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Oenological Tannins from Different Sources and Their Impact on Color and Phenolic Evolution of a Rosé Wine

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Abstract

This study evaluates the impact of eight commercial oenological tannins—sourced from grape seed, grape skin, cherry, quebracho, acacia, tara, chestnut, and oak—on the phenolic composition and color evolution of a rosé wine during oxidative storage. The tannins were initially characterized for their phenolic richness, antioxidant capacity, oxygen consumption rate, and iron chelating ability. Their effects were then assessed in a lab-scale rosé wine produced without sulfur dioxide, where each tannin was added individually. Results revealed that condensed tannins, particularly from grape skins, significantly enhanced the initial color intensity, while hydrolyzable tannins such as chestnut and oak better preserved color stability over time. Chestnut tannin showed the highest antioxidant and oxygen consumption activities, correlating with its greater performance in limiting oxidative degradation. Although some tannins contributed to anthocyanin loss, evidence suggests a role in promoting pigment polymerization and color stabilization.

Keywords: wine oxidation; anthocyanins; CIELab indexes; oxygen consumption; iron chelation; antioxidant capacity

1. Introduction

Wine's taste, smell, and mouthfeel are greatly influenced by phenolic compounds, which could play a crucial role in the overall acceptance of oenological products by consumers [1]. In wines, these molecules include flavonoids such as condensed tannins and anthocyanins, as well as, to a lesser extent, flavones and phenolic acids [2]. During the winemaking process and as wine ages, certain phenolics could evolve and/or degrade, leading to changes in composition and alterations in the wine's sensory profile. Anthocyanins, for example, may undergo oxidative and condensation phenomena, turning into orange-shaded pigments [3], while phenolic acids and flavanols oxidize, becoming prooxidant species [4]. To counteract these effects and enhance the wine's overall quality, the use of exogenous oenological tannins has emerged in recent years as a valuable technological tool [5,6]. In winemaking, a wide variety of exogenous tannins are used, differing in origin, structure, and composition, and offering producers a broad range of functional properties to select from [5]. Additionally, their effectiveness is influenced by the chemical composition, particularly the type and concentration of active tannin molecules [6].

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The oenological use of tannins is now widespread thanks to their recognized properties [7]. These include acting as antioxidants to protect wine from oxidation and scavenging free radicals [8,9]. It has been reported that oenological tannins can chelate iron and directly consume dissolved oxygen [10,11], co-pigment with existing pigments, enhancing the color, and even contribute to the formation of entirely new pigments [9]. Tannins are commonly divided into two main classes: hydrolyzable and condensed tannins [5,7]. Hydrolyzable tannins have a complex structure centered around a sugar unit (glucose) esterified with various phenolic acids. They can be classified as gallotannins or ellagitannins based on whether they contain gallic acid or ellagic acid moieties [12]. Some examples of hydrolyzable tannins comprise nut galls, chestnut (*Castanea sativa* Mill.), and oak (*Quercus* spp.) tannins. Condensed tannins may come from various plants, including grapes (*Vitis vinifera* L.), quebracho (*Schinopsis lorentzii* L.), and acacia (*Acacia catechu* Lf.), among others [6]. They contain flavan-3-ol oligomers and polymers, which after hydrolysis give (+)-catechin, (−)-epicatechin, profisetidin or prorobinetidin [13]. While the impact of oenological tannins on red wine stability has been explored in various studies [6,9], their application in rosé wines remains relatively understudied. Rosé wines, in fact, differ from red wines in their production process, which involves shorter macerations, lighter color, lower phenolic content and a fresher flavor profile. They often exhibit delicate fruit and floral notes, contrasting with the structured, harsher features of red wines. The anthocyanin to tannin ratio determines the color range of rosé wines (from pale pink to darker shades) and their respective proportions influence the overall color evolution during shelf life [14]. Puyo et al.'s research [15] stands among the few studies that have investigated the effects of oenological tannins in rosé wines, concluding that hydrolyzable tannins can protect the color of rosé musts vinified in the absence of sulfite.

In our study, eight oenological tannins from diverse sources were chemically characterized in terms of phenolic content, oxygen consumption rate, and antioxidant capacity. Additionally, their impact on the color evolution of a rosé wine during oxidative storage was assessed. Samples were analyzed by both spectrophotometric and HPLC approaches to highlight the changes in wine phenolic composition and color attributes during a two-month storage time. The research aimed to determine the beneficial impact of the various tannins on rosé wine color quality, especially in terms of better color retention and resistance to phenolic degradation during storage.

2. Materials and Methods

2.1. Reagents

Ascorbic acid, (+)-tartaric acid, catechin-(+), gallic acid, Fe(II) sulphate heptahydrate, Fe(III) chloride, sodium acetate, 4-dimethylaminocinnamaldehyde (DMAC) and potassium chloride were obtained from Sigma-Aldrich (Milano, Italy). We additionally acquired HPLC-grade acetonitrile, acetic acid, formic acid, 37% HCl, 97% ethanol, methanol for HPLC, Folin–Ciocalteu phenol reagent (FC), sodium carbonate, and ethylenediaminetetraacetic acid (EDTA). Potassium persulfate (di-potassium peroxydisulfate) was obtained from Carlo Erba (Milano, Italy). 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p′-disulfonic acid monosodium salt hydrate (Ferrozine), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) and 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) were purchased from Fluka (Charlotte, NC, USA). MilliQ water was used for all the solutions.

2.2. Oenological Tannins, Wine Samples and Storage Conditions

Eight commercially available oenological tannins of different origins were obtained from Bioenol S.r.l. (Broni, Italy) and grouped as condensed tannins (procyani-

dins/prodelphinidins (PC/PD) and profisetidins/prorobitenidins (PF/PR)) and hydrolyzable tannins (gallotannin (GT) and ellagitannins (ET)) (Table 1). They were characterized in a model wine solution composed of 4 g/L tartaric acid and 12% ethanol, buffered at pH 3.2 with 2 M NaOH, and their concentration varied from 0.05 to 5 g/L based on the analytical determination being performed.

Table 1. Code, botanical origin, and classification of investigated oenological tannins.

Tannin Code		Botanical Origin	Tannin Class	Tannin Subclass *
GSK	Grape skin	*Vitis vinifera* L.	Condensed	PC/PD
GSE	Grape seeds	*Vitis vinifera* L.	Condensed	PC/PD
PRU	Cherry	*Prunus avium* L.	Condensed	PC/PD
ACA	Acacia	*Acacia catechu* Lf.	Condensed	PF/PR
SCH	Quebracho	*Schinopsis lorentzii* L.	Condensed	PF/PR
TAR	Tara	*Caesalpinia spinosa* L.	Hydrolyzable	GT
OAK	Oak	*Quercus petraea* L.	Hydrolyzable	ET
CHT	Chestnut	*Castanea sativa* Mill.	Hydrolyzable	ET

*: PC/PD = Procyanidins/Prodelphinidins; PF/PR = Profisetidins/Prorobitenidins; GT = Gallotannins; ET = Ellagotannins.

A lab-scale vinification was conducted using a blend of 70% Sangiovese and 30% Merlot grapes. Grapes were pressed using a manual press and macerated in three 5 L bottles for approximately 12 h until a typical rosé wine color was achieved (about 0.5 Abs units at 520 nm). Racked must was inoculated with UVAFERM CM™ Saccharomyces cerevisiae yeasts (Lallemand, Blagnac, France) after the rehydration of about 1.5×10^6 CFU mL^{-1} cells. Sealed glass fermenters, specifically designed to be airtight to prevent contamination and oxygen ingress, were employed after being thoroughly cleaned and sterilized. Both maceration and fermentation were conducted without the addition of sulfur dioxide (SO_2). Fermentation progress was monitored by tracking fermenters' weight loss up to the completion of fermentation (indicated by a constant weight for 36 h). Following cold stabilization (48 h at 2 °C), the oenological tannins were individually added to each of the three rosé wines, at a final concentration of 200 mg/L, resulting in eight distinct triplicated treatments (500 mL each). For each replicated series, a control sample, consisting of the same rosé wine without any tannin addition, was also included. Wines (20 mL) were poured into 25 mL screw-capped glass vials (5 mL of headspace was left) and the color and phenolic evolution of the samples were observed over two months of storage in the dark at 20 °C. Samples were analyzed at four sampling points (7, 21, 35 and 56 d) for a total of 108 experimental samples. All the following analyses were done in duplicate.

2.3. Characterization of Tannins Phenolic Richness

Following the spectrophotometric approach proposed by OIV for the determination of the botanical origin of tannins [16], the phenolic content of the eight tannins was evaluated as a function of the response to the FC, Bate-Smith (BS), and DMAC assays and absorbance at 280 nm. A similar set of spectrophotometric methods was used by Vignault to characterize 36 oenological tannins [5]. Phenolic content was expressed as richness % (g of phenolics/100 g of commercial formulation).

The total polyphenol index (TPI) was determined using the FC colorimetric method, according to the method of Singleton et al. [17]. Briefly, in a 20 mL flask, 1 mL of tannin solution diluted in water (1:20), 1 mL of Folin–Ciocalteu reagent and 4 mL of aqueous sodium carbonate (10% w/v) were added and brought to the mark. After 120 min, the absorbance at 750 nm was measured against a blank made by substituting the sample with 1 mL of water. The results were expressed as grams of gallic acid equivalents (GAE) per 100 g of product.

In addition, the spectrophotometric absorbance at 280 nm of each tannin solutions, appropriately diluted with 10% ethanol/water, was acquired to determine total phenols. Phenolic richness was expressed as GAE [1] in the case of hydrolyzable tannins and catechin equivalents (CE) for condensed tannins [5].

