Chapter

Properties of Wine Polysaccharides

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Abstract

Polysaccharides are the main macromolecules of colloidal nature in wines, and play a fundamental role in the technological properties and organoleptic characteristics of the wines. The role of the different wine polysaccharides will depend on their quantity but also on their chemical composition, molecular structure and origin. Wine polysaccharides originate from grapes and yeast acting during the winemaking. The main polysaccharides present in wines can be grouped into three major families: (i) polysaccharides rich in arabinose and galactose (PRAG), (ii) polysaccharides rich in rhamnogalacturonans (RG-I and RG-II), which both come from the pectocellulosic cell walls of grape berries, and (iii) mannoproteins (MP) released by yeasts. This paper describes the origin, structure and role of the different wine polysaccharide families through a bibliographic revision of their origin and extraction into the wines, as well as their technological and sensory properties.

Keywords: wine, rhamnogalacturonans, polysaccharides rich in arabinose and galactose, rhamnogalacturonans, mannoproteins, technological and sensory properties

1. Introduction

Polysaccharides are the main macromolecules of colloidal nature in wines. Therefore, these compounds play a fundamental role in the technological properties and organoleptic characteristics of the wines.

The content of the different polysaccharide families in the wines depends mainly on the grape variety and its degree of maturation, the winemaking technology used (including type of strain of yeast and bacteria), and the transformation of the polysaccharides during the wine aging process [1–5]. These macromolecules show different technological properties in wines. Wine polysaccharides are widely known for their effect on the physicochemical stabilization of wine; thus, they are able to interact with the colloidal particles present in wines, reducing their reactivity and limiting their aggregation and flocculation [6]. These macromolecules have the ability to interact and aggregate with tannins [7], prevent the formation of protein haze in white wines [8], and delay or even arrest the outgrowth of the crystals of potassium bitartrate to a macroscopic visual size [9]. Wine polysaccharides have also been associated to the mouthfeel perceptions because they are able to modify the sensory properties of wines [7, 10]. Several authors [10, 11] have observed that wine

polysaccharides can modulate the astringency perception, increasing the sweetness sensation and body. Astringency is usually defined as the array of tactile sensations felt in the mouth including shrinking, puckering and tightening of the oral surface. In addition, polysaccharides are able to interact with wine volatile compounds [12], and thus affect the aroma of the wines.

Polysaccharides are extracted during the mechanical operations applied to the grapes (destemming-crushing, pressing and pumping of the crushed destemmed grapes) and during some stages of the winemaking. Therefore, polysaccharides are released in white, rosé and red winemaking during the premaceration process before starting the alcoholic fermentation, but also during the maceration fermentation of the red wine elaborations, and during the aging of the wines on their lees. On the contrary, other stages of the winemaking, such as filtration, produce a decrease in the content of wine polysaccharides [5].

Wine polysaccharides come from both the cell walls of the grape itself, and the yeasts and other microorganisms that act during the winemaking process. **Figure 1** shows a classification of the polysaccharides present in wines according to their origin.

From an oenological point of view, polysaccharides from grapes and yeasts are the most important both quantitatively and qualitatively. Therefore, the main polysaccharides present in wines can be grouped into three major families: (i) polysaccharides rich in arabinose and galactose (PRAG) [13] and (ii) polysaccharides rich in rhamnogalacturonans (RG-I and RG-II), which both come from the pectocellulosic cell walls of the grape berries [13], and (iii) mannoproteins (MP) produced and released by yeasts during the fermentation and the aging of wines on their lees [8]. Other wine polysaccharides such as glucans, produced by *Botrytis cinerea*, only become relevant when an infection with this fungus occurs, causing difficult clarifications and filtrations. Bacterial polysaccharides are present in the wines in very low concentrations. Polysaccharides exogenous to wine include carboxymethylcellulose and arabic gum, which are additives allowed by the International Organization of Vine and Wine (OIV).

Among all these types of polysaccharides, not all show the same behavior with respect to wines, and their concrete effects and properties will depend on their size, chemical composition, molecular structure and origin.

The objective of the present paper is to describe the origin, structure and key role of the different wine polysaccharide families through a bibliographic revision of their origin and extraction into the wines, as well as their technological and sensory properties.

