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The polysaccharides of winemaking: From grape to wine.

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ABSTRACT

Background: Polysaccharides are a major class of complex macromolecules present in the wine matrix. These polysaccharides can be classified as being either grape or yeast derived. The key polysaccharides identified within the wine matrix are the pectic polysaccharides: polysaccharide rich in arabinose and galactose (PRAG), rhamnogalactouronans (RG-I and RG-II) and yeast mannoproteins (MP). The transformation of grapes into wine induces significant changes in the chemical composition and profile of these polysaccharides.

Scope and approach: This review aims to summarise and discuss the prevalence of polysaccharides in wine, with a focus on their profile during the transformation from grape to wine. This study emphasises the chemical complexity of the wine matrix, highlighting the many factors influencing the profile and abundance of polysaccharides which could in turn assist winemakers in making informed decisions.

Key findings and conclusions: Many factors during grape maturation and throughout the winemaking process have been shown to influence the profile and chemical composition of polysaccharides. Environmental factors can significantly influence the polysaccharide profile of grape berries prior to harvest. Fermentation is responsible for the largest modification in the polysaccharide profile throughout vinification. Overall, the transition of must to wine is characterised by an increase in grape derived AGPs and RG-II, as well as a dramatic and progressive increase in yeast mannoproteins, especially true for wines aged on yeast lees.

1. Introduction

Wine is a culturally important alcoholic beverage that has been consumed for thousands of years, with some of the earliest archaeological records concerning wine dating as far back as 5500 B.C (Jackson, 2008). Wine is produced from the crushing and pressing of grape berries, followed by the anaerobic transformation of grape must, utilising alcoholic fermentation, a process that uses yeast to convert glucose to ethanol, resulting in considerable alterations in the chemical composition of the medium (Jackson, 2008; Moreno & Peinado, 2012; Moreno-Arribas & Polo, 2009). Several other steps during the winemaking process can also cause marked changes in the chemical profiles of the wine polysaccharides, some of which will be highlighted in this review. An overview of the winemaking process is illustrated in Fig. 1. Some of these steps are considered optional and many internal factors contribute to governing when to perform each step and how long each step will be performed for. The sometimes-subtle differences in these steps allow for variations in stylistic design, characteristics and organoleptic properties of the final wine, which are often crafted by winegrowers to fit the desires of their consumer base.

The relevance of various winemaking techniques and how they influence the extractability and thus the profile and content of polysaccharides in wine will be explained in later sections. However, it must be noted that there are many factors that can be implemented throughout this process to introduce variations in the final wine; these include chemical additives (Martínez-Lapuente, Guadalupe, Ayestarán, Ortega-Heras, & Pérez-Magariño, 2013), enzymes (Apolinar-Valiente, Romero-Cascales, Gómez-Plaza, & Ros-García, 2016; Blanco, Sieiro, & Villa, 1999; Ducasse et al., 2010; Gao et al., 2019) and yeast selections (Bindon et al., 2019; Ciani & Comitini, 2011; Del Barrio-Galán, Pérez-Magariño, Ortega-Heras, Guadalupe, & Ayestarán, 2012; González-Royo et al., 2017González-Royo et al., 2017; Malfeito-Ferreira, 2011).

This review aims to examine the prevalence of polysaccharides in wine, discussing their profile during the transformation from grape to

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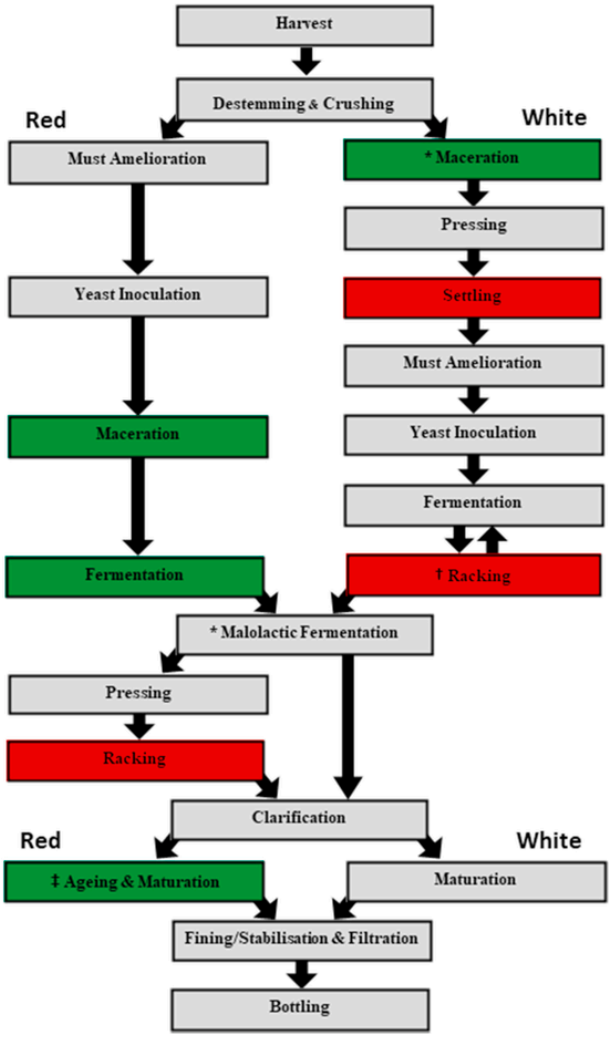

