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Alternatives to Traditional Aging of Bobal Red Wines from Semi-Arid Climate: Influence on Phenolic Composition and Related Properties

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Abstract: The effect of oak chips on the phenolic composition, color characteristics, and antioxidant capacity of Bobal red wines caused by contact with oak chips at different stages of the winemaking process has been studied. Performance liquid chromatography–diode array detection (HPLC-DAD) was used to determine the detailed phenolic composition of wines and antioxidant activity, and chromatic characteristics were determined by spectrophotometric methods. Standard red winemaking process was applied to make the Bobal control wine. The rest of the wines were elaborated with oak chip contact at two dose levels (3 and 6 g/L) in different phases of the winemaking process: during alcoholic fermentation (AF), during malolactic fermentation (MLF), and in young wines. The phenolic composition, antioxidant activity, and chromatic characteristics of Bobal control wines were slightly but significantly modified by contact with the oak chips. Wines in contact with oak chips during malolactic fermentation showed a decrease in the concentration of resveratrol-monomer stilbenes, monomeric anthocyanins, and pyranoanthocyanins. In general, the concentration of total resveratrol is influenced by the dose level used, resulting in a 10% decrease when the dose level is 6 g/L compared to the 3 g/L dose.

Keywords: bobal wine; oak chips; phenolic composition; antioxidant capacity; color characteristics

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1. Introduction

In warm regions, challenging climate conditions often hinder the elaboration of wines with stable and intense colors defined as high-quality red wines. This discrepancy arises because phenolic maturity does not align with the technological maturity (sugar) of the grapes during harvest. Consequently, different levels of phenolic compounds and sugar concentrations coexist at the time of picking [1]. In such cases, grapes may have higher concentrations of sugar but immature phenolic compounds. So, an extra contribution of tannins may be desirable in order to stabilize the color, astringency, and bitterness of wines [1].

Moreover, wines that have been aged in wooden barrels are highly valued by consumers [2]. This preference is further supported by recent market research, which found that 88% of respondents favored red wines aged in wood over younger red wines [3].

The process of aging wine in wooden barrels results in noticeable changes in the wine's color, structure, and, most notably, its aroma. Nevertheless, the traditional method of aging wine in oak barrels entails a significant financial burden for wineries due to the expensive nature of the barrels themselves, the extended duration the wine must remain within them, and the operational and logistical challenges associated with barrel aging [2].

In an effort to reduce costs and expedite the aging process, wineries have begun to explore more economical and efficient alternatives in recent years. One such method involves the use of small wood fragments, often referred to as "oak chips". This technique allows wines to acquire characteristics like those aged in barrels but in a shorter timeframe and at a reduced cost. Oak chips are small pieces of wood with dimensions ranging from a minimum of 2 mm (called granulates, tabacs, or wood rice) up to about 20 mm (called shavings, copeaux, or fragments). Smaller size chips have more exchange surface area that can be used in different phases of winemaking: during alcoholic fermentation, before malolactic fermentation, or during wine aging. Delegated Regulation 2019/934 (EU) currently regulates their use in oenology.

The effect of oak wood chips on phenolic compounds, chromatics characteristics, and volatile compounds has been extensively reviewed. In this sense, several investigations are focused on the effect of oak chip contacts on the volatile composition of wines—Airén, Asyrtiko, Chardonnay, Merlot, Bobal, and Moravía Agria grape varieties [4–11]. Nevertheless, few studies have been found on phenolic composition and its influence on the color of red wines macerated with chips [12–15].

Bobal grape variety is a traditional variety cultivated in the La Mancha region, whose market is mainly based on its high tannin concentration and color intensity [16]. The phenolic composition, sensory characteristics, and volatile compounds of Bobal grapes and wines cultivated in the La Mancha region have been studied in previous works [17,18]. Bobal grapes and wine persist due to their great concentrations of flavanols such as catechin, epicatechin and epigallocatechin, flavonols, quercetin and myricetin, and anthocyanins —principally malvidin [17,18], so this variety has a polyphenolic composition suitable for good aging in contact with oak woods. The sensory characteristics and the volatile compounds of young Bobal wines, elaborated with and without oak chip addition, have already been studied [19,20], but no references about the influence of oak chip contact on phenolic composition have been found.

As a result, the objective of this research was to study the influence on phenolic composition, color effects, co-pigmentation, and physicochemical properties (including antioxidant capacity) of Bobal wines in contact with oak chips at two different dose rates (3 and 6 g/L) and in different winemaking stages—during alcoholic fermentation, during malolactic fermentation, and during one week in young wines—in order to reduce the overall maturation time and associated costs and obtain wines according to consumer demand.

2. Materials and Methods

2.1. Wine Samples

Vitis vinifera c.v. Bobal grape variety is from La Mancha region (middle-southeast) Spain. The climate in the area is classified as semi-arid continental Mediterranean, characterized by hot and dry summers as well as cold and moderately rainy winters. The region experiences a wide annual temperature range, with a thermal amplitude of 21.50 °C. The average annual temperature is 14.82 °C, and the reference evapotranspiration (ETo) is 1285 mm, whereas the annual rainfall amounts to 377 mm. Usually, only 40 % of the total rainfall occurs during the grapevine growing season.

Grapes were manually harvested at their optimum ripening point and under good sanitary stage. The winemaking process involved seven batches of grapes (each weighing 8 kg) macerated in 10 L vats until alcoholic fermentation occurred. The red Bobal experimental wines were added with oak chips (a blend with medium toast of French and American oak) in two different dosages (3 and 6 g/L) in different stages: during alcoholic fermentation for 7 days (AFA3 and AFA6), during malolactic fermentation for 20 days (MFA3 and MFA6) and in young wines for one week (PFA3 and PFA6) at 24 °C. The control wine was produced without oak chips (CW). The grapes were stemmed and crushed, and 100 mg/L of SO_2 was added as $K_2S_2O_7$. Alcoholic fermentation was conducted at 24 °C with *Saccharomyces cerevisiae* selected yeasts (UCLM S325, Fould-Springer). Manual punching down was performed twice a day, and the separation from solids occurred based

on relative density (0.994 g/L). Subsequently, malolactic fermentation was induced using *Oenococcus oeni* (Lactobacter SP1; Laffort, Guipúzcoa, Spain), and the end of malolactic fermentation was evaluated using Thin Layer Chromatography analysis. Then, the wines were racked, filtered through 1.2 µm membranes (Millipore, Bedford, MA, USA), bottled, and stored in dark and at controlled temperature of 16–18 °C. All fermentations were conducted in duplicate.

