow release of sugars from raisins during alcoholic fermentation is consistent with the observed ethanol levels, which were not directly predicted by initial sampling of the berries at harvest. Again, this was likely due to the inability of raisins to quickly release their sugar content. Practically speaking, winemakers seeking to achieve an accurate read of sugar levels at harvest are suggested to soak crushed Zinfandel berries for at least 48 to 72 h before proceeding to take a reading of sugar content of the must.

Wine pH was generally higher in the wines from Young relative to Old vines, and accordingly, titratable acidity was slightly lower in Young wines. On the other hand, Dry-farmed Control wines showed residual levels of malic acid, indicating these wines failed to complete malolactic fermentation (MLF). This could be due to a combination of low pH and exceedingly high ethanol levels, though other treatments showed similar chemical features and did, nonetheless, complete MLF. Volatile acidity was higher in Irrigated Young wines, also reflecting the slower rate of alcoholic fermentation (Figure 1B).

Table 1. One-way analysis of variance (ANOVA) of the basic chemical composition of Zinfandel wines produced from vines of different ages and submitted to irrigation or dry farming (non-irrigated). Averages followed by the standard error of the mean (SEM) (n = 3).

Irrigation	Vine Age	Ethanol (% *v*/*v*)	pH	Titratable Acidity (g/L Tartaric Acid)	Glucose + Fructose (g/L)	Malic Acid h(g/L)	Lactic Acid (g/L)	Acetic Acid (g/L)
Irrigated	Control	16.1 ± 0.44 ab	3.36 ± 0.09 b	8.05 ± 0.53 a	0.50 ± 0.09 a	0.09 ± 0.01 b	1.21 ± 0.12 bc	0.24 ± 0.03 c
	Young	14.2 ± 1.14 b	3.79 ± 0.12 a	6.78 ± 0.23 c	0.81 ± 0.31 a	0.09 ± 0.03 b	1.81 ± 0.17 a	0.75 ± 0.08 a
	Old	16.7 ± 0.86 a	3.36 ± 0.11 b	7.42 ± 0.01 abc	2.96 ± 1.49 a	0.12 ± 0.01 b	1.07 ± 0.11 c	0.44 ± 0.09 bc
Dry-farmed	Control	16.7 ± 0.73 a	3.57 ± 0.11 ab	7.77 ± 0.18 ab	2.64 ± 2.12 a	1.75 ± 0.15 a	0.07 ± 0.02 d	0.41 ± 0.13 bc
	Young	17.1 ± 0.43 a	3.64 ± 0.06 ab	7.05 ± 0.05 bc	3.46 ± 2.82 a	0.11 ± 0.01 b	1.52 ± 0.11 ab	0.37 ± 0.09 bc
	Old	17.8 ± 0.38 a	3.43 ± 0.05 b	7.51 ± 0.12 abc	3.03 ± 0.83 a	0.13 ± 0.02 b	0.94 ± 0.07 c	0.59 ± 0.06 ab
p-value		0.0663	0.0340	0.0393	0.6939	<0.0001	<0.0001	0.0235

Different letters within a column indicate significant differences for Fisher's LSD test and $\alpha < 0.05$.

