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Effect of soluble polysaccharide addition against oxidation of rosé wines

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ABSTRACT

Rosé wines, due to lower phenolic compounds and antioxidant content, are especially vulnerable to oxidation. Moreover, the valorization of winemaking byproducts is gaining interest, as it has the potential to reduce the environmental impact of wine production. For these reasons, the aim of this study was to investigate the effect of the addition of soluble polysaccharides, obtained from white grape pomace, on the phenolic oxidation of Syrah rosé wines. The soluble polysaccharides were extracted, characterized and added to the wines, which were periodically saturated with oxygen. The evolution of the phenolic composition and color parameters (CIELAB) was monitored by means of HPLC-DAD-MS and UV–vis spectrophotometry, respectively. The polysaccharide extract was mainly formed by homogalacturonans, type-II rhamnogalacturonans and polysaccharides rich in arabinose and galactose. The addition of this soluble extract seemed to promote the formation of acetaldehyde-mediated derived pigments in rosé wines, with an increase in color intensity and sulfite bleaching resistance. During oxygenation, a protective trend against the degradation of flavanols and phenolic acids was also observed in the polysaccharide-added rosé wines, which exhibited, at the end of this study, concentrations of these compounds that were 43.7 % and 11.5 % higher, respectively, than those in control samples. Therefore, these results suggest a protection of wine polyphenols, which reveals the potential use of these waste-derived extracts as a new oenological adjuvant for enhancing the phenolic and color stability of rosé wines.

1. Introduction

World consumption of rosé wine has increased by 30% since 2002, currently representing more than 10% of total still wine consumption (Peres et al., 2020). According to the OIV (2015), France stands as the largest producer of rosé wines worldwide, whereas Spain, the second country in terms of production, is the leading exporter of this product.

The color of rosé wines is thought to be a significant factor contributing to their increasing success and their growing attractiveness, as it constitutes the primary criterion for consumers when selecting a rosé wine (Flanzy et al., 2009). As a consequence, the market offers a wide range of rosés, varying in color hues and intensity from light salmon-orange tones to intense pinks (Centre de Recherche et d'Expérimentation sur le Vin Rosé, 2023).

Analogous to red wines, the color of rosés is a direct consequence of the presence of anthocyanin pigments extracted from red grape skins during the maceration process. In contrast to the prolonged macerations in the red winemaking process, rosé winemaking involves pressing after a short prefermentative maceration with the grape pomace (Wirth et al., 2012). The limited extraction of phenolic compounds, mainly from the skins, results in a distinct phenolic composition, different from that of red or white wines, and even diverse among rosés (Leborgne et al., 2023; Wirth et al., 2012). Additionally, factors such as grape variety, maturity and winemaking conditions (temperature, pressing, use of enzymes, etc.) play a crucial role in shaping the final organoleptic characteristics of rosé wines (Flanzy and Cayla, 2006).

Phenolic compounds have a remarkable impact on the overall quality of the wines, influencing its color, taste and astringency (Lambert et al., 2015). The major phenolic compounds found in rosé wines are hydroxycinnamic acids, whereas anthocyanins and flavanols are present at lower concentrations, making these wines more susceptible to oxidation. This fact can favor the oxidation of the

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hydroxycinnamic acids, which leads to a browning of musts and wines (Cheynier et al., 1997; Lambert et al., 2015; Leborgne et al., 2023). Therefore, understanding the evolution and changes in the phenolic composition of the wines under oxygen exposure, especially in the case of an understudied matrix such as rosé wines, is of prime interest (Wirth et al., 2012). Indeed, although color evolution and stabilization are widely studied in red wines (Waterhouse and Laurie, 2006; Zhang et al., 2022), oxidative evolution studies in rosés gain significance due to their popularity and wide variety of color and phenolic composition (Wirth et al., 2012).

Reactive oxygen species (ROS) from dissolved oxygen can cause the oxidation of several molecules present in wine, such as ethanol, polyphenols, and organic acids (Oliveira et al., 2011). Studies show that anthocyanins are the main target of oxidation in wines, undergoing autooxidation processes as well as reacting with other compounds such as acetaldehyde (Wirth et al., 2010). Eventually, at longer oxygen exposure times, the concentration of tannins and phenolic acids likewise decreases (Wirth et al., 2010).

In terms of color, oxidative changes toward orange and yellowish tones are primarily driven by the oxidative evolution of phenolic compounds (Wirth et al., 2012; Zhang et al., 2022). Oxygen exposure has been shown to cause the degradation of anthocyanins (Wirth et al., 2010), and the modification of wine tannins' nature and properties, thereby influencing the organoleptic attributes of the final product (Waterhouse and Laurie, 2006).

The relative concentration of anthocyanins and flavanols directly affects wine behavior under oxygen exposure (Petrozziello et al., 2018). Thus, the complexity of the phenolic evolution upon oxidation in rosé wines increases the interest in oenological strategies for managing the oxidation process (Peres et al., 2020; Wirth et al., 2010).

In the context of climate change, the chemical composition of grapes is changing due to alterations in the phenological stages of grapevines. This has led to the search of new strategies to mitigate these changes and protect wine quality (Oyón-Ardoiz et al., 2022). From a commercial and sustainability perspective, the focus is on potential natural additives, ideally derived from winemaking by-products. This could be the case of mannoproteins from winemaking yeasts, polysaccharide extracts from grape skins, or seed-derived products (Alcalde-Eon et al., 2019; Oyón-Ardoiz et al., 2022). In this framework, grape pomace has gained attention due to its technological properties. In wine-producing countries such as France, Italy or Spain, grape pomace generation, typically regarded as a waste, can amount to several thousand tons per year (Beres et al., 2017). Among the components of pomace, grape skins offer numerous interesting applications due to their content of phenolic compounds and polysaccharides, even after the maceration process (Martínez-Lapuente et al., 2019).

The main groups of polysaccharide families derived from grape cell walls are polysaccharides rich in arabinose and galactose (PRAGs) and type I and II rhamnogalacturonans (RG-I and RG-II). Constituting the so-called PRAGs, arabinans, arabinogalactans and arabinogalactan-proteins (AGP) can be found. Polysaccharides extracted from grape cell walls show chemical and organoleptic characteristics of significant oenological interest. For instance, they can stabilize foam in sparkling wines, act as protective colloids, modulate astringency or contribute to the sensation of body in still wines (Canalejo et al., 2021; Martínez-Lapuente et al., 2019). Despite their potential, grape-derived polysaccharides are not currently commercially available. However, maceration techniques and studies are underway to enhance the extraction of these elements from the skins (Martínez-Lapuente et al., 2019).