2.2. Conventional Analysis

The most usual parameters of wines, pH, titrable acidity as g/l of tartaric acid, volatile acidity as g/l acetic acid, alcohol strength (% *v*/*v*), and free and total SO_2 were determined according to the OIV methods (OIV, 2022) [21].

2.3. Antioxidant Capacity

The wine samples were diluted with methanol (1/20), and 100 µL of the diluted wine was added to 2.9 mL of methanolic solution of DPPH (2,2-diphenyl-1-picrylhydracyl, procured from Fluka Chemie, Buchs, Switzerland). The concentration of the DPPH radical in the solution was 6×10^{-2} mol/L. Subsequent to a duration of 25 min, the decrement in absorbance at a wavelength of 515 nm was quantified using a UV-Visible Spectrophotometer (Helios Gamma 9423 UVG 1002E; CT, USA). The recorded measurement was required to be within the range of 20–80% of the initial DPPH absorbance. In order to quantify the antioxidant capacity calibration curves with methanolic solutions of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, sourced from Fluka Chemie, Buchs, Switzerland), with concentration range between 10 and 45 mmol/L and R^2 = 0.9996 (Table S1) [22].

2.4. Total Polyphenols Content

The spectrophotometric method proposed by Mazza et al. (1999) [23] was used to analyze the total polyphenols of studied wines in duplicate and after two months of storage. To 0.5 mL of wine diluted 1:10 with 10% (*v*/*v*) ethanol in water were added 0.5 mL of 2% HCl in 96% ethanol and 9.1 mL of HCl 1 N. After 15 min, absorbance at 280 nm was measured in 1 cm quartz cells using water as blank using a UV-Visible Spectrophotometer (Helios Gamma 9423 UVG 1002E). Calibration curves with different concentrations of gallic acid were used for the quantification (concentration range = 100–2000 mg/L as gallic acid equivalents, R^2 = 0.9967, Table S1). While the total phenolic content of red wine provides limited insight into the impact of phenolic compounds on key properties, we conducted a detailed analysis of various phenolic compound classes. Monomeric anthocyanins, monomeric flavan-3-ols, resveratrol-monomer stilbenes, pyranoanthocyanins, flavonols, and hydroxycinnamic acid derivatives were the phenolic compound families analyzed.

2.5. Wine Sample Preparation for Determination of Non-Anthocyanin Phenolic Compounds

Prior to the analysis of non-anthocyanin phenolic compounds, particularly flavonols, it is necessary to eliminate anthocyanin-type pigments commonly found in wine samples in order to eliminate interference during their chromatographic separation. Three milliliters of sample wine were diluted with three milliliters of 0.1 M hydrochloric acid. The near-total elimination of anthocyanin pigments was achieved through solid-phase extraction, utilizing a blend of reversed-phase and cation-exchange materials. This process employed Oasis® MCX cartridges (Waters—6 cm^3 capacity containing 500 mg of absorbent), enabling the isolation of wine flavonols. The prepared samples were passed through the MCX cartridges, which had been previously conditioned with five milliliters of methanol and five milliliters of water. After washing with five milliliters of 0.1 M hydrochloric acid and five milliliters of water, the flavonol fraction was eluted with three portions of five milliliters of methanol. This fraction also contained other neutral or acidic polyphenols (flavan-3-ols or tannins and hydroxycinnamic acid derivatives, respectively). The eluate-containing flavonols were dried in a rotary evaporator at 40 °C and re-dissolved in three milliliters of solvent A used in

the HPLC separation. To regenerate the cartridge, fixed anthocyanins were removed using three portions of five milliliters of 2% NH4OH in 55% methanol, followed by five milliliters of 2% NH4OH in 80% methanol, and the cation-exchange material was regenerated with three portions of five milliliters of 2% HCl in 80% methanol [24].

2.6. Determination of Phenolic Composition by HPLC-DAD

2.6.1. Chemicals

In this study, all solvents were of HPLC quality, and the chemicals used were of analytical grade (>99%). Ultrapure water, with a conductivity of 18.2 MΩ cm, was generated through the Milli-Q purification system by Millipore (USA). Commercial standards from Phytolab (Vestenbergsgreuth, Germany) included malvidin 3-glucoside, caffeic acid, p-coumaric acid, trans-piceid, and (-)-epigallocatechin. Extrasynthese (Genay, France) provided commercial standards for isorhamnetin, quercetin, syringetin, and kaempferol, as well as the 3-glucosides of kaempferol and myricetin. Sigma-Aldrich (Madrid, Spain) supplied trans-resveratrol, *(+)*-catechin, and *(-)*-epicatechin. Through UV irradiation (366 nm light for 5 min in quartz vials) of 25% MeOH solutions of the *trans* isomers, the *cis* isomers of resveratrol and piceid (resveratrol 3-glucoside) were obtained. All standards were used for identification and quantification based on calibration curves, which covered expected concentration ranges. When a standard was unavailable, quantification was performed using the calibration curve of the most similar compound, with subsequent molecular mass correction, malvidin 3-glucoside was used for all native grape anthocyanins and flavonol 3-glycosides with non-available standards, as their corresponding 3-glucoside derivatives.

2.6.2. HPLC-DAD-ESI-MS/MS: Separation and Identification of Phenolic Compounds

The analysis utilized an Agilent 1100 series system (Agilent, Waldbronn, Germany) equipped with a DAD photodiode detector (G1315B) and an LC/MSD Trap VL (G2445C VL) electrospray ionization mass spectrometry (ESI-MS/MS) system, both coupled to an Agilent Chem Station (version B.01.03) for data processing. Wine samples were directly injected for anthocyanin and pyranoanthocyanin analysis, while an anthocyanin-free wine phenolic extract was used for non-anthocyanin phenolic compounds (Section 2.5). After filtration (0.20 µm, polyester membrane, Chromafil PET 20/25, Machery-Nagel, Düren, Germany), 50 µL of the samples were injected onto a reversed-phase column (Zorbax Eclipse XDB-C18, 4.6 × 250 mm; 5 µm particle; Agilent) at 40 °C. The MS detector settings followed previously established parameters. Anthocyanins and flavan-3-ols were identified using positive ESI-MS/MS mode, while flavonols, hydroxycinnamic acid derivatives, and stilbenes were analyzed in both positive and negative modes. Phenolic compound standards were used for confirmation, and other compounds were tentatively identified based on UV-vis and MS/MS spectral data, which are consistent with prior reports [25,26].