An adaptation of the BS method was also performed on tannins at a concentration of 5 g/L, as reported by Vignault et al. [5]. Sample (20 µL), water (1.48 mL) and hydrochloric acid (1.5 mL, 37%) were placed in two test tubes. Tube A was placed in an ice bath (0 °C) while tube B was placed in a hot bath (100 °C). After 30 min, 600 µL of ethanol was added to both the tubes. The absorbance of each test tube was measured in a spectrophotometer (Model V 730, Jasco, Cremella, Italy) at 550 nm using deionized water as the blank. The absorbance difference was multiplied by the factor 19.33 (the absorptivity coefficient of cyanidin after the acidic cleavage of the condensed tannins [18]) and was expressed as tannin equivalents (g of tannin/100 g of commercial formulation). Although this method is specific for procyanidins, it was also applied to hydrolyzable tannins to verify the purity of those formulations.

Tannins were also tested by the DMAC assay [16,19]. Briefly, the DMAC reagent was prepared daily by dissolving 100 mg of 4-dimethylaminocinnamaldehyde in 75 mL of 100% methanol and the volume was adjusted to 100 mL with 37% HCl. The concentration of tannin solutions varied depending on the tannin source and its response to the DMAC assay; e.g., hydrolyzable tannins were used at 5 g/L while condensed tannins were tested at 0.5 g/L. A 500 µL diluted tannin solution (1:5) was mixed with 2.5 mL of the reagent. The absorbance was measured at 640 nm using a 10 mm cuvette once it reached its maximum value (within 3 to 5 min). The concentration as catechin equivalents (CE) resulted from a calibration curve, made by dissolving (+)-catechin in 10% ethanol. Stock solutions were prepared at 0.1; 0.2; 0.5, 1; 2; 5; 10 mg/L.

2.4. Oxygen Consumption of Oenological Tannins

The kinetics of oxygen consumption of pure tannins over two weeks were investigated according to Pascual et al. [11]. The analyses were carried out in a model wine solution consisting of 12% ethanol (*v*/*v*), 4 g/L tartaric acid, and pH adjusted to 3.2. Once saturated with oxygen after 12 h agitation at open air, the model wine was supplemented with 5 mg/L of Fe(II) in the form of ferrous sulphate, and each tannin solution was prepared at a concentration of 5 g/L in model wine. Measurements were conducted in clear 50 mL tightly closed bottles completely filled with the model wine solutions and provided with sensor patches (PreSens Precision Sensing GmbH, Regensburg, Germany) to be read by luminescence with a Nomasense Oxygen Analyzer (Nomacorc S.A., Thimister Clermont, Belgium) in a non-invasive fashion. Oxygen consumption (OC) was monitored for two weeks. All analytical procedures were triplicated for increased data reliability and expressed as OCRt0 (mgO_2/L·day·g) following the calculation proposed by Pascual et al. [11]. For each tannin solution this calculation allowed the comparison of instantaneous oxygen consumption to assess their efficacy under that specific experimental condition.

2.5. Antioxidant, Chelating and Reducing Capacity of Oenological Tannins

The antioxidant capacity of the different oenological tannins was measured using TEAC (Trolox equivalent antioxidant capacity) assay [20]. The ABTS radical solution was prepared the day before using 7 mM ABTS (equivalent to 3.84 g/L) and 2.45 mM potassium persulfate (equivalent to 0.66 g/L) dissolved in water. This solution was then stored in darkness at room temperature for 12–16 h. Ethanol was subsequently added to achieve the desired absorbance of 0.70 ± 0.02 au. A 2 mL solution was then mixed with 20 µL of each tannin solution at 200 mg/L, or with ethanol to in the case of the blank. The

absorbance was measured at 734 nm immediately (t = 0) and every minute up to 6 min (t = 6). The antioxidant capacity was calculated as the percentage inhibition using the formula (absorbance of blank (t = 6)—absorbance of sample at (t = 6))/absorbance of ABTS at t = 0. This percentage inhibition was then converted to Trolox equivalents using a calibration curve with a Trolox standard solution. The iron chelating ability (ICA) was determined on tannins dissolved in model solution at 250 mg/L [21]. A 1 mL solution was transferred to a tube containing 10 µL of a 3.5% ferrozine aqueous solution. The contents of the test tube were briefly mixed and we immediately added 1.5 mL EDTA at 0.005% aqueous solution. The absorbance measurements were made 1 min after the addition of EDTA to determine Fe(II) contents in the solutions. For total iron determination, EDTA was replaced with 1.5 mL of ascorbic acid aqueous solution (0.1%) in a separate tube. Absorbance measurements were taken after the absorbance stabilized and all Fe(III) had been completely reduced to Fe(II), which took up to 30 min. All absorbance measurements were made at 562 nm against a blank (2.5 mL model wine, 10 µL ferrozine solution). The obtained absorbance values were used to calculate the concentrations of Fe(II) and total iron (Fe(tot)) based on a calibration curve built by using stock solutions of ferrous sulphate heptahydrate at 0.1; 0.2; 0.5; 1; 2; 4; 5 mg/L. The concentration of Fe(III) was calculated by subtracting the Fe(II) concentration from the Fe(tot) concentration.

The validated ferrozine method [21] was also used by our research group to build a novel assay to evaluate the reducing capacity of the tannins. This method is here referred to as the RAFI (Reducing Activity on Ferric Ions) assay and may be considered another way to express the antioxidant activity of a sample. In the RAFI assay, solutions containing 200 mg/L of each of the eight tannins were prepared, and the amount of Fe(II) produced by each tannin after its addition to a 2 mg/L Fe(III) solution was recorded. To this aim, 20 µL of a 3.5% ferrozine aqueous solution was added to 2 mL of tannin solution (200 mg/L) and 2 mL of an Fe(III) solution (4 mg/L Fe using $FeCl_3$) and read at 562 nm in a 1 cm cuvette after 5 min. For blank, ferrozine was substituted with 10% hydroalcoholic solution. Results were expressed as Trolox equivalents (mg Trolox/g tannin) obtained by means of a calibration curve where Trolox is used in the cuvette instead of the sample as a reference antioxidant molecule.

2.6. CIELAB Color Parameters and Tannin Content of Laboratory-Scale Rosé Wine

The color evolution of the base wine and the eight rosé wines after tannin addition was monitored according to Glories [1]. Measurements were performed with a Jasco V-730 spectrophotometer equipped with the Chromnav software suite ver. 1.11.02 (Jasco, Cremella, Italy) and a 1 cm path-length cuvette. The derived index dA% (percentage of red produced by the flavylium cation) [22] and the CIELAB parameters L^*, a^* and b^* were also obtained. Additionally, color differences (ΔE^*_{ab}) [23] and color density (CD) were calculated as follows:

$$\Delta E^*_{ab} = \sqrt{\left(L_2^* - L_1^*\right)^2 + \left(a_2^* - a_1^*\right)^2 + \left(b_2^* - b_1^*\right)^2} \qquad CD = \frac{420\ nm}{520\ nm}$$

Total anthocyanin concentration (TA) in wines was determined by using the differential method described by Giusti et al. [24]. For each sample, two tubes were prepared. One of them was diluted with a potassium chloride buffer at pH 1.0, and the other with a sodium acetate buffer at pH 4.5. After 15 min, the absorbance of each dilution was measured at 520 nm, along with measurements at 700 nm (for haze correction), using a blank cell filled with distilled water as a reference. The results were expressed as mg/L of malvidin equivalent (MVDE) using the molar extinction coefficient (ε = 28,000 $M^{-1} * cm^{-1}$) and considering the dilution factor. The determination of phenolic and iron content was also performed

during the wine storage time, using the same methods previously employed in the tannin characterization, e.g., BS [5] and DMAC assays [19] and iron chelating activity [21].

2.7. Anthocyanin Content in Rosé Wines

The anthocyanins in wine samples were quantified according to an established method by Chinnici et al. [25], using an HPLC system equipped with a Jasco PU-2089 quaternary gradient pump, a Jasco AS-2057 Plus Intelligent Sampler autosampler, and a Jasco UV/Vis MD-910 PDA detector (Jasco, Tokyo, Japan) set at 250–600 nm. The column used was a Synergi 4 µm Hydro-RP 80A (Phenomenex, Castel Maggiore, Italy) measuring 250 × 3.0 mm, operating at 0.47 mL/min. Injection volume was 40 µL. The elution program followed this sequence: initial conditions: 85% Solvent A (7% formic acid in bidistilled water) and 15% Solvent B (formic acid:acetonitrile:bidistilled water at a ratio of 7:45:48); at 17 min, the ratio shifted to 70% A and 30% B; after 45 min, the ratio became 27% A and 73% B; at 48 min, it shifted to 0% A and 100% B; by 52 min, it transitioned to 0% A, 0% B, and 100% C (acetonitrile at 100%) and at 55 min, the conditions returned to the initial state with 85% A and 15% B. Quantification was carried out using a calibration curve generated from a pure standard of malvidin-3-*O*-glucoside.