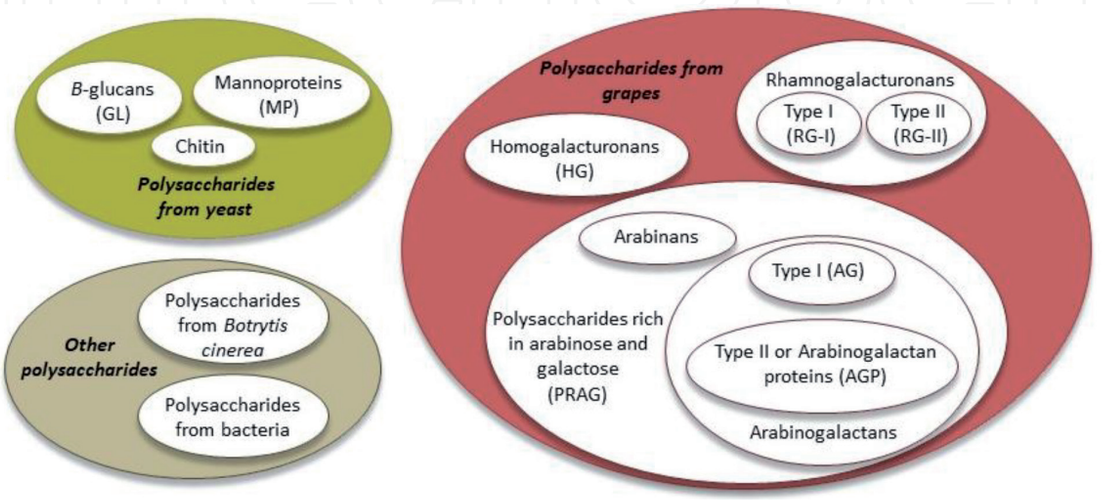

Figure 1.
Classification of the main polysaccharides of wines according to their origin.

2. Grape polysaccharides: origin, structure and functions

The plant cell wall is composed of a highly integrated and structurally complex network of polysaccharides, including celluloses, hemicelluloses and pectins, and also structural proteins [14]. Pectins are a family of heteropolysaccharides characterized by a high content of α-D-galacturonic acid residues partially methyl esterified [15]. These heteropolysaccharides are located in the middle lamella of the primary cell walls, and are mainly composed of a galacturonic acid backbone and chains of several monosaccharides. The smooth region is represented by homogalacturonans (HG), which are galacturonic acid chains more or less methylated/acetylated; the hairy region (high density of side chains) is composed of rhamnogalacturonans type I (RG-I) and type II (RG-II) [16]. RG-I consists of rhamnose and galacturonic acid and represents a very small proportion of grape-based pectins; RG-II is formed in the grape berry during the maturation and is released into the wine during the winemaking. Arabinogalactan proteins (AGP) are glycoproteins also located in the plant cell walls and extracted during the winemaking. They are themselves sidechains of the backbone that arise from the hairy region of pectins and are connected via specific hydroxyproline-rich proteins and, together with arabinogalactans, contribute to the so-called *polysaccharides rich in arabinose and galactose* (PRAG) [17]. Hemicellulose is formed by several polymeric structures in which xyloglucan (a backbone of cellulose with side chains containing xylose, galactose and fucose) is the most abundant [18]. Cellulose microfibrils represent the major constituent of the cell wall polysaccharides, and they are interacting with hemicellulose and pectic polysaccharides, improving the structural integrity of the plant cell wall [19].

Grape berries are composed of three main tissue types [20]: the skins, the pulp and the seeds. The structural properties of the cell walls of grape berries, especially the cell walls from the exocarp (the skin), determine the mechanical resistance, the texture, and the ease of processing berries. Grape skins represent about 5–10% of the total dry weight of the grape berry, and act as a hydrophobic barrier to protect the grapes from physical and climatic injuries, dehydration, fungal infection and UV light. The grape skin itself can be divided into three superimposed layers (**Figure 2**) [21]: (1) the outermost layer, the cuticle, is composed of hydroxylated fatty acids called cutin, and is covered by hydrophobic waxes; (2) the intermediate epidermis, assumed to consist of one or two layers, which appears as a regular tilling of cells; and (3) the inner layer, the hypodermis, which is the layer closest to the pulp, and which is composed of several cell layers that contain most of the phenolics