In this context, evaluating soluble polysaccharides derived from winemaking by-products as a potential oenological additive seems necessary, with the aim of protecting or modulating the organoleptic characteristics of wines, which are directly linked to its phenolic composition, against oxidation and decay (Canalejo et al., 2021; Martínez-Lapuente et al., 2019).

The effect of the addition of grape and pomace-derived polysaccharides has been previously demonstrated in white wines, where they have been shown the ability to modulate flavor characteristics by interacting with polyphenols and volatile compounds in the wine (Canalejo et al., 2023; Pérez-Magariño et al., 2022). However, to our knowledge, no studies have reported the effect of the addition of pectic polysaccharides in rosé wine matrices.

White grape pomace contains lower levels of antioxidant compounds compared to red grape pomace, which makes it even more underused as a source of phenolic compounds (Pinelo et al., 2006). However, for the addition of pomace-derived extracts to white or rosé wines, the absence of anthocyanins in white grapes makes white grape pomace a more suitable option, as these pigments would otherwise undesirably modify the color in white and rosé wines.

Therefore, the main objective of this study was to determine, for the first time, the effect on the oxidation of rosé wines of the addition of soluble polysaccharides obtained from winemaking by-products. To do this, the extraction and characterization of soluble polysaccharides from white grape pomace skins has been performed. Furthermore, the evolution of phenolic composition and color parameters in a rosé wine subjected to periodic oxygenation was monitored to investigate the effects of adding the previously extracted polysaccharides.

2. Materials and methods

2.1. Chemicals

All reagents used were of analytical grade and all solvents were of HPLC grade.

Ultrapure water from a Milli-Q Gradient water purification system (Millipore, Billerica, MA, USA) was used for all solutions. Ethanol was acquired from Scharlab S.L. (Barcelona, Spain), and methanol from VWR International (Briare, France). Trifluoroacetic acid (TFA) was purchased from Riedel-de Haën (Hanover, Germany), acetonitrile from Supelco (Darmstadt, Germany) and chlorohydric acid (HCl, 35 %) was obtained from Panreac (Darmstadt, Germany).

2.2. Extraction and purification of soluble polysaccharide extract

Soluble polysaccharides were extracted from a white grape pomace from *Vitis vinifera* L. (cv. Verdejo) obtained under white winemaking conditions ('Bodega Cuatro Rayas').

The extraction was carried out following the method described by Martins et al. (2017) with some modifications, as Manjón et al. (2023) have previously reported. The skins were firstly separated from the seeds and other solids. Then, 60 g of skins were weighed and extracted by decoction with 1.6 L distilled water, maintained at constant boiling for 2 h. After filtration, the solid residue was subjected to a second extraction under the same conditions to maximize the polysaccharide extraction. The supernatant from both processes was concentrated to half its volume under reduced pressure and then subjected to freeze-drying. To remove phenolic compounds, the resulting freeze-dried extract was divided into 1 g portions and placed in Falcon tubes, then washed with 96% cold ethanol (30 mL per tube) and centrifuged at 14,400×*g* for 10 min (4 °C). This washing operation was repeated until the absorbance at 280 nm of the supernatant reached below 0.2 units. The precipitate was then redissolved in a hydroalcoholic solution (200 mL/L of ethanol in water) and centrifuged under the same conditions. The supernatant, containing the soluble polysaccharides, was reserved. This process was repeated once, and the remaining precipitate was discarded. The supernatants were then combined, concentrated under vacuum and freeze-dried to obtain the soluble polysaccharide fraction of the grape pomace skins. Following the extraction and purification process of the soluble polysaccharide extract from white grape skins, a yield of 47 mg of soluble polysaccharide extract per gram of pomace skins was achieved.

Once the extract was obtained, further characterization was

conducted. In order to ensure the absence of free polyphenols in the extract, HPLC-DAD-MS of a filtered 0.5 mg/mL PS sample was performed (as described in Section 2.8). The search for any residual phenolic compound in the extract was carried out at 280, 320 and 360 nm. Protein content in the extract was determined by the Bradford method (Bradford, 1976) using the 96 Well Plate Assay Protocol as described by the supplier (Sigma-Aldrich, St. Louis, MO, USA), testing a range of PS concentrations (0.1, 0.2, 0.4, 0.5, 1 and 2 mg/mL) and a bovine serum albumin calibration curve (Sigma-Aldrich, St. Louis, MO, USA) (calibration curve included in Supplementary Material).

2.3. Analysis of soluble polysaccharide weight distribution

The molecular weight distribution of the polysaccharide extract was analyzed by high-resolution size exclusion chromatography, with a refractive index detector (HRSEC-RID), following the method described by Guadalupe and Ayesterán (2007) with some modifications. Briefly, 2 mg of the polysaccharide extract were dissolved in 500 μL of lithium nitrate (0.1 mol/L) (Thermo Fisher Scientific Inc., Waltham, MA, USA), filtered through a Nylon filter (0.45 μm Millex syringe-driven filter unit; Millipore Corp., Bedford, MA, USA) and analyzed using an HPLC chromatograph (Agilent 1260 Infinity - Agilent Technologies, Palo Alto, CA, USA). The chromatograph was equipped with two columns in series: Shodex OHpak SB-803 HQ and SB-804 HQ (8 mm × 300 mm; Showa Denko Europe GmbH, Germany) equilibrated at 1 ml/min in 0.1 mol/L $LiNO_3$, along with a refractive index detector (RID). To assess the weight distribution of the polysaccharide extract, it was compared with pullulan commercial standards of different molecular weights (Sigma-Aldrich, St. Louis, MO, USA): Mw 342 Da (P1), Mw 1320 Da (P2), Mw 6200 Da (P3), Mw 10,000 Da (P4), Mw 21,700 Da (P5), Mw 48,800 Da (P6), Mw 113,000 Da (P7), Mw 200,000 Da (P8), Mw 348,000 Da (P9) and Mw 805,000 Da (P10) (Manjón et al., 2020) (calibration curve included in Supplementary Material).

2.4. Monosaccharide analysis of the soluble polysaccharide extract

Monosaccharide composition of the polysaccharide extract was analyzed following a modified version of the method described by Ruiz-Garcia et al. (2014). The soluble polysaccharide extract (1 mg) was hydrolyzed in 2 mol/L TFA at 100 °C for 3 h. Afterwards, it was cooled on ice and centrifuged at 9190×*g* for 5 min. The supernatant was collected for the subsequent derivatization reaction with 1-phenyl-3-methyl-5-pyrazonone (PMP; SigmaAldrich, St. Louis, MO, USA). The conditions for HPLC-DAD-MS analysis were previously optimized by Manjón et al. (2023) (see Supplementary Material for further details on monosaccharide analysis).