2.6.3. Quantification of Phenolic Compounds by HPLC-DAD

The quantification of wine phenolic compounds was carried out using the same chromatographic system as the one used for identification, which follows established methods [25,26]. DAD-chromatograms extracted at 520 nm were used to quantify native grape anthocyanins and pyranoanthocyanins. For non-anthocyanin phenolic compounds (including flavonols, hydroxycinnamic acids, flavan-3-ol monomers, and resveratrol-type stilbenes), DAD-chromatograms were extracted at 360 nm (flavonols), 320 nm (hydroxycinnamic acid derivatives and resveratrol-type stilbenes), and280 nm (flavan-3-ol monomers).

Calibration curves were generated using the provided standards (Section 2.6.1), covering the expected concentration ranges (typically 0–100 mg/L, except for malvidin 3-glucoside, which covered a range of 0–1000 mg/L and with $R^2 \geq 0.998$, Table S1). Vitisin-like and hydroxyphenyl-like pyranoanthocyanins were quantified using previously obtained calibration curves for vitisin A and 10-dihydroxyphenyl-pyranomalvidin-3-glucoside (10-DHP-pyrmv-3-glc or pinotin A) [27]. When a standard was unavailable, quantification was performed using the calibration curve of the most similar compound

(with subsequent molecular mass correction). For instance, malvidin 3-glucoside was used for all native grape anthocyanins, and flavonol 3-glycosides without available standards were quantified using their corresponding 3-glucoside derivatives. Hydroxycinnamic acid derivatives were quantified using the calibration curve of their corresponding free hydroxycinnamic acid.

2.7. Copigmented Anthocyanins

The percentage of copigmented anthocyanins contributing to the overall wine color at pH 3.6 was determined using Boulton's method, as described by Hermosín-Gutiérrez (2003) [28]. Although this pH value may not match the specific conditions of each individual wine, it serves as a consistent basis for comparing color components across all wines, given their pH-dependent effects.

2.8. CIELAB Parameters of Wines

The chromatic characteristics in the space CIELAB L*, C*, and h* were determined from the absorbances at 450, 520, 570, and 630 nm of sample wine previously filtered through 0.45 µm nylon membranes (Millipore) using a simplified method specifically designed for red wines [29]. To mitigate pH effects, all measurements were adjusted to a common reference value (pH 3.6), which was also used for estimating copigmented anthocyanins.

2.9. Data Analysis

In order to determine significant differences between the mean concentration of all studied parameters of wines, the Student–Newman–Keuls test was applied using the SPSS version 28.0 for Windows statistical package.

3. Results and Discussion

3.1. Conventional Parameters

The basic physicochemical composition of wines is reported in Table 1 and in Figure S1 of Supplementary Materials. All determinations were carried out at the moment of wine bottling. These values align with typical characteristics observed in Bobal wines from the La Mancha region and in wines from other red grape varieties cultivated in this region [17,18]. Specifically, ethanol content, total acidity, and pH fall within the accepted range for red wines in semi-arid regions. Although produced independently, the samples showed no significant differences. The free and total SO_2 concentrations are within the legal limits

Table 1. Mean values and SD (n = 2) of conventional parameters, Total Polyphenols and Antioxidant Capacity.

	Alcoholic Degree (% *v*/*v*)	pH	Total Acidity (g/L as Tartaric Acid)	Volatile Acidity (g/L as Acetic Acid)	SO_2 Free (mg/L)	SO_2 Total (mg/L)	Total Polyphenols (mg/L as Gallic Acid)	Antioxidant Capacity (mmol/L of Trolox Equivalents)
CW	13.8 0.55	3.75 0.10	4.05 0.15	0.49 0.07	16.5 071	34.5 ^{b} 1.41	1457.8 47.8	21.2 1.32
AFA3	14.7 0.41	3.75 0.11	4.16 0.12	0.56 0.08	16.0 0.71	33.5 ^{b} 1.41	1435.7 73.2	20.8 1.21
AFA6	13.4 0.52	3.79 0.15	4.27 0.17	0.53 0.06	15.0 0.71	31.5 ^{b} 2.83	1400.3 86.4	20.1 1.35
MFA3	14.7 0.60	3.80 0.10	3.98 0.17	0.55 0.07	15.5 0.10	31.5 ^{b} 1.41	1350.2 30.3	20.3 1.22
MFA6	14.6 0.71	3.84 0.12	4.08 0.12	0.51 0.06	16.0 0.71	27.0 ^{a} 1.41	1462.3 53.9	20.9 1.38
PFA3	13.9 0.62	3.76 0.15	4.16 0.11	0.51 0.07	16.0 0.71	32.0 ^{b} 0.70	1380.5 43.4	21.1 1.20
PFA6	14.3 0.40	3.77 0.14	4.09 0.13	0.50 0.06	14.5 0.80	33.0 ^{b} 0.71	1412.9 69.1	22.9 1.22

According to the Student–Newman–Keuls test ($p < 0.05$), different letters (a,b) on the same column indicate significant differences in the mean values.

3.2. Antioxidant Activity

The antioxidant capacity of the studied Bobal control wines and Bobal wines in contact with oak chips in different winemaking stages at the two dose levels considered (Table 1 and Figure S1) ranged within 20.1 to 22.9 mmol/L (as Trolox equivalents); the values fall within the reported range for red wines, 1.2–25.5 mmol/L as Trolox equivalents [30,31] without significant differences between samples. Despite variations in the phenolic concentration due to oak chip addition, the overall antioxidant capacity remained consistent. While some phenolic families decreased (e.g., red pigments and stilbenes), others increased (e.g., flavonols and hydroxycinnamic acid derivatives), resulting in a balanced effect on antioxidant properties.

3.3. Total Polyphenols

All wines displayed total polyphenol contents (as indicated in Table 1) that fall within the typical ranges for young red wines [32]. These levels were consistent with previously reported phenolic compound concentrations for Bobal wines [17]. Notably, no significant differences were detected between the wines in contact with oak chips and the control wine (CW), independent of the winemaking stage and dosage.