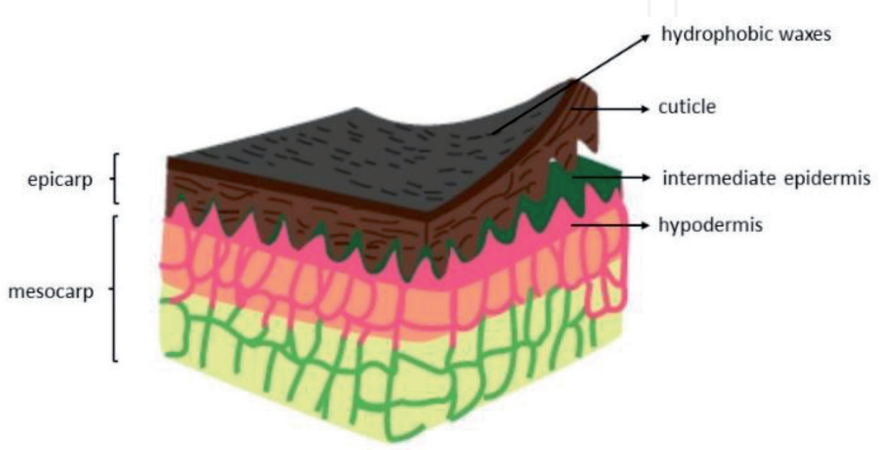

Figure 2.
Different layers of the grape skin.

in grape skin [22]. The cuticle, that covers the skin, is the primary interface between the plant and the environment and is a protective layer (against pathogens and minimizes water loss) that consists of waxes (soluble lipids) embedded in or deposited on the cutin-rich matrix [23]. Gao et al. [24] describe that this wax layer most probably, in red winemaking, albeit not proven, prevents cell wall degrading enzymes from penetrating into the inner tissues (skin and pulp), thus enzymes can only penetrate effectively from the pulp exposed during grape crushing.

The cell walls from the skin form a barrier to the diffusion of components such as aromas and polyphenols, which are important to the quality of the wines. Phenolic compounds contribute to color, astringency and bitterness of the red wines. Aroma is one of the major factors that determine the quality of the wine, showing the skins more than a half of the volatile compounds present in the grape berries [19]. It is well known that the grape berry skin cell walls consist of cellulose, hemicellulose, and are particularly rich in pectin [13, 25]. This pectin component contains a number of polymers HG, RG-I, side chains such as arabinans and galactans, RG-II and AGP [25, 26], and was proposed to be associated with other cell wall polymers (cellulose and hemicellulose) [27].

The pulp (i.e., flesh, also known as pericarp) is the main storage tissue for free sugars (i.e., glucose and fructose) and organic acids (i.e., tartaric acid) [28]. Pulp cells and tissues expand significantly during and after the veraison stage by volume compared to skin cells which expand by net surface area (i.e., a surface-to-volume ratio) [27]. Pulp tissue cell wall layers comprise mainly cellulose and pectin polysaccharides in addition to extension proteins [27].

The ease of skin degradation is directly linked to the skin cell wall composition and morphology [29], and the grape origin [29] and cultivar. Ortega-Regules et al. [30] points out that the differences among morphology and composition of the skin and pulp cell wall of three different red grape varieties (Monastrell, Syrah, Cabernet Sauvignon, Merlot) could explain the different anthocyanin extractability during the winemaking process. Moreover, the liberation of polysaccharides into the wine from the degradation of the grape cell wall could also be affected by an increase of the cell wall rigidity.

Grape berry ripening consists of a cell division (green) phase followed by a cell expansion (ripe) phase [25]. The onset of this second phase known as veraison is marked by the initiation of events such as sugar accumulation, a decrease in organic acids, color development, berry expansion and fruit softening.

The process of ripening, characterized in many fruits by softening of the fleshy tissues, is primarily due to textural changes partially correlated with cell wall polysaccharide remodeling [31]. Berry ripening links with size and morphological changes and a series of coordinated biochemical processes. Both biosynthetic and degradative metabolism of cell wall components involve numerous plant enzymes. Several reviews [32–34] discuss in detail the processes and the enzymes involved in plant cell wall turnover. In grapes, the changes in the cell wall structure involve the solubilization of galacturonan, with a concomitant reduction in the abundance of the arabinogalactan side chains of pectins [35], which can play a role in phenolic extractability [36]. It is thought that the loss of these components opens the interior of the cell wall to several degrading enzymes, causing further depolymerization, and an increased porosity [37]. The progressive pectin degradation of the grape skin cell walls [38] that takes place thorough ripening, should favor polysaccharide solubilization in the juice and thus in wine [39]. Martínez-Lapuente et al. [40] observed that the grape ripening stage (premature and mature grapes) showed a significant impact on the content, composition, and evolution of polysaccharides of sparkling wines. PRAG, RG-II, and oligosaccharides in base wines increased with maturity.