2.8. Low-Molecular-Weight Phenolics of Rosé Wines

The phenolic composition of wines was analyzed by an HPLC-DAD method [26]. The instrumentation was the same as previously described. Analysis was carried out at 35 °C on a Poroshell 120 2.7 mm (4.6 × 150 mm) C18 column (Agilent technologies, Palo Alto, CA, USA) with a flow of 0.8 mL/min. Samples were injected at 10 µL. Elution started with 98% eluent A (2% acetic acid in HPLC-grade water) and 2% eluent B (2% acetic acid in HPLC-grade acetonitrile). Then the gradient was 95% A in 10 min, to 90% A in 7 min, to 83% A in 6 min, to 70% A in 6 min, to 0% A in 6 min, to 98% A in 2 min. Identification was accomplished by using standard solutions of gallic acid (0.2–10 mg/L), protocatechuic acid (0.2–5 mg/L), caffeic acid (0.2–50 mg/L), coumaric acid (0.2–20 mg/L), ferulic acid (0.2–20 mg/L), (+)-catechin (0.2–50 mg/L), (−)-epicatechin (0.2–50 mg/L), quercetin (0.2–20 mg/L), tyrosol (0.2–50 mg/L), and hydroxymethylfurfural (HMF) (0.2–20 mg/L). For each compound, 6 solutions at known concentrations were injected in duplicate. Quantification of phenolic compounds was carried out at each specific wavelength (256 nm for gallic and protocatechuic acids, 280 nm for flavanols and tyrosol, 310 nm for coumaric acid and its tartaric esters, 320 nm for caffeic and ferulic acids and their tartaric esters and derivatives, 360 nm for quercetin) using an external calibration curve obtained by injecting solutions of standard compounds at known concentrations and plotting peak areas vs. concentrations. The amount of tartrate esters of caffeic, coumaric and ferulic acids and Grape reaction Product (GRP) were expressed as the respective hydroxycinnamic acid.

2.9. Statistical Data Processing

ANOVA processing was applied to the data to identify significant differences within the samples for each individual analysis. A Tukey test (HSD) at a significance level of $p < 0.05$ was considered for this purpose and carried out using XLSTAT version 2019.2.2 (Addinsoft, Paris, France) statistical package.

3. Results

3.1. Physicochemical Characterization of the Oenological Tannins

Table 2 shows the phenolic richness, expressed as percentage (g of tannin per 100 g of commercial product), of the eight oenological tannins measured by applying four different spectrophotometric indexes. In previous studies, cherry tannin was indistinctly classified

as hydrolyzable [6] or condensed [27] because of the presence of both gallic polymers and proanthocyanidins. In the present research, cherry was considered as condensed tannin following the results on its phenolic characterization, which will be further discussed below. When tannin richness was calculated by the FC method, the average richness of all the oenological tannins studied was 84.6 ± 12.5%, suggesting these tannins were highly purified. Cherry tannin showed the lowest richness (66.3 ± 2.3%), while grape seed and oak tannin exhibited the highest richness (98.6 ± 0.7% and 98.4 ± 0.9% respectively). No significant differences were found considering the two groups, condensed vs. hydrolyzable, and this may depend on the limited selectivity of this method, which detects phenolic molecules with no differentiation between gallic acid, flavanol monomers, dimers, and larger phenolic compounds [28]. As a faster alternative to FC, the TPI value was obtained by measuring the absorbance at 280 nm (Table 2).

Table 2. Mean phenolic richness of the eight enological tannins as determined by four distinct spectrophotometric indexes. Richness is expressed as a percentage (g of tannin per 100 g of commercial product). In the same column, different lowercase letters indicate significant differences among the single tannins at $p < 0.05$ (n = 6); different uppercase black letters indicate significant differences among the tannins' classes (condensed or hydrolyzable) at $p < 0.05$ (n = 6). For sample codes, see Table 1. FC = Folin–Ciocalteu method; TPI = Total Phenolic Index; DMAC = 4-dimethylaminocinnamaldehyde assay; BS = Bate-Smith assay.

Tannins		FC	TPI (280 nm) *	DMAC	BS
		Richness (%)			
PC/PD	GSK	89.4 ± 1.5 b	92.5 ± 0.7 b	38.1 ± 0.7 c	62.4 ± 0.9 a
	GSE	98.6 ± 0.7 a	99.2 ± 0.2 a	77.3 ± 0.7 a	61.0 ± 1.1 a
	PRU	66.3 ± 2.3 d	68.2 ± 0.5 d	22.8 ± 0.0 d	17.3 ± 0.9 d
PF/PR	ACA	72.9 ± 1.1 c	76.4 ± 0.7 c	57.9 ± 1.0 b	38.3 ± 0.3 c
	SCH	91.4 ± 1.3 b	93.1 ± 0.3 b	8.6 ± 0.1 e	43.3 ± 0.9 b
Condensed		*83.7 ± 13.5 A*	*85.9 ± 13.0 A*	*40.9 ± 27.4 A*	*44.5 ± 18.5 A*
GT	TAR	72.2 ± 1.1 c	22.4 ± 0.3 f	0.5 ± 0.0 f	0.0 ± 0.1 f
ET	OAK	98.4 ± 0.9 a	20.8 ± 0.1 f	0.1 ± 0.0 f	2.3 ± 0.1 e
	CHT	87.5 ± 1.6 b	26.4 ± 0.4 e	0.1 ± 0.0 f	0.0 ± 0.0 f
Hydrolyzable		*86.0 ± 13.2 A*	*23.2 ± 2.9 B*	*0.2 ± 0.2 B*	*0.8 ± 1.4 B*

* expressed as CE (catechin equivalent) for PC/PD and PF/PR, as GAE (gallic acid equivalent) for GT and ET. The italicized text is to highlight that the raw is the mean of the cells above.

In this case, the average richness of tannins was lower with respect to the FC method (62.4 ± 33.9%), in particular for hydrolyzable tannins, which however are in line with other reports [5,27]. Significant differences were found, in fact, in the richness of condensed and hydrolyzable tannins, where grape seed tannin (99.2 ± 0.2%), grape skin tannin (92.5 ± 0.7%), and quebracho tannin (93.1 ± 0.3%) were significantly higher in richness than other tannins. Despite some drawbacks of this method, such as the interference from non-phenolic compounds and the lack of information about the type of phenolics measured [28], according to Vignault et al. [5] it may represent an easy way to discriminate tannins as a function of their class. In contrast, BS and DMAC assays offer a more targeted approach, specifically estimating the total proanthocyanidin content [29]. Due to this, those methods have been reported not to be suitable to analyze hydrolyzable tannins, because of their negligible content of proanthocyanidins [28]. Still, it was interesting to check all the tannins to confirm their respective origins. The BS assay is a colorimetric method based on the highly specific hydrolytic reaction of proanthocyanidins in a heated acidic medium to give colored anthocyanin pigments [30]. As expected, this method revealed significant

differences between the two groups: condensed tannins exhibited, in fact, higher richness (44.5 ± 18.5%) compared to hydrolyzable tannins (0.8 ± 1.4%). For condensed tannins, these percentages confirmed the ones obtained in a previous study [6]. It is worth mentioning that the marked differences between PC/PD and PF/PR may depend on the resistance to acidic hydrolysis of the latter [31]. Furthermore, cherry emerged as the poorest in the Bate-Smith assay among the condensed tannins. The DMAC assay [19] is based on a condensation reaction between 4-dimethylaminocinnamaldehyde and flavanol A rings at positions 6 and 8. This method is considered to be more specific than BS for flavanols with a low degree of polymerization (DP) and unaffected by non-phenolic components in wine [32]. This is evident by comparing both assays for hydrolyzable tannins (Table 2), which should be poor, in principle, in proanthocyanidins: while DMAC gave very low percentages (≤0.5%) for all the samples, BS provided values equal to 2.3 ± 0.1% in oak tannin, suggesting the existence of some interfering compounds, such as for example, Maillard products formed during the acid treatment at high temperatures. Consequently, DMAC could be considered as a more valid tool than BS for rapid colorimetric discrimination between condensed and hydrolyzable tannins. Additionally, some studies highlighted a pronounced sensitivity of DMAC toward monomeric flavanols, for which the response was deemed to be up to three times higher than oligomers [32,33]. In light of this, the DMAC and BS assays may provide complementary information. For instance, richness values given by BS vs. DMAC for grape skin and grape seed tannins (62.4% vs. 38.1% and 61.0% vs. 77.3%, respectively) could suggest higher DP for the former with respect to the latter. At the same time, cherry showed higher oligomeric content, supported by DMAC assay (22.8 ± 0.0%), than polymers evaluated by BS (17.3 ± 0.9%), while quebracho turned out to probably be the poorest in oligomers (8.6 ± 0.1%, DMAC value) among condensed tannins.

Table 3 shows data on antioxidant capacity and iron chelating and oxygen consumption ability of the tannins. In the ABTS assay, gallotannins emerged as the most efficient antioxidant, exhibiting an activity of 2336 ± 11 mg Trolox/g. Grape seed displayed moderate activity (1751 ± 83 mg Trolox/g), followed by chestnut (1422 ± 43 mg Trolox/g), while the lowest activity was observed for cherry tannin (1058 ± 24 mg Trolox/g). Our results are consistent with those reported by other authors for the same oenological tannins in model solutions [5,6,8] and suggest the large variability in the antioxidant activities within each tannin class. For hydrolyzable tannins, the high antioxidant capability could be due to the presence of ellagic polymers and gallic acid, which already demonstrated relevant antioxidant properties [5,8]. Unlike what was found in other studies [8], we did not find any significant correlation between ABTS and FC (Table S1) even though both the essays are based on electron transfer from the antioxidant to the oxidizing species.

Table 3. TEAC (Trolox equivalent antioxidant capacity), RAFI (Reducing Activity on Ferric Ions), ICA (iron chelating ability) and OCRt0 (oxygen consumption rate) of the oenological tannins. For sample codes, see Table 1. In the same column, different lowercase letters indicate significant differences among the single tannins at $p < 0.05$ (n = 6); different uppercase black letters denote significant differences among the tannins' classes (condensed or hydrolyzable) at $p < 0.05$ (n = 6).