3.3.1. Monomeric Anthocyanins and Pyroanthocianins

The phenolic compounds responsible for wine color are anthocyanins [33]. Table 2 shows the results of monomeric anthocyanins and proanthocyanins in studied Bobal wines. The monomeric anthocyanins present in Bobal wines included the expected derivatives: the 3-glucoside (3-glc), 3-(6″-p-coumaroyl)-glucoside (3-cmglc), and 3-(6″-acetyl)-glucoside (3-acglc) of cyanidin, peonidin, delphinidin, petunidin, and malvidin (cy, pn, dp, pt and mv, respectively). The percentages of each individual anthocyanin over the total amount in graphed in Figure S2 of Supplementary Materials (Figure S2A 3-glucoside (3-glc; Figure S2B 3-(6″-p-coumaroyl)-glucoside (3-cmglc) and Figure S3B and 3-(6″-acetyl)-glucoside (3-acglc) and 3-cfglc, 3-(6″-caffeoyl)glucoside). Also, lower concentrations of the 3-(6″-caffeoyl)-glucoside (3-cfglc) derivative were found, specifically associated with malvidin. The monomeric anthocyanin profiles of Bobal wines from Castilla-La Mancha were predominantly characterized by B-ring tri-substituted anthocyanidin structures (delphinidin, petunidin, and malvidin), consistent with the patterns commonly observed in most widespread *V. vinifera* varieties. Among these, mv-3-glc was the most significant individual contributor, accounting for 53.39–57.46% of the total anthocyanin content in *V. vinifera* red wines. Pt-3-glc (10.78–12.30%) and dp-3-glc (8.20–10.97%) also contributed to the pool of anthocyanin. Non-acylated anthocyanins constituted 85–87% of the total, while caffeoylated, p-coumaroylated, and acetylated anthocyanins represented <0.4%, 5–6%, and 8–9%, respectively. These results align with well-established differences between the anthocyanin profiles of the grapes and their respective wines. A previous study on Bobal grapes reported 0.4–0.9% caffeoylated anthocyanins, 80–83% non-acylated anthocyanins (including 44–45% mv-3-glc) and approximately 5% acetylated, 12–14% p-coumaroylated, and [17].

The contact of oak chips with wines at different winemaking stages did not significantly alter the primary constituents to anthocyanin profiles, specifically acetylated and non-acylated anthocyanins. Minor differences were observed for certain pn-3-cmglc and cis and trans isomers of mv-3-cmglc (p-coumaroylated derivatives) and the mv-3-cfglc (caffeoylated derivative), particularly in wines in contact with chips during malolactic fermentation (MFA wines). Overall, MFA wines experienced a reduction in anthocyanin content, accompanied by decreased percentages of the aforementioned minor anthocyanins. Most studies on oak chip use in red wine production focus on post-malolactic fermentation chip addition. Notably, a recent study involving Mencía wines in contact with chips along alcoholic fermentation exhibited no significant differences in total anthocyanin content and profiles compared to control wines after bottling [34], similar to our findings for analogous AFA wines. Oak chip addition during the post-fermentative phase (after alcoholic and

malolactic fermentations) led to reduced anthocyanin content only in wines treated with the lowest doses (PFA3), which is consistent with reported data for chip-treated wines post-malolactic fermentation [35–37]. Importantly, the total concentration of monomeric anthocyanins in Bobal wines, regardless of the point of addition of the oak chips and the dose used, fell within the typical range reported for red wines [17,38–40].

Table 2. Percentages of each individual anthocyanin over the total amount and mean concentration of total anthocyanins (SD; n = 2).

Anthocyanin	CW		AFA3		AFA6		MFA3		MFA6		PFA3		PFA6	
dp-3-glc	10.97	1.91	9.33	0.35	8.35	1.38	9.51	0.21	9.85	0.68	8.20	1.89	8.53	1.68
cy-3-glc	0.52	0.03	0.45	0.04	0.47	0.02	0.41	0.05	0.46	0.02	0.40	0.08	0.68	0.19
pt-3-glc	12.22	1.61	10.78	1.14	11.36	0.44	11.25	0.29	12.30	1.54	11.29	0.66	11.94	0.22
pn-3-glc	9.08	1.24	9.21	1.31	8.96	0.25	9.01	0.79	7.15	1.47	8.58	0.35	9.15	1.41
mv-3-glc	53.39	2.84	55.63	1.98	56.46	1.74	55.15	1.54	55.48	2.02	57.46	2.74	56.14	1.85
dp-3-acglc	1.93	0.47	1.91	0.31	1.73	0.18	1.45	0.44	1.25	0.35	1.69	0.15	1.98	0.43
cy-3-acglc	1.01	0.09	0.95	0.08	0.93	0.07	0.95	0.05	1.31	0.36	0.81	0.31	0.75	0.41
pt-3-acglc	1.09	0.11	1.06	0.08	1.04	0.12	1.14	0.09	1.43	0.35	1.13	0.07	0.88	0.05
pn-3-acglc	0.67	0.18	0.73	0.12	0.63	0.11	0.69	0.13	0.79	0.08	0.58	0.10	0.55	0.09
mv-3-acglc	4.16	0.24	4.31	0.31	4.31	0.15	4.41	0.15	4.65	0.41	4.23	0.19	4.08	0.38
dp-3-cmglc	1.05	0.07	1.19	0.09	1.15	0.11	1.12	0.07	1.15	0.07	1.01	0.09	1.00	0.10
cy-3-cmglc	0.42	0.13	0.31	0.07	0.37	0.04	0.36	0.04	0.44	0.09	0.40	0.03	0.38	0.04
pt-3-cmglc	0.24	0.03	0.22	0.06	0.21	0.04	0.24	0.04	0.29	0.04	0.22	0.03	0.24	0.04
pn-3-cmglc	0.92 ^{a}	0.08	1.07 ^{a,b}	0.09	1.17 ^{b}	0.11	1.19 ^{b}	0.09	1.05 ^{a,b}	0.05	1.11 ^{b}	0.11	1.08 ^{a,b}	0.08
mv-3-*cis*-cmglc	0.13 ^{a}	0.04	0.20 ^{b}	0.04	0.10 ^{a}	0.03	0.10 ^{a}	0.02	0.64 ^{c}	0.09	0.07 ^{a}	0.03	0.07 ^{a}	0.04
mv-3-*trans*-cmglc	2.07 ^{b}	0.21	2.30 ^{b}	0.31	2.42 ^{b,c}	0.22	2.74 ^{c}	0.22	1.52 ^{a}	0.24	2.48 ^{c}	0.13	2.29 ^{b}	0.15
mv-3-cfglc	0.13 ^{a}	0.06	0.35 ^{b}	0.07	0.33 ^{b}	0.06	0.28 ^{b}	0.07	0.24 ^{a,b}	0.07	0.35 ^{b}	0.07	0.26 ^{b}	0.05
Total Anthocyanin *	473.5 ^{c}	12.11	493.7 ^{c}	13.71	499.3 ^{c}	19.21	379.4 ^{a}	9.35	368.3 ^{a}	11.29	450.1 ^{b}	11.98	488.2 ^{c}	9.54

According to the Student–Newman–Keuls test ($p < 0.05$), different letters (a,b,c) on the same row reveal significant differences in the mean values. nd, not detected. dp, delphinidin; cy, cyanidin; pt, petunidin; pn, peonidin; mv, malvidin; 3-glc, 3-glucoside. 3-acglc, 3-(6″-acetyl)glucoside. 3-cmglc, 3-(6″-*p*-coumaroyl)glucoside (*trans* isomer if not indicated). 3-cfglc, 3-(6″-caffeoyl)glucoside; * mg/L, as malvidin 3-glucoside equivalents.