Pectins are among the plant polysaccharides found in wines, and are present in concentrations ranging from around 200 to 1500 mg/L [41]. Polysaccharide amounts depend on different parameters that include the grape variety, terroir, maturity stage, vintage, the wine-making techniques, and the treatments leading to increased solubilization of the macromolecular components of grape berry cell walls [4].

Several researches have studied the effect of techniques and treatments that could increase the solubilization of the polysaccharides of the grape cell walls. Some of them looked for the bursting of the grape cells, thus promoting the breakdown of the linkages stiffening the structure of the grape cell walls and allowing an increase in the release of the polysaccharides. The press fractioning, for example, allowed to segregate the grape juices with different qualities. Jégou et al. [42] observed significant changes in the polysaccharide and oligosaccharide base wine composition and concentration as the pressing cycle of the grapes progressed. The crushed berry is other technique used to physically break the grape berry cell walls, causing depectination and the release of cell wall polysaccharides in significant amounts into the fermenting must [2, 24]. Another technique consists in lowing the temperature of the entire or broken grapes. Low temperature techniques (cold prefermentative maceration, addition of dry ice at the beginning of the fermentation, and grape skin freezing) are additional tools used for degrading the cell wall and achieving greater extraction of polysaccharides [4]. Dry ice addition at the beginning of the fermentation has also proven a significant influence on the polysaccharide concentration and composition of the wines made from a given cultivar, whereas cold prefermentative maceration or grape skin freezing showed no effect [4, 43]. Flash release and heating accelerated the extraction of grape polysaccharides [44]. On the contrary, wines obtained by pressing immediately after flash release contained lower amounts of polyphenols and grape polysaccharides than those made with pomace contact, indicating that the extraction continued during the maceration. Flash release, consisting of the heating of the grapes in a closed tank and then placing them under vacuum, is used to break the cell walls and cool the must.

Other techniques such as modified skin contact times enhanced the release of polysaccharides. Prefermentative maceration at 18°C could also be applied to increase the content of polysaccharides in the wines [3]. The polysaccharides are gradually extracted during the maceration and the alcoholic fermentation due to grape tissue breakdown and degradation of the grape berry cell wall [2, 36]. Polysaccharide concentration increases during skin contact and is much higher in red wines than in white wines [45]. The commercial enzymes have been traditionally used in wine elaborations in order to produce a progressive cell wall disassembly during the winemaking and, hence, improve the release of valuable grape skin compounds such as the anthocyanins [46], aroma components [47], polysaccharides and oligosaccharides [48, 49]. Ayestarán et al. [50] analyzed the influence of commercial enzymes on the wine polysaccharide content, and reported that wines treated with commercial enzymes had higher concentrations of AGP and RG-II than control wines, probably due to the ability of commercial enzymes to hydrolyze the grape pectic polysaccharides during the maceration-fermentation stage. However, contradictory results have been obtained in other studies [48, 51, 52], probably due to the different activities and nature of the commercial preparations. RG-II, containing rare sugars, is also abundant in wines as it resists enzymatic degradation [53].

Guadalupe and Ayestarán [2] studied the changes occurring on the must and wine polysaccharide families of the grape cell walls during the different stages of the red wine processing, including maceration-fermentation and post maceration, malolactic fermentation, and oak aging and bottle aging. Passing from must to wine produced a loss of low-molecular-weight grape structural glucosyl polysaccharides,