All monosaccharides were characterized according to their mass spectra, fragmentation patterns and retention times. For quantitative analysis, calibration curves were prepared using previously PMP-derivatized monosaccharide standards of D-(+)-glucose, D-(+)-xylose, D-(+)-mannose (SigmaAldrich, St. Louis, MO, USA), D-(+)-galactose, L-rhamnose, D-(+)-galacturonic acid, D-(+)-galacturonic acid, D-(+)-fucose and D-(−)-arabinose (Alfa-Aesar, Karlsruhe, Germany). Using the concentration data of the different monosaccharides, the polysaccharide profile of the extract was estimated using the iterative method described by Arnous and Meyer (2009). This method systematically distributes the previously identified monosaccharides into known polysaccharide structures based on established plant cell wall models. All analyses were conducted in triplicate.

2.5. Wine samples

The experimental rosé wine was produced by the Food Color and Quality Research Group from the University of Seville. Grapes from *V. vinifera* cv. Syrah, belonging to the Condado de Huelva D.O., were harvested after reaching technological maturity. The oenological parameters of the wine were: pH of 3.55; total acidity of 5.1 g/L (expressed as tartaric acid equivalents); 64.0 mg/L of total sulfites, and 30.07 mg/L of free sulfites.

Samples were prepared by placing 120 mL of rosé wine into transparent glass bottles, capped with a silicone lid, leaving enough headspace for the oxygenation process. To investigate the impact of the polysaccharides on wine oxidation, three control samples (wine without polysaccharide addition) and three wine samples with a concentration of 400 mg/L of soluble polysaccharide extract (PS) were analyzed and monitored. This concentration was chosen based on the maximum mannoprotein addition permitted by the OIV (2023), given that these are a type of polysaccharide.

2.6. Oxygen monitoring

Dissolved oxygen in the wines was daily measured with the FireSting®-PRO Multichannel Optical Multianalyte Meter (PyroScience GmbH, Aachen, Germany), using the OXROB10 oxygen probe calibrated between 0 and 230 μmol/L O_2 (100% oxygen saturation in water at the specific conditions of temperature, atmospheric pressure and salinity). When the samples reached a consistently low dissolved oxygen level (below 100 μmol/L O_2), the wines were saturated by shaking: two cycles of shaking for 1 min (>50% of headspace) followed by 30 s of rest for air renewal. The wines were considered oxygen-saturated once a value of 200 μmol/L O_2 had been reached. The bottles were then recapped and stored in the dark at a constant room temperature (24 °C). Fig. S1 in the Supplementary Material shows oxygen evolution during the experiment.

On days 0 (before oxygen saturation), 5, 11 and 27 of the experiment, aliquots of all the samples were analyzed by means of HPLC-DAD-MS. An additional aliquot was used on day 19 for the colorimetric analysis.

2.7. Analysis of native and derived anthocyanins

The analysis of anthocyanins was carried out by HPLC- DAD-MS. To each 2 mL sample, 70 μL of a 3 mol/L HCl solution were added, followed by filtration through a 0.45 μm filter (Millex syringe-driven filter unit; Millipore Corp., Bedford, MA, USA). The analysis was performed on an Agilent 1100 Series HPLC (Agilent Technologies, Palo alto, CA, USA) equipped with a C18 reverse phase column (5 μm, 150 mm × 4.6 mm; Aqua®, Phenomenex, Torrance, CA, USA) thermostated at 35 °C. The solvents used were (A) an aqueous solution (1 mL/L) of TFA and (B) 100% HPLC-grade acetonitrile. The following gradient was established to perform the analysis: isocratic 10% B for 5 min, from 10 to 15% B for 15 min, isocratic 15% B for 5 min, from 15 to 18% B for 5 min and from 18 to 35% B for 20 min, at a flow rate of 0.5 mL/min. Detection was carried out at a wavelength of 520 nm, and spectra were recorded from 220 to 600 nm (Alcalde-Eon et al., 2006). For MS analysis, detection was carried out in positive mode (ESI+) (see Supplementary Material for further details on MS analysis).

A total of 34 pigments were identified based on their absorption spectra, retention times, *m/z* ratios, and fragmentation patterns (Alcalde-Eon et al., 2019). The concentration of each pigment was determined using a malvidin-3-*O*-glucoside (Mv3glc) (Extrasynthèse, Genay, France) calibration curve (see Supplementary Material).

2.8. Analysis of flavanols and phenolic acids

The analysis of flavanols and phenolic acids was conducted using HPLC-MS following a previously published method (García-Estévez et al., 2017a). Briefly, wine samples were diluted 1:1 with acidified water (0.1 mol/L HCl) and loaded onto an Oasis MCX cartridge (Waters Corp., Milford, MA, USA), which was pre-conditioned with methanol and water. The elution of these compounds was carried out with 8 mL of methanol, followed by drying in a rotary evaporator and re-dissolving in 500 μL of ultrapure water. Chlorogenic acid (Alfa-Aesar, Karlsruhe,

Germany) was added as an internal standard (0.025 mg/mL) and samples were filtered using 0.45 μm filters before their analysis by HPLC-DAD-MS.

The identification and quantification of flavanols were carried out by mass spectrometry using the MRM analysis method, following the conditions described by García-Estévez et al. (2017a). Calibration curves of (+)-catechin, (−)-epicatechin, (+)-gallocatechin (Sigma-Aldrich, St. Louis, MO, USA), B1 and B2 dimers, C1 trimer, (−)-epicatechin gallate, and (−)-epigallocatechin (Extrasynthèse, Genay, France) were used for the quantification of flavanols. For phenolic acids, a calibration curve for each acid (Sigma-Aldrich, St. Louis, MO, USA) was used for their respective quantification (calibration curves included in Supplementary Material).

2.9. Color properties and sulfite bleaching resistance

For colorimetric analysis, samples were filtered to remove potential suspended particles. The absorbance spectrum between 190 and 770 nm was measured using a Hewlett-Packard 8435 UV–vis spectrophotometer (Agilent Technologies, Waldbronn, Germany) with a quartz cuvette (1 cm of path length). From the visible spectrum data (380–770 nm), CIELAB parameters (L^*, a^*, b^*, C^*_{ab} and h_{ab}) were obtained using the CromaLab® software (Heredia et al., 2004).

To assess the resistance of rosé wines to bisulfite bleaching, absorbance spectra of decolorized samples were also measured. For this, 45 μL of a 200 g/L solution of potassium metabisulfite (Panreac, Darmstadt, Germany) in distilled water were added to 3 mL of the rosé wine samples. After 1 min of reaction, the absorbance was measured in the UV–vis spectrophotometer previously stated, using a quartz cuvette (1 cm of path length). To determine the percentage of bisulfite resistance, the absorbance (520 nm) of the decolorized samples was compared with its absorbance before bisulfite addition.