Grape monomeric anthocyanins play a crucial role in reactions occurring immediately after their transfer during must fermentation and wine aging. These processes lead to the formation of new polymeric red pigments anthocyanin-derived, including polymers of tannin-anthocyanin linked by acetaldehyde and non-polymeric pyranoanthocyanins [41]. The mean concentration of individual and total pyranoanthocyanins in Bobal control wines and wines in contact with oak chips are shown in Table 3.

Table 3. Mean concentration and SD (n = 2) of individual and total pyranoanthocyanins.

pyranoanthocyanin	CW		AFA3		AFA6		MFA3		MFA6		PFA3		PFA6	
vitisin A *	9.15 ^{d}	0.31	11.61 ^{f}	0.18	10.48 ^{e}	0.21	6.00 ^{b}	0.26	4.32 ^{a}	0.27	8.17 ^{c}	0.19	8.37 ^{c}	0.34
vitisin B *	1.96 ^{c}	0.11	1.63 ^{b}	0.31	1.28 ^{b}	0.15	0.50 ^{a}	0.17	1.28 ^{b}	0.09	0.83 ^{a}	0.19	0.81 ^{a}	0.17
total vitisins *	11.11 ^{d}	0.34	13.25 ^{e}	0.37	11.75 ^{d}	0.28	6.50 ^{b}	0.31	5.60 ^{a}	0.21	9.00 ^{c}	0.17	9.18 ^{c}	0.28
10-MHP-pyrmv-3-glc **	0.53 ^{b}	0.12	0.49 ^{b}	0.08	0.61 ^{b}	0.09	0.21 ^{a}	0.15	0.17 ^{a}	0.11	0.63 ^{b}	0.08	0.60 ^{b}	0.10
10-MHP-pyrmv-3-cmglc **	0.06	0.02	0.06	0.01	0.08	0.02	0.04	0.01	0.02	0.01	0.08	0.02	0.07	0.01
10-DHP-pyrmv-3-glc **	0.16 ^{b}	0.03	0.14 ^{b}	0.03	0.15 ^{b}	0.03	0.08 ^{a}	0.02	0.06 ^{a}	0.01	0.14 ^{b}	0.02	0.12 ^{b}	0.03
10-DHP-pyrmv-3-cmglc **	0.04	0.01	0.05	0.02	0.07	0.03	0.05	0.01	0.03	0.01	0.03	0.01	0.04	0.02
total hydroxyphenyl-pyranonthocyanins **	0.78 ^{c}	0.19	0.74 ^{c}	0.18	0.90 ^{c}	0.17	0.38 ^{b}	0.05	0.28 ^{a}	0.04	0.87 ^{c}	0.18	0.82 ^{c}	0.16

According to the Student–Newman–Keuls test ($p < 0.05$), different letters (a,b,c) on the same row indicate significant differences in the mean values. nd, not detected. * mg/L, as vitisin A equivalents ** mg/L, as 10-DHP-pyrmv-3-glc equivalents. Pyrpn, pyranopeonidin; pyrmv, pyranomalvidin. 3-glc, 3-glucoside; 3-cmglc, 3-(6″-*p*-coumaroyl)glucoside; 10-MHP, 10-(4‴-monohydroxy)phenyl. 10-DHP, 10-(3‴,4‴-dihydroxy)phenyl.

Vitisin-type compounds are predominated over hydroxyphenyl-type in all research wines. The pyranoanthocyanin found in higher concentration in all wines was vitisin A (10-carboxy-pyranomalvidin 3-glucoside) with concentrations ranging from 4.32 to 11.61 mg/L—consistent with reported values [27]. Pyruvic acid and acetaldehyde, yeast metabolites, are respectively linked to the development of vitisin A and vitisin B.

Our findings indicate that the contact of wine with oak chips during alcoholic fermentation (AFA wines) enhanced the production of vitisin A over vitisin B, when compared to control wines (CW). In contrast, the contact of wine with oak chips after alcoholic fermentation, especially during malolactic fermentation and in a dose level of 6 g/L (MFA6 wines), led to decreased concentrations of both vitisins A and B. During alcoholic fermentation, only vitisin A is produced, while during oxidative wine aging vitisin B can also form, with subsequent concentration decline [42].

Furthermore, the fate of vitisin-like pyranoanthocyanins appears to be accelerated by oak chip addition, particularly when applied during malolactic fermentation. Previous studies on Merlot and Petit Verdot wines in contact with chips after malolactic fermentation reported slight decreases in B-type vitisins and nearly unchanged levels of A-type vitisins [36,37].

Interestingly, the total content of vitisin-like pyranoanthocyanins closely correlates with the total monomeric anthocyanin content in each wine (regression coefficient, $R^2 = 0.828$). Therefore, all types of monomeric anthocyanins and vitisin-like pyranoanthocyanins decreases with the addition of oak chips during malolactic fermentation. This effect may be attributed to the longer duration of chip maceration during malolactic fermentation (approximately 20 days) compared to other treatments (7 days).

In terms of hydroxyphenyl-pyranoanthocyanins, the primary compound found in all studied wines was 10-(4‴-monohydroxy)phenyl-pyranomalvidin 3-glucoside (10-MHP-pyrmv-3-glc), formed by the reaction of mv-3-glc with p-coumaric acid. This was followed by 10-(3‴,4‴-dihydroxy)phenyl-pyranomalvidin 3-glucoside (10-DHP-pyrmv-3-glc), also known as pinotin A, resulting from the reaction of mv-3-glc with caffeic acid. These findings align with reported data for young red wines [27].

Wines treated with oak chips during malolactic fermentation (MAF wines) exhibited lower quantities of 10-MPH-pyrmv-3-glc and 10-DHP-pyrmv-3-glc compared to other wines, including the control wine. This effect was more pronounced with higher chip doses (MFA6 wines). Similar to vitisin-type pyranoanthocyanins, the total content of hydroxyphenyl-pyranoanthocyanins correlated with the total monomeric anthocyanin content ($R^2 = 0.839$), although their formation can be influenced by other competitive reagents, such as condensed tannins which are responsible for the astringent and bitter properties of wines [43].

In summary, oak chip treatment during malolactic fermentation resulted in less favorable outcomes in terms of anthocyanin-related pigments. Although the characteristic anthocyanin profile remained largely unchanged, a significant decrease in total monomeric anthocyanin content was observed. Additionally, parallel reductions in pyranoanthocyanin concentrations were closely associated with this loss of monomeric anthocyanins.

