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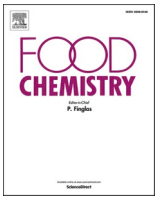

The composition and structure of plant fibers affect their fining performance in wines

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ABSTRACT

In recent years, the wine industry has shifted towards plant-based fining agents for food safety reasons and consumer preferences. This study analysed the interaction of five plant fibers with red wine phenolic compounds to determinate their performance as fining agents. Chemical composition, polysaccharide profile, and physical properties were examined. Pea, cellulose, and *Sauvignon Blanc* pomace fibers effectively reduced tannin content while minimally affecting the concentration of anthocyanins, flavonols and wine color. Contrary to previous beliefs, the presence of pectins in fibers didn't play a crucial role in phenolic compound interaction since cellulose-rich fibers with low pectin concentration also bound tannins effectively, especially those with small particle size and high contact surface. Pea fiber, rich in cellulose and pectins, showed remarkable tannin retention while minimally affecting wine color. This research highlights the potential of plant fibers as effective fining agents in wine production and how their composition affects their performance.

1. Introduction

Fining is a technique that involves the addition of an agent capable of eliminating undesirable compounds. These agents interact through hydrophobic interactions, hydrogen bonding, or adsorption and absorption phenomena with various components of the wine to remove them through precipitation (Kemp et al., 2022). The fining process should be reasonably fast, and the amount of product lost in the sediment should be minimal. The removed compounds may be those that adversely affect the color or clarity of the wine, as well as its sensory characteristics or food safety. An excessive extraction of phenolic compounds in the wine during winemaking, especially tannins, has been associated with undesirable characteristics in wine, such as an increase in bitterness and astringency (Cheynier et al., 2006).

The most common fining agents traditionally used in enology are made from proteins of animal origin such as gelatin, albumin, or casein. However, due to the potential for allergic reactions that some of them present, and with many consumers having a vegan food style, the trend has shifted towards using plant-based proteins (pea, potato, soy, gluten) as well as synthetic polymers like PVPP and earth materials such as bentonite.

Within the framework of searching for new plant-based fining agents, studies such as those conducted by Bindon and Smith (2013), Guerrero et al. (2013), and Jiménez-Martínez et al. (2019) demonstrated that insoluble fibers derived from Cell Wall Material (CWM) of apples and various grape varieties could be considered as fining agents for red wines. In addition, the effectiveness of CWM as fining agents has been shown to be competitive in comparison with some animal-derived ones, like gelatins. The International Organisation of Vine and Wine (OIV) approved the use of plant fibers as fining agents for the removal of undesirable compounds such as ochratoxin A (OTA) or phytosanitary residues (OIV-OENO 684 A-2022), at a maximum allowed concentration of 2 g/L or 1.5 Kg/m^2 when fibers are used during filtration.

Studies with grape pomace derived fibers showed differences in their behaviour during the interaction with the phenolic compounds present in the wine, even when they were from the same grape variety (Guerrero et al., 2013). This may be assigned attributable to different parameters, such as particle size, porosity, surface, or differences in cell wall

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composition, like polysaccharide profile or lignin content. Particle size and porosity affect the contact surface, which play an important role in the number of binding sites available for phenolic compounds. However, and on top of that, Renard et al. (2001) and Le Bourvellec et al. (2007) pointed out that the adsorption of proanthocyanidins to apple cell wall material was not fully described by Langmuir isotherms, which means that the number of proanthocyanidins retained was not proportional to the available binding sites, making the affinity of these compounds to CWM hard to predict. For this reason, to have a better understanding of how these fibers work as fining agents, and with the aim of find new plant derived fining agents, the composition and physical properties of these fibers and its relationship with their efficiency as finning agents are to be studied.

Cell walls are constituted of 90% polysaccharides and 10% structural proteins (McNeil et al., 1984). These polysaccharides, mainly cellulose, pectins, and hemicelluloses, demonstrate noteworthy interactions with phenolic compounds found in wine, such as proanthocyanidins and anthocyanins (McManus et al., 1985), due to the hydroxyl and aromatic groups, that enable the formation of hydrogen bonds, hydrophobic interactions and electrostatic interactions (Garrido-Bañuelos et al., 2021; Jones-Moore et al., 2021; Le Bourvellec, Bouchet, & Renard, 2005; Bindon and Smith, 2013).

This ability of cell walls to interact with condensed tannins or proanthocyanidins has been deeply studied, both in model solution (Bindon, Smith, Holt, and Kennedy, 2010, Bindon, Smith, and Kennedy, 2010., Castro-López et al., 2016) and in wine (Bautista-Ortín et al., 2015; Guerrero et al., 2013; Jiménez-Martínez et al., 2019). The nature of these interactions is not only influenced by the properties of the CWM as stated before but it may also be influenced by factors related to phenolic composition such the nature of the phenolics (flavonoids or not flavonoid phenolics) and their specific properties as the degree of galloylation and molecular weight of proanthocyanidins (Bautista-Ortín et al., 2014) or anthocyanin acylation or cyclation to form pyranoanthocyanins (Bautista-Ortín et al., 2016).

Given all these facts, the search of the best vegetal fibers for fining proposes needs a deeper knowledge of the role of their composition for their behaviour as fining agent.

In order to increase our knowledge in this field this study determines the physico-chemical composition and structure of various plant fibers from different sources and correlates this composition with their affinity towards different wine phenolic compounds.

2. Materials and methods

For this study, five fibers of different plant origins were used, three of them, *Sauvignon Blanc* pomace (SBF), pea (PF) and cellulose (CF) provided by AGROVIN S.A. (Alcazar de San Juan, Ciudad Real, Spain), and one, from vine leaf (VLF). The dried vine leaves (Explotaciones Hermanos Delgado SL, Socuéllamos, Ciudad Real) were treated with a hydroalcoholic solution for 48 h on a shaker at 250 rpm. Afterwards, they were dried at room temperature and crushed in an electric grinder with blades. The resulting powder was passed through a 125 μm aperture sieve.

In addition, the composition and fining effect of one commercial plant fiber (CoF) (Flowpure, Laffort, 33,072, Bordeaux Cedex, France) was studied together with two commercial fining agents of synthetic and mineral origin, PVPP (Divergan F) and Bentonite (Maxibent G), respectively, also provided from AGROVIN S.A.

2.1. Fining trial

The wine used for the experiment was a young Monastrell wine, elaborated in 2022 at the pilot winery from University of Murcia, with a maceration length of 7 days. Wine was sulphited at a dose of 60 mg/L, botted in January 2023 and stored at 20 °C during one month until the analyses. The wine presented a final ethanol percentage of 14% and a titratable acidity of 5.1 g/L, expressed as tartaric acid.

The fining agents were weighed into 125 mL bottles and combined with 100 mL of wine. The concentration of the plant fibers was of 2 g/L, the maximum amount allowed by OIV (OIV-OENO 684 A-2022), for PVPP was of 0.5 g/L and for bentonite of 0.8 g/L, both the maximum amounts recommended by the commercial house. Then the samples were sonicated for 30 min at 20 °C and remained in static conditions during 48 h at 25 °C. Each treatment was made in triplicate, and a wine without treatment was used as control. After the fining treatment, the wine was centrifuged at 12,880 *g* for 5 min and the supernatants were filtered (0.45 μm nylon) before analyses.

2.2. Chromatic parameters

Color intensity (CI) was obtained by the sum of the absorbances at 620 nm, 520 nm and 420 nm (Glories, 1984). Total anthocyanins (TA) and polymeric anthocyanins (PA) were determined by the method described by Ho et al. (2001). The total tannins were measured by the method of precipitation with methylcellulose (Smith, 2005).

2.3. Proanthocyanidin analysis by HPLC

The phloroglucinol reagent was used to measure the tannin concentration and composition, following the method by Busse-Valverde et al. (2010) by high-performance liquid chromatography (HPLC). Briefly, 4 mL of wine was evaporated using a centrivap concentrator (Labconco, USA), then reconstituted in 2 mL of water, and passed through a C18-SPE column (Waters, Milford, MA) that had been prerinsed with 20 mL of water. The target compounds were eluted with 10 mL of methanol, which was then evaporated and reconstituted in 0.4 mL of methanol. The sample was analysed using HPLC. The solvents for elution were water/formic acid (98:2, *v*/v) (A) and acetonitrile/solvent A (80:20, v/v) (B), with a flow rate of 0.8 mL/min. The injection volume was 10 μL and the oven temperature of 30 °C. Elution began with 100% A for 5 min, followed by a linear gradient from 100% to 90% A over 30 min, then from 90% to 80% A over another 30 min, concluding with column washing and re-equilibration. Identification and quantification of flavan-3-ols were performed at 280 nm, and proanthocyanidins were quantified using (+)-catechin as the quantitative standard.

2.4. Determination of phenolic compounds by HPLC

Anthocyanins, flavonols and phenolic acids were separated using the column Poroshell120 EC-C18 core-shell column (150 mm × 2.1 mm, 2.7 μm, Agilent Technologies, Santa Clara, CA, USA) in a Waters Acquity Arc liquid chromatograph (Waters, Milford, MA, USA) as described by Pérez-Porras et al. (2022). The elution gradient began with 100% A (1% formic acid in Milli-Q water) for 2 min, then increased linearly from 0 to 15% B (1% formic acid in methanol: acetonitrile mixture 1:1 (*v*/v)) in 33 min, 15 to 21% B in 15 min, and 21 to 30% B in 20 min, followed by cleaning and re-equilibration of the column. The flow rate was of 0.3 mL/min, and the injection volume was of 5 μL. The column oven was kept at 55 °C. Using a Waters 2998 diode array detector (Waters, Mildford, MA, USA), the phenolic compounds were identified and quantified based in their UV spectra at 520 nm (anthocyanins), 360 nm (flavonols) and 280 nm and 320 nm (phenolic acids).

The measurement of various phenolic compounds was carried out using external standards. Specifically, anthocyanins and vitisins were measured using malvidin-3-glucoside chloride, flavonols using quercetin-3-glucoside, phenolic acids using gallic acid for hydroxyphenolic acids (280 nm) and caffeic acid for hydroxycinnamic derivatives (320 nm).

2.5. Fiber composition analysis

2.5.1. Comprehensive microarray polymer profiling (CoMPP) analysis

CoMPP technique detects glycan epitopes of plant tissue with high specificity thanks to the binding capacity of monoclonal antibodies (mABS) and carbohydrate binding molecules (CBMs), as described by Moller et al. (2008). 10 mg of the alcohol insoluble residue (AIR) of each fiber was weight in a Metller Toledo XS204 (Barcelona, Spain) analytical scale and sequentially extracted in 300 μL of 50 mM trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CDTA) and then with 4 M NaOH in 0.1% (*v*/v) $NaBH_4$. CDTA solvent is used to primarily extract pectic polysaccharides and NaOH primarily hemicellulosic polysaccharides. A piezoelectric array printer (Marathon, Arrayjet, United Kingdom) dot each sample, in triplicates, on a nitrocellulose membrane, creating a profile array that is probed with plant cell wall specific primary antibodies. To visualise the binding of the primary antibodies to their epitopes the following appropriate secondary antibody with alkaline phosphatase was used. Each microarray is developed with BCIP/NBT (5-bromo-4-chloro-3′-indoly-phosphate/nitro-blue tetrazolium chloride) which allows to see the printed dot profile. The dry microarrays are scanned using a flatbed scanner (Canon 8800) and the intensity of each dot is measured by the ImaGene 6.0 microarray analysis software. The data is processed with the highest signal set to 100, and every signal bellow 5 is equalled to 0. The processed data is converted into a heatmap using excel software.

2.5.2. Protein and phenol quantification

Both parameters were measured from 10 μL of supernatant obtained after treating 10 mg of fiber with 1 mL of 1 M NaOH, at 100 °C for 10 min. Following the Bradford method (Bradford, 1976), the protein content was determined by the colorimetric reaction of a mixture of the sample, 200 μL of Bradford and 790 μL of H_2O. After 15 min, the absorbance at 595 nm was measured. The phenol content was determined using the diluted Folin-Ciocalteu reactive (1:2 *v*/v). A mixture of the sample, 40 μL of 1 M NaOH, 790 μL of H_2O and 40 μL of the diluted reactive, was measured after 1 h at 700 nm.

2.5.3. Analysis of lignin, uronic acids, cellulosic glucose, and noncellulosic glucose

All analyses were conducted by triplicate with a quantity of 10 mg. Total glucose and uronic acids were estimated after two sequential hydrolysis, first by using 72% aqueous H_2SO_4 (*v*/v) for 1 h at 30 °C, then using 5.4% H_2SO_4 (v/v) for 3 h at 100 °C. Noncellulosic glucose was estimated after only the later hydrolysis. Both total glucose and noncelullosic glucose were estimated using D-glucose kit (R-Biopharm AG, Damstadt, Germany). Cellulosic glucose was obtained of the difference between total glucose and noncellulosic glucose. Uronic acids were measured colorimetrically with the 3,5-dimethylphenol reagent, at 397 and 450 nm. Klason lignin was estimated weighing the dried residual material.

2.5.4. Particle size and contact surface

The sample was previously prepared using HydroEV, a shaker that scatters the sample in an appropriate amount of water. Once the sample is fully dispersed and clot free, the particle size is determined using Mastersizer 3000E (IESMAT, Alcobendas, Madrid, Spain), that measure the intensity of the light that is scattered when the laser beam passes through a sample of dispersed particles. This information is then analysed to calculate the particle size and contact surface that creates the dispersion pattern by Mastersizer 3000E software.

2.6. Statistical analysis

Significant differences were determined using one-way analysis of variance (ANOVA) followed by a LSD (least significant difference) test ($P < 0.05$), using STATGRAPHICS Centurion XVI.3 (Statpoint Technologies, INC., The Plains, VA, USA).

3. Results and discussion

The different fining fibers were tested for their ability to reduce wine tannins, since they are associated to the wine perceived astringency. However, when using fining agents to reduce tannins for improving the sensations of astringency and bitterness, the effect on other wine phenolic compounds which may contribute positively to red wine color needs to be also evaluated. Those fining agents capable of reducing tannins without affecting the colored pigments are those that offer the most interesting properties for the industry.

Table 1 shows the tannin profile of the wine after fining, measured by the methylcellulose precipitation (MCPT) method and by HPLC after acidic depolymerization in the presence of phloroglucinol (TT). The plant fibers reduced MCPT within a range that varied from 9.9% to 27.4%, with PF being most effective in tannin removal and VLF the least effective. SBF reduced total tannins by 15.7%, being very close to the value reported by Guerrero et al. (2013) using different grape pomace fibers from Cabernet Sauvignon at a dose of 5 mg/mL. B and PVPP reduced tannin content by 19.5% and 22.7%, respectively.

The tannin concentration measured by HPLC differed from those obtained by methyl cellulose. With this method, only SBF showed a significant reduction in tannin content. It is important to note that the phloroglucinolysis method only allow to measure those tannins susceptible to depolymerisation in acid medium, while the methylcellulose precipitation method measures also oxidized tannins and those bound to anthocyanins. The differences in results between the two methods may be attributed to a higher affinity of the fibers for oxidized tannins and/or to those bound to anthocyanins, which are also non-depolymerizable. This phenomenon has been already reported in studies by Bautista-Ortín et al. (2014) and Le Bourvellec et al. (2009), indicating that non-depolymerizable tannins, such as oxidized tannins, exhibit high affinity for the polysaccharides in the cell wall. Renard et al. (2001) and Le Bourvellec et al. (2004) proposed that proanthocyanidins bind to the cell wall, and then interact with other proanthocyanidins by hydrogen bonds, to increase the number of molecules bound to the polysaccharides of the cell wall, and that this effect is more pronounced for highly polymerized structures. Furthermore, in studies such as those conducted by Jiménez-Martínez et al. (2019), it was also observed that the addition of a higher dose of pomace cell walls (6 mg/mL) than used

Table 1
Effect of the addition of the different fining agents on the concentration and composition of the tannins remaining in the solution.

	MCPT (mg/L)	TT (mg/L)	mDP	%Gal	%EGC
Control	1041.83 ± 44.34d	480.37 ± 3.57bc	6.17 ± 0.05bc	2.23 ± 0.01c	16.48 ± 0.05b
SBF	878.49 ± 49.90bc	438.70 ± 31.60a	5.95 ± 0.04ab	2.27 ± 0.02c	16.35 ± 0.23b
VLF	938.18 ± 27.72c	479.15 ± 15.54bc	6.17 ± 0.04c	2.10 ± 0.02a	16.18 ± 0.28ab
CoF	796.35 ± 38.87ab	478.00 ± 26.74bc	6.11 ± 0.07bc	2.12 ± 0.11ab	16.11 ± 0.22ab
PF	756.85 ± 80.63a	470.51 ± 32.20ab	5.81 ± 0.14a	2.23 ± 0.03c	15.72 ± 0.43a
CF	841.40 ± 17.86ab	468.90 ± 28.33ab	6.14 ± 0.08bc	2.09 ± 0.05a	19.63 ± 0.49d
B	838.85 ± 91.58ab	512.62 ± 6.19c	6.77 ± 0.18d	2.21 ± 0.05bc	18.93 ± 0.02c
PVPP	805.20 ± 53.26ab	449.78 ± 12.22ab	6.87 ± 0.24d	2.13 ± 0.09ab	18.95 ± 0.01c

Abbreviations: SBF, Sauvignon Blanc fiber; VLF, vine leaf fiber; CoF, commercial fiber; PF, pea fiber; CF, cellulose fiber; B, bentonite; MCPT, tannins measured by methylcellulose precipitation; TT, total tannins measured by phloroglucinolysis method; mDP, mean degree of polymeration; %Gal, percentage of galloylation; %EGC, percentage of epigallocatechin.

in this study produced minimal changes in the wine tannin concentration measured by phloroglucinolysis, while much more important reductions of tannins were measured when using the methylcellulose method.

So, considering the previous results and the values of anthocyanin-tannin complexes, that we measured as polymeric anthocyanins (Table 2), we can determinate how each fining agent interacted with tannins. SBF could remove both oxidazed and non oxidized tannins. The reduction of tannins caused by CoF and B was mainly due to the binding of both oxidized tannins and anthocyanin-tannin complexes, since they reduced MCPT and also decreased polymeric anthocyanins. CF and PVPP reduced oxidized tannins measured by methylcellulose but they did not affect depolymerizable tannins since no changes in the values of tannins measured by phloroglucinolysis were observed. They did not react with anthocyanin-tannin complexes, since they did not change PA values.

The MCPT values showed that all the plant fibers can reduce tannin concentration in wine to a similar or higher level than when the commercial PVPP and bentonite were used, and this reduction may be associated with a reduction of wine astringency (Medel-Marabolí et al., 2017).

Regarding the tannin composition, the mDP of the tannins that remained in the wine decreased when PF was used, probably due to preference for the retention of highly polymerized tannins, as previously observed. Contrary to that, PVPP and B produced an increase in tannin mDP, probably due to this treatment being effective in the elimination of depolymerizable tannins with low degree of polymerization and high galloylation, as supported by the decrease in the galloylation percentage values. PVPP is a fining agent that in white and rosé wines is used to reduce low molecular phenolic compounds associated with browning and astringency (Jackson, 2020), acting through hydrogen and Van der Waals bonds and hydrophobic interactions (Laborde et al., 2006). On the other hand, He et al. (2020) reported that the fining with Ca—Na bentonite resulted in the lowest concentrations of flavanols in white wines, while that in red wine, bentonite effect on low degree of polymerization tannins depended of wine composition (González-Neves et al., 2014).

VLF, CF and PVPP produced a minor but statistically significant reduction of the galloylation percentage which may produce a decrease of astringency and bitterness sensation in these wines (Ma et al., 2014).

As stated before, the impact of the use of different fining agents on the wine color was also evaluated since it may be an important issue in the outcome of the fining process (Table 2). All fining treatments resulted in a slight although statistically significant decrease in color index, compared to the control wine. The treatments with CoF, VLF and B showed the highest impact on color, and especially when CoF was used, which produced a color reduction of 18.7%. These reductions were mainly due to a decrease in total anthocyanin content that ranged from 8.6 to 10.9%. Similar to our findings, González-Neves et al. (2014), when using 0.5 g/L of bentonite in young red wines, found decreases of 9.8% to 11.6% in total anthocyanins and 11 to 14.9% decreases in color intensity. Bentonite is a montmorillonite clay used as fining agent mainly to reduce positive charged and uncharged polar molecules, especially proteins, with the aim of reducing protein haze in white wine (Marchal et al., 1995).

Table 2
Effect of the addition of the different fining agents on the chromatic parameters.

	CI	TA (mg/L)	PA (mg/L)
Control	8.06 ± 0.03f	281.00 ± 5.29c	35.28 ± 2.26 cd
SBF	7.60 ± 0.12d	273.33 ± 14.74bc	32.89 ± 0.22bc
VLF	6.99 ± 0.06b	257.00 ± 14.73ab	32.95 ± 0.72bc
CoF	6.55 ± 0.13a	250.33 ± 11.15a	28.60 ± 0.18a
PF	7.53 ± 0.04d	268.33 ± 3.51abc	32.93 ± 0.84bc
CF	7.82 ± 0.13e	289.50 ± 13.31c	35.57 ± 3.64cd
B	6.91 ± 0.06b	257.00 ± 11.36ab	31.94 ± 1.32b
PVPP	7.30 ± 0.03c	272.33 ± 6.35bc	36.71 ± 0.97d

Abbreviations: SBF, Sauvignon Blanc fiber; VLF, vine leaf fiber; CoF, commercial fiber; PF, pea fiber; CF, cellulose fiber; B, bentonite; CI, color intensity; TA, total anthocyanins; PA, polymeric anthocyanins.

PVPP, CF and SBF caused minimal decreases in the color index due to not significant changes in total anthocyanin content. The capacity of PVPP to bind phenolic compounds has also been studied in model solutions (Durán-Lara et al., 2015) and in red and rosé wine (Carrasco-Sánchez et al., 2018; Gil et al., 2017). In red wine, Carrasco-Sánchez et al. (2018) obtained a 35.9% reduction of phenolics using a PVPP concentration of 5 mg/mL, a dose 10 times greater than that used in this work.

CoF and bentonite removed the highest amount of stable colored pigments (PA), the reduction being of 18.9% and 9.5% respectively, while these compounds were not affected by the rest of fining agents. Therefore, PF, CF, and SBF exhibit an interesting behaviour as fining agents, since they can remove a high tannin quantity without producing important changes in the anthocyanin concentration and the final wine color.

Anthocyanins are the phenolic compounds that primarily determine the color of wine and, therefore, play a crucial role in its perceived quality. Even though phenolic compounds usually interact with cell wall polysaccharides via hydrogen bonding or hydrophobic interactions, anthocyanins can also bind with polysaccharides through electrostatic interactions thanks to charged groups (Koh et al., 2020).

Although anthocyanins were spectrophotometrically determined, they were also evaluated as individual compounds by HPLC. The results (Table 3) showed all treatments led to an overall decrease in monomeric anthocyanins, B and CoF causing the most significant losses for non-acylated anthocyanin content while the acylated anthocyanin content was more affected by CoF and PVPP, followed by the use of VLF and B. Among the grape fibers, a major impact in these compounds was observed when VLF was used, while the treatment with SBF removed less monomeric anthocyanin.

In the case of stable pigments, such as A and B type vitisins, a lower interaction with the different fining agents was observed compared with this of free anthocyanins, causing again CoF and B the most significant reductions of these compounds. Vitisins exhibit a great color intensity and stability against pH changes and SO_2 bleaching when compared to monomeric anthocyanins (Marquez et al., 2013) and therefore the low effect of some fining agents on these compounds is positive for wine color.

Flavonols are important compounds in red wine, particularly due to their antioxidant effects and their contribution to copigmentation in young wines. Their concentration was reduced by all treatments (Table 4), with PVPP and CoF causing significant decreases. Gil et al. (2017) described that PVPP has a higher affinity for flavonols than for anthocyanins in rosé wines, similar to what is observed in this study, which is attributed to a selective adsorption. Specifically, quercetin, myricetin-3-glucoside, quercetin-3-glucuronide, and quercetin-3-glucoside were the compounds which showed the highest interaction capacity with the fining agents. Among the fibers, SBF had the least impact in the flavonol concentration.

PVPP, VLF, CoF, and CF showed an interesting ability to reduce quercetin effectively. Quercetin aglycone is a complex derived from the glycosylated derivatives of quercetin and when its concentration is over 5 mg/L may precipitate and form yellow deposits (Boulton, 2001). Due to climate change, some red grape varieties are oversynthetizing quercetin glycosides, so the search for ways to reduce it is an emerging topic (Gambuti et al., 2020; Luciano et al., 2024). PVPP reduced quercetin by 89%, VLF by 79%, CoF by 77% and CF by 49%. PVPP is often used to reduce quercetin in white wines, but in red wines it is not commonly used. The results indicate that some plant fibers as CF could be used to reduce the formation of yellow deposits in red wines caused by quercetin without largely affect its chromatic characteristics.

The presence of phenolic acids is also important in wines. They can

Table 3
Effect of the addition of the different fining agents on the concentration of free anthocyanins and vitisins (mg/L) by HPLC.

Compounds	Control	SBF	VLF	CoF	PF	CF	B	PVPP
Non-acylated anthocyanins								
Delphidin-3-glucoside	8.06 ± 0.22f	7.58 ± 0.11e	6.65 ± 0.16c	6.68 ± 0.15c	7.28 ± 0.07d	7.26 ± 0.05d	6.40 ± 0.08b	6.11 ± 0.05a
Cianidin-3-glucoside	3.27 ± 0.25d	3.05 ± 0.16c	2.69 ± 0.01ab	2.57 ± 0.02a	2.83 ± 0.03b	2.77 ± 0.02b	2.57 ± 0.01a	2.52 ± 0.04a
Petunidin-3-glucoside	13.64 ± 0.47e	12.71 ± 0.32d	11.52 ± 0.02b	11.18 ± 0.01b	12.06 ± 0.11c	12.13 ± 0.09c	10.59 ± 0.02a	11.25 ± 0.04b
Peonidin-3-glucoside	8.35 ± 0.47d	7.85 ± 0.15c	7.39 ± 0.15b	6.68 ± 0.31a	7.34 ± 0.07b	7.47 ± 0.07bc	6.68 ± 0.22a	7.23 ± 0.14b
Malvidin-3-Glucoside	80.19 ± 1.94 g	75.78 ± 0.84e	71.60 ± 0.38c	68.54 ± 0.26b	74.45 ± 0.33de	74.03 ± 0.50d	64.37 ± 0.12a	71.79 ± 0.44c
Σtotal	113.51 ± 3.22f	106.96 ± 1.24e	99.85 ± 0.56c	95.64 ± 0.47b	103.95 ± 0.45d	103.66 ± 0.58d	90.61 ± 0.36a	98.90 ± 0.43c
Acylated anthocyanins								
Malvidin-(6-acetyl)-3-glucoside	8.08 ± 0.48d	7.15 ± 0.54c	6.28 ± 0.17ab	5.86 ± 0.46a	6.97 ± 0.56c	6.78 ± 0.23bc	6.15 ± 0.07ab	6.27 ± 0.25ab
Cyanidin-(6-coumaroyl)-3-glucoside	1.27 ± 0.12d	1.15 ± 0.07bc	1.01 ± 0.01b	0.99 ± 0.01a	1.20 ± 0.03cd	1.21 ± 0.05 cd	1.21 ± 0.04 cd	0.92 ± 0.03a
Petunidin-(6-coumaroyl)-3-glucoside	2.49 ± 0.19e	2.30 ± 0.17d	1.74 ± 0.03b	1.51 ± 0.09a	2.08 ± 0.06c	1.96 ± 0.09c	1.91 ± 0.09bc	1.38 ± 0.07a
Malvidin-(6-coumaroyl)-3-glucoside cis	1.41 ± 0.23cd	1.43 ± 0.07d	1.28 ± 0.03bc	1.12 ± 0.01a	1.35 ± 0.04cd	1.35 ± 0.04 cd	1.25 ± 0.03abc	1.17 ± 0.03ab
Peonidin-(6-coumaroyl)-3-glucoside	1.95 ± 0.10f	1.77 ± 0.05e	1.39 ± 0.08b	1.29 ± 0.07ab	1.72 ± 0.05de	1.62 ± 0.05 cd	1.54 ± 0.03c	1.27 ± 0.02a
Malvidin-(6-coumaroyl)-3-glucoside	14.12 ± 0.52g	12.53 ± 0.10f	9.75 ± 0.10c	8.07 ± 0.43a	12.11 ± 0.10ef	11.91 ± 0.27e	10.30 ± 0.15d	8.58 ± 0.15b
Σtotal	29.32 ± 1.57e	26.32 ± 0.81d	21.54 ± 0.38b	18.84 ± 0.92a	25.42 ± 0.76 cd	24.83 ± 0.49c	22.36 ± 0.18b	19.60 ± 0.28a
Σtotal free anthocyanins	142.83 ± 4.65e	133.29 ± 1.93d	121.38 ± 0.82b	114.49 ± 1.27a	129.38 ± 0.93c	128.49 ± 1.03c	112.96 ± 0.20a	118.49 ± 0.70b
A-type vitisins								
Delphidin-3-glucoside-pyruvic acid	0.94 ± 0.01d	0.92 ± 0.01bcd	0.93 ± 0.01 cd	0.92 ± 0.01bc	0.92 ± 0.01bcd	0.91 ± 0.01ab	0.90 ± 0.00a	0.91 ± 0.02abc
Cianidin-3-glucoside-pyruvic acid	1.19 ± 0.01d	1.17 ± 0.00c	1.14 ± 0.00b	1.11 ± 0.01a	1.16 ± 0.01bc	1.16 ± 0.02c	1.09 ± 0.01a	1.16 ± 0.02bc
Malvidin-(6-acetyl)-3-glucoside-pyruvic acid (acetylvitisin A)	1.01 ± 0.01cd	1.01 ± 0.02cd	1.01 ± 0.01d	0.97 ± 0.01ab	0.99 ± 0.01bc	0.99 ± 0.00bc	0.96 ± 0.03a	0.99 ± 0.01bcd
Malvidin-3-glucoside-pyruvic acid (vitisin A)	4.02 ± 0.08e	3.81 ± 0.03c	3.79 ± 0.03c	3.54 ± 0.05b	3.96 ± 0.02de	3.92 ± 0.04d	3.44 ± 0.05a	3.96 ± 0.03de
Malvidin-(6-coumaroyl)-3-glucoside pyruvic acid	1.57 ± 0.03f	1.46 ± 0.02d	1.41 ± 0.01c	1.23 ± 0.04a	1.50 ± 0.01de	1.51 ± 0.02e	1.36 ± 0.01b	1.47 ± 0.04de
Σtotal	8.74 ± 0.12d	8.36 ± 0.02b	8.29 ± 0.04b	7.77 ± 0.06a	8.53 ± 0.04c	8.49 ± 0.03c	7.76 ± 0.05a	8.50 ± 0.04c
B-type vitisins								
Petunidin-3-glucoside-acetaldehyde	1.09 ± 0.10b	1.05 ± 0.09ab	1.04 ± 0.01ab	1.00 ± 0.02a	1.10 ± 0.03b	1.08 ± 0.04ab	1.00 ± 0.02a	1.09 ± 0.00ab
Malvidin-3-glucoside-acetaldehyde (vitisin B)	2.99 ± 0.12d	2.69 ± 0.07c	2.47 ± 0.05b	2.24 ± 0.08a	2.79 ± 0.03c	2.83 ± 0.09c	2.12 ± 0.17a	2.81 ± 0.09c
Malvidin-(6-coumaroyl)-3-glucoside acetaldehyde	1.14 ± 0.14cd	1.06 ± 0.01bc	1.00 ± 0.03b	0.90 ± 0.03a	1.15 ± 0.03cd	1.17 ± 0.02d	0.98 ± 0.05ab	1.07 ± 0.03bc
Σtotal	5.22 ± 0.33d	4.79 ± 0.10c	4.52 ± 0.08b	4.14 ± 0.12a	5.04 ± 0.06cd	5.08 ± 0.09d	4.10 ± 0.20a	4.96 ± 0.10 cd
Σtotal free anthocyanins and vitisins	156.79 ± 5.09e	146.44 ± 2.04d	134.19 ± 0.79b	126.40 ± 1.37a	142.94 ± 0.88 cd	142.06 ± 1.14c	124.82 ± 0.14a	131.95 ± 0.77b

contribute to the color stabilization of red wines due to the copigmentation effect and/or participate in the formation of anthocyanin-derived pigments (i.e., pinotins and portisins) (Bloomfield et al., 2003; He et al., 2012). Phenolic acids were the phenolic compounds the least affected by the different treatments. Only PVPP and CoF led to a small although significant decrease, with a reduction of 6 and 2%, respectively.

As a resume of the different fining agent's behaviour towards wine phenolic compounds and even though PVPP, B and CoF showed a good tannin concentration reduction, they also had a great affinity with anthocyanins and flavonols, leading to a poorer phenolic content in wine. SBF, CF and specially PF, seemed to lead to a more balanced wine, effectively reducing tannins and only slightly affecting other phenolic compounds. Trying to understand the reason behind the different behaviour of the different tested fibers, in terms of their capacity of interaction with phenolic compounds in wine, we focused our attention to their composition, analysing the main chemical composition (Table 5), their polysaccharide profile (Fig. 1) and particle size and surface (Table 6).

When studying the fiber composition, CoF and CF fibers showed very low amounts of uronic acids, indicating an absence of pectic polysaccharides in these fibers. Contrary to that, a high content of these compounds was observed for VLF, SBF and PF, especially for the latter. The highest content of cellulose glucose was detected in the CF, followed by PF and CoF fibers, while the lowest amount was found for the VLF. In

Table 4
Effect of the addition of the different fining agents on the concentration (mg/L) of flavonols and phenolic acids by HPLC.

Compounds	Control	SBF	VLF	CoF	PF	CF	B	PVPP
Flavonols								
Myricetin-3-glucoside	19.57 ± 0.29g	18.93 ± 0.06f	17.85 ± 0.19c	17.19 ± 0.02b	18.80 ± 0.08ef	18.56 ± 0.26de	18.31 ± 0.07d	14.98 ± 0.28a
Quercetin-3-galactoside	2.66 ± 0.07bc	2.59 ± 0.01b	2.67 ± 0.03c	2.25 ± 0.01a	2.61 ± 0.02bc	2.59 ± 0.04b	2.60 ± 0.01b	2.24 ± 0.06a
Quercetin-3-glucuronide	14.57 ± 0.17e	14.09 ± 0.07d	14.95 ± 0.10f	12.76 ± 0.06b	14.07 ± 0.03d	13.80 ± 0.30c	14.18 ± 0.07d	11.24 ± 0.21a
Quercetin-3-glucoside	10.78 ± 0.17f	10.26 ± 0.04e	10.06 ± 0.13d	8.62 ± 0.06b	9.98 ± 0.02 cd	9.79 ± 0.15c	9.89 ± 0.04 cd	8.11 ± 0.18a
Isorhamnetin-3-glucoside	1.06 ± 0.02f	1.03 ± 0.02ef	0.99 ± 0.01cd	0.89 ± 0.01a	1.02 ± 0.01def	1.01 ± 0.03de	0.98 ± 0.02c	0.93 ± 0.02b
Syringetin-3-glucoside	1.65 ± 0.03e	1.60 ± 0.02d	1.55 ± 0.02c	1.40 ± 0.02a	1.60 ± 0.00d	1.60 ± 0.02d	1.50 ± 0.01b	1.53 ± 0.01bc
Quercetin	5.74 ± 0.67e	3.83 ± 0.08d	1.23 ± 0.10b	1.32 ± 0.09b	3.41 ± 0.17cd	2.92 ± 0.29c	3.39 ± 0.30 cd	0.62 ± 0.08a
Σtotal	56.02 ± 1.35f	52.34 ± 0.16e	49.30 ± 0.56c	44.42 ± 0.24b	51.49 ± 0.26de	50.27 ± 1.06 cd	50.84 ± 0.37d	39.66 ± 0.78a
Phenolic acids								
Caftaric acid	10.97 ± 0.24c	10.77 ± 0.02ab	11.27 ± 0.03d	10.76 ± 0.01ab	10.81 ± 0.02ab	10.79 ± 0.08ab	10.84 ± 0.02bc	10.67 ± 0.03a
Coutaric acid	8.24 ± 0.12d	8.05 ± 0.08a	8.14 ± 0.02abc	8.11 ± 0.01ab	8.19 ± 0.01bc	8.18 ± 0.06bc	8.22 ± 0.01d	8.05 ± 0.02a
Caffeic acid	2.02 ± 0.03cde	2.03 ± 0.00cde	2.00 ± 0.04bc	1.98 ± 0.01b	2.06 ± 0.02e	2.00 ± 0.02bcd	2.04 ± 0.02de	1.73 ± 0.02a
P-Coumaric acid	4.12 ± 0.31c	4.09 ± 0.05c	4.05 ± 0.10bc	3.86 ± 0.06ab	4.16 ± 0.01c	4.05 ± 0.04bc	4.08 ± 0.02c	3.75 ± 0.04a
Gallic acid	9.26 ± 0.03bc	9.47 ± 0.01d	9.25 ± 0.02bc	9.18 ± 0.12b	9.34 ± 0.04c	9.24 ± 0.08bc	9.33 ± 0.04c	8.33 ± 0.03a
Σtotal	34.60 ± 0.65c	34.41 ± 0.14c	34.71 ± 0.20c	33.89 ± 0.16b	34.55 ± 0.03c	34.25 ± 0.30bc	34.51 ± 0.06c	32.53 ± 0.07a

Abbreviations: SBF, Sauvignon Blanc fiber; VLF, vine leaf fiber; CoF, commercial fiber; PF, pea fiber; CF, cellulose fiber.

Table 5
Composition (mg/g fiber) of the plant fibers used in the study.

	C glu	Non-C glu	Uronic acids	FC	Proteins	Lignin
SBF	75.29 ± 11.80b	11.68 ± 1.68a	79.75 ± 4.91c	41.69 ± 2.20d	24.00 ± 0.96d	767.09 ± 1.07d
VLF	31.85 ± 0.10a	40.16 ± 4.13b	60.33 ± 1.91b	17.57 ± 2.15c	24.79 ± 3.33d	825.52 ± 7.18e
CoF	263.79 ± 15.77c	33.01 ± 0.99b	0.99 ± 1.41a	11.91 ± 0.19b	9.34 ± 0.18b	681.05 ± 15.53c
PF	322.19 ± 6.90d	31.77 ± 2.48b	98.99 ± 6.81d	10.31 ± 0.49b	16.68 ± 1.64c	520.07 ± 15.62b
CF	489.18 ± 15.74e	65.11 ± 1.026c	3.07 ± 5.32a	4.34 ± 0.54a	5.96 ± 1.28a	433.77 ± 21.31a

Abbreviations: SBF, Sauvignon Blanc fiber; VLF, vine leaf fiber; CoF, commercial fiber; PF, pea fiber; CF, cellulose fiber; C glu, cellulosic glucose; Non-C glu, noncellulosic glucose; FC, phenolic compounds.

the case of proteins, lignin and phenolic compounds, the highest values of these compounds were showed by VLF and SBF fibers and the lowest values by CF. PF showed the major amount of non cellulose glucose, while the lowest content was found for SBF.

Le Bourvellec et al. (2005) reported the differences in the affinity of different cell wall components for tannins, being highest for pectins, followed by xyloglucans and then cellulose, while Bindon et al. (2012) demonstrated that some pomace skin cell wall components may negatively influence the interaction with tannins, such as high lignin amounts, since this may represent a greater cell wall structural rigidity, exposing a smaller surface area for interaction with tannins. On the other hand, it has been reported the possibility that cell wall-bound protein, particularly the hydroxyproline rich glycoproteins, may strongly adsorb tannins (Hanlin et al., 2010) and, therefore, a high pectin and protein content and a low lignin content in the PF could explain its major adsorption capacity for tannins compared to the SBF and VLF, although the wall composition may not explain the behaviour of CoF and CF.

In order to obtain more information about the complex polysaccharide composition of the cell walls of the fibers used, the CoMPP methodology was employed (Fig. 1). This technique involves polymer profiling microarrays and allows to detect specific epitopes with antibodies. In CoMPP analysis, two fractions are obtained: one using CDTA, from which mainly pectins are extracted since this solvent is capable of removing Ca^{2+} ions, and another using NaOH. The NaOH solvent targets hemicelluloses, unbranched RG-I, galactan and xyloglucans. Also, strongly associated pectins like highly esterified HG and RG-I could be solubilized in this solvent (Gao et al., 2016).

The CoMPP results confirmed the absence of pectins in CF and CoF fibers. Additionally, they also show a lack of arabinogalactan epitopes. No polysaccharides are detected for these fibers in the CDTA fraction, and the NaOH fraction indicates that both fibers have similar levels of xyloglucans and xylans. CF stood out for its high mannose content. These results correlate with those found in the composition analysis of the fibers (Table 5).

The CDTA fraction for the SBF fiber indicated that it is rich in arabinogalactans (JIM17 epitope) and highly methyl esterified homogalacturonan (JIM7 epitope) and, although in a minor amount, epitopes for rhamnogalacturonan, mannose, and low methyl esterificated homogalacturonan (JIM5 epitope) were also detected. SBF, together with VLF presented mannose epitopes in the CDTA fraction, indicating the presence in these fibers of highly exposed mannans. The NaOH fraction for these fibers showed the presence of xyloglucan epitopes (LM15 and LM25 epitopes), arabinans (LM6 epitope) and galactans (LM5 epitope). VLF exhibited a similar polysaccharide profile to SBF, but in general, with a lower response of different epitopes.

The PF, showed the highest content of pectins in the CDTA fraction, coinciding with the results obtained with composition analysis by spectrophotometric methods (Table 4). In this fiber, the highest amount of high esterification grade (DE) homogalacturonan (JIM7 epitope) and RG-I (LM6 and LM13 epitopes) epitope were detected, together with significant levels of low DE homogalacturonan epitopes (JIM5 epitope). The arabinogalactans were also presented in this fiber, although in a lower amount than that found in SBF and VLF fibers. In the NaOH fraction an increase of the quantity of arabinans was observed, along with epitopes of rhamnogalacturonans, mannoses, and xyloglucans. Moreover, a similar amount of xylans compared to that shown by CoF and CF was also observed.

Some studies (Fernandes et al., 2020) indicated that lowly-methylated pectins (JIM7 epitopes) have a higher anthocyanin binding affinity than highly methylated pectins (JIM5 epitope). Therefore, the highest content of these pectins in VLF could be associated with its major impact on wine color, causing a reduction of 13%. The CoMPP analysis showed VLF has approximately the same levels of high and low DE pectins, while SBF and PF have higher DE pectins than low DE pectins. Furthermore, Brandão et al. (2020) reported that polysaccharides with higher number of branched chains interact more with proanthocyanins, therefore the greater amount of RG-I side chain epitopes (LM6 and LM13 epitopes) in PF may justify that this fiber was the most effective to reduce tannin content in the wine.

Regarding arabinogalactan proteins, PF and VLF have similar high

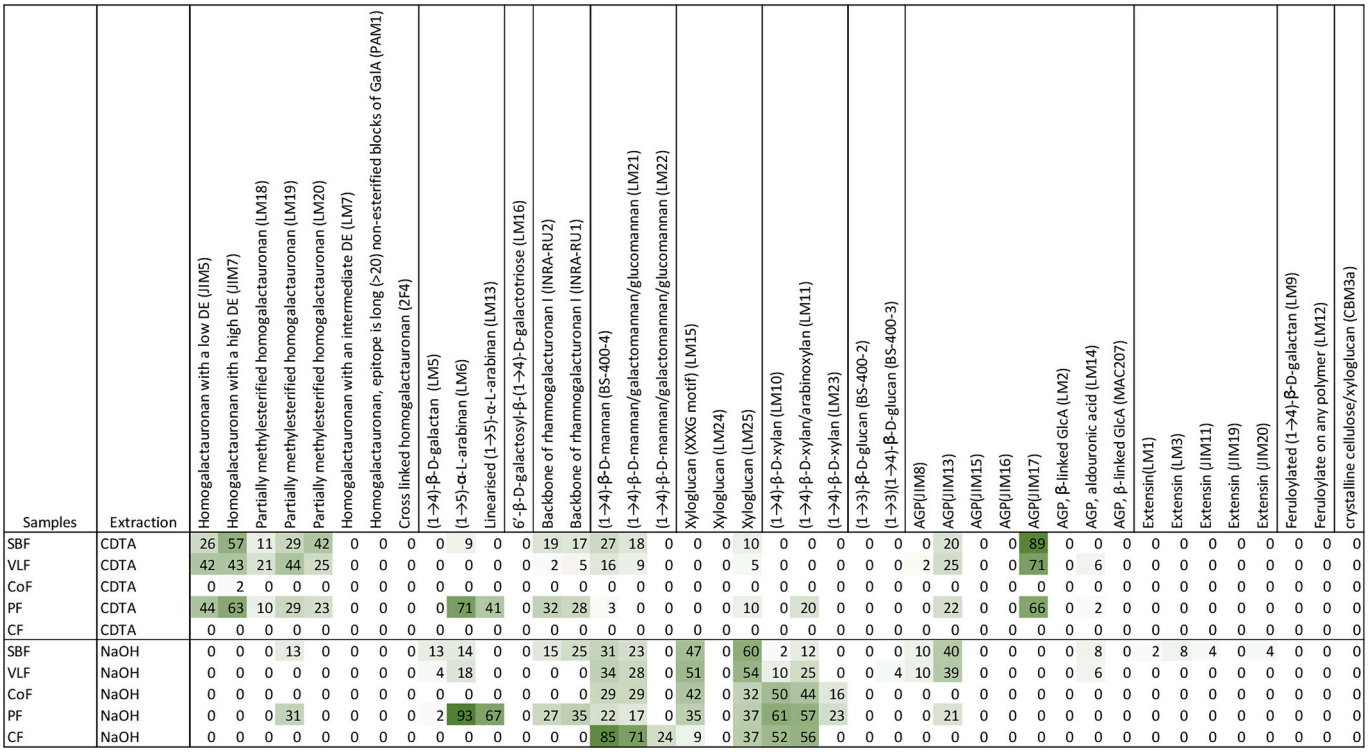

Fig. 1. Heatmap of glycan epitope prevalence (0−100) found in the pectin (CDTA) and hemicellulose (NaOH) fractions extracted from cell walls of the plant fibers. Abreviations: SBF, Sauvignon Blanc fiber; VLF, vine leaf fiber; CoF, commercial fiber; PF, pea fiber; CF, cellulose fiber; DE, methyl esterification degree; GalA, galacturonic acid; AGP, arabinogalactan protein.

Table 6
Particle size and contact surface of the plant fibers.

	Size (μm)	Surface (m^2/Kg)
SBF	454.0	31.4
VLF	53.0	310.4
CoF	34.5	379.9
PF	81.3	183.1
CF	118.0	132.5

Abbreviations: SBF, Sauvignon Blanc fiber; VLF, vine leaf fiber; CoF, commercial fiber; PF, pea fiber; CF, cellulose fiber.

levels detected and SBF display the highest signal of arabinogalactan protein. Arabinogalactan proteins are glycoproteins rich in hydroxyproline formed from proteins complex with arabinogalactan II, a pectic polysaccharide whose glycosidic fraction is over 90% of the structure (Jones-Moore et al., 2021). Some studies (Brandão et al., 2017; Lei et al., 2023) reported the ability of this molecules to reduce astringency by intervening in the formation of compounds between tannins and saliva proteins, but this property has been attributed to an interaction of arabinogalactans with salivary protein (Kuhlman et al., 2024). The specific ability of these proteins to interact with phenolic compounds of wine still needs to be studied.

CoF, PF and CF stands out above VLF and SBF for their high levels of cellulosic glucose, and at the same time are the ones that show higher tannin retention. Suominen et al. (2023) studied the interaction between hydrolysable tannins (HT) and proanthocyanidins with bacterial cellulose, obtaining different levels of retention (from 0 to 75%) depending on the tannin structural features, molecular weight, mDP and galloylation. Overall, for HT, galloylation and hydrophobicity seems to increase the affinity to cellulose, due to hydrophobic interaction. Regarding the proanthocyanidin type tannins, this study showed that it bound cellulose in a similar way, from 8 to 32%. Galloylation increased the proanthocyanidin's affinity for cellulose, while prodelphinidins and B-type proanthocyanidins presented a higher binding capacity than procyanidin and A-type proanthocyanidin in pure solutions. The relation between molecular weight and affinity to cellulose was not clear either for HT or proanthocyanidin. These results together with the results of this study show that the role of cellulose in interaction with tannins should not be underestimated.

Other parameters worth taking in consideration are particle size and contact surface of the fibers, shown in Table 6. It is widely recognised that low particle size and high contact surface increase the interaction possibilities. Furthermore, surface data also gives us information about porosity. This is noticed when the contact surface is increased in the fibers, and also, with the smaller particle size, they remain more time in suspension without precipitating, and, therefore, there is more time for the fibers to interact with the phenolic compounds of wine. CoF and VLF have the smallest particle size and biggest surface area, over 300 m^2/Kg, and SBF has by far the biggest particle size and smallest surface, 31.4 m^2/Kg. Some of these parameters could explain the difference between some of the fibers used in this study, for example the capacity of CoF to reduce tannins and anthocyanins more effectively in comparison with CF, despite having a very similar composition and CoMPP profile. Also, CoF and VLF both produced the biggest color reduction among the fibers, despite not having a similar polysaccharide composition or profile. In summary, there is not a direct correlation between contact surface and interaction with phenolic compounds. This is likely due to the nature of this interaction depends on the polysaccharide content of each fiber. This content determines which phenols each fiber interacts with and to what extent they retain them. The role of the contact surface is that when it increases, the possibility and quantity of these interactions also increases.

4. Conclusion

The first part of this study shows that plant fibers of very different origins can be used to effectively reduce tannins from a young wine, and

the proportion and nature of the bound tannins and how the fibers affected other phenolic compounds and wine color differed depending on characteristics such as fiber composition, polysaccharide profile, particle size and contact surface. SBF, CF and specially PF effectively bound tannins while minimizing the effect on anthocyanins and color. CF also presented an important capacity of reducing quercetin in wines, which makes this fiber a very interesting fining agent to prevent the formation of yellow precipitates in red wine.

Moreover, it showed for first time that the presence of pectins in the fiber composition is not fundamental in the interaction with wine tannins since fibers with high content of cellulose and lack of pectins like CoF and CF bound tannins more effectively than other fibers that had pectins in their structure, like SBF and VLF. Although the highest content of cellulose and pectins showed by PF, stand out for the major reduction of tannins.

The fiber with low size and high contact surface values increased the reduction of wine tannins in absence of pectins, as was the case of CoF but with a great impact in the chromatic characteristics, making this agent unsuitable for red wine. Moreover, it is especially remarkable the high capacity to retain tannins with little alteration in wine color showed by SBF, when it had the lowest contact surface value. It would be interesting for this fiber to carry out further studies to verify if a reduction of its size could enhance its interaction capacity with tannins without affecting the color of the wine.

Therefore, not only the polysaccharide composition of fibers will influence the ability to remove tannins from the wine, but will also be influenced by their size and contact surface and for some of the fibers studied this may be detrimental for the color of red wine.

CRediT authorship contribution statement

Lucía Osete-Alcaraz: Writing – original draft, Methodology, Investigation, Formal analysis. **Encarna Gómez-Plaza:** Writing – review & editing, Validation, Supervision, Investigation, Funding acquisition, Conceptualization. **Bodil Jørgensen:** Writing – review & editing, Validation, Supervision, Methodology, Formal analysis. **José Oliva:** Writing – review & editing, Methodology, Investigation, Data curation, Conceptualization. **Miguel Angel Cámara:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Ricardo Jurado:** Resources, Investigation, Conceptualization. **Ana Belén Bautista-Ortín:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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