and an important increase of grape-derived AGP, and RG-II. AGP were more easily extracted tan RG-II, and small quantities of RG-II monomers and galacturonans were detected. Post maceration produced a reduction in all grape polysaccharide families, particularly acute in AGP. The reduction of polysaccharides during malolactic fermentation only affected grape AGP. Wine oak and bottle aging was associated with a relative stability of the polysaccharide families. AGP were thus the majority polysaccharides in young wines. Precipitation of polysaccharides was noticeable during the winemaking, and it mainly affected to the high-molecular-weight AGP. Hydrolytic phenomena affected the balance of wine polysaccharides during late maceration-fermentation. Other authors [3, 54, 55] have observed a change to lower molecular weight polysaccharides during the wine aging, suggesting a partial degradation of the polysaccharides during the aging on lees, and a modification of their properties and solubilization. Pati et al. [56] concluded that the aging on lees led to an increase in all wine polysaccharide glycosyl residues, with the exception of glucose, xylose and myo-inositol, and to volatile profile modifications. The concentrations of cell wall polysaccharides are affected by the filtration process. Therefore, cross-flow microfiltration has shown to produce the highest retention of polysaccharides and proanthocyanidins in all the wines, mainly PRAG and highly polymerized phenols [5]. AGP greatly affected the filtration processes [57].

The final concentrations of cell wall polysaccharides that are extracted during the maceration and alcoholic fermentation are important for wine colloidal stability. RG-II and AGP can enhance or inhibit tannin self-aggregation [7, 58, 59]. Watrelot et al. [60] describe that the main interactions that occur between tannins and polysaccharides are hydrophobic interactions and hydrogen bonds, which differently affect the body, structure and mouthfeel sensations of the wines [10, 61]. Brandão et al. [11] studied the effect of two wine polysaccharides (AGP and RG-II) on the salivary proteins-polyphenol interactions. In general, both polysaccharides were effective to inhibit or reduce salivary proteins-polyphenol interactions and aggregations, and thus both polysaccharides were able to affect the astringency of wines and other beverages and foods. Different researches also point out that AGP show a protective effect against protein haze in white wines [8, 62], while RG-II increases tartrate crystallization at low concentrations and inhibit it at high concentrations [63]. Recent studies suggest that grape AGP do not affect the foamability of sparkling wines but increase foam stability [64, 65].

Aroma compounds can physically or chemically interact with other wine matrix components such as polyphenols, glycoproteins, and polysaccharides. One of the most important factors that can limit the rate of release of aroma compounds during wine consumption could be the interaction between aroma and non-volatile matrix components. This interaction can change the distribution of the aroma compounds between the aqueous solution and the vapor phase (partition coefficient), and thus, alter the odorant volatility, and influence the headspace partitioning of volatiles producing two opposite effects: a retention effect, decreasing the amount of aroma in the headspace, or a “salting out” effect, causing an increase in the headspace concentration of a volatile compound because of the increase in the ionic strength of the solution [66]. Some authors [67, 68] have observed that the addition of arabinogalactan compounds to wines at low concentrations increases the volatility of the aroma compounds.

3. Yeast polysaccharides: origin, structure and functions

Mannoproteins (MP) are polysaccharides released into the wines by *Saccharomyces cerevisiae* yeast either during the fermentation when yeast are actively

growing, or after the yeast autolysis by the action of glucanases on the cell wall during aging [69]. The amount of MP released by yeast depends on the specific yeast strain [70] and the winemaking and aging conditions [57]. MP are the second most abundant class of polysaccharides found in wine [2, 13, 42]. It is estimated that MP is around 35% of total polysaccharides in red wines [13], ranging approximately from 100 to 150 mg/L [71].

MP are located in the outermost layer of the yeast cell wall and can account for up to 50% of the cell wall dry mass of *Saccharomyces cerevisiae* [72]. The structure of MP present in wines has been described in several papers [8, 73]; basically, it consists of many small chains with one-to-four D-mannose residues in α-(1 → 2) or (1 → 3), which are linked to polypeptide chains on serine or threonine residues (**Figure 3**).

Wine MP are often highly glycosylated, with carbohydrate fractions consisting mainly of mannose (>90%) and glucose [69], and proteins ranging from 1 to 10% [13, 42, 72]. It has been reported sizes that vary within the range 5–800 kDa [1], with typical range between 50 and 500 kDa [13]. MP can be hydrolyzed by α-mannosidases and proteases, releasing small peptidomannans into the wine [1]. At wine pH, MP carry negative charges and they may establish electrostatic and ionic interactions with other components of the wine [74], resulting in the formation of complexes in a process that is dependent on their net electrical charge and on the structure of their functional groups [75].

MP in wines have great relevance from both a technological and a sensorial point of view [76], although they may be responsible for a decrease in wine color intensity or lower filterability [77, 78]. The different oenological functions of the yeast MP are discussed below.