2.10. Statistical analysis

The results were subjected to statistical analysis using SPSS Statistics 26 software (IBM). The Student's t-test was used to determine the statistical significance of the differences between samples with (PS) and without polysaccharide addition (control). In all cases, differences were considered statistically significant for $p < 0.05$.

3. Results and discussion

3.1. Characterization of soluble polysaccharide extract

After obtaining the soluble polysaccharide extract, HPLC-DAD-MS analysis was performed to study the presence of free polyphenols in the extract. The resulting chromatogram recorded at different wavelengths (280, 320 and 360 nm) showed the absence of phenolic compounds. Additionally, protein presence in the extract was ruled out by the Bradford assay (Bradford, 1976), where no protein was detected at any PS concentration.

The distribution of the PS molecular weight was analyzed by HRSEC-RID. The soluble polysaccharide extract comprised three main constituents, as shown in Table 1. The first constituent, with a molecular weight of 105 kDa, constituted 26.1 % of the total polysaccharides determined. The second, with a molecular weight of 8.4 kDa, accounted for 15 %. Finally, the third constituent, with a molecular weight of 1.74 kDa, represented over half of the polysaccharide extract (59.4 %). The greater presence of the polysaccharide fraction with the smallest molecular weight (1.74 kDa) suggested that the soluble polysaccharide extract consisted mainly of low molecular weight oligomers(<2 kDa). Given the conditions of the polysaccharide extraction from the grape pomace and the purification performed in order to isolate the soluble fraction, low molecular weight polysaccharides were expected. Additionally, this finding aligns with previous studies (Canalejo et al., 2021; Pérez-Magariño et al., 2022) where polysaccharides extracted from white grape pomace (cv. Verdejo) exhibited over 50 % of fractions with a molecular weight lower than 5 kDa.

Table 1
Distribution of molecular weights of the soluble polysaccharide extract obtained from white grape pomace skins.

Constituent	Molecular weight (kDa)	Percentage
1	105 ± 6	26.1 ± 0.3
2	8.4 ± 0.3	15 ± 1
3	1.74 ± 0.01	59.4 ± 0.8

Values are means ± their standard deviations (n = 3).

From the monosaccharide composition of the soluble polysaccharide extract determined by HPLC-DAD-MS (see Table S1 in the Supplementary Material), the polysaccharide profile was estimated using iterative calculation (Arnous and Meyer, 2009). Table 2 shows the concentration of the main polysaccharide families in the extract, with homogalacturonans (38.1 %), type II rhamnogalacturonans (29.1 %) and PRAGs (22.1 %) being the predominant families. These results are in agreement with findings from Canalejo et al. (2021), who reported that different polysaccharide extracts obtained from white grape skin mainly consists of PRAGs and polysaccharides rich in rhamnogalacturonans (RG-II). These polysaccharides are considered principal constituents of the pectic matrix in grape cell walls (Martínez-Lapuente et al., 2019; Vidal et al., 2001), which can explain the composition of the obtained extract.

The identification of mannose among the monosaccharide units likely corresponded to the presence of mannans in the extract. Mannans are linear chains of mannose naturally present in grape pericarp (Canalejo et al., 2021; Vidal et al., 2001). Considering that the grape pomace employed was derived from winemaking by-products, which are in direct contact with yeasts, the presence of mannoproteins from yeast cell walls was also possible. Yeasts, mainly *Saccharomyces cerevisiae*, could be native of the grape itself, or come from the winery during the different stages of the winemaking process. Additionally, the detection of glucans could also suggest the presence of yeast-derived polysaccharides in the extract (Ayestarán et al., 2004). The trace amounts of lees in the skins could explain the minor and very similar concentrations of both mannans and glucans in the extract.

Xylose residues would correspond to the xyloglucans present in the sample. Minor carbohydrates such as fucose, aceric acid or 2-*O*-methyl xylose are expected to be part of the type II rhamnogalacturonans polymeric structure (Ayestarán et al., 2004; Canalejo et al., 2021).

Thus, the main soluble polysaccharides determined in the extract obtained from white grape skin consisted of galacturonic acid, arabinose and galactose as major constituent monosaccharides, which would act as the building blocks for homogalacturonans, rhamnogalacturonans, arabinogalactans and arabinans. These results are in agreement with those reported by Manjón et al. (2023) in their analysis of soluble polysaccharide extracts obtained from grape cell wall material.

Table 2
Polysaccharidic composition of the soluble extract obtained from white grape pomace skins.

Polysaccharide Family	Percentage (w/w)
Homogalacturonan (HG)	38.6 ± 0.6
Rhamnogalacturonan II (RGII)	29 ± 2
PRAGs	22.40 ± 0.01
Rhamnogalacturonan I (RGI)	3.80 ± 0.06
Glucans	2.7 ± 0.4
Mannans	2.60 ± 0.06
Xyloglucan	0.71 ± 0.07

Values are means ± their standard deviations (n = 3).

3.2. Effect of the addition of soluble polysaccharide extract to rosé wine

The previously characterized soluble polysaccharide extract (section 3.1) was added to Syrah rosé wines. The maximum concentration of mannoprotein addition to wine allowed by the OIV (2023) is 400 mg/L. Given that mannoproteins are a type of polysaccharide, it was decided to adopt the same concentration to assess the impact of the soluble polysaccharide on the oxidative evolution of rosé wine. The maximum dose (400 mg/L) was chosen in order to determine a possible effect of the polysaccharide extract, setting the ground for further optimization studies. This extract was added to three wine samples (PS), while other triplicate was kept as control samples.

3.2.1. Evolution of native and derived anthocyanins

The HPLC-DAD-MS analysis allowed the identification and quantification of 34 pigments in the rosé wine samples exposed to an oxygenation process, both with and without soluble polysaccharide addition (see Table S2 in the Supplementary Material). These pigments were grouped into 7 families to simplify the discussion of results: total monoglucoside anthocyanins (5 compounds), total acylated derivatives (15 compounds), vitisin A, group B vitisins (4 compounds), ethyl-linked flavanol-anthocyanin condensates (3 compounds), flavanol-anthocyanin condensates (2 compounds) and vinylphenol-type vitisins (4 compounds).

Fig. 1 shows the evolution of monoglucoside anthocyanins, acylated derivatives (the sum of both would constitute the native anthocyanins) and total pigments (the sum of the 34 quantified pigments, indicated above). The wines showed a gradual decrease in the concentration of native anthocyanins and total pigment concentration throughout the oxygenation process. This decrease was more than 34 % at 27 days for total pigments. However, no significant differences between the evolution of control and polysaccharide-added wines were observed in the case of native and total pigments.