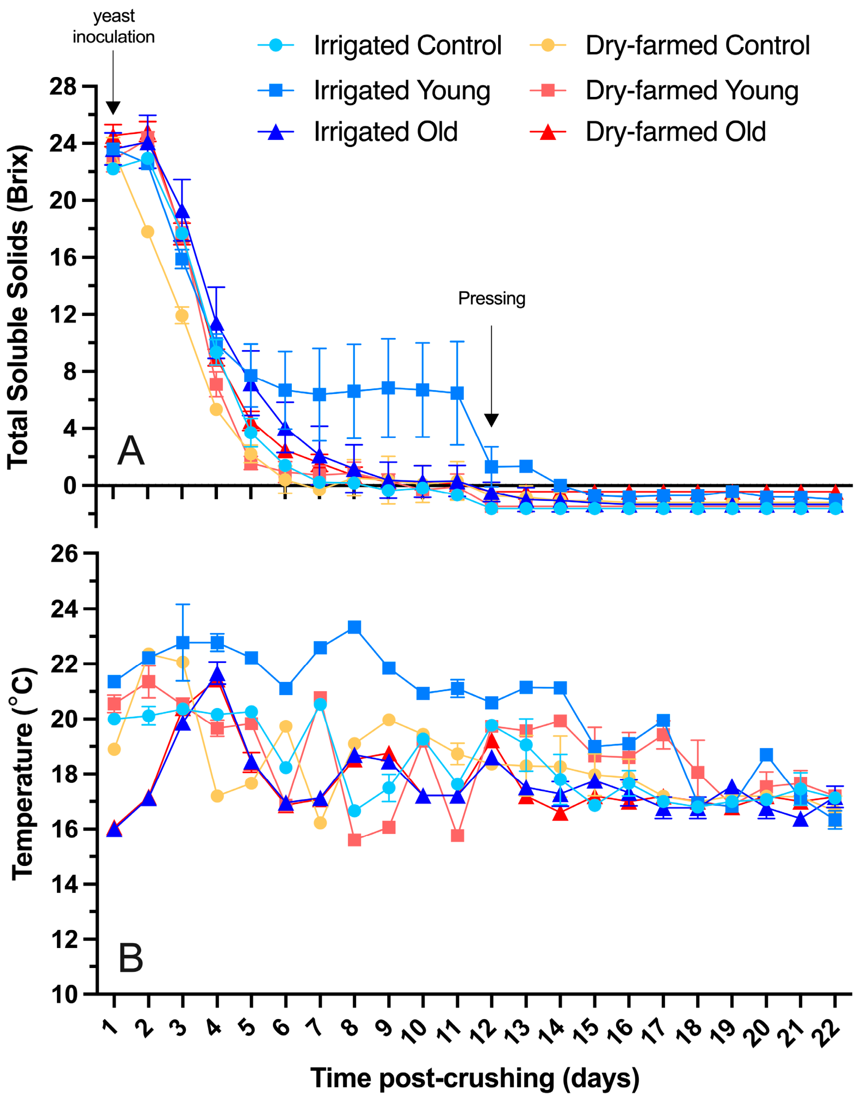

Figure 1. Evolution of (**A**) sugar consumption (Brix), and (**B**) temperature and during alcoholic fermentation of Zinfandel wines produced from vines of different age and submitted to irrigation or dry farming (non-irrigated). Each data point represents the average of three tank replicates (n = 3) and error bars indicate the standard error of the mean. If not shown, error bars are obscured by treatment symbols.

3.3. Phenolic Composition of the Wines

The wines of the different treatments were followed throughout winemaking and up to 15 months of bottle aging to assess the impact of both irrigation and vine age on key phenolic classes. Anthocyanins decreased post-pressing, with comparable rates within treatments (Figure 2A). After 15 months of bottle aging, anthocyanins were higher in Dry-farmed Young wines, but only relative to Irrigated Control and Irrigated Old wines, and Dry-farmed Control wines. Thus, from the perspective of the final anthocyanin content, irrigation of Young vines generally resulted in slightly lower anthocyanins. However, these differences were minor in magnitude and, conversely, during the establishment of a projected dry-farmed vineyard, the irrigation of young vines may be beneficial for root development and proper rootstock establishment.