MP seem to protect wines against protein precipitation. Protein haze is due to the instability of the grape proteins that occur naturally in wines [79], their denaturation and precipitation. It is often related to exposure to high temperatures but can also develop in properly stored wines [80, 81]. Moine-Ledoux and Dubourdieu [82] identified a 32-kDa fragment of *S. cerevisiae* invertase capable of reducing protein haze in white wines, and similar properties were observed for the intact protein [83]. Other yeast cell wall proteins have been shown to stabilize wine against protein haze [84] by reducing protein aggregate particle size [84]. In fact, MP could interact with heat-unfolded proteins, thus preventing protein self-aggregation by limiting the

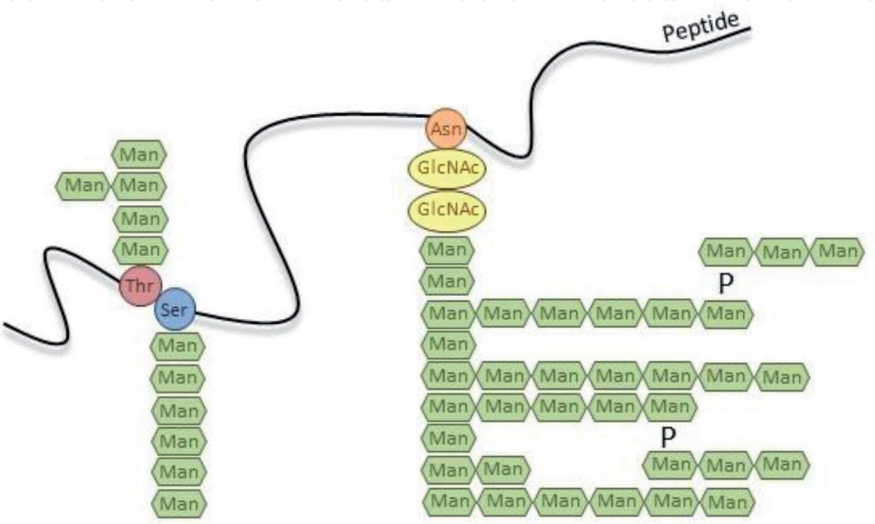

Figure 3.
Chemical structure of yeast exocellular mannoproteins. Asn, asparagine; GNAc, N-acetylglucosamine; man, mannose; P, phosphate; Ser, serine; Thr, threonine.

availability of some protein binding sites with a steric hindrance mechanism [85]. This effect seems to be dependent on the yeast used and the composition and size of the polysaccharides released [86] as well as pH and the ionic strength [87]. However, other authors have revealed that polysaccharides modulate the aggregation kinetics and final haziness, interfering with the aggregation process, but could not prevent it [87]. The ability of a yeast MP to stabilize wine proteins has been attributed specifically to the glycan portion of the proteoglycan [88]. Moreover, protein stabilization effectiveness in white wines has been related to MP chemical composition, concretely with their high mannose to glucose ratio [89].

MP play also an important role in tartrate salt crystallization. Several studies have shown that MP inhibit the crystallization of tartrate salts by lowering the crystallization temperature, particularly sharply glycosylated MP of medium molecular weight (30–50 kDa) [63, 90]. Other authors mention that MP affect the rate of crystal growth by binding to the nucleation points and preventing the expansion of the crystal structure [91]. The mechanism of mannoprotein's impact on tartrate stability is thought to be based on a competitive inhibition, which limits crystal formation [92]. MP act in the first stage of the formation of bitartrate crystals, and also during its growth, preventing the precipitation of the crystals [92]. It is also described that MP do not prevent potassium bitartrate nucleation. Instead, these compounds seem to delay or even arrest the outgrowth of the crystals to a macroscopic, visual size [9]. According to Moine-Ledoux and Dubourdieu [90], the stabilizing effect of MP may delay the appearance of crystals for a month in relation to the untreated wine. It was observed that a dose of 25 g/HL mannoproteins inhibited bitartrate salt precipitation in wines even after having been kept at −4°C for 6 days. Yeast MP are efficient inhibitors at concentrations of 20 g/HL. However, for highly saturated wines, in which a higher concentration is needed to achieve the same inhibitory effect, MP flocculation may occur that counteracts the expected effect [93]. In a recent study, Guise et al. [94] reported that MP did not tartaric stabilized the wines. In fact, MP showed a variable effect, and thus needed preliminary tests to evaluate their effectiveness and the optimal dose, which was specific to the wine being treated [90, 95]. In conclusion, the effect of MP on tartaric acid stabilization is still a continuing matter of debate [94].