Tannins		TEAC	RAFI	ICA	OCRt0
		mg Trolox/g Tannin		%	(mgO_2/L·day·g)
PC/PD	GSK	1315.0 ± 71.9 cd	303.5 ± 8.1 b	5.2 ± 0.3 c	2.1 ± 0.0 c
	GSE	1751.0 ± 83.4 b	285.0 ± 0.0 cd	8.1 ± 0.0 b	0.5 ± 0.0 g
	PRU	1058.0 ± 23.9 e	296.9 ± 21.7 bc	3.6 ± 1.0 cd	1.8 ± 0.0 d
PF/PR	ACA	1122.0 ± 71.5 de	306.4 ± 8.2 b	4.8 ± 0.2 cd	2.3 ± 0.0 b
	SCH	1141.0 ± 91.0 de	283.9 ± 7.1 cd	3.0 ± 0.9 d	0.6 ± 0.0 f

Table 3. *Cont.*

Tannins		TEAC	RAFI	ICA	OCRt0
Condensed		*1277.4 ± 281.3 B*	*295.1 ± 10.3 A*	*4.9 ± 2.0 A*	*1.5 ± 0.9 A*
GT	TAR	2336.0 ± 11.0 a	271.9 ± 19.7 d	4.4 ± 0.6 cd	0.1 ± 0.0 h
ET	OAK	1172.0 ± 29.4 de	292.6 ± 13.3 bc	3.2 ± 0.3 cd	1.5 ± 0.0 e
	CHT	1422.0 ± 42.5 c	380.4 ± 17.6 a	13.2 ± 1.0 a	2.7 ± 0.0 a
Hydrolyzable		*1643.3 ± 612.8 A*	*314.9 ± 57.6 A*	*6.9 5.5 A*	*1.4 ± 1.3 A*

The italicized text is to highlight that the raw is the mean of the cells above.

Table 3 also shows RAFI data, in which chestnut tannin exhibited the strongest iron-reducing activity (380 ± 18 mg Trolox/g), while tara tannin was the weakest iron reducer (272 ± 20 mg Trolox/g). Considering the tannin groups, however, no significant differences were found because of the large variability in reducing ability of their respective representants. Other studies using FRAP assay to evaluate the reducing capacity of tannins also found the hydrolyzable tannins to share the highest values [5]. FRAP method could be considered similar to RAFI as both measure the samples' reducing capacity toward ferric ions. However, and contrary to our results, in those studies, tara tannin had a tendentially higher reducing activity while acacia had lower mean values. This could suggest that the mechanisms involved in RAFI and FRAP methods are different. Also noteworthy is the significant positive correlation of RAFI with chelating power (ICA) and oxygen consumption (OCR T0) (Table S1).

Chestnut tannin was the most efficient in terms of Fe chelation (13.2 ± 1.0%) and oxygen consumption (2.7 $mgO_2/L \cdot day \cdot g$) in accordance with other researchers [5,6,10]. Grape seed tannins showed relevant chelating values (8.1%) but, together with tara and quebracho, demonstrated the lowest OCRt0 (0.1 and 0.5 $mgO_2/L \cdot day \cdot g$, respectively), which is also consistent with previous findings [5,34]. It is worth mentioning that, although quebracho demonstrated low OCRt0 values, it consumed about the same amount of the available oxygen as chestnut in the longer term (over 98% in 13 days), suggesting that OCRt0 may not be always or so obviously linked to the overall ability of a tannin to consume oxygen (Figure 1).

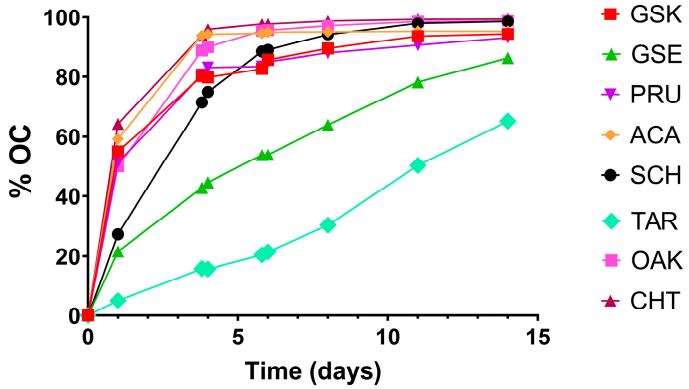

Figure 1. Oxygen consumption kinetics (% OC) of the different tannins in a model wine solution during 14 days of measurements. For sample codes, see Table 1.

In general, OCRt0 and ICA values appeared weakly correlated (Table S1), probably due to the independence of the phenomena underlying those features (at least, at the conditions we used in the present work).

3.2. Color and Phenolic Parameters of Starting Rosé Wines After the Addition of the Oenological Tannins

The overall color and phenolic parameters at T0 of the lab-scale rosé wines added with tannins are presented in Table S2 and Table 4, respectively.

Table 4. Phenolic parameters of rosé wines added with the different oenological tannins at T0. For sample codes, see Table 1. TA = total anthocyanins; FC = Folin–Ciocalteu method; TPI = Total Phenolic Index; DMAC = 4-dimethylaminocinnamaldehyde assay; BS = Bate-Smith assay. In the same column, different lowercase letters indicate significant differences among the tannins at $p < 0.05$ (n = 6); different uppercase black letters denote significant differences among the tannins' classes (condensed or hydrolyzable) at $p < 0.05$ (n = 6).

	T0	**TA mg/L MVDE**	**FC mg/L GAE**	**TPI (280 nm) mg/L CE**	**DMAC mg/L CE**	**BS mg/L**
	Control	5.57 ± 0.19 bcd	295 ± 8 d	659 ± 1 f	51 ± 2 f	414 ± 10 d
PC/PD	GSK	5.68 ± 0.16 abc	340 ± 2 c	824 ± 3 d	127 ± 1 c	539 ± 8 a
	GSE	5.90 ± 0.11 ab	387 ± 5 a	858 ± 3 c	206 ± 2 a	541 ± 19 a
	PRU	5.50 ± 0.16 cde	352 ± 7 bc	884 ± 7 c	97 ± 2 d	448 ± 8 c
PF/PR	ACA	6.02 ± 0.15 a	351 ± 5 bc	764 ± 4 e	167 ± 4 b	490 ± 9 b
	SCH	6.05 ± 0.19 a	363 ± 8 b	876 ± 29 c	69 ± 1 e	502 ± 13 b
Condensed		*5.83 ± 0.24 A*	*359 ± 18 A*	*841 ± 49 B*	*133 ± 55 A*	*504 ± 38 A*
GT	TAR	5.77 ± 0.21 abc	381 ± 6 a	1230 ± 6 a	56 ± 2 f	424 ± 16 cd
ET	OAK	5.26 ± 0.07 de	359 ± 5 b	883 ± 1 c	52 ± 2 f	431 ± 7 cd
	CHT	5.13 ± 0.02 e	359 ± 2 b	975 ± 7 b	52 ± 2 f	421 ± 11 cd
Hydrolyzable		*5.39 ± 0.34 A*	*366 ± 13 A*	*1029 ± 179 A*	*54 ± 2 B*	*425 ± 5 B*

The italicized text is to highlight that the raw is the mean of the cells above.

These tables aim to highlight the initial impact on those features due to the addition itself. In agreement with previous surveys dealing with the color diversity of rosé wines, the CIELAB and phenolic parameters of our laboratory-scale wine could be considered representative of intermediate nuances [14,35]. All the tannins visibly influenced the initial color of wines (Table S2) except tara, which exhibited $\Delta E^*_{ab} < 1.0$, hence not discernible to the naked eye [22]. Grape skin tannin expressed the greatest impact on color ($\Delta E^*_{ab} = 11.48$), followed by chestnut ($\Delta E^*_{ab} = 5.18$) and quebracho ($\Delta E^*_{ab} = 4.31$). This order appeared to be somehow dependent on the tannin contribution to yellowness (coordinate b^* in Table S2), which increased to a major extent after grape skin, chestnut or quebracho addition. Grape skin tannin also generates the highest variation in a^* and b^* (as shown in Figure 2), color density (CD), hue (h_{ab}) and lightness (L^*) of wine, making it the most impactful tannin on the wine's initial color.

According to their richness, added tannins proportionally contributed to the phenolic content of the starting rosé wine (Table 4). The specific DMAC and BS values of each tannin (Table 2), for instance, were perfectly reflected in the respective wine phenolic content. Grape seed, grape skin and acacia tannins, in fact, augmented wine phenolics the most (with an increase of 76–154 mg/L for DMAC and 76–127 mg/L for BS) while, as expected, all the hydrolyzable tannins barely changed those parameters. Wine added with tara tannin showed the highest TPI values at 280 nm (1230 ± 6 mg/L CE), probably due to the prompt dissolution of compounds with high absorption at those wavelengths (e.g., gallic acid). For the same parameter, and quite unexpectedly if the tannin original richness is considered (see TPI values in Table 2), hydrolyzable tannins gave wines with significantly higher values (1029 ± 179 mg/L CE) with respect to condensed ones (841 ± 49 mg/L CE) (Table 4). This may depend on the catechin calibration curve used in this assay for all the wines, which

overestimates TPI when compared to gallic acid used to quantify phenolics in the hydrolyzable tannin solutions (Table 2). On the other hand, no significant differences were found between tannin groups for FC assay, reflecting the data coming from their characterization.