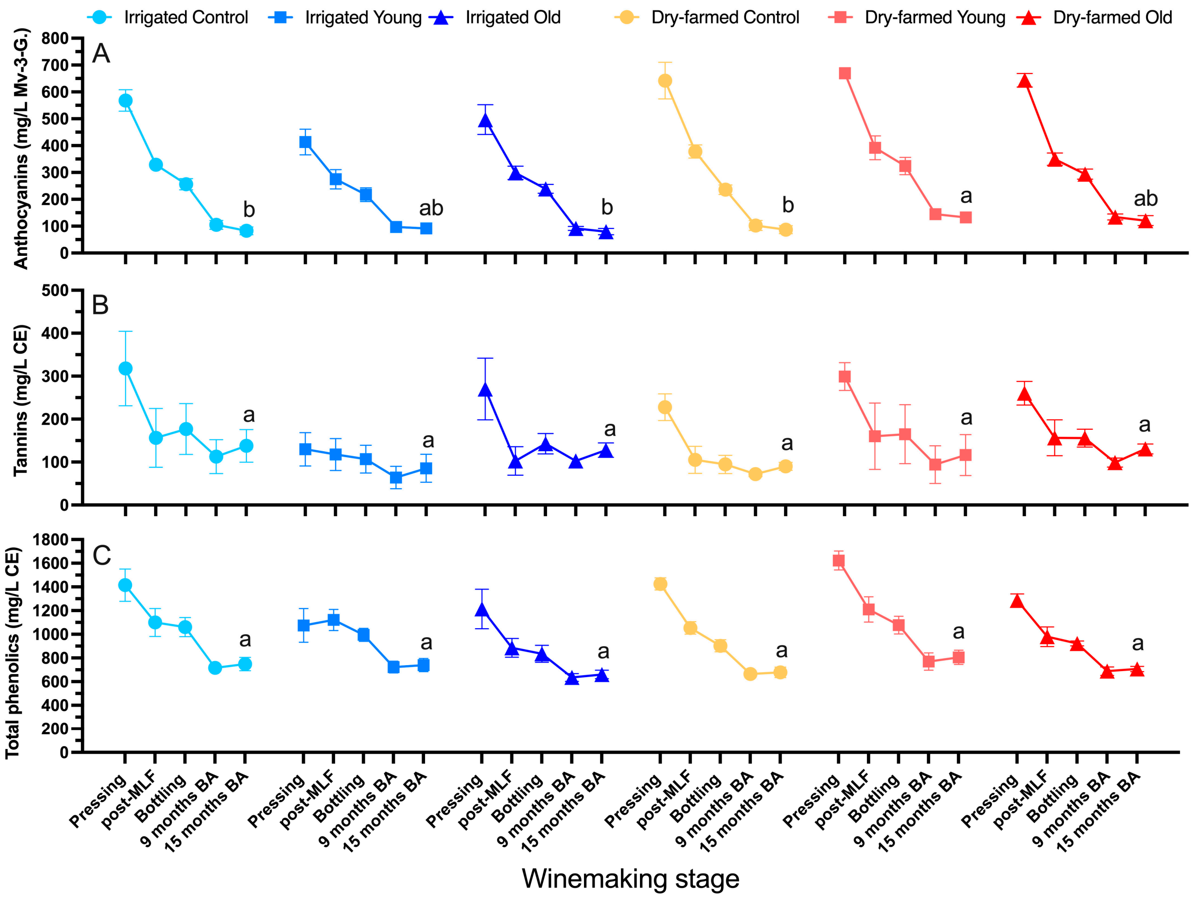

Figure 2. Evolution of (**A**) anthocyanins, (**B**) tannins, and (**C**) total phenolics during winemaking of Zinfandel wines produced from vines of different age and submitted to irrigation or dry farming (non-irrigated). Each data point represents the average of three tank replicates (n = 3) and error bars indicate the standard error of the mean. If not shown, error bars are obscured by treatment symbols. Different letters in the last sampling point (15 months of bottle aging), indicate significant differences for Fisher's LSD test and $p < 0.05$. CE: catechin equivalents. BA: bottle aging.

The detailed anthocyanin composition, as well as the proportion of the different anthocyanin classes, is shown in Figure 3. Malvidin-3-glucoside was the prevailing anthocyanin, accounting for 60 to 65% of the total anthocyanin content of the wines at bottling (Figure 3), and then decreasing proportionally throughout bottle aging. At the end of the 15-month period of bottle aging, anthocyanin derivatives accounted for up to 60% of the total anthocyanin content in Irrigated Old vines (Figure 3, bottom panel). Anthocyanin-derived pigments include pyranoanthocyanins such as Vitisin A and Vitisin B, as well as low-molecular-weight adducts between anthocyanins and flavanols of direct condensation or mediated by acetaldehyde [26] and polymeric pigments [11]. These pigments are form through aging and display less color than intact anthocyanins due to generally comparatively lower molar extinction coefficients [11,27]. However, these anthocyanin-derived pigments may be key contributors of the color of aged red wines as they display color at pH 4 and above and are also resistant to bisulfite bleaching. They also display characteristic hues, including brick-red and garnet hues [26], thereby explaining the typical color of aged Zinfandel wines.