Wine MP can also modify wine aroma composition, either affecting the volatility and perception of wine aroma compounds or by releasing exogenous volatiles [96, 97]. The physicochemical interactions between aroma substances and MP depend on the nature of the volatile compounds, since a greater degree of interactions is often observed with hydrophobic compounds [96], as well as the conformational structure of the MP [12]. This fact implies a longer aromatic perception because the volatile compounds retained by MP will be slowly released [98, 99]. Some authors attribute the retention of the aroma substances to MP containing a high proportion of proteins as the protein fraction of MP is the main responsible for the aromatic stability [96]. However, Chalier et al. [12] have shown that both the glycosidic and peptidic parts of the MP may interact with the aroma compounds. Different authors have reported the role of yeast derivatives as a source of MP on wine aroma [97, 98, 100–102]. Dosage appears to be fundamental since low amounts of MP increased the volatility of some esters, giving more flowery and fruity notes to the wine; while higher amounts increased fatty acid content, producing yeasty, herbaceous and cheese-like smells [97]. In still wines, the use of free yeast strains with higher concentrations of MP resulted in higher concentration of positive aroma compounds, such as terpenes and C13-norisoprenoids associated with the fresh, fruity, and floral notes [103]. On the other hand, the addition of commercial products rich in MP in sparkling wines resulted in higher content of some fruity esters [102], and improved the perception of fruity [100, 101]

and flowery characters [100]. It has been proposed that MP can be used to remove or reduce the occurrence of wine off-flavors as ethyl phenols (4-ethylguaiacol and 4-ethylphenol). In fact, the sorption of these compounds to the yeast walls could be due to the interactions of 4-ethylphenol and 4-ethylguaiacol with the functional groups of the MP and the free amino acids on the surface of the cell walls [104].

More interestingly, yeast MP have been described for their positive effect on the color stabilization [105, 107], reduction of astringency [10, 61, 108–110], and increased body and mouthfeel [10, 69, 99, 108, 111]. Studies performed in synthetic wines indicated that yeast MP can interact with tannins, probably through steric interactions, and prevent their aggregation and precipitation [7, 59]. This phenomenon seems to be dependent on the MP concentration and molecular weight, and on the conditions of the medium (ethanol content and ionic strength). The formation of tannin and polysaccharide complexes influences their association with salivary proteins, which then leads to a decrease in the astringency perception. This fact has been demonstrated in model solutions by several authors using different polysaccharide fractions [7, 10, 59]. It has also been evidenced not only the existence of interactions between MP and flavonols but also between MP and salivary proteins. This interaction could form proteins/polyphenol/mannoprotein soluble aggregates that probably affect the astringency perception [112]. Other studies suggested that MP did not stabilize or prevent the aggregation of tannin particles but they could increase tannin aggregation, leading to their precipitation [69, 108, 113]. The combination tannin-mannoproteins could result in high-molecular-weight structures that would be unstable and precipitate, leading to a decrease in the total proanthocyanidin content and thus, in a decrease in the astringent sensation [69, 108, 113]. More recently, Gonzalez Royo et al. [114] have shown that the decrease of the astringency sensation in wines was related to two different phenomena. The first was associated to the release of MP by inactive yeasts, which would increase the mouthfeel and inhibit the interactions between salivary proteins and tannins. The second was attributed to a direct effect of MP on the precipitation or absorption of proanthocyanidins. In fact, MP could act as stabilizers or flocculating polymers depending on factors such as tannin concentration and structure, and MP concentration, origin, molecular weight, charge, and structure [69]. It has also been reported that the addition of commercial inactive yeasts in grape juice during winemaking decreased the proanthocyanidin content of red wines coinciding with a decrease in high molecular weight MP [111, 115]. This fact suggests that the co-aggregates mannoprotein-tannin precipitated during this treatment [114]. Del Barrio-Galán et al. [99, 111] observed in the sensory analysis that some of MP commercial products reduced green tannins, thereby increasing softness on the palate. MP play also an important role in the stabilization of the color of red wines. MP are adsorbed by the colloidal molecules of anthocyanin-tannin, copigmented anthocyanins, and so forth, completely covering the surface of these colloids, avoiding their degradation and precipitation [116], leading to an increase in color stability [57, 105]. However, studies that analyze the effect of MP on wine color have shown contradictory results [7, 69, 99, 108, 109, 111, 113]. Our research group carried out a detailed study in order to know the effect of MP on the color of red wines. Several researches were carried out, such as the addition of commercial MP preparations before alcoholic fermentation [113], the use of MP overproducing yeast strains [69], aging on lysated lees [55], and combinations of all these treatments [55, 108]. Contrary to what was described in model solutions by using MP purified preparations [7, 59], our results showed that the use of MP in real vinification situations did not maintain the extracted polyphenols in colloidal dispersion, and neither seemed to ensure color stability [108, 113].