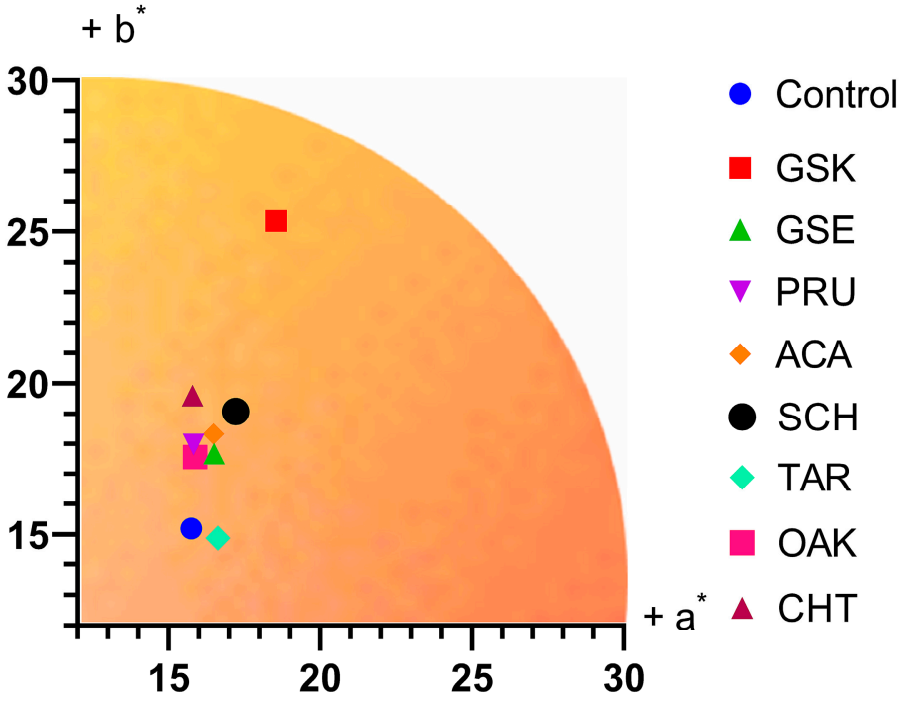

Figure 2. Effects on *a** and *b** CIELAB parameters of the rosé wine color due to the addition of different tannins at T0. While the actual *a** and *b** coordinates were used for each tannin to build the figure, the CIELAB color space shown does not accurately represent the true color at each specific value; it was only provided for illustrative purposes to suggest the changes in wine color toward redder or yellower hues due to each tannin addition. For sample codes see Table 1.

3.3. Impact of Oenological Tannins on Color Evolution of Rosé Wines During Storage

After 56 days of storage, the color of rosé wines evolved differently depending on the tannin used or the class to which it belonged (Table 5).

Table 5. Final variation (T56-T0) in color parameters of rosé wines added with the different oenological tannins. For sample codes see Table 1. CD = color density; ΔE^*_{ab} = total color difference with respect to the same sample at T0; dA% = contribution to color of flavylium ions. In the same column, different lowercase letters indicate significant differences among the tannins at $p < 0.05$ (n = 6); different uppercase black letters denote significant differences among the tannins' classes (condensed or hydrolyzable) at $p < 0.05$ (n = 6).

ΔT56-T0	*L**	*a**	*b**	C^*_{ab}	h_{ab}	ΔE^*_{ab}	CD	dA%
Control	0.4 ± 0.2 a	−0.25 ± 0.24 e	5.91 ± 0.15 de	4.30 ± 0.19 d	0.15 ± 0.00 b	5.94 ± 0.15 de	0.04 ± 0.01 e	−5.8 ± 0.8 cd
GSK	−0.8 ± 0.2 b	1.33 ± 0.11 b	9.55 ± 0.24 b	8.72 ± 0.22 b	0.12 ± 0.00 de	9.67 ± 0.24 b	0.15 ± 0.01 b	−4.9 ± 0.2 b
GSE	−1.6 ± 0.2 d	1.52 ± 0.20 b	9.24 ± 0.54 b	8.22 ± 0.56 b	0.13 ± 0.01 cd	9.50 ± 0.55 b	0.15 ± 0.01 b	−5.2 ± 0.3 bc
PRU	−1.4 ± 0.1 d	0.78 ± 0.02 c	7.17 ± 0.10 c	6.23 ± 0.18 c	0.12 ± 0.00 e	7.35 ± 0.11 c	0.13 ± 0.01 c	−5.4 ± 0.1 bc
ACA	−3.1 ± 0.0 e	1.94 ± 0.05 a	10.90 ± 0.15 a	9.95 ± 0.12 a	0.14 ± 0.00 c	11.50 ± 0.15 a	0.23 ± 0.00 a	−7.0 ± 0.2 e
SCH	−0.9 ± 0.2 bc	0.46 ± 0.02 cd	7.42 ± 0.09 c	6.11 ± 0.10 c	0.12 ± 0.00 de	7.49 ± 0.12 c	0.10 ± 0.01 d	−5.5 ± 0.3 bcd
Condensed	*−1.5 ± 0.9 B*	*1.21 ± 0.59 A*	*8.86 ± 1.56 A*	*7.85 ± 1.66 A*	*0.12 ± 0.01 A*	*9.10 ± 1.72 A*	*0.15 ± 0.05 A*	*−5.6 ± 0.8 A*
TAR	0.0 ± 0.1 a	−0.65 ± 0.10 f	6.50 ± 0.12 d	4.43 ± 0.16 d	0.16 ± 0.00 a	6.54 ± 0.11 d	0.06 ± 0.01 e	−7.3 ± 0.1 e
OAK	−1.2 ± 0.1 cd	0.23 ± 0.04 d	6.05 ± 0.07 d	4.91 ± 0.06 d	0.12 ± 0.00 de	6.18 ± 0.09 d	0.12 ± 0.00 cd	−6.4 ± 0.3 de
CHT	0.3 ± 0.1 a	0.18 ± 0.11 d	5.33 ± 0.12 e	4.46 ± 0.09 d	0.10 ± 0.00 f	5.34 ± 0.13 e	0.04 ± 0.00 e	−3.5 ± 0.2 a
Hydrolyzable	*−0.3 ± 0.8 A*	*−0.08 ± 0.50 B*	*5.96 ± 0.59 B*	*4.60 ± 0.27 B*	*0.13 ± 0.03 A*	*6.02 ± 0.61 B*	*0.07 ± 0.04 B*	*−5.7 ± 2.0 A*

The italicized text is to highlight that the raw is the mean of the cells above.

In general, the CIELAB color parameters for all the wines increased, except for L^* which decreased by an average of 1.5 units for condensed tannins. Among the hydrolyzable tannins, tara exhibited no variation in lightness compared to its initial value at T0, while chestnut only slightly increased over time, similarly to the control. Overall, and as expected, the changes in L^* of the samples were moderate if compared to previous studies on red wines [36,37]. Apart from L^*, for all the remaining color parameters the addition of condensed tannins led to significantly higher variations with respect to hydrolysable tannins. These latter, in particular, changed similarly to the control sample (see, for instance, the values of ΔE^*_{ab}, CD, C^*_{ab} and b^* in Table 5), suggesting that this class of tannins did not significantly influence the kinetics involved in the oxidative color evolution of wines. On the contrary, the presence of condensed tannins caused the highest overall color modification (ΔE^*_{ab}) due to significant increases in both a^* and b^* with respect to control. After about 2 months of storage, b^* values increased in all the wines, with chestnut tannin promoting the lowest changes. Specifically, in the wine with this tannin, b^* values rose by 5.33 ± 0.12 units compared to the same wine at T0. In contrast, acacia samples exhibited the largest increase in b^* values (10.90 ± 0.15 units), making it the least effective in maintaining the initial yellow tonalities. The increase in red color (a^*) could be attributed to both copigmentation and creation of anthocyanin–tannin adducts through direct or indirect condensation reactions, as suggested by other authors [38,39]. The analysis on copigmentation we conducted on the wines, however, failed in confirming this assumption due to an extreme variability, probably because the overall color of our samples was too low to permit the reliable execution of that assay [40]. The changes in hue (h_{ab}) (Table 5) suggest a transition from the initial pale-pink hues towards more red-orange shades. However, the color tonality of almost all the wines added with tannins (with the exception of tara) evolved to a lesser extent with respect to the initial rosé wine, tendentially preserving more reddish notes. As a whole, acacia showed the highest global variation in wine color with ΔE^*_{ab} values up to 11.50 ± 0.15 units, while chestnut emerged for its low influence on the color evolution of wines (ΔE*ab 5.34 ± 0.13). This oenological tannin, which provided the highest reducing activity and oxygen consumption ability (Table 3), may have contributed to counteracting oxidation and the resulting browning. Supporting this observation, the dA% values (which reflect the contribution of flavylium species to the overall color [22]) indicated that chestnut significantly limited red color loss in wine compared to other ones.

3.4. Effects of Oenological Tannins on Spectrophotometric Phenolic Indexes and Iron Content

Table 6 shows the changes in wine phenols and total anthocyanins at the end of the experimentation. The DMAC values varied differently depending on the class of tannins considered. As expected, hydrolyzable tannins showed losses comparable to the control. In contrast, grape seed tannin, which contributed the most to wine flavonoid contents (Table 4), lost the highest amount of these compounds (87 ± 3 mg/L) during the storage (Table 6). This trend was observed in all the other condensed tannins, where the loss of flavonoids correlated with their initial content. For example, quebracho tannin, with a low initial flavonoid content, showed the poorest loss in flavonoids (14 ± 1 mg/L).

Also, in the case of the BS assay, all hydrolyzable tannins should reflect the behavior of the control, given the unresponsiveness of the BS method to these tannins. However, chestnut tannin seemed to protect the wine from phenolic degradation better than tara and oak tannins, which had the same phenolic content loss as the control. Regarding condensed tannins, although grape skin and grape seed tannins had similar initial values as measured by the BS assay (Table 4), the former exhibited superior preservation over time. This suggests that grape skin tannin might offer better protective ability than grape seed as it decreased the initial BS value by only 52 mg/L, compared to grape seed tannin,

which lost 191 mg/L (Table 6). In a similar way, in the wines added with PF/PR tannins the phenolic content did not decrease during oxidative storage. TPI as measured with FC and Abs at 280 nm both did not show significant differences between the two classes of tannins, due to the large variability among the respective representants. However, the addition of cherry, acacia and quebracho tannins (condensed) and oak tannin (hydrolyzable) led to decreases in TPI (280 nm) with respect to their initial content, while in the control wine TPI slightly increased. Further details on the evolution of low-molecular-weight phenolics are discussed below.