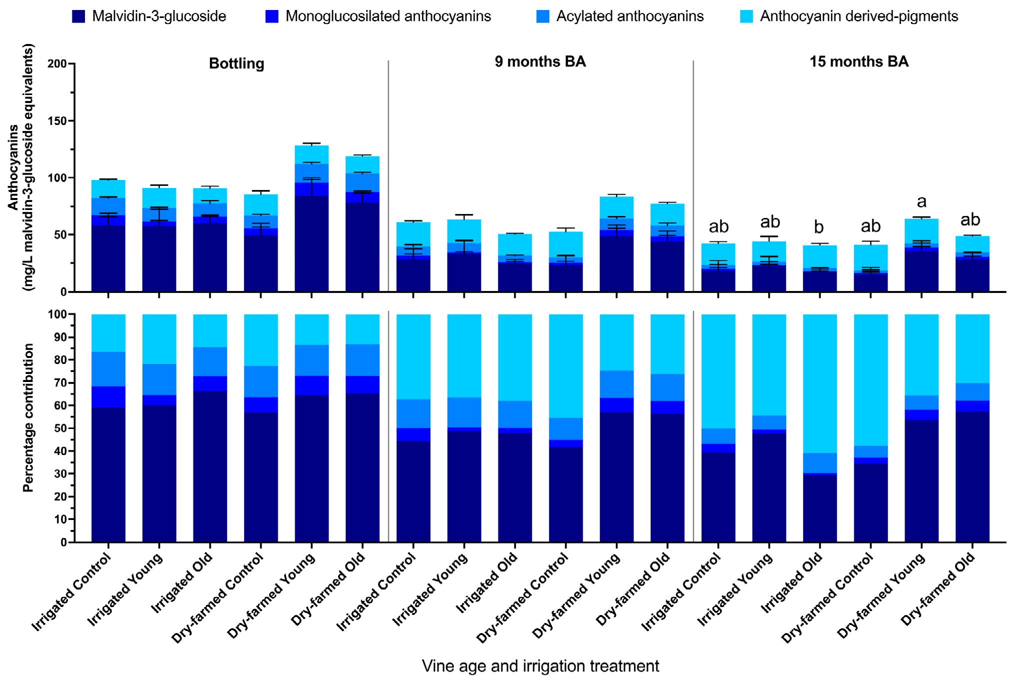

Figure 3. Evolution of the concentration (top panel) and percentage contribution (bottom panel) of malvidin-3-glucoside, the remaining monoglucosylated anthocyanins (peonidin-3-glucoside + petunidin-3-glucoside + delphinidin-3-glucoside + cyanidin-3-glucoside), acylated anthocyanins and anthocyanin-derived pigments during the winemaking of Zinfandel wines produced from vines of different age and submitted to irrigation or dry farming (non-irrigated). Different letters in the last sampling point (15 months of bottle aging) indicate significant differences for Fisher's LSD test and $p < 0.05$. BA: bottle aging.

The remaining monoglucosylated anthocyanins and acylated anthocyanins accounted for about 4% and 7% of the anthocyanin content after 15 months of bottle aging. At this time, Dry-farmed Young wines showed higher total anthocyanin concentration only relative to Irrigated Old wines, with no overall effects of the remaining treatments (Figure 3).

The evolution of both tannins and total phenolics are shown in Figure 2B,C, respectively. Tannins peaked at pressing in all the wines, decreasing especially after malolactic fermentation. After 15 months of bottle aging, tannin levels ranged from 85 mg/L (Irrigated Young wines) to 137 mg/L (Irrigated Control wines). These represent low tannin levels and highlight this as a chemical feature of Zinfandel wines grown in Mediterranean climates such as the Central Coast of California. A previous survey of tannins on 182 commercial Zinfandel wines from California reported an average tannin content of 652 mg/L [13], which is about five times higher than the tannin levels observed in the present study. Conversely, tannin levels of Zinfandel wines from the Central Coast of California, specifically Paso Robles, were reported to be between 250 and 500 mg/L [7], though these were measured immediately post-bottling, unlike the present study.