The degradation of anthocyanins, in particular of the major pigment, Mv3glc, primarily results in the production of syringic acid as degradation product (Lopes et al., 2007). Thus, the evolution of both syringic acid and Mv3glc concentrations was studied. The concentration of syringic acid remained constant over time, suggesting that the degradation of these pigments was not the main pathway for the decrease in native Mv3glc concentration. Therefore, the formation of derived pigments may explain this decrease.

Fig. 2 shows the evolution of the derived pigments during the oxygenation process. The group of type B vitisins (Vit B) and ethyl-linked condensates (F-et-A) are the derived pigments that exhibited a major increase in concentration over time. In both cases, the effect of the presence of the polysaccharide was significant at the end of the study (27 days), with higher concentration in PS samples compared to the control samples. To be precise, an increase of 10.1 % in the case of Vit B, and of 8.5 % for F-et-A was observed.

Fig. 3 shows the evolution in PS and control wines of native monoglucoside anthocyanins and of the main derived pigments in the samples (Vit B and F-et-A). As indicated above, native pigments decrease their concentration over time during oxygenation, while derived anthocyanins increase. This notable increase in these derived pigments suggested the presence of acetaldehyde in the wines, which is necessary for mediating the formation of these products (Leborgne et al., 2023; Wirth et al., 2012). This may indicate that the periodic oxygenation of rosé wine samples would result in the oxidation of ethanol to acetaldehyde, which, in turn, promotes the formation of these derived pigments. The presence of polysaccharide revealed a potential trend of steering the evolution of anthocyanins towards the formation of pyranoanthocyanins.

Additionally, the percentage of resistance to bisulfite bleaching was measured during the experiment. As shown in Fig. 4, the resistance of the wines to discoloration increased with time. Furthermore, a slight tendency towards greater resistance was observed in the polysaccharide-added rosés. All these findings led to the conclusion that the evolution of native anthocyanins in wines subjected to oxidation possibly occurred primarily towards pyranoanthocyanin derived pigments, as they inherently exhibit higher sulfite bleaching resistance (Zhang et al., 2022).

Previous studies of enological tannin and its effect on pigment evolution in wines have shown that its addition promotes the formation of vitisins and acetaldehyde-mediated condensates (García-Estévez et al., 2017b). Thus, it could be suggested that the presence of soluble polysaccharide would favor the formation of pyranoanthocyanins, in an analogous way to the aforementioned tannins, potentially limiting other evolution pathways.

Different polysaccharides can interact and associate with polyphenolic compounds in wines (Fernandes et al., 2020; Manjón et al., 2023; Oyón-Ardoiz et al., 2022). Previous studies have shown that mannoproteins can interact with anthocyanins, providing colloidal protection against precipitation by cold (Alcalde-Eon et al., 2019; Oyón-Ardoiz et al., 2022). However, other studies on anthocyanin interactions with white grape soluble polysaccharides (cv. Muscat) do not show significant effects on red wine pigments (Manjón et al., 2023), which would be in agreement with the lack of differences between the evolution of total pigments in control and PS wines shown in Fig. 1. Nevertheless, grape variety can greatly influence the polysaccharide

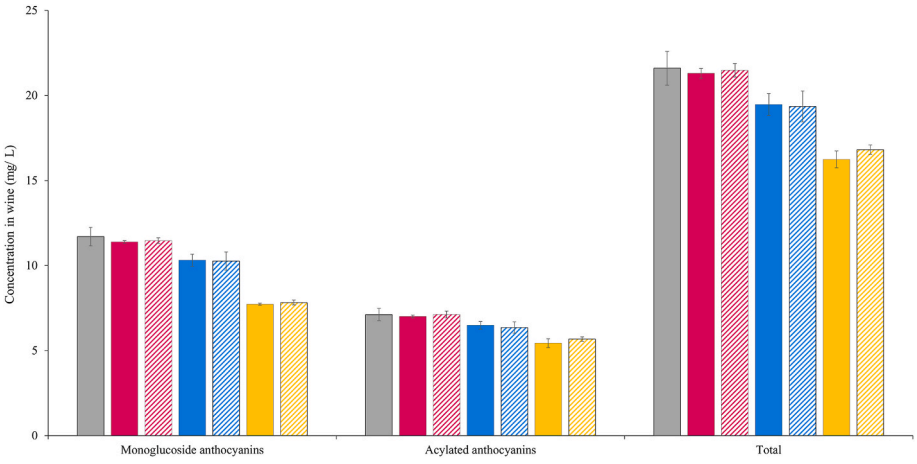

Fig. 1. Evolution of the concentration of monoglucoside anthocyanins, their acylated derivatives and total pigments. The evolution of samples without polysaccharide (flat color) and added with 400 mg/L polysaccharide (PS; stripe pattern) is shown for each group at 0 days (grey), 5 days (pink), 11 days (blue) and 27 days (yellow). The error bars represent the standard deviation of the triplicates. Significant differences ($p < 0.05$) between PS samples and their respective control are denoted with an asterisk.

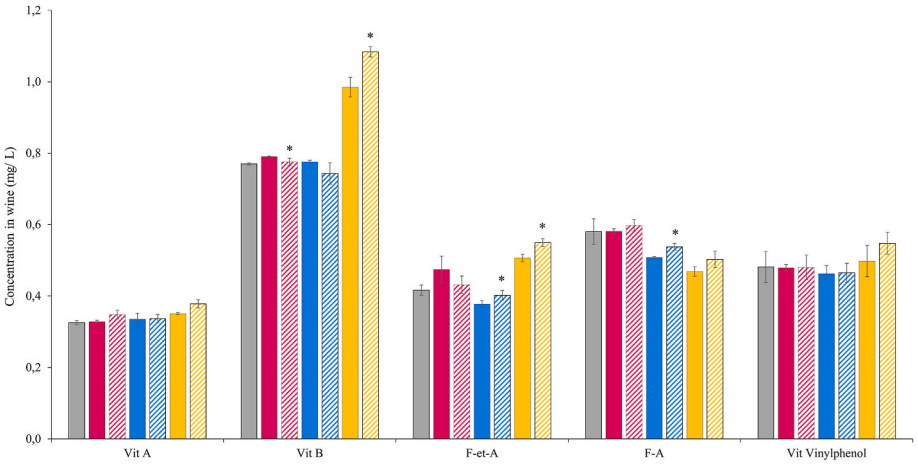

Fig. 2. Evolution of the concentration of vitisin A (Vit A), vitisin B (Vit B), flavanol-ethyl-anthocyanin condensates (F-et-A), direct flavanol-anthocyanin condensates (F–A) and vinylphenol-type vitisins (Vit Vinylphenol). The evolution of samples without polysaccharide (flat color) and added with 400 mg/L polysaccharide (PS; stripe pattern) is shown for each group at 0 days (grey), 5 days (pink), 11 days (blue) and 27 days (yellow). The error bars represent the standard deviation of the triplicates. Significant differences ($p < 0.05$) between PS samples and their respective control are denoted with an asterisk.