3.3.2. Flavonols

The flavonol composition in the studied Bobal wines closely resembled that found in other red wines. These flavonols consist of a diverse blend of native grape flavonol 3-glycosides (such as 3-galactosides, 3-glucuronides, and 3-glucosides of quercetin, kaempferol, and myricetin) along with their respective free flavonol aglycons, which are liberated through hydrolysis in the winemaking process [24].

In order to make the statistical analysis of flavonol profiles, the flavonols were classified based on their common aglycon structure and respective 3-glycosides. A total of six aglycon-type flavonol groups were identified. The main families of flavonol were quercetin-type and myricetin-type, accounting for 24.77–33.14% and 27.93–30.66%, respectively. Isorhamnetin-, syringetin-, laricitrin-, and kaempferol-type flavonols followed, with varying percentages (Table 4).

Interestingly, the flavonol profile of Bobal wines differed significantly from that of their respective grapes [17]. Non-methoxylated flavonols decreased in percentage (e.g., 49.06–42.82% for quercetin-type, 31.35–36.63% for myricetin-type, and 6.94–7.43% for kaempferol-type flavonols in grapes), while methoxylated flavonols increased (e.g., 3.79–4.00% for isorhamnetin-

type, 5.40–6.27% for laricitrin-type, and 3.25–4.05% for syringetin-type flavonols in grapes). These differences persisted regardless of oak chip treatment for quercetin-, laricitrin-, and kaempferol-type flavonols, likely due to variations in solid-liquid partition coefficients.

Table 4. Mean molar percentages of aglycon-type flavonol profiles and mean concentration (µmol/L) of total flavonol (SD n = 2).

Flavonol	CW		AFA3		AFA6		MFA3		MFA6		PFA3		PFA6	
myricetin-type	28.99	1.51	27.93	1.21	30.66	1.64	28.21	1.74	30.51	1.82	28.00	1.14	29.99	3.21
quercetin-type	24.77 ^{a}	2.31	27.78 ^{b,c}	1.58	26.21 ^{b}	2.11	30.94 ^{c}	2.11	31.76 ^{c}	1.58	33.14 ^{c}	2.21	30.20 ^{c}	2.44
laricitrin-type	8.02	0.98	8.01	0.78	9.15	0.65	9.09	0.40	9.28	0.94	9.51	0.31	8.75	0.35
kaempferol-type	3.57	0.17	4.05	0.41	3.68	0.32	3.95	0.24	3.98	0.21	3.88	0.14	3.75	0.21
isorhamnetin-type	14.49 ^{a}	0.31	15.07 ^{a}	0.28	16.39 ^{b}	0.19	16.62 ^{b}	0.18	16.37 ^{b}	0.17	16.34 ^{b}	0.24	16.79 ^{b}	0.24
syringetin-type	20.16 ^{g}	0.15	17.15 ^{f}	0.41	13.90 ^{e}	0.18	11.20 ^{d}	0.22	8.11 ^{a}	0.14	9.13 ^{b}	0.21	10.52 ^{c}	0.31
total flavonols *	273.6 ^{a}	8.24	281.4 ^{a}	10.11	279.8 ^{a}	7.21	270.3 ^{a}	9.21	286.4 ^{a}	8.75	299.1 ^{a,b}	11.14	305.3 ^{b}	7.54

According to the Student–Newman–Keuls test ($p < 0.05$), different letters (a,b,c) on the same row indicate significant differences in the mean values * µmol/L.

However, the percentages of quercetin-, isorhamnetin-, and syringetin-type flavonol families were significantly higher in oak chip-added wines, especially when contact of wine and chips occurs during malolactic fermentation (MFA) and with young wines (PFA). This indicates that oak chips affect not only the sensory attributes but also the insolubilization, precipitation, hydrolysis flavonol 3-glycoside, and flavonol oxidation in wine.

Overall, the total concentration of flavonol Bobal wines remained relatively stable, even with oak chip addition (Table 4). Only a slight, yet significant, increase in total flavonols was observed when the contact of wines and chips occurs in young red wines (PFA wines). Despite these variations, all Bobal wines exhibited high flavonol levels (mean value, 270.3–305.3 µmol/L), which are consistent with the reported concentrations for red wines (ranging from 81 to 274 µmol/L) [44].

3.3.3. Flavan-3-ols

Table 5 and Figure S5 of Supplementary Materials include the results of the flavan-3-ol monomers *(+)*-catechin, *(-)*-epicatechin, and *(-)*-epigallocatechin that were detected in the studied red wines, consistent with previous research [17,38,39]. The main flavan-3-ol monomer across all wines was *(+)*-catechin (mean concentration ranging from 29.54 to 38.54 mg/L), followed by *(-)*-epicatechin (mean concentration ranging from 20.14 to 27.66 mg/L) and *(-)*-epigallocatechin (mean concentration ranging from 3.89 to 6.21 mg/L). Interestingly, the amounts of these flavan-3-ols remained relatively stable or showed slight decreases when the wines were in contact with oak chips.

Table 5. Mean Concentration (mg/L) and SD (n = 2) of Flavan-3-ol profiles.

	(+)-Catechin	(-)-Epicatechin	(-)-Epigallocatechin
CW	38.54 ^{c} 1.12	26.66 ^{c} 1.54	5.27 ^{b} 0.45
AFA3	30.44 ^{a} 1.54	20.14 ^{a} 1.07	4.12 ^{a} 0.34
AFA6	34.74 ^{b} 1.14	20.55 ^{a} 0.89	5.44 ^{b} 0.44
MFA3	35.21 ^{b} 0.98	21.87 ^{a} 1.04	3.89 ^{a} 0.34
MFA6	38.22 ^{c} 1.05	25.68 ^{b,c} 2.12	6.21 ^{c} 0.74
PFA3	29.54 ^{a} 0.97	23.07 ^{b} 0.77	3.98 ^{a} 0.61

Table 5. *Cont.*

	(+)-Catechin	(-)-Epicatechin	(-)-Epigallocatechin
PFA6	35.78 [b]	23.11 [b]	4.39 [a,b]
	1.11	0.82	0.47

[a,b,c] According to the Student–Newman–Keuls test ($p < 0.05$), different letters on the same column indicate statistical differences among mean values.

3.3.4. Hydroxycinnamic Acid Derivatives (HCAD)

Table 6 and Figure S6 of Supplementary Materials show the hydroxycinnamic acid derivatives (HCAD), including the anticipated hydroxycinnamoyl-tartaric acids native to grapes (such as caftaric and coutaric acids) as well as certain byproducts formed during the winemaking process. These derivatives included caffeic and p-coumaric acids (free hydroxycinnamic acids) that were released via hydrolysis, ethyl caffeate, and ethyl coumarate.