Table 6. Final variation (T56-T0, mg/L) in phenolic parameters of rosé wines added with the different oenological tannins. For sample codes see Table 1. TA = total anthocyanins; FC = Folin–Ciocalteu method; TPI = Total Phenolic Index; DMAC = 4-dimethylaminocinnamaldehyde assay; BS = Bate-Smith assay. In the same column, different lowercase letters indicate significant differences among the tannins at $p < 0.05$ (n = 6); different uppercase black letters denote significant differences among the tannins' classes (condensed or hydrolyzable) at $p < 0.05$ (n = 6).

	ΔT56-T0	**TA**	**FC**	**TPI (280 nm)**	**DMAC**	**BS**
		mg/L MVDE	**mg/L GAE**	**mg/L CE**	**mg/L CE**	**mg/L**
	Control	−2.40 ± 0.38 a	−24 ± 5 bc	56 ± 7 ab	−3 ± 1 a	−180 ± 11 de
PC/PD	GSK	−2.78 ± 0.04 a	−14 ± 3 abc	87 ± 12 a	−47 ± 1 d	−52 ± 13 b
	GSE	−2.97 ± 0.16 a	−9 ± 16 abc	32 ± 4 bc	−87 ± 3 f	−191 ± 21 e
	PRU	−2.85 ± 0.27 a	0 ± 8 ab	−132 ± 8 f	−30 ± 2 c	−93 ± 15 c
PF/PR	ACA	−2.99 ± 0.29 a	−6 ± 4 ab	−19 ± 3 d	−70 ± 4 e	0 ± 15 a
	SCH	−2.79 ± 0.04 a	−32 ± 13 c	−90 ± 20 e	−14 ± 1 b	−1 ± 2 a
Condensed		*−2.87 ± 0.10 A*	*−12 ± 12 A*	*−24 ± 88 A*	*−49 ± 29 B*	*−67 ± 79 A*
GT	TAR	−2.67 ± 0.24 a	1 ± 8 a	81 ± 30 a	−8 ± 2 ab	−186 ± 3 de
ET	OAK	−2.85 ± 0.09 a	−11 ± 8 abc	−26 ± 4 d	−5 ± 2 a	−150 ± 10 d
	CHT	−2.88 ± 0.19 a	−8 ± 6 abc	2 ± 6 cd	−4 ± 2 a	−1 ± 19 a
Hydrolyzable		*−2.80 ± 0.11 A*	*−6 ± 6 A*	*19 ± 55 A*	*−6 ± 2 A*	*−113 ± 98 A*

The italicized text is to highlight that the raw is the mean of the cells above.

Interesting results were also observed when evaluating the iron chelation action of tannins once added to the wines (Figure 3).

Similarly to the phenolic data, these findings are consistent with the ones coming from tannin characterization (Table 3), where chestnut tannin exhibited the highest chelating activity (Table S3). At the end of the experimentation, it chelated 0.14 ± 0.01 mg/L of the initial wine total iron content (0.69 mg/L), and no precipitate was visible at the bottom of the containers. Therefore, it is unlikely that the undetected iron content was due to precipitation as iron oxide.

3.5. Influence of Oenological Tannins on Some Individual Phenolic Compounds

As shown in Table 4, although all the samples shared a common rosé base wine, the addition of tannins led to significant differences in the initial anthocyanin content. This was likely due to the lack of specificity of the method or the interference in that assay by the presence of oenological tannins.

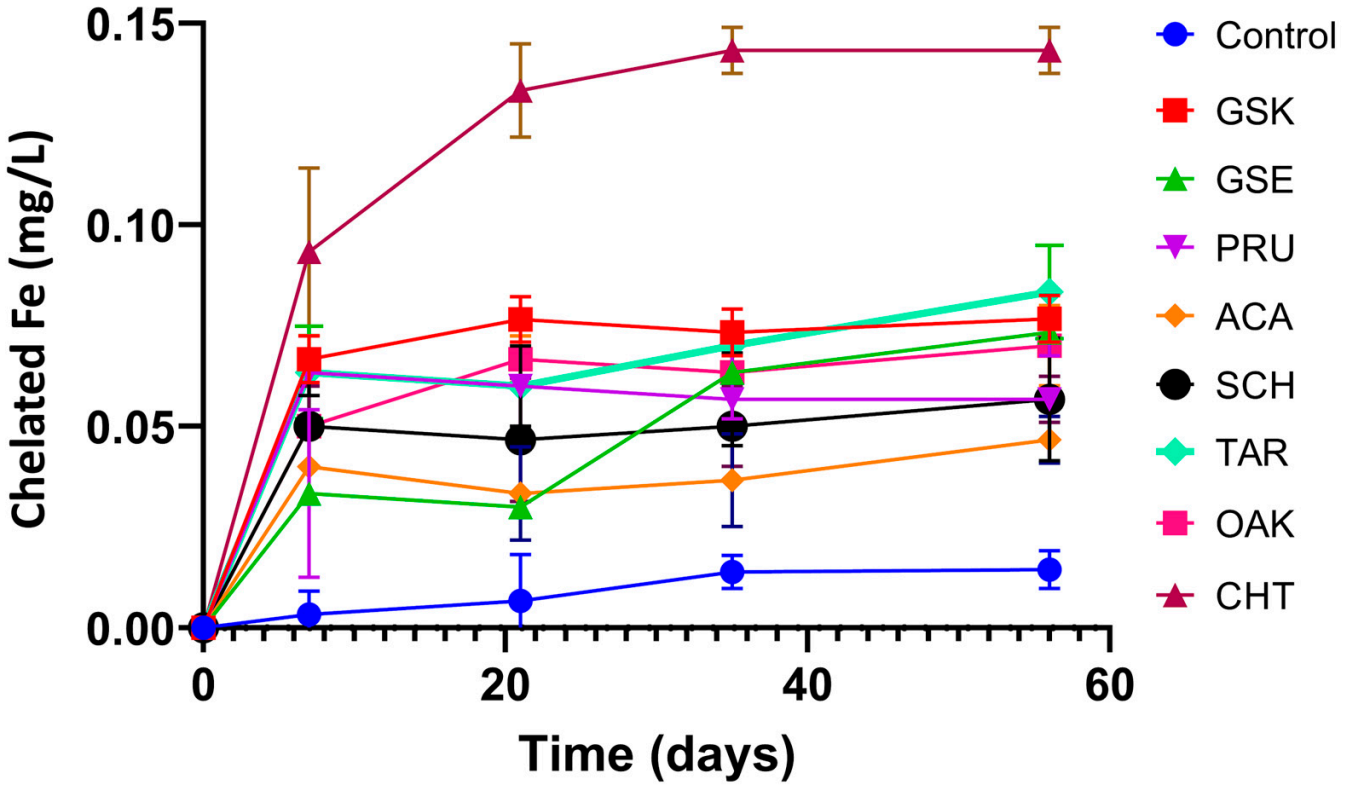

Figure 3. Chelation of Fe (mg/L) by the different tannins in the rosé wine during 56 days of storage. For sample codes see Table 1.

At T56 all the wines lost the same amount of total anthocyanins as the control, suggesting that tannins had poor impact on anthocyanin degradation (Table 6), even if variations among individual monomeric anthocyanin should not be excluded. To assess this eventuality, single anthocyanins were also quantified by HPLC-DAD and grouped into six chemical families (Table S4). They include native compounds like glucosides, acetylglucosides, and coumaroylglucosides, as well as their derivatives such as vitisins, vinylphenol, and ethyl-bridged adducts. Contrarily to the results coming from the spectrophotometric determination, no significant differences were found at T0 among the wines added with the different tannins, supporting the hypothesis that oenological tannins may partially impair the quantification of anthocyanins carried out via that method. The HPLC quantification of anthocyanins reflected the results found by other authors on red and rosé wines [3,35], in which anthocyanin 3-*O*-glucosides were the predominant pigments (Table S4). However, when evaluating the degradation of those pigments over time, they are expected to be less resistant than vitisins [14]. Their variations from T0 to T56 were hence calculated to verify this hypothesis (Table S5). Anthocyanins decreased in all the wines up to about 50%, and grape skin and grape seed tannins caused the highest diminution, indicating a potentially enhanced reactivity of monomeric anthocyanins in those samples. Interestingly, the same wines had the highest increment in red tonalities at T56 (a^* parameter in Table 5), and this may imply that a portion of monomeric anthocyanins could have been involved in polymerization phenomena [41] with stabilizing effects on the rosé hues of the wines. As expected, pigments such as vitisins (pyranoanthocyanins) and vinyl adducts were more stable than the native ones, with variations of about −20% and +1% respectively for the former as opposed to >−60% for the latter [14].