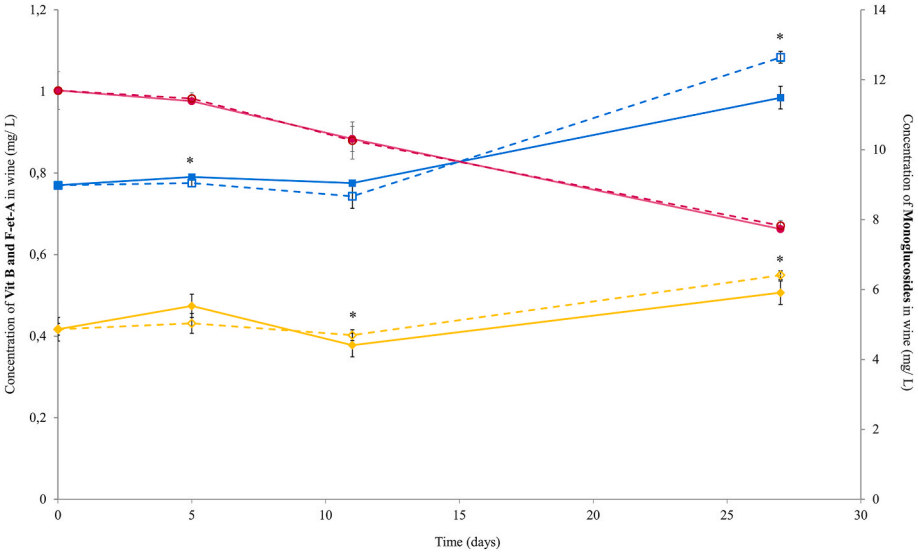

Fig. 3. Evolution over time of the concentration of monoglucoside anthocyanins (pink circles; secondary y-axis) and their derivatives (primary y-axis): vitisin B (Vit B; blue squares) and flavanol-ethyl-anthocyanin condensates (F-et-A; yellow diamonds). The evolution of control samples without polysaccharide (solid line) and added with 400 mg/L polysaccharide (PS; dashed line) is shown. The error bars represent the standard deviation of the triplicates. Significant differences ($p < 0.05$) between PS samples and their respective control are denoted with an asterisk.

composition (Ortega-Regules et al., 2008) and, consequently, its behavior and interactions in the wine matrix. Furthermore, the polyphenolic composition of red and rosé wines varies greatly (Leborgne et al., 2023), thereby affecting these interactions.

Thus, a slight colloidal protection of the pigments due to the polysaccharide extract, as seen in the case of arabinogalactans derived from *Acacia* gum (Nigen et al., 2019), would be expected to hinder the direct oxidation of native anthocyanins in rosé wines. Consequently, more dissolved oxygen would be free in the wine matrix, capable of reacting with ethanol and generating acetaldehyde. This increase in acetaldehyde, as previously mentioned, would favor the formation of acetaldehyde-mediated derivatives such as Vit B and F-et-A, which could explain the higher concentrations of these compounds in the polysaccharide-added wines. The differences and trends found in polysaccharide added rosé wines can set the ground for further studies of wine waste derived extracts as an additive in this type of wine.

3.2.2. *Evolution of flavanols*

A total of 19 flavanols (mainly proanthocyanidins) were identified and quantified, including monomers ((+)-catechin, (−)-epicatechin and (+)-gallocatechin), prodelphinidin (PD) dimers, (epi)catechin-(epi)gallocatechin dimers (mixed PD dimer), as well as procyanidin (PC) dimers, trimers and tetramers. These compounds were grouped into 3 categories based on the number of monomeric units in their structure, distinguishing monomeric flavanols (sum of identified monomers), dimeric proanthocyanidins (sum of PD dimers, PC dimers and mixed PD dimers) and oligomeric proanthocyanidins (sum of identified PC trimers and tetramers).

Fig. 5 shows a decrease in all compounds as oxidation progresses, which is in agreement with the findings of Atanasova et al. (2002) and Rinaldi et al. (2021). In the case of total flavanols, the decrease was significantly lower in the polysaccharide-added rosé wines (43.3 %) than in the control samples (60.6 %). This result suggests a protective role of the polysaccharide extract in preventing flavanol degradation

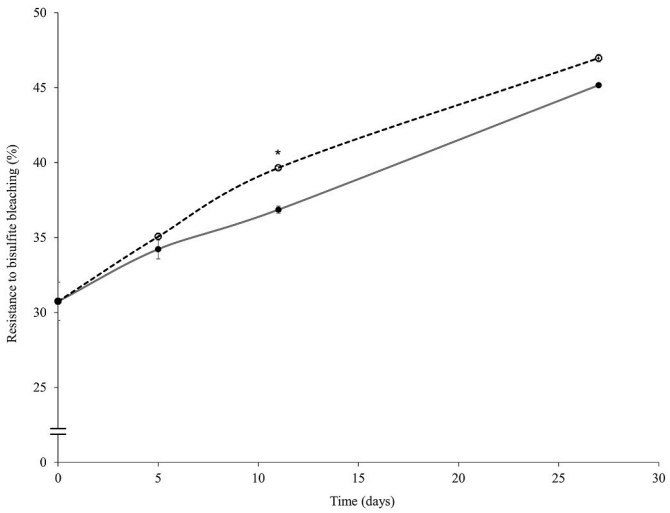

Fig. 4. Evolution of the percentage of bisulfite bleaching resistance. The evolution of control samples without polysaccharide (solid line) and added with 400 mg/L polysaccharide (PS; dashed line) is shown. The error bars represent the standard deviation of the triplicates. Significant differences ($p < 0.05$) between PS samples and their respective control are denoted with an asterisk.

under oxidation, particularly over extended periods (27 days).