Total phenolics include vicinal o-dihydroxyls, such as tannins, flavan-3-ols and flavanols, but monohydroxylated phenols and anthocyanins are not included [28]. Because tannins are important constituents of the total phenolic content of wines, it was reasonable to expect a similar evolution of the total phenolic content of the wines (Figure 2C). Maximum levels of total phenolics were attained at pressing, following a similar decrease as reported for tannins (Figure 2B). After 15 months of bottle aging, no differences in total phenolics were observed within treatments. Overall, total phenolics and especially tannin levels in the Zinfandel wines of the present study were low or moderate at best, highlighting differences with other Zinfandel growing regions in California. Predictably, low astringency levels may be expected in the Zinfandel wines of the present study. This is not only because these Zinfandel wines were low in tannins, but also because of their very high ethanol level. Indeed, increases in ethanol (from 10 to 15%) decrease hydrophobic interactions between tannins and proteins, thus decreasing perceived astringency [29], as may be plausible for the wines of the present study.

Figure 4 shows the evolution of small and large polymeric pigments. Small polymeric pigments (SPP) include low-molecular-weight pigments that are unable to precipitate with proteins [30], hence unlikely to contribute to astringency. Large polymeric pigments include large-molecular-weight adducts between anthocyanins and tannins that can engage with proteins [30], thus potentially contributing to mouthfeel and astringency [31]. Polymeric pigments increased gradually throughout the winemaking, but most increases occurred early in the period post-MLF (Figure 4). After 15 months of bottle aging, the polymeric pigment content of these Zinfandel wines was largely due to SPP with small contributions of LPP, with the latter increasing over time. The proportion of SPP to the total polymeric pigment content of the wines was 74%, 74%, 71%, 78%, 70% and 72% for Irrigated Control, Irrigated Young, Irrigated Old, Dry-farmed Control, Dry-farmed Young and Dry-farmed Old wines, respectively. Considering the total polymeric pigment at 15 months of bottle aging, Dry-farmed Young wines showed the highest amount, but only relative to Irrigated Control and Irrigated Old wines (Figure 4).

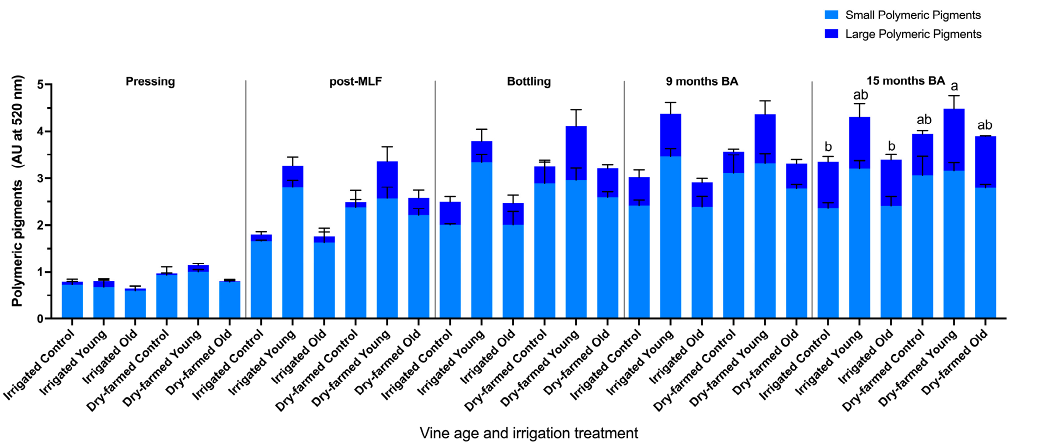

Figure 4. Evolution of small and large polymeric pigments during winemaking of Zinfandel wines produced from vines of different age and submitted to irrigation or dry farming (non-irrigated). Each data point represents the average of three tank replicates (n = 3) and error bars indicate the standard error of the mean. If not shown, error bars are obscured by treatment symbols. Different letters in the last sampling point (15 months of bottle aging) indicate significant differences for Fisher's LSD test and $p < 0.05$. AU: absorbance units. BA: bottle aging.