HPLC was also utilized to evaluate the content of low-molecular-weight phenolics of wines (Table 7). Only tara, cherry and grape seed tannins significantly augmented the phenolic richness of the base rosé wine at T0, respectively up to 102 mg/L, 95 mg/L and 94 mg/L, with an increase of about 5–10%. In accordance with the respective chemical class, tara tannin mainly released gallic acid (15.67 ± 3.21 mg/L as a total) while grape seed tannin incremented the amount of flavanols such as (+)-catechin and procyanidin B2 (8.17 ± 0.41 mg/L and 1.17 ± 0.10 mg/L as a total). Cherry tannin released both (+)-catechin and gallic acid (up to 6.65 ± 0.51 mg/L and 4.02 ± 0.14 mg/L), confirming its dual nature of condensed and hydrolyzable tannin [6,27,42]. For grape seed tannin, these findings agree with the results from the DMAC assay on tannin solutions in model wine (Table 2) and when added to the wines (Table 4). Indeed, these analyses highlighted that grape seed tannins had the highest amount of monomers/oligomers at T0. Tara tannin, on the other hand, contributed with the greatest amount of gallic acid, confirming the results of TPI at 280 nm (Table 4); similarly, cherry tannin also achieved noticeable values in the DMAC assay and TPI. Although grape skin tannin provided high DMAC values (Table 4), it did not significantly release mono/dimeric flavanols to the wine (Table 7). This is probably due to its higher content of polymers rather than monomers, as supported by the BS assay (Table 4), which were not quantified by our RP-HPLC method. During storage, phenolic acids evolved to a different extent depending on the added tannin. Table 8 presents the changes in phenolic compound levels in wines after two months of storage (T56). It shows that condensed tannins drove to evolutions similar to that of control, with little decreases or no significant changes for those compounds as a sum. For grape seed and cherry tannins, the main variation is due to the partial decrease in that amount of (+)-catechin which was initially released to the wine (Table 7), probably due to its involvement in oxidative depletion and/or coupling phenomena. On the contrary, the initial higher amount of (+)-catechin given by acacia tannin remained substantially unchanged during storage. For wines added with hydrolyzable tannins, the total amount of phenolic compounds significantly increased, particularly for tara tannin. Interestingly, both the two other hydrolyzable tannins (oak and chestnut) evolved differently from each other, since oak tannin appeared to generate considerable amounts of gallic acid while chestnut tannin did not exhibit this behavior (Table 8). Indeed, for gallotannins such as tara, gallic acid could derive from the hydrolysis of the respective oligomers [43]. Furthermore, the difference in composition (presence of depside bonds and/or gallate esters) may also justify the distinct behavior of oak and chestnut tannins during storage. It has been reported, for instance, that the depside bonds are considerably easier to break than the core ester linkages, making the tannins richer in those molecules poorly resistant to acidic hydrolysis [44]. Regarding hydroxycinnamate derivatives, they overall showed no clear evolution, neither as a function of the compound nor the added tannin considered. *t*-caftaric acid appeared to be the compound most involved in quantitative fluctuations, as expected, being the main constitutive phenolic acid in the base rosé wine (Table 7).

Table 7. Quantification (mg/L) of individual low-molecular-weight phenolics in rosé wines treated with different oenological tannins at the initial time point (T0). For sample codes see Table 1. Different lowercase letters within the same row indicate statistically significant differences among the tannin treatments for each compound ($p < 0.05$; n = 6). Different uppercase letters in the "Total sum" row indicate significant differences in the total concentration of phenolic acids among the tannin treatments ($p < 0.05$; n = 6). Data are expressed as mean ± standard deviation.

T0	Control mg/L	GSK mg/L	GSE mg/L	PRU mg/L	ACA mg/L	SCH mg/L	TAR mg/L	OAK mg/L	CHT mg/L
Tyrosol	50.05 ± 0.86 a	50.10 ± 0.89 ab	50.38 ± 1.35 ab	51.05 ± 0.47 a	49.83 ± 0.17 ab	49.19 ± 0.29 b	51.51 ± 1.48 a	50.47 ± 1.96 ab	49.77 ± 1.41 b
(+)-Catechin	1.96 ± 0.29 d	2.82 ± 0.22 c	8.17 ± 0.41 a	6.65 ± 0.51 b	7.70 ± 0.19 a	1.77 ± 0.08 d	1.94 ± 0.10 d	1.79 ± 0.20 d	1.86 ± 0.03 d
Procyanidin-B2	0.16 ± 0.03 cd	0.23 ± 0.03 bc	1.17 ± 0.10 a	0.16 ± 0.01 cd	0.29 ± 0.03 b	0.15 ± 0.02 cd	0.16 ± 0.03 cd	0.15 ± 0.01 d	0.16 ± 0.00 cd
(−)-Epicatechin	0.06 ± 0.02 ab	0.07 ± 0.00 a	0.05 ± 0.00 bc	0.02 ± 0.00 e	0.05 ± 0.01 bc	0.02 ± 0.00 e	0.07 ± 0.00 a	0.03 ± 0.00 de	0.04 ± 0.01 cd
Gallic acid	1.67 ± 0.01 d	1.60 ± 0.08 d	2.78 ± 0.22 bcd	4.02 ± 0.14 bc	1.51 ± 0.06 d	2.07 ± 0.11 cd	15.67 ± 3.21 a	3.90 ± 0.05 bc	4.72 ± 0.13 b
HMF	0.78 ± 0.06 bc	0.74 ± 0.00 cd	0.77 ± 0.01 bc	0.79 ± 0.05 bc	0.69 ± 0.03 d	0.71 ± 0.01 cd	0.83 ± 0.00 b	0.72 ± 0.05 cd	0.95 ± 0.05 a
c-Coutaric Acid	1.19 ± 0.02 b	1.21 ± 0.04 ab	1.25 ± 0.09 ab	1.32 ± 0.10 a	1.19 ± 0.05 b	1.16 ± 0.02 b	1.27 ± 0.06 ab	1.24 ± 0.07 ab	1.24 ± 0.04 ab
t-Coutaric Acid	2.06 ± 0.13 ab	2.07 ± 0.08 ab	2.10 ± 0.24 ab	2.26 ± 0.05 ab	2.04 ± 0.02 ab	2.02 ± 0.03 b	2.29 ± 0.16 a	2.17 ± 0.18 ab	2.16 ± 0.08 ab
Coumaric derivative	0.10 ± 0.01 cde	0.11 ± 0.01 bcd	0.09 ± 0.00 ef	0.12 ± 0.00 ab	0.13 ± 0.00 a	0.09 ± 0.01 de	0.07 ± 0.00 f	0.11 ± 0.01 abc	0.13 ± 0.01 a
c-Caftaric Acid	1.20 ± 0.02 c	1.27 ± 0.02 abc	1.33 ± 0.09 a	1.33 ± 0.01 a	1.23 ± 0.06 c	1.21 ± 0.02 c	1.31 ± 0.03 ab	1.23 ± 0.03 bc	1.22 ± 0.03 c
t-Caftaric Acid	19.86 ± 0.45 ab	18.95 ± 0.97 ab	19.45 ± 0.84 ab	20.31 ± 0.20 a	18.72 ± 0.99 b	18.43 ± 0.07 b	19.94 ± 0.75 ab	19.57 ± 1.36 ab	18.88 ± 0.45 ab
t-GRP	2.60 ± 0.17 c	2.93 ± 0.03 ab	3.01 ± 0.22 a	2.87 ± 0.01 ab	2.80 ± 0.23 abc	2.76 ± 0.05 abc	2.79 ± 0.13 abc	2.86 ± 0.11 abc	2.67 ± 0.02 bc
t-Fertaric Acid	0.99 ± 0.02 a	0.96 ± 0.02 a	0.93 ± 0.02 a	1.03 ± 0.13 a	0.96 ± 0.06 a	0.96 ± 0.02 a	0.97 ± 0.04 a	0.97 ± 0.01 a	0.98 ± 0.02 a
t-Caffeic Acid	1.73 ± 0.17 a	1.77 ± 0.09 a	1.83 ± 0.18 a	1.91 ± 0.02 a	1.73 ± 0.06 a	1.69 ± 0.02 a	1.91 ± 0.11 a	1.76 ± 0.16 a	1.76 ± 0.01 a
Ferulic Acid	0.20 ± 0.02 ab	0.18 ± 0.02 b	0.19 ± 0.01 b	0.22 ± 0.01 ab	0.18 ± 0.03 b	0.18 ± 0.00 b	0.24 ± 0.03 a	0.18 ± 0.04 b	0.18 ± 0.01 b
Ethylcaffeoate	0.45 ± 0.00 b	0.42 ± 0.03 b	0.42 ± 0.06 b	0.52 ± 0.02 a	0.42 ± 0.02 b	0.41 ± 0.00 b	0.45 ± 0.04 b	0.44 ± 0.03 b	0.42 ± 0.01 b
Quercetin	0.03 ± 0.00 a	0.03 ± 0.00 a	0.02 ± 0.01 a	0.03 ± 0.02 a	0.02 ± 0.00 a	0.02 ± 0.00 a	0.02 ± 0.01 a	0.01 ± 0.00 a	0.02 ± 0.01 a
Total sum	85.11 ± 0.80 DE	85.45 ± 2.01 DE	93.93 ± 2.76 B	94.63 ± 1.47 B	89.49 ± 1.56 C	82.86 ± 0.34 E	101.47 ± 0.68 A	87.59 ± 3.65 CD	87.17 ± 1.93 CD

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Table 8. Final variation (ΔT56–T0, mg/L) in the content of individual low-molecular-weight phenolics in rosé wines treated with different oenological tannins. For sample codes see Table 1. Different lowercase letters within the same row indicate statistically significant differences among the tannin treatments for each compound ($p < 0.05$; n = 6). Different uppercase letters in the "Total sum" row indicate significant differences in the total variation of phenolic acids among the tannin treatments ($p < 0.05$; n = 6). Data are expressed as mean ± standard deviation.