Manjón et al. (2023) previously observed that soluble polysaccharides from grape skins could reduce the amount of flavanols in wine due to their interaction and precipitation, thereby reducing the astringency of red wines. However, given that rosé wines usually contain a much smaller concentration of these compounds, this interaction could provide a protective effect without leading to their precipitation. Other studies have concluded that the structure of pectic polysaccharides can directly influence their interaction with polyphenols (Fernandes et al., 2020). The size and branching degree of the polysaccharide, as well as the polymerization degree of procyanidins can influence their interactions, with stronger effects observed for low-branched polysaccharides and more polymerized flavanols (Fernandes et al., 2020). During the initial stages of oxidation, the effect of the polysaccharides was more pronounced in the case of oligomers. However, at longer durations, this became more noticeable for monomeric and total flavanols. Therefore, the presence of polysaccharides could decrease their polymerization, rather providing a colloidal stabilization of flavanols. This observation was also found by Canalejo et al. (2023), concluding that the presence of polysaccharide extracts in white wines positively contributes to the modulation of astringency and bitterness, which would be related to the reduction of proanthocyanidins and their polymerization degree. Consequently, in prolonged times of oxygen exposure, the polysaccharide-polyphenol interaction may favor the formation of derived pigments with anthocyanins, such as ethyl-linked adducts, through the presence of acetaldehyde in the wines (He et al., 2012; Leborgne et al., 2022).

3.2.3. *Evolution of phenolic acids*

The identified and quantified phenolic acids (a total of 12 compounds) were grouped into three families (Fig. 6): hydroxybenzoic acids (HBA; gallic, protocatechuic and syringic acids), hydroxycinnamic acids (HCA; caffeic, *p*-coumaric and ferulic acids) and cinnamoyl tartaric acids (HCTA; *cis* and *trans* caffeoyltartaric, coumaroyltartaric and feruloyltartaric acids). According to the findings reported by Leborgne et al. (2023), rosé wines exhibited a substantial content of phenolic acids, particularly of their tartaric derivatives (HCTA).

Although no significant differences were observed, the addition of polysaccharide appeared to exert a slight protective effect against global phenolic acid oxidation (total concentration of phenolic acids was 11.5 % higher in PS wines than in the control at 27 days). This effect suggested a parallel behavior of the soluble extract, similar to that observed for other polyphenols (anthocyanins and flavanols).

Fernandes et al. (2020), by means of isothermal titration calorimetry (ITC), demonstrated that phenolic compounds, such as hydroxycinnamic acid derivatives (chlorogenic acid), can interact with arabinans and other pectic polysaccharides (mainly by hydrophobic interactions). Although the studied compound, caffeoyl quinic acid, is not present in grapes or wine, hydroxycinnamic tartaric derivatives (the main polyphenols in rosé wine), due to their structural similarity to caffeoyl quinic acid, might exhibit similar interactions with the soluble polysaccharides in the samples.

These results implied an interaction between the phenolic acids in rosé wine and the polysaccharide extract, providing a potential protection that could partially prevent their degradation.

3.3. *Colorimetric analysis*

Table 3 summarizes the analysis of CIELAB parameters representing hue (h_{ab}), lightness (L^*), and chromaticity (C^*_{ab}) to describe the evolution of wine color (according to the OIV Method OIV-MA-AS2-11).

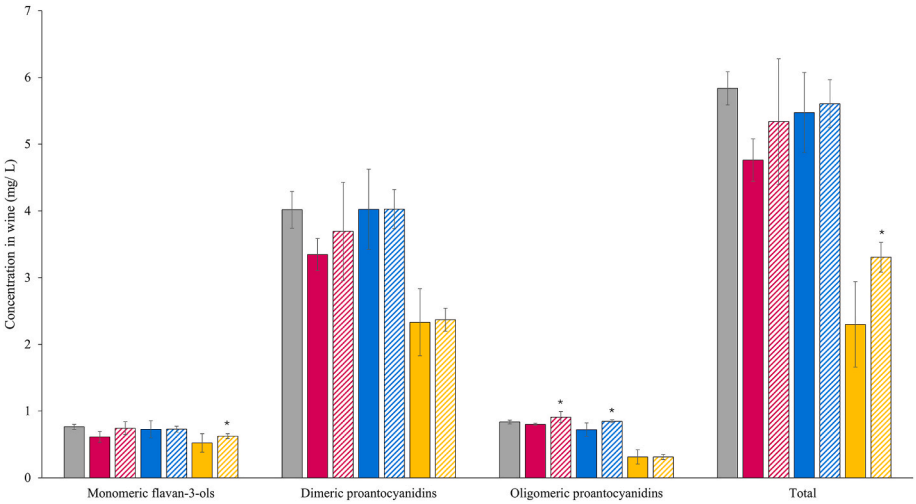

Fig. 5. Evolution of the concentration of monomeric, dimeric, oligomeric and total flavanols. The evolution of samples without polysaccharide (flat color) and added with 400 mg/L polysaccharide (PS; stripe pattern) is shown for each group at 0 days (grey), 5 days (pink), 11 days (blue) and 27 days (yellow). The error bars represent the standard deviation of the triplicates. Significant differences ($p < 0.05$) between PS samples and their respective control are denoted with an asterisk.

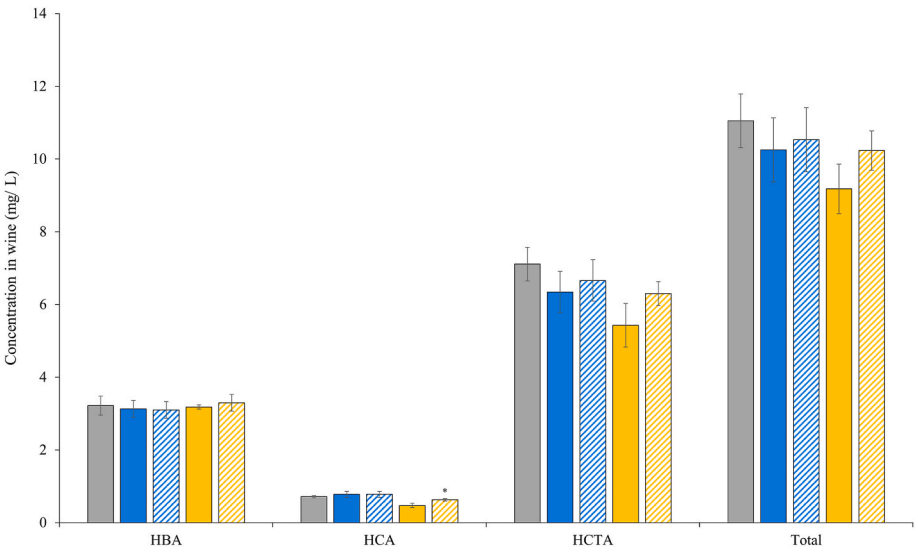

Fig. 6. Evolution of the concentration of phenolic acids, including hydroxybenzoic (HBA), hydroxycinnamic (HCA), hydroxycinnamoyl tartaric (HCTA) and total phenolic acids. The evolution of samples without polysaccharide (flat color) and added with 400 mg/L polysaccharide (PS; stripe pattern) is shown for each group at 0 days (grey), 11 days (blue) and 27 days (yellow). The error bars represent the standard deviation of the triplicates. Significant differences ($p < 0.05$) between PS samples and their respective control are denoted with an asterisk.