Although astringency levels were not determined in the wines of the present study, a closer analysis of their chemical composition allows for some extrapolations. For example, a study suggested that Nebbiolo wines with a tannin-to-anthocyanin ratio of 16 but very low polymeric pigment content (below 1 AU) may be felt as drying and exceedingly astringent [32]. Conversely, wines with a more balanced tannin-to-anthocyanin ratio and higher levels of polymeric pigments (above 4 AU) may potentially display positive astringency subqualities such as "velvety", "suede" or "round" [32]. The tannin-to-anthocyanin ratio of the Zinfandel wines of the present study was on average 1.23, and the polymeric pigment content close to 4 AU (Figure 4). Coupled with very high ethanol levels (which may lower perceived astringency), it is possible to surmise a rounder and "resolved" type of astringency in the wines of the present study.

3.4. Chromatic Composition of the Wines

The detailed CIELab composition of the wines is shown in Figure 5. Lightness (Figure 5A) provides information about the total amount of color saturation, with lower values indicating more saturated wines and higher values indicating wines with comparatively lower color saturation. Lightness (L*) increased over time in all the wines, suggesting a loss of color saturation, and this was related with the progressive degradation of anthocyanins (Figure 2) and the concomitant formation of polymeric pigments (Figure 4). After 15 months of bottle aging, lower L* values (indicating darker wines) were observed in Dry-farmed Young wines. This could be explained by the comparatively higher anthocyanin content in Dry-farmed Young wines, both as measured spectrophotometrically (Figure 2) and by HPLC (Figure 3). The opposite trend was observed for a*, which indicates the amount of red color to the total hue of the wine. That is, a* decreased progressively through aging, indicating a lower contribution of the red color to the total color of these wines, again, in parallel with an increase in polymeric pigments. This result also suggests these polymeric pigments may be indeed less red in hue than intact anthocyanins. Dry-farmed Young and Dry-farmed Old wines showed comparatively higher values relative to Irrigated Young wines (Figure 5B).