Table 6. Molar percentages of hydroxycinnamic acid derivatives (HCAD) profiles and mean concentration total (SD n = 2) of HCAD.

HCAD	CW		AFA3		AFA6		MFA3		MFA6		PFA3		PFA6	
caftaric acid	61.20 [b]	2.22	61.03 [b]	1.78	58.37 [b]	2.24	62.63 [b]	1.91	60.27 [b]	2.54	52.91 [a]	1.32	50.98 [a]	1.39
coutaric acid	17.03 [a,b]	1.19	15.01 [a]	0.97	19.17 [b]	1.01	14.59 [a]	0.98	14.66 [a]	0.99	14.48 [a]	1.07	15.71 [a]	1.14
caffeic acid	7.08 [a]	0.76	8.14 [a]	0.85	8.00 [a]	0.79	7.27 [a]	0.83	8.62 [a]	0.95	10.06 [a,b]	1.03	11.15 [b]	0.52
p-coumaric acid	5.20 [a]	0.82	6.08 [a]	0.91	6.39 [a]	0.75	6.98 [a]	0.96	7.36 [a]	1.08	12.95 [b]	0.54	13.20 [b]	0.77
ethyl caffeate	1.04 [a,b]	0.32	1.51 [b]	0.21	0.78 [a]	0.12	0.67 [a]	0.23	1.06 [a,b]	0.15	1.88 [b]	0.19	1.82 [b]	0.29
ethyl coumarate	8.46 [b]	0.32	8.25 [b]	0.31	7.31 [a]	0.39	7.86 [a,b]	0.16	8.03 [b]	0.25	7.73 [a,b]	0.45	7.14 [a]	0.47
total amount *	178.94 [a,b]	11.4	176.33 [a,b]	12.1	182.87 [a,b]	12.3	163.13 [a]	12.1	160.12 [a]	11.9	194.57 [b]	12.1	205.90 [b]	9.91
caffeic-type	69.31 [b]	2.01	70.67 [b]	1.28	67.14 [b]	1.81	70.56 [b]	1.89	69.95 [b]	1.95	64.84 [a]	0.54	63.94 [a]	1.68
p-coumaric-type	30.69 [a]	1.33	29.33 [a]	1.25	32.86 [a]	1.45	29.44 [a]	1.77	30.05 [a]	1.57	35.16 [b]	1.17	36.06 [b]	1.22
% hydrolysis **	22.22 [a]	1.56	21.09 [a]	1.78	25.55 [a,b]	2.74	21.57 [a]	1.98	22.02 [a]	1.47	27.43 [b]	1.48	28.91 [b]	1.07
% ethyl esters	9.50	0.87	9.75	1.02	8.08	1.01	8.53	0.74	9.08	0.49	9.60	0.65	8.96	0.88

According to the Student–Newman–Keuls test ($p < 0.05$), different letters (a,b) on the same row indicate significant differences in the mean values.* µmol/L; ** total sum of percentages of caffeic and *p*-coumaric acids (free hydroxycinnamic acids) and their ethyl esters.

When comparing the wines, there were no notable differences detected between the control wine and wines in contact with oak chips during alcoholic fermentation (AFA wines) and malolactic fermentation (MFA wines). Nevertheless, young Bobal wines in contact during seven days (PFA wines) exhibited distinct hydroxycinnamic acid derivative profiles, primarily associated with increased hydrolysis (27.43% and 28.91%). Remarkably, the percentage of ethyl esters did not significantly change in these cases. Among the PFA wines, PFA3 and PFA6 had the lowest levels of caffeic-type hydroxycinnamic acids and the highest levels of p-coumaric-type. Also, the concentration of hydroxycinnamic acid derivative concentrations was elevated (194.57 and 205.90 µmol/L, respectively). The overall impact of oak chip addition on these differences was not significantly influenced by the number of chips added, except for a higher proportion of coutaric acid and a lower percentage of ethyl esters observed in AFA6 wines compared to AFA3 wines.

3.3.5. Resveratrol-Based Monomeric Stilbenes

Table 7 includes the results obtained for stilbene monomers based on resveratrol, *cis* and *trans* isomers of resveratrol and its 3-glucoside (piceid) these compounds in the studied wines (Figure S7 of Supplementary Materials). The natural form of resveratrol that exists in grapes is piceid, which, during the vinification process, decreases its solubility due to its partial hydrolysis. Additionally, the *trans* isomers of piceid and resveratrol of grapes can be easily transformed under UV light into their corresponding *cis* isomers.

Table 7. Mean concentration (SD n = 2) of resveratrol, piceid and total resveratrol, and molar percentages of *trans*- and *cis*- isomers.

	***trans*-Piceid ***	***cis*-Piceid ***	***trans*-Resveratrol ***	***cis*-Resveratrol ***	**% total *trans*-Isomers**	**% total *cis*-Isomers**	**total Resveratrol ****
CW	12.18 ^{e} 0.67	72.53 ^{f} 0.62	11.12 ^{b} 0.28	29.13 ^{c} 1.11	18.65 1.11	81.35 1.21	34.74 ^{f} 1.14
AFA3	10.75 ^{d} 0.27	64.50 ^{e} 0.97	8.95 ^{a} 0.77	23.30 ^{b} 0.92	18.33 1.25	81.67 1.29	29.88 ^{e} 0.88
AFA6	9.56 ^{b,c} 0.57	58.26 ^{d} 0.70	8.56 ^{a} 0.49	21.79 ^{b} 0.81	18.46 1.12	81.54 1.61	27.29 ^{d} 1.13
MFA3	9.87 ^{c} 0.28	47.61 ^{c} 0.81	8.28 ^{a} 0.59	23.07 ^{b} 0.77	20.43 1.30	79.57 1.89	24.70 ^{c} 1.21
MFA6	8.80 ^{b} 0.46	43.25 ^{b} 0.85	7.58 ^{a} 0.57	20.45 ^{a} 1.21	20.45 1.29	79.55 1.02	22.26 ^{b} 1.14
PFA3	7.95 ^{b} 0.66	44.68 ^{b} 0.91	8.05 ^{a} 0.59	22.80 ^{b} 0.82	19.17 1.18	80.83 1.29	23.21 ^{b} 0.99
PFA6	6.51 ^{a} 0.56	38.99 ^{a} 0.84	7.38 ^{a} 0.69	19.76 ^{a} 0.71	19.12 1.29	80.88 1.31	20.19 ^{a} 1.14

According to the Student–Newman–Keuls test ($p < 0.05$) different letters (a,b,c,d,e,f) on the same column indicate significant differences of the mean values. * µmol/L. ** mg/L, as resveratrol equivalents.