A progressive decrease in rosé wine lightness was observed over the oxygenation period, reflecting a darkening of the wines. Previous studies showed that this parameter is negatively correlated to derived pigments and, consequently, with oxidation (Leborgne et al., 2022). The color intensity (chromaticity), on the other hand, increased over time, theoretically resulting in a more intense color. This increase in the C^*_{ab} parameter was significantly greater in the presence of soluble polysaccharide. Finally, considering hue, a progressive decrease was observed (significantly less important in the case of PS samples), meaning that the wines were leaning towards redder tones (Fan et al., 2023). This evolution of the hue is particularly noteworthy, since, unlike other oxidation trials where the wines tended to develop yellowish hues (Rinaldi et al., 2021), in this case the color of the wine shifted towards more intense reddish tones. Pigment evolution, according to the HPLC analysis, showed a decrease in native anthocyanins, parallel to an increase in pyranoantocyanins. This would theoretically translate into an orangish hue in the wines due to the hypsochromic shift of the absorption maximum of various derived pigments (Alcalde-Eon et al., 2006; Leborgne et al., 2023; Zhang et al., 2022).

Wirth et al. (2010) associated higher levels of oxygen exposure in bottled wines with a higher color intensity. Accordingly, other studies in red and rosé wines have shown color enhancement due to oxidation, attributed to the consumption of SO_2 followed by a release of flavylium cations from their colorless bisulfite adducts, enhancing the red color of the wines (Leborgne et al., 2022; Wirth et al., 2012).

Color degradation by means of oxidation is highly dependent on specific factors of the medium such as polyphenol composition or pH, which has been reported in other beverages, like rosé cider (Février et al., 2017). These factors could highly vary from one rosé wine to another. Nevertheless, in this study, oxidative color degradation in a rosé wine was evaluated in presence or absence of 400 mg/L of the polysaccharide extract under the same composition of wine, which allows for the attribution of possible differences exclusively to the presence of exogenous polysaccharides.

Therefore, polysaccharide-added rosé wine showed a greater color intensity variation, with a smaller variation in hue towards red. Additionally, it exhibited lower lightness values than the control samples. Considering color differences, a value greater than 3 in ΔE^*_{ab} (OIV Method OIV-MA-AS2-11) implies a difference in wine color that is perceptible by the human eye (Martínez et al., 2001). In this case, control and PS-added wines showed ΔE^*_{ab} values of 7.1 ± 0.4 and 7.0 ± 0.3, respectively, between the last and first day of the experiment. This means that wine color perceptively changed throughout the assay. This change was slightly higher in wines without PS addition. Although not statistically significant, this observation further supports the previously established protective trend of the PS in rosé wine. Nevertheless, color differences between treated and control wines at 27 days would not be perceptible by the human eye ($\Delta E^*_{ab} = 1.5 \pm 0.2$).

Previous studies have shown that the presence of soluble polysaccharide extracted from grape pomace has an effect on the color of Mv3glc solutions, showing higher intensity and lower hues (Torres-Rochera et al., 2023). In previous works, the colloidal stabilization of wine coloring matter by the presence of polysaccharides (mannoproteins) has been observed (Oyón-Ardoiz et al., 2022). Furthermore, interactions between grape-derived polysaccharides and polyphenols (flavanols) have also been reported by means of ITC

Table 3
Evolution of CIELAB parameters: L* (lightness), C^*_{ab} (chroma) and h_{ab} (hue), of the control wine samples and with the addition of 400 mg/L of soluble polysaccharide extract (PS) during the oxygenation period. Standard deviation of each triplicate is provided. Significant differences ($p < 0.05$) between PS samples and their respective control for each CIELAB parameter are denoted with an asterisk.

Time (days)	Control			PS		
	L^*	C^*_{ab}	h_{ab}	L^*	C^*_{ab}	h_{ab}
0	76.7 ± 0.4	32.6 ± 0.1	46.2 ± 0.4	–	–	–
5	75.7 ± 0.1	33.5 ± 0.2	44.7 ± 0.3	74.99 ± 0.07 *	34.63 ± 0.09 *	45.9 ± 0.2 *
11	74.5 ± 0.1	35.0 ± 0.1	44.0 ± 0.1	73.1 ± 0.4 *	36.0 ± 0.2 *	45.82 ± 0.08 *
19	73.3 ± 0.3	36.2 ± 0.1	43.66 ± 0.06	72.8 ± 0.1 *	37.4 ± 0.1 *	44.8 ± 0.1 *
27	72.0 ± 0.3	37.5 ± 0.2	43.5 ± 0.1	71.1 ± 0.3 *	38.5 ± 0.1 *	44.56 ± 0.09 *

(Manjón et al., 2023). Thus, it is possible that the interaction of the polysaccharide extract could be exerting a similar effect to known copigments, such as flavonols, on the anthocyanin pigments, providing a hyperchromic effect (Torres-Rochera et al., 2023; Zhang et al., 2022), combined with the aforementioned colloidal protection. Further studies regarding sensory evaluation and tasting may be performed in order to understand the role of polysaccharides addition in the mouthfeel of wines, which would be complementary to the color study performed in this work.

4. Conclusion

The results obtained in this study, focused on the effects of pomace-derived soluble polysaccharides added to rosé wines, suggest that soluble polysaccharides from white grape pomace could exert a potential protection for native anthocyanins, flavanols and phenolic acids, against their progressive degradation in environments with high oxygen exposure. Rosé wines showed a higher polyphenol content (especially in the case of flavanols and phenolic acids) when the polysaccharide extract was added, as well as greater color intensity and bisulfite resistance. Thus, this can set the ground for the addition of this type of soluble polysaccharides as a protective measure against rosé wine oxidation.

Therefore, given the increasing popularity of rosé wines and the growing interest in natural products contributing to a circular economy and a sustainable winemaking industry, the use of by-products, such as soluble polysaccharide extracts from grape pomace, presents a viable and promising opportunity for the enological industry from economic, commercial and ecological perspectives. Further studies could be performed to establish the optimal conditions (dose, winemaking conditions, etc.) for the application of this proposed additive in the wine industry.

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CRediT authorship contribution statement

Iván Puerta-García: Resources, Investigation, Data curation, Formal analysis, Visualization, Writing – original draft. **Montserrat Dueñas:** Methodology, Investigation, Formal analysis, Validation, Visualization, Writing – review & editing. **Ignacio García-Estévez:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition. **Erika Salas:** Methodology, Formal analysis, Investigation, Writing – review & editing. **M. Teresa Escibano-Bailón:** Conceptualization, Project administration, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare no competing financial interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2025.101009.

Data availability

Data will be made available on request.

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