Fig. 1. A generalised summary of the steps involved in the winemaking process. Note that some of these steps are optional and other steps can be included or excluded depending on the type and stylistic desire of the final wine. * Optional Steps. † Often performed several times through fermentation. ‡ Ageing on Lees. The coloured boxes highlight steps which involved alterations in polysaccharide profile/content of the wine, with green and red showing increases and decreases, respectively. Figure adapted from Unterkofler et al., Moreno-Arribas et al., and Jackson (Gao, Zietsman, Vivier, & Moore, 2019; Jackson, 2008; Moreno-Arribas & Polo, 2009; Unterkofler, Muhlack, & Jeffery, 2020). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

wine. Polysaccharides are key wine macromolecules (Apolinar-Valiente et al., 2013) and have been isolated, characterised and studied in some depth over the past 30 years. These relatively complex and diverse structures are reported in wine at concentrations ranging from 0 to 2 g L^{-1} (Doco, Quellec, Moutounet, & Pellerin, 1999; Dufour & Bayonove, 1999; Guadalupe, Ayestarán, Williams, & Doco, 2014). It is widely accepted that the majority of wine polysaccharides originate from grape berries and yeast cells, Fig. 2 serves to summarise and illustrate this. Grape derived pectic polysaccharides are released from the skin and pulp of the grapes in the must. These pectic polysaccharides are specific components of pectin and are released from the complex cell wall network by several types of endogenous and exogenous enzymes (Guadalupe et al., 2014). Pectin is a galacturonic acid rich hetero-polysaccharide with galacturonic acid (GalA) comprising approximately 70% of the 1,4-glycosidic linkages (Eliaz & Raz, 2019; Ochoa-Villarreal, 2012) present in the structure. Pectin, together with cellulose and hemicellulose, are the three major components that form the cell wall network of higher plants (Harholt, Suttangkakul, & Scheller, 2010; Ochoa-Villarreal, 2012; Voragen, Coenen, Verhoef, & Schols, 2009). The second source of wine polysaccharides is parietal mannoproteins which are liberated from yeast cells (Ayestarán, Guadalupe, & León, 2004; Dufour & Bayonove, 1999; Escot, Feuillat, Dulau, & Charpentier, 2001; Guadalupe & Ayestarán, 2007; Marangon et al., 2018; Unterkofler et al., 2020). Previous studies have reported that pectic polysaccharides present in grape must and wine include polysaccharides rich in arabinose and galactose (PRAGs), which comprise arabinans and arabinogalactans (AG-I and AG-II), and rhamnogalacturonans (RG-I and RG-II) (Ayestarán et al., 2004; Doco et al., 1999; Doco, Williams, Pauly, O'Neill, & Pellerin, 2003; Guadalupe & Ayestarán, 2007; Vidal, Williams, Doco, Moutounet, & Pellerin, 2003; Vidal, Williams, O'Neill, & Pellerin, 2001). However, the most and abundant grape polysaccharides in wine are arabinogalactan proteins (AGP), RG-I and RG-II (Ayestarán et al., 2004; Guadalupe et al., 2014; Vidal et al., 2001, 2003).

Arabinogalactan II, unlike AG-I, often exists as a complex with proteins and is therefore classified as an arabinogalactan protein (AGP). AGP contains a backbone of linked (1 → 3)-D-galactose residues with substitutions of (1 → 6) linked D-galactose residues. Other saccharides can be attached to these residues including (1 → 3) and (1 → 5) linked α-L-arabinose, (1 → 4) linked α-L-rhamnose and (1 → 6) linked β-D-glucuronic acid, creating further branching as illustrated in Fig. 3 (Guadalupe et al., 2014; Knoch, Dilokpimol, & Geshi, 2014; Voragen et al., 2009). AGP is a hydroxyproline-rich glycoprotein (HRGP) where the protein moiety is attached to the saccharide backbone via a (1 → 4)-β-D-galactose linkage. AGP contains a high content of the monosaccharides galactose and arabinose (Fincher & Stone, 1983, pp. 47–70; Knoch et al., 2014), and it has been reported that the saccharide portion constitutes the majority (>90%) of the structure (Fincher & Stone, 1983, pp. 47–70; Knoch et al., 2014; Pellerin, Waters, & Brillouet, 1993; Voragen et al., 2009). Other important HRGP include extensin and proline-rich proteins (PRP), and together with AGP, these molecules are involved in the plant's primary defence response. The rapid production of reactive oxygen species (ROS) in plant cells, such as hydrogen peroxide (H_2O_2), in plant cells is also a crucial response involved in plant defence. Stress-related production of ROS is required for the rapid crosslinking of plant cell wall components, including HRGP (Ribeiro et al., 2006). H_2O_2-induced extensin-deposition and crosslinking creates a dense, fibrillar extensin network, independent of the cellulosic network, that can span the width of the cell wall and help immobilize polymers to increase cell-wall rigidity and resistance to digestion by exogenous lytic enzymes (Nunan, Sims, Bacic, Robinson, & Fincher, 1998). Conceivably, H_2O_2-induced extensin-crosslinking could play a key role in assisting grape tissue to resist enzymatic digestion during early stages of winemaking, in turn having an impact on the extraction of crucial components. Furthermore, H_2O_2 is capable of driving the non-enzymatic, oxidative cleavage of polysaccharides, altering cell-wall properties, and subsequently, this could affect the polysaccharide profile of a wine during early winemaking steps.

Rhamnogalacturonan I (RG-I) is a branched polysaccharide with a backbone comprised of the repeating disaccharide unit (1,2)-α-D-galacturonic acid-(1,4)-α-L-rhamnose where acetylation can occur at *O*-2 and/or *O*-3 (Tanhatan Naseri et al., 2008). The rhamnose residues of the RG-I backbone have been identified to be substituted with several different polysaccharides at *O*-4. Some of these substitutions include arabinan, galactan and arabinogalactans I and II (AG-I and AG-II) (Ochoa-Villarreal, 2012; Tanhatan Naseri et al., 2008; Vidal et al., 2001; Voragen et al., 2009) (Fig. 4).

Rhamnogalacturonan II (RG-II) is a highly conserved, low-molecular weight polysaccharide domain of pectin and contributes less than 10% to the overall structure of pectin. Unlike RG-I, RG-II contains four different, but characteristic side chains as illustrated in Fig. 5. These side chains contain glycosyl residues and glycosidic linkages that

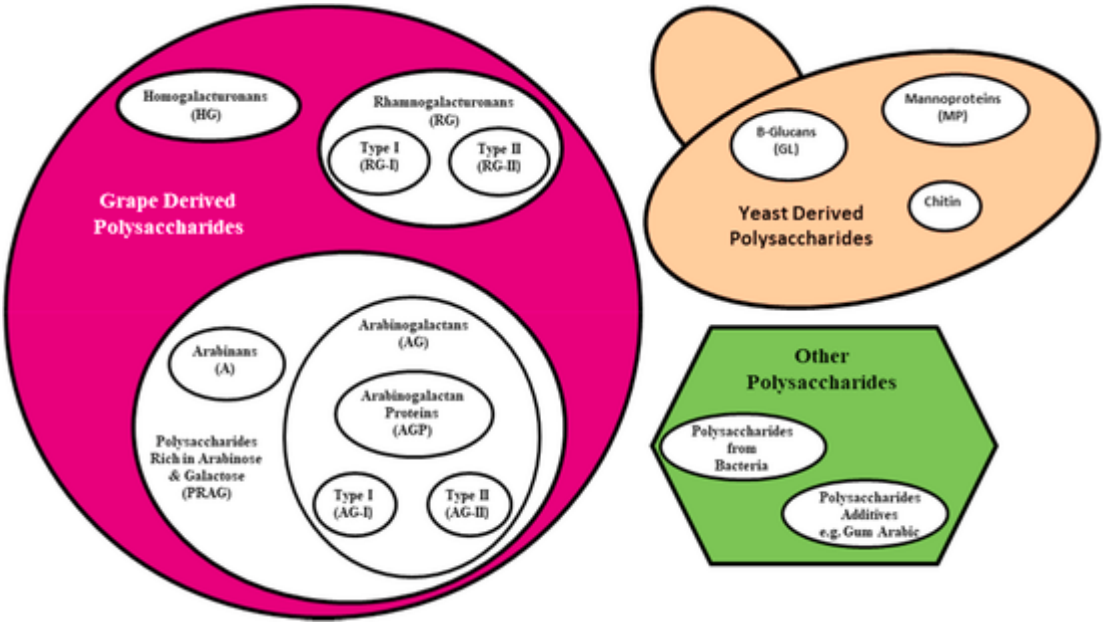

Fig. 2. A summary illustration of the polysaccharides of wine from their respective origins. Adapted from Martínez-Lapuente et al. (Martínez-Lapuente, Guadalupe, & Ayestarán, 2019).

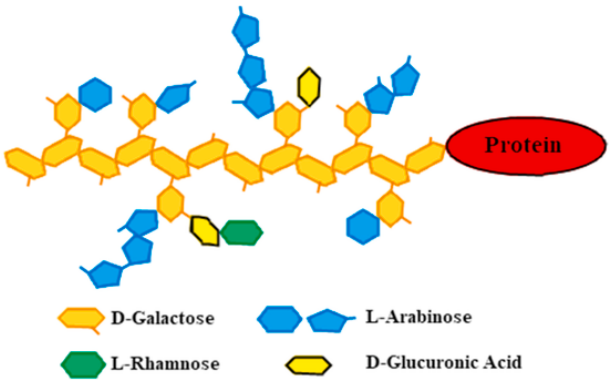

Fig. 3. The structural components of the pectic polysaccharide type II-arabinogalactan, complexed with a hydroproline-rich peptide entity to form an AGP, a major polysaccharide of wine. The (1 → 3)-D-galactose backbone can contain galactose substituents via (1 → 6) linkages. Illustration adapted from Guadalupe et al. (Guadalupe et al., 2014) and other authors (Eliaz & Raz, 2019; Fincher & Stone, 1983, pp. 47–70; Harholt et al., 2010; Knoch et al., 2014; Tanhatan Naseri, Thibault, & Ralet-Renard, 2008; Ochoa-Villarreal, 2012; Pellerin et al., 1993; Pellerin, Vidal, Williams, & Brillouet, 1995; Saulnier & Brillouet, 1989; Verhertbruggen, Marcus, Chen, & Knox, 2013; Voragen et al., 2009).

are uncommon and unique to plant polysaccharides. These include apiose, 2-*O*-methyl xylose, 2-*O*-methyl fucose, aceric acid, 2-keto-3-deoxy-D-lyxo heptulosaric acid (Dha) and 2-keto-3-deoxy-D-manno octulosonic acid (Kdo) (Ayestarán et al., 2004; Doco & Brillouet, 1993; Doco, Williams, Vidal, & Pellerin, 1997; Guadalupe & Ayestarán, 2007; Guadalupe et al., 2014; Harholt et al., 2010; Tanhatan Naseri et al., 2008; Ochoa-Villarreal, 2012; Pellerin et al., 1996; Vidal et al., 2003; Voragen et al., 2009). These characteristic saccharides allow for easy identification and characterisation of RG-II in wine samples (Guadalupe et al., 2014). Interestingly, RG-II can form a complex with boron, through its apiosyl-residues (Doco & Brillouet, 1993; Pellerin et al., 1996) to yield a borate-diol ester linkage between two pectin molecules and thus RG-II exists as a dimer (dRG-II). This dimerisation contributes to the mechanical stability and 3-D structure of the pectic network in plants (Doco et al., 1997; Harholt et al., 2010; Ochoa-Villarreal, 2012; Pellerin et al., 1996; Tanhatan Naseri et al., 2008) (see Fig. 6).

Polysaccharides derived from yeast include mannans, glucans and mannoproteins (MP), and originate from the cell wall material, accounting for up to 90% of the dry weight of the cell wall (Escot et al., 2001; Guadalupe et al., 2014). Mannoproteins are important molecules within the wine matrix and are predominately comprised of mannose, but can contain trace amounts of glucose (Waters, Pellerin, & Brillouet, 1994). Mannoproteins are attached to proteins via an *N*-acetyl glucosamine linkage, shown in Fig. 7. Mannoproteins contain a backbone of (1 → 6) linked D-mannose residues, which is often highly branched with other mannose units through (1 → 2) or (1 → 3) glycosidic linkages. Phosphate entities have been identified in the exocellular mannoprotein portion of the yeast cell walls and this can create further branching (Guadalupe et al., 2014).

The research field of polysaccharides in wine has seen an increase in interest over the past 30 years. Several pioneering authors including Ayestarán, Doco, Guadalupe, Pellerin, Vidal and Williams, along with others, have produced a comprehensive platform of information detailing the wine matrix. Guadalupe et al. (Guadalupe et al., 2014) published an extensive summary of the analytical techniques many researchers have used to characterise components of the wine matrix. The most common technique used to obtain purified wine polysaccharides employs high resolution size exclusion chromatography (HRSEC) to separate and fractionate components based on their molecular weights (Ayestarán et al., 2004; Doco & Brillouet, 1993; Doco, Williams, et al., 2003; Dufour & Bayonove, 1999; Guadalupe & Ayestarán, 2007; Guadalupe et al., 2014; Pellerin et al., 1996; Vidal et al., 2001; Vidal et al., 2003). This technique can often be used in combination with high performance anion exchange chromatography (HPAEC) (Ayestarán et al., 2004; Brillouet, Bosso, & Moutounet, 1990; Doco & Brillouet, 1993; Dufour & Bayonove, 1999; Pellerin et al., 1996; Vidal et al., 2003) to readily isolate charged, acidic species (e.g. galacturonic acids) from those that are neutral (e.g. PRAGs). Gas chromatography coupled with a mass spectrometer have also been used by many in the field as to ascertain the glycosyl-residues present in the polysaccharides (Brillouet et al., 1990; Doco & Brillouet, 1993; Doco, Williams, et al., 2003; Doco et al., 1997; Dufour & Bayonove, 1999; Guadalupe & Ayestarán, 2007; Guadalupe et al., 2014; Pellerin et al., 1996; Vidal et al., 2001). Other techniques such as low-angle laser-light-scattering (LALLS) (Doco &

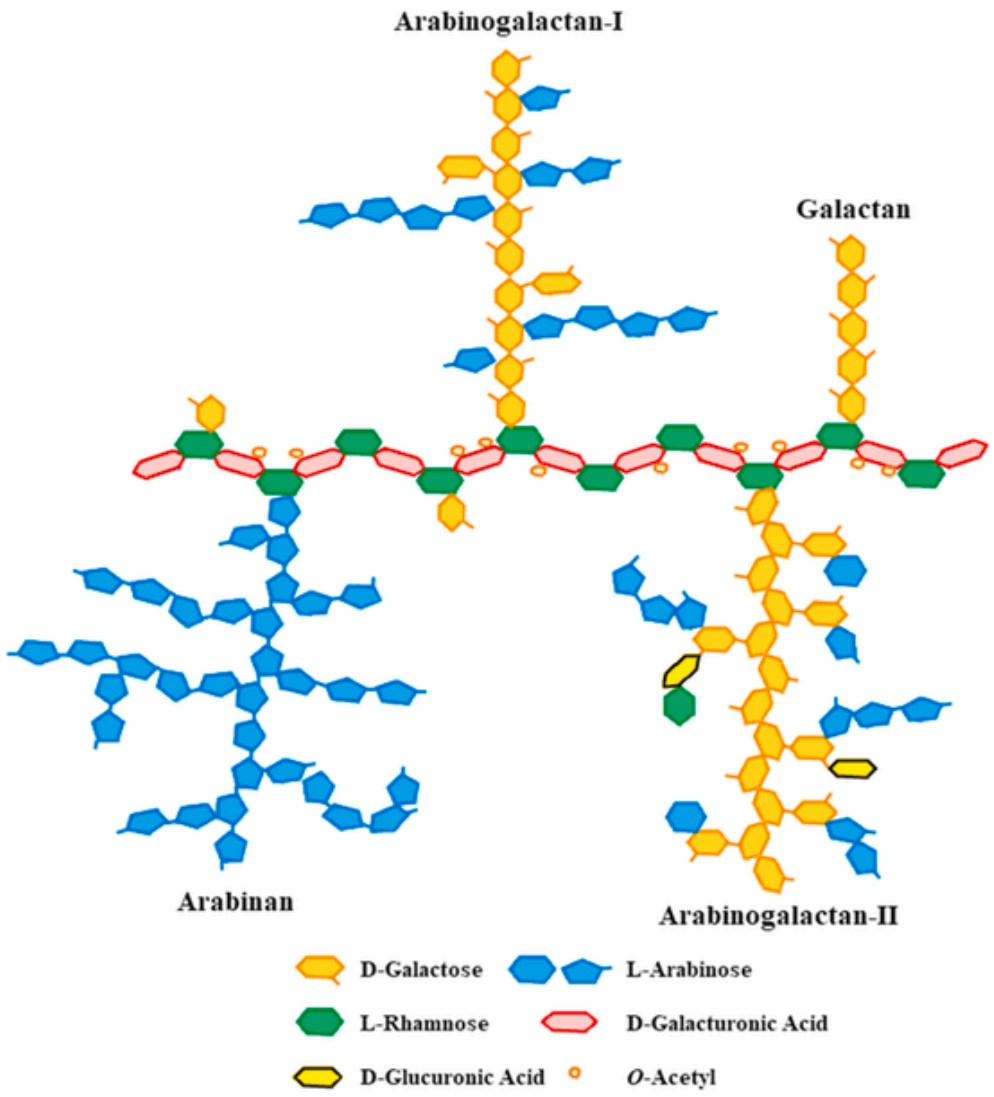

Fig. 4. A depiction of the structural components of the pectic polysaccharide type I-rhamnogalactouronan (RG-I), a polysaccharide of the wine matrix. RG-I contains a backbone of repeating (1,2)-α-D-galacturonic acid-(1,4)-α-L-rhamnose residues, where substitutions can occur at the *O*-4 position of the (1,4)-α-L-rhamnose residues. The substitutions can include the PRAGs arabinan, arabinogalactan I and II and galactan. Illustration adapted and designed from Guadalupe et al. (Guadalupe et al., 2014) and other authors (Eliaz & Raz, 2019; Fincher & Stone, 1983, pp. 47–70; Harholt et al., 2010; Knoch et al., 2014; Tanhatan Naseri et al., 2008; Ochoa-Villarreal, 2012; Pellerin et al., 1993, 1995; Saulnier & Brillouet, 1989; Verhertbruggen et al., 2013; Voragen et al., 2009).

Brillouet, 1993) to determine molecular weights and concanavalin A affinity (CAA) (Brillouet et al., 1990; Guadalupe et al., 2014; Marangon et al., 2018; Pellerin et al., 1996) to purify and isolate mannosylated polysaccharide fractions have also been performed by several groups in the study of polysaccharides in wine. Comprehensive microarray polymer profiling (CoMPP) is another popular technique (Garrido-Bañuelos et al., 2019b; Moore, Fangel, Willats, & Vivier, 2014), and recently has been used in conjunction with recombinant pectinase additions and GC techniques to better understand the cellular deconstruction process during enzyme-mediated maceration, characterise grape tissue and to propose a model for the grape cell wall (Gao et al., 2019; Gao, Fangel, Willats, Vivier, & Moore, 2016).

2. Polysaccharides profiles of grapes and wine in the vinification process

2.1. Factors that affect polysaccharide profile of grapes prior to vinification

A number of studies over the past 25 years have been dedicated to the understanding and quantification of the polysaccharides in grapes and wine throughout the vinification process. Some of these studies have attempted to identify influential factors involving the grape berries that could lead to alterations in their polysaccharide profile. Modifications to cell wall polysaccharides in grape are an important factor affecting firmness at *veraison* and throughout the ripening stages. During maturation and ripening the berry undergoes many compositional changes (Garrido-Bañuelos et al., 2019b; Jackson, 2008; Moreno & Peinado, 2012) which can have an impact on the final chemical composition and overall polysaccharide profile at the time of harvest.

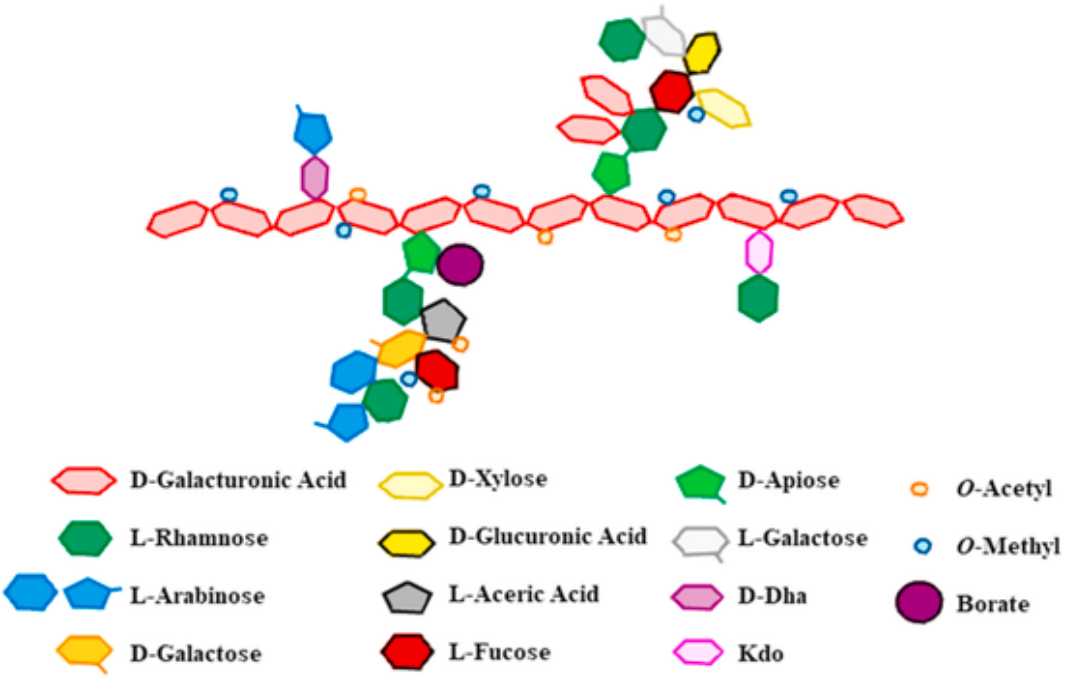

Fig. 5. The structure of type II-rhamnogalacturonan (RG-II), an important pectic polysaccharide within the wine matrix. RG-II contains a (1 → 4) linked galacturonic acid backbone with four characteristic and highly conserved side chains, containing several uncommon saccharides and glycosidic linkages. Illustration adapted and designed from Guadalupe et al.(Guadalupe et al., 2014) and other authors (Eliaz & Raz, 2019; Fincher & Stone, 1983, pp. 47–70; Harholt et al., 2010; Knoch et al., 2014; Ochoa-Villarreal, 2012; Pellerin et al., 1993, 1995; Saulnier & Brillouet, 1989; Tanhatan Naseri et al., 2008; Verhertbruggen et al., 2013; Voragen et al., 2009).

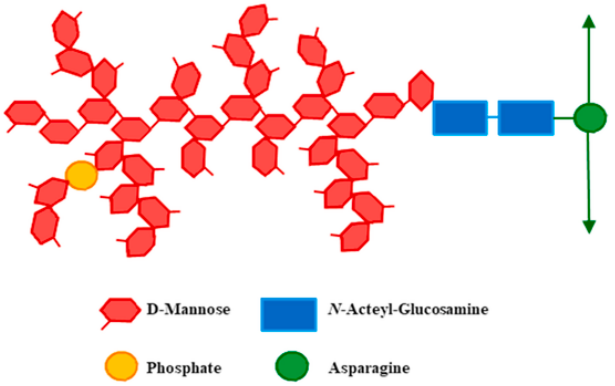

Fig. 6. A structural depiction of a yeast-derived mannoprotein, an important polysaccharide present in wine matrix. Mannoproteins contain a backbone of (1 → 6) linked D-mannose residues, which is often highly branched with other mannose residues. The saccharide motif is connected to the peptide backbone (shown by the green arrow) through an *N*-acetyl glucosamine linkage. Illustration adapted and designed from Guadalupe et al.(Guadalupe et al., 2014) and Martínez-Lapuente et al. (Martínez-Lapuente et al., 2019). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Veraison describes the point at which a series of developmental events during grape berry maturation are initiated, including the accumulation of sugars, a decrease in acidity, berry expansion, and softening (Nunan et al., 1998). Softening involves significant changes in the properties of cell wall polysaccharides. Significant modification of specific polysaccharide components and large changes in protein content can be observed during softening and ripening (Nunan, Davies, Robinson, & Fincher, 2001).

More recently, Moore et al. (Moore et al., 2014) used CoMPP and molecular probes for specific polysaccharide epitopes to track changes in polysaccharide abundance and composition during the ripening stages. Combinations of cell wall probes were able to characterise distinct ripening phases in grapes, and cell wall modifications in ripening grapes were shown to involve the rearrangement of networks composed of pectin, xylogucans and cellulose. Also, pectin, extensin and AGP showed strong correlations with ripening, with a significant increase in abundance of extensin and AGP epitopes at *veraison,* correlating to mesocarp cell expansions events.

Fasoli et al. (Fasoli et al., 2016) used FTIR to monitor differences in the polymer modifications (including the extent of esterification, depolymerisation and solubilisation), and dynamics between the epidermal and inner skin surfaces of grape. The most significant changes occurred from *veraison* and mid-ripening until full ripeness, with Fasoli et al. noting that major changes in the surfaces were due to hemicellulose and pectin modifications in the internal layer, and primarily cellulose (with pectin to a lesser degree) modification in the epidermal layer. Fasoli et al. also found that pectin depolymerisation and solubilisation correlated with skin wall swelling, concluding that pectic depolymerisation and de-esterification were key processes leading to increased cell wall porosity and fruit softening during ripening.

Vicens et al. (Vicens et al., 2009) examined the evolution and extractability of polysaccharides from Shiraz grape skins throughout ripening. Changes were observed in the composition of cell wall polysaccharides, namely a decrease in galactose content and the de-esterification of methoxylated uronic acids. A two-fold increase was observed in the concentration of water-soluble saccharides throughout ripening, an event well-documented during the ripening of fruits (Jackson, 2008; Moreno & Peinado, 2012). Ortega-Regules et al. (Ortega-Regules, Ros-García, Bautista-Ortín, López-Roca,; Gómez-Plaza, 2008) obtained similar findings during their study investigating the changes of the chemical composition within the skin cell wall during maturation of Cabernet Sauvignon (CS), Merlot (M), Syrah (S) and Monastrell (MJ & MB) grapes. Ortega-Regules et al. reported that the different grape varieties experienced different changes in polysaccharide profiles throughout maturation, reporting an increase or no change

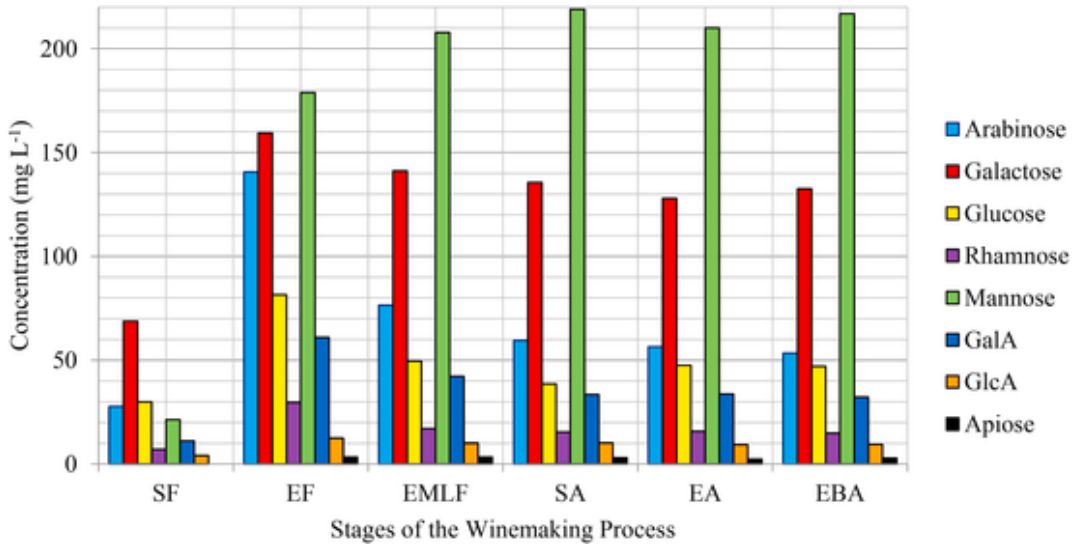

Fig. 7. A summarised version of results for the concentration of eight selected saccharides monitored throughout different stages of the winemaking process to illustrate the changes in saccharide profile, taken from the research of Guadalupe et al. (Guadalupe & Ayestarán, 2007) SF = Start Fermentation, EF = End Fermentation, EMLF = End of Malolactic Fermentation, SA = Start of Ageing, EA = End of Ageing and EBA = End of Bottled Ageing. For simplicity, errors values have not been included and only a select set of saccharides are represented in this figure. Apiose was selected to represent and illustrate potential changes in RG-II throughout different stages of the process. For ease of illustrational purposes, these values are the sum of several Tempranillo wine and juice/must fractions isolated using HRSEC, placed together in a single graph.

in the concentration of arabinose. Rhamnose however, was more varied, either increasing (CS), remaining constant (M & MJ) or decreasing slightly (S & MB). Furthermore, Vicens et al. reported that the overall protein content increased during the stages of ripening; interestingly, a dramatic increase in the amino acid hydroxyproline was also reported. Several researchers have observed hydroxyproline as a major amino-acid component of AGP (Fincher & Stone, 1983; Pellerin et al., 1993, 1995, pp. 47–70; Saulnier & Brillouet, 1989) and AGPs are abundant polysaccharides in harvested grape berries (Doco, Brillouet, & Moutounet, 1996; Vidal et al., 2001). Perhaps this increase in hydroxyproline could be correlated to an increased complexation of AG-II with protein moieties, as Vicens et al. proposed that an increase in hydroxyproline indicates the involvement of HRGP in the cell wall during the ripening process. Nunan et al. (Nunan et al., 1998) corroborated this idea, suggesting it is plausible that the expansion of mesocarp cells during ripening require the reinforcement of the cell walls with HRGP, which saw a 3.5-fold increase in content, as to maintain cell wall integrity during softening.

Further studies involving grape maturity and polysaccharide profiles have been performed by Martínez-Lapuente et al. (Martínez-Lapuente et al., 2016) and Gil et al. (Gil et al., 2015). Gil et al. reported that the total concentration of medium to low molecular weight polysaccharides in Cabernet Sauvignon cultivar grapes increased with greater grape maturity. This was thought to be due to grape polygalacturonase (PG) activity, an endogenous enzyme responsible for the degradation of pectic polysaccharides, increasing following *veraison*, and triggering pectin polysaccharide degradation and depolymerisation associated with ripening events (Fasoli et al., 2016; Gil et al., 2015). Martínez-Lapuente et al., who primarily focused their studies on sparkling wines (Martínez-Lapuente et al., 2016, 2013; Martínez-Lapuente, Guadalupe, Ayestarán, & Pérez-Magariño, 2015; Martínez-Lapuente et al., 2018Martínez-Lapuente et al., 2018) investigated the influence of grape maturity on the polysaccharide profile of red sparkling wines during winemaking and ageing. One key difference between sparkling and still red wines was that sparkling red grapes must be harvested earlier so as to have lower amounts of soluble sugars (Gil et al., 2015) to compensate for an increase in alcohol content during secondary fermentation (Martínez-Lapuente et al., 2016), as well as a lower pH and higher titratable acidity to support long ageing on yeast lees. Martínez-Lapuente et al. reported that ripeness did influence the polysaccharide content of the final wines, stating that major differences among the glycosyl composition contents of arabinose, galactose and rhamnose were observed. Interestingly, Martínez-Lapuente et al. argued that the concentration of pectic polysaccharides increased with grape maturity as a result of increased enzymatic activity, which corroborates the results from Gil et al. (Gil et al., 2015) Polygalacturonase activity has been reported to be very low during early stages of berry growth, but increases after