ΔT56-T0	Control	GSK	GSE	PRU	ACA	SCH	TAR	OAK	CHT
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Tyrosol	0.50 ± 0.50 a	0.75 ± 0.85 a	−0.04 ± 0.78 a	−1.88 ± 1.91 a	1.44 ± 0.65 a	0.00 ± 0.45 a	−1.36 ± 1.77 a	−0.64 ± 1.80 a	0.82 ± 1.15 a
(+)-Catechin	−0.78 ± 0.12 bc	−1.05 ± 0.15 c	−2.69 ± 0.01 d	−2.32 ± 0.39 d	−0.51 ± 0.22 b	−0.77 ± 0.04 bc	−0.12 ± 0.09 a	−0.86 ± 0.12 c	−0.85 ± 0.02 c
Procyanidin-B2	−0.05 ± 0.01 a	−0.08 ± 0.03 a	−0.45 ± 0.09 b	−0.06 ± 0.01 a	−0.04 ± 0.04 a	−0.04 ± 0.02 a	−0.04 ± 0.02 a	−0.04 ± 0.00 a	−0.04 ± 0.00 a
(−)-Epicatechin	−0.02 ± 0.01 d	−0.02 ± 0.00 d	0.05 ± 0.01 a	0.00 ± 0.00 c	0.00 ± 0.00 c	0.02 ± 0.00 b	−0.03 ± 0.00 d	0.01 ± 0.00 c	0.01 ± 0.00 c
Gallic acid	−0.03 ± 0.06 c	0.54 ± 0.10 c	0.71 ± 0.16 c	0.29 ± 0.25 c	0.22 ± 0.08 c	0.27 ± 0.13 c	27.76 ± 4.16 a	17.67 ± 0.22 b	0.69 ± 0.03 c
HMF	0.45 ± 0.02 bc	0.48 ± 0.04 bc	0.38 ± 0.03 c	0.45 ± 0.04 bc	0.54 ± 0.03 ab	0.50 ± 0.01 ab	0.23 ± 0.12 d	0.48 ± 0.01 b	0.59 ± 0.04 a
c-Coutaric Acid	0.05 ± 0.03 a	0.10 ± 0.17 a	0.03 ± 0.14 a	−0.19 ± 0.01 b	0.07 ± 0.04 a	0.00 ± 0.01 a	0.01 ± 0.04 a	0.05 ± 0.05 a	0.05 ± 0.01 a
t-Coutaric Acid	−0.09 ± 0.03 ab	0.00 ± 0.27 a	−0.15 ± 0.09 ab	−0.26 ± 0.22 ab	0.00 ± 0.03 a	−0.17 ± 0.00 ab	−0.29 ± 0.19 b	−0.22 ± 0.05 ab	−0.01 ± 0.02 a
Coumaric derivative	−0.01 ± 0.00 bc	0.00 ± 0.01 b	0.01 ± 0.00 a	−0.02 ± 0.00 cd	−0.02 ± 0.01 d	0.00 ± 0.01 b	−0.01 ± 0.00 cd	−0.03 ± 0.00 e	−0.02 ± 0.01 d
c-Caftaric Acid	0.02 ± 0.07 a	−0.09 ± 0.08 ab	−0.12 ± 0.11 abc	−0.28 ± 0.02 c	−0.10 ± 0.02 ab	−0.09 ± 0.05 ab	−0.11 ± 0.11 ab	−0.13 ± 0.13 bc	−0.16 ± 0.02 bc
t-Caftaric Acid	−0.67 ± 0.94 ab	0.63 ± 1.79 a	−0.75 ± 1.04 ab	−1.82 ± 0.94 b	0.53 ± 0.45 a	−0.18 ± 0.11 ab	−1.08 ± 1.38 ab	−1.05 ± 1.48 ab	0.26 ± 0.36 ab
t-GRP	−0.18 ± 0.11 a	−0.66 ± 0.08 c	−0.61 ± 0.28 bc	−0.49 ± 0.00 abc	−0.21 ± 0.18 ab	−0.40 ± 0.10 abc	−0.48 ± 0.37 abc	−0.68 ± 0.26 c	−0.22 ± 0.11 ab
t-Fertaric Acid	−0.23 ± 0.02 c	−0.11 ± 0.01 a	−0.20 ± 0.01 bc	−0.24 ± 0.04 c	−0.10 ± 0.01 a	−0.24 ± 0.06 c	−0.19 ± 0.09 abc	−0.24 ± 0.03 c	−0.13 ± 0.01 ab
t-Caffeic Acid	0.11 ± 0.09 ab	0.22 ± 0.02 a	−0.09 ± 0.12 cd	−0.12 ± 0.04 cd	0.20 ± 0.15 a	0.06 ± 0.14 abc	−0.16 ± 0.05 d	−0.02 ± 0.03 bcd	0.13 ± 0.05 ab
Ferulic Acid	−0.04 ± 0.00 d	−0.01 ± 0.00 abc	−0.03 ± 0.01 d	−0.08 ± 0.00 e	0.00 ± 0.01 a	−0.02 ± 0.01 cd	−0.08 ± 0.01 e	−0.02 ± 0.02 bcd	0.00 ± 0.01 ab
Ethylcaffeoate	−0.05 ± 0.00 bc	0.01 ± 0.01 a	−0.03 ± 0.03 ab	−0.09 ± 0.04 c	0.02 ± 0.02 a	−0.03 ± 0.00 ab	−0.05 ± 0.02 bc	−0.06 ± 0.05 bc	0.01 ± 0.01 a
Quercetin	−0.02 ± 0.00 cd	0.00 ± 0.00 a	−0.01 ± 0.00 bc	−0.02 ± 0.01 d	0.00 ± 0.00 ab	0.00 ± 0.00 ab	−0.01 ± 0.00 bc	0.00 ± 0.00 ab	0.00 ± 0.00 ab
Total sum	−1.03 ± 2.20 CD	0.71 ± 3.63 C	−4.00 ± 3.43 CD	−7.09 ± 4.63 D	2.02 ± 0.20 C	−1.09 ± 0.35 CD	23.99 ± 8.08 A	14.20 ± 4.13 B	1.12 ± 1.67 C

4. Limitations

This study has been conducted on an experimental rosé wine with an average content of pigments and phenolic compounds. However, among the marketed rosé wines there is a vast variability in color tonalities and densities, which could span from pale pink to deep salmon, to coppery or orange hues. Depending on both the grape cultivar used and the choices made during winemaking, each shade also entails distinct anthocyanin to tannin ratios. Since it has been demonstrated that the relative proportion between pigments and procyanidins may affect the oxidative behavior of rosé wines, our results may not be entirely pertinent to wines with extremely faint or deep rosé nuances.

A second limitation of the present investigation relates to the oenological tannins involved. Although our experiment was planned to represent all the tannin classes and subclasses, not all the possible tannin formulations were tested. In addition, within each class and for the same type of oenological tannin, large differences in chemical composition and phenolic richness may exist due to the starting raw material and the extraction methods adopted by the producers. Consequently, even if the results effectively describe the overall features of condensed and hydrolysable tannins, the specific effects on rosé wines of other commercial formulations based on condensed and/or hydrolysable polymers may diverge.

5. Conclusions

The physicochemical characterization of the oenological tannins revealed significant differences in their phenolic richness and behavior when analyzed using various spectrophotometric methods. Overall, grape seed tannin exhibited the highest phenolic values both as measured by FC and DMAC methods and by absorbance at 280 nm, while chestnut tannin emerged for its antioxidant capacity, reducing activity and oxygen consumption.

The addition of tannins significantly influenced the initial color of rosé wine as a function of their origin and phenolic specificity. Condensed tannins, particularly those from grape skins, intensified the color, contributing to reddish and yellowish tonality, while hydrolyzable tannins had a milder initial impact. During storage, condensed tannins prompted the highest color variation but with differences among individual tannins, while hydrolyzable tannins, in particular chestnut, appeared to better preserve the initial color of the wine as suggested by limited ΔE^*_{ab} and hue evolution. In addition, grape skin and grape seed tannins led to the highest decline in native pigments, probably due to their transformation into red polymers. During wine storage the different tannins showed distinct susceptibility to undergo hydrolysis, enriching the wines with constitutive monomers which could influence the color evolution in the long term.

Further studies may be needed to dive into the specific mechanisms underlying the observed effects and to optimize tannin usage in winemaking.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/beverages12030028/s1: Table S1: Correlation among some physicochemical parameters of the studied oenological tannins. Values in bold are significantly correlated at $p \geq 0.5$ (n = 6); Table S2: Color parameters of rosé wines added with the different oenological tannins at T0. ΔE^*_{ab} was calculated with respect to control wine at T0. In the same column, different lowercase letters indicate significant differences among the tannins at $p < 0.05$ (n = 6); different uppercase black letters denote significant differences among the tannins' classes (condensed or hydrolyzable) at $p < 0.05$ (n = 6). CD = color density; ΔE^*_{ab} = total color difference; dA% = contribution to color of flavylium ions; TA = total anthocyanins; Table S3: Chelation of Fe (mg/L) by the different oenological tannins added to wines (initial content 0.69 mg/L). In the same column, different letters indicate significant differences among the tannins at $p < 0.05$ (n = 6); Table S4: Quantification (mg/L) of individual anthocyanins and their respective classes (bold) in the different rosé wines at the starting point (T0). In the same row, different lowercase letters denote

significant differences among the tannins at $p < 0.05$ (n = 6); different uppercase black letters represent significant differences among the tannin families at $p < 0.05$ (n = 6); different uppercase red letters indicate significant differences in the total sum of all detected anthocyanins among the tannins at $p < 0.05$ (n = 6); Table S5: Final variation (ΔT56-T0) in anthocyanin concentrations (mg/L) and their representative families, highlighting changes in pigment levels and degradation over time. In the same row, different lowercase letters denote significant differences among the tannins at $p < 0.05$ (n = 6); different uppercase black letters represent significant differences among the tannin families at $p < 0.05$ (n = 6); different uppercase red letters indicate significant differences in the total sum of all detected anthocyanins among the tannins at $p < 0.05$ (n = 6).

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