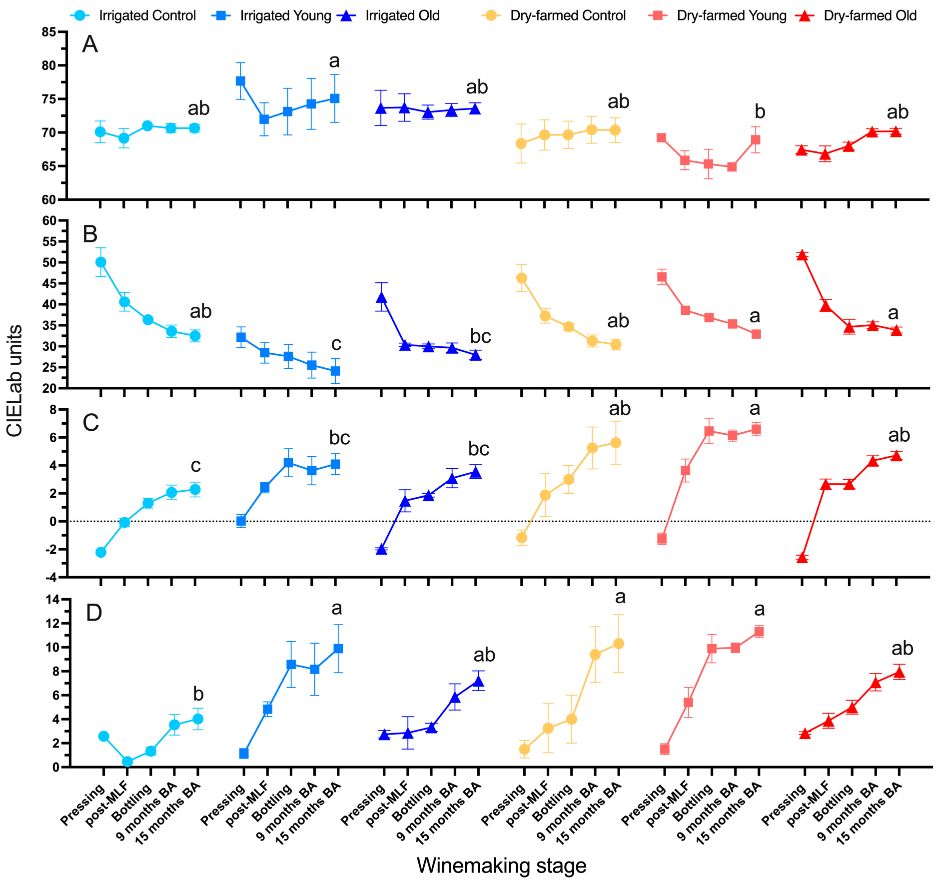

Figure 5. Evolution of CIELab parameters: (**A**) lightness; (**B**) a* (red color when positive); (**C**) b* (yellow color when positive), and (**D**) H* (hue angle), during winemaking of Zinfandel wines produced from vines of different age and submitted to irrigation or dry farming (non-irrigated). Each data point represents the average of three tank replicates (n = 3) and error bars indicate the standard error of the mean. If not shown, error bars are obscured by treatment symbols. Different letters in the last sampling point (15 months of bottle aging) indicate significant differences for Fisher's LSD test and $p < 0.05$. BA: bottle aging.

The CIELab parameter b* informs about the proportion of yellow hues (Figure 5C), whereas H* (hue angle) is effectively an angle between 0° and 360°, with 0° representing maximum redness and 90° representing maximum yellowness. These Zinfandel wines were very red in color and very low in yellow hues early at pressing (Figure 5C,D). However, the proportion of yellow hue increased over time, peaking at the last sampling point, and so it did the hue angle, indicating a more pronounced contribution of yellow hues to the overall hue of these wines. After 15 months of bottle aging, a* values were higher in Dry-farmed Young wines (Figure 5C), whereas H* values were higher in Irrigated Young wines, and in Dry-farmed Control and Dry-farmed Young wines (Figure 5D). Overall, these chromatic differences between the wines of the different treatments were relatively small in magnitude, but sensory analysis may have to confirm this assumption.

4. Conclusions

The present study builds upon a previous one reporting the effect of supplemental irrigation in a dry-farmed Zinfandel vineyard, in which vines were further segregated by age, including Young vines (5 to 12 years old), Old vines (40 to 60 years old) and Control (2:1 ratio of Old to Young vines, as representative of the vineyard) vines [19]. Herein, the wines of the individual treatments were made into wine and followed up to 15 months of bottle aging.

Overall, the aggregate of the data suggests that the most affected treatments were Irrigated Young wines and Dry-farmed Young wines. For example, Irrigated Young wines showed lower alcohol, anthocyanins, and tannins, as well as a higher pH and hue angle values (H*) than the remaining treatments, whereas Dry-farmed Young wines were higher in anthocyanins and small polymeric pigments, and showed higher color saturation and red hue. This may initially suggest that, from the perspective of wine chemistry, irrigation was more detrimental when applied to Young vines than Old vines, highlighting an interactive effect of vine age and irrigation on wine chemistry. However, it must be emphasized that the magnitude of these differences was small at best, and unlikely to hold any commercial relevance from the perspective of the quality of the finished wines. This outcome is likely the result of equally small differences observed in the fruit obtained from the original irrigation treatments imposed in the field. This further highlights the fact that the performance of Old vine and their respective wines is significant, in light of a previous finding in Zinfandel indicating overall higher yields in Old rather than in Young vines [7]. Over a 15-month period of bottle aging, irrespective of the treatment, Zinfandel wines went from a 60 to 65% preponderance of malvidin-3-glucoside in their anthocyanin profile, to up to 60% of it being dominated by anthocyanin derivatives, highlighting a rather fast evolution of anthocyanin and their derivatives during aging of Zinfandel wines. Moreover, small polymeric pigments accounted for more than 70% of the total polymeric pigment content of the wines after bottle aging.

Lastly, Irrigated Old wines and Dry-farmed Old wines did not differ to any significant extent in their basic chemistry, phenolic chemistry (including detailed anthocyanin composition), and chromatic composition. This suggests that in case emergency irrigation during the growing season has to be applied to Old Vine Zinfandel vineyards in the Central Coast of California, no adverse chemical effects on the wines are to be expected. Rather, applying emergency or just supplementary irrigation in Mediterranean regions in the event of unexpected weather conditions (i.e., heat waves) can not only save the crop but also preserve and ensure chemical and sensory quality.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/fermentation9110974/s1, Supplemental Figure S1: Field experimental design, showing the selected Control, Young and Old vines, as well as the application of the irrigation treatment.

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