The concentrations of piceid and resveratrol, along with their cis/trans isomers, were significantly higher in the control wine (CW) compared to wines treated with oak chips. The total resveratrol content (sum of all resveratrol forms, expressed as mg/L of resveratrol equivalents) varied based on the timing of oak chip addition: Alcoholic Fermentation Addition (AFA) > Malolactic Fermentation Addition (MFA) > Post Fermentation Addition (PFA). Furthermore, the total resveratrol content depended on the amount of oak chips added (3 g/L > 6 g/L), with the 6 g/L dose resulting in a 10% decrease compared to the 3 g/L dose. This reduction could be attributed to the preferential adsorption of resveratrol-type stilbenes onto the oak chips.

When considering only trans-resveratrol, the highest levels were observed in wine control (CW), while the wines in contact with oak chips wines did not significantly differ in their trans-resveratrol content. Interestingly, no clear trend was observed regarding the extent of trans/cis isomerization and piceid hydrolysis based on the timing and dose of oak chip addition.

Overall, the concentration of total resveratrol content in Bobal wines from La Mancha region (ranging from 20.19 to 34.7 mg/L, expressed as resveratrol equivalents) exceeded reported values for other red wines from Spain (ranging from 0.60 to 8.0 mg/L) [45], Italian wines (ranging from 0.17 to 10.79 mg/L) [46], and wines from Argentina, Australia or United States exhibit mean concentrations ranged between 5 and 6 mg/L [47]. Consequently, these Bobal wines, including those treated with oak chips, can be labeled as having a high content of total resveratrol. Furthermore, when focusing solely on trans-resveratrol, these Bobal wines nearly reach the highest levels observed in red wines.

3.4. Chromatic Characteristics and Co-Pigmentation Degree

The hue of red wine results from a sophisticated interaction of physical and chemical mechanisms, with anthocyanins playing a central role. These mechanisms encompass proton transfer, anthocyanin hydration, co-pigmentation with other often colorless phenolic compounds, and the creation of pigments derived from anthocyanins. Accurately forecasting the precise color attributes of red wines based solely on their anthocyanin content proves to be difficult.

Chromatic characteristics and the influence of co-pigmented anthocyanins on the overall wine color at pH 3.6 are shown in Table 8. Interestingly, contact of wines with oak

chip shavings did not significantly modify the color intensity L* (luminosity). However, the chroma parameter (C*) was modified by the contact of the wine with the oak chips. Control wines and wines in contact during alcoholic fermentation at the 3 and 6 g/L dose levels exhibited higher C* values, suggesting more vivid colors compared to the other samples, which appeared duller. These findings imply that adding oak chips during later stages of winemaking (during or after malolactic fermentation) may reduce color purity (MFA and PFA wines).

Table 8. Mean values and SD (n = 2) of CIELCh parameters and % of copigmentation.

	L*	C*	h*	% Copigmentation
CW	79.12 2.35	22.16 ^{b} 1.07	357.8 ^{b} 1.50	5.45 ^{a} 2.04
AFA3	78.15 2.15	23.72 ^{b} 1.67	354 ^{a,b} 2.76	6.33 ^{a} 0.87
AFA6	78.11 2.81	22.84 ^{b} 1.57	355.5 ^{a,b} 2.91	7.21 ^{a,b} 1.99
MFA3	81.23 2.49	20.48 ^{a,b} 2.13	352.2 ^{a} 1.40	6.44 ^{a} 0.79
MFA6	80.36 1.92	19.51 ^{a} 1.16	351.4 ^{a} 1.15	8.21 ^{b} 0.59
PFA3	82.77 1.95	17.71 ^{a} 2.34	351.1 ^{a} 1.25	8.31 ^{b} 0.44
PFA6	79.75 2.17	19.73 ^{a} 0.71	351.3 ^{a} 1.87	8.44 ^{b} 0.54

According to the Student–Newman–Keuls test ($p < 0.05$), different letters (a,b) on the same column show statistically differences among the mean values.

The extent of copigmentation increased with the dose of oak chips and the timing of their addition. Greater copigmentation led to an increase in violet tones (lower h*, hue angle), consistent with the expected bathochromic effect associated with copigmentation. Additionally, the greater concentration of vitisin-type pigments (Table 3) related to the red-orange tones found in CW and AFA wines could influence the less pronounced violet tones in their red color (highest h* values).

4. Conclusions

The addition of oak chips to Bobal wines at the 3 and 6 g/L dose levels in different winemaking stages influenced their antioxidant activity, chromatic characteristics, and phenolic composition, but only slightly significant differences were observed. The primary contributors to anthocyanin profiles, specifically non-acylated and acetylated anthocyanins, were not significantly altered by the contact of oak chips with wines at different winemaking stages, and the overall antioxidant capacity remained consistent. Wines in contact with oak chips after both fermentations (PFA wines) exhibited distinct hydroxycinnamic acid derivative profiles. Notably, oak chip addition during malolactic fermentation had the most pronounced effects, particularly in reducing the content of non-polymeric red pigments and enhancing the level of copigmentation, which are probably attributed to the prolonged contact time of wines and oak chips at this stage. Wines in contact with 6 g/L of oak chips, regardless of the point of addition, generally presented lower total resveratrol concentrations compared to when 3 g/L were used.

These findings may serve as valuable guidance for winemakers to select the point of addition and the dose level according to the sensory profile demanded by consumers in La Mancha Bobal wines due to the minimal changes in phenolic profiles and related properties during the stage of contact between Bobal wine and oak chips.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/beverages10030089/s1, Figure S1: Mean values of conventional analysis of Bobal wines. * mg/L of tartaric acid; ** mg/L of acetic acid; *** mg/L as gallic acid; **** mmol/L of Trolox equivalents; Figure S2: Percentages of each individual anthocyanin over the total amount; Figure S3: Mean concentration of individual and total pyranoanthocyanins; * mg/L, as vitisin A equivalents; ** mg/L, as 10-DHP-pyrmv-3-glc equivalents; Figure S4: Mean molar percentages of aglycon-type flavonol profiles; Figure S5: Mean Concentration of Flavan-3-ol profiles; Figure S6: Molar percentages of *cis* and *trans* resveratrol and piceid isomers; Figure S7: Mean concentration of *cis* and *trans* resveratrol and piceid isomers; Table S1: Details on the calibration curves for phenolic compounds and antioxidant activity.

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