Other interesting oenological property of MP is their capacity to stimulate the growth of lactic acid bacteria and consequently the malolactic fermentation [117, 118]. In fact, MP can stimulate the malolactic bacteria through two mechanisms. Firstly, the adsorption of the medium chain fatty acids synthesized by Saccharomyces. These compounds have been shown to inhibit lactic acid bacteria growth and hence their removal by MP promotes the detoxification of the medium [119]. Secondly, the enzymatic hydrolysis of yeast MP and/or other macromolecules and polysaccharides by lactic acid bacteria can enhance the nutritional content of the medium, and thus potentially stimulate the lactic acid bacteria growth [117].

In the same way, yeast MP are able to adsorb the ochratoxin A (OTA), which is a dangerous mycotoxin [120]. This adsorption seems to be more effective in white wines than in red wines, due to the competition between polyphenols and OTA for the same binding sites on the surface of the yeast cells [106, 121]. There are several factors that can significantly affect the ability of OTA adsorption by MP as yeast strain [122, 123], mannosylphosphate content in the MP of wine yeasts, dissimilar fermentation, and cell sedimentation dynamics, cell dimension, and flocculence [120].

MP also affect the foam quality of sparkling wines [64, 65, 124–126]. Specifically, these molecules play a major role in foam stabilization [65, 127], particularly the MP with low content of protein (5%) [127]. The hydrophobic nature of MP causes them to preferentially adsorb to the gas/liquid interface of foam bubbles [128, 129], resulting in more stable foam [125]. In fact, the use of MP or cell wall extracts as additives has been proposed to improve the foam properties of sparkling wines elaborated by the traditional method. Therefore, the addition of yeast cell wall MP with a relative molecular weight between 10 and 30 kDa improved the foaming of sparkling wines [124]. However, the addition of commercial dry yeast products rich in MP to the tirage liquor did not modify the foam properties of sparkling wines [101]. In a previous work it was shown that MP and PRAG were poor foam formers but good foam stabilizers. Moreover, a higher positive correlation was found between foam stability time and PRAG (r = 0.723) than MP (r = 0.465) [65].

Finally, MP also contribute to the flocculation of yeast strains [130], and thus improve their elimination from the bottle during disgorging. MP could also serve as markers to follow the autolysis process because they are the major polysaccharides released by yeast [1, 3, 54]. Moreover, MP also seem to participate in film forming yeast or flor velum in Sherry type wines [131]. These wines are produced by "biological aging" that follows alcoholic fermentation. According to the study conducted by Alexandre et al. [132], a 49 kDa hydrophobic cell wall MP present in a velum yeast has been correlated with velum formation during the aging system used in sherry wine (Spain) or Vin Jaune (France).

4. Conclusions

Polysaccharides are one of the main groups of macromolecules in wines. They play an important role in both the technological and organoleptic properties of the wines. The oenological interest of polysaccharides has induced the development of several commercial products. In fact, there are nowadays in the market different commercial products based on purified MP or yeast derived cell walls, which are used in many wineries in order to improve the tartaric or proteic stability of the wines, or the sensory properties of some wines. However, these products have not always shown a clear effect in the wines. Recent studies indicate that other oligosaccharides and polysaccharide families from grapes could have a great potential to modify and improve the sensory and physicochemical properties of the wines. Unfortunately, these polysaccharide families are very difficult to obtain and they

are not present in commercial formulates. Therefore, there are only a few studies regarding their effects and mechanisms of action, and more researches have to be done to better known their role and applicability into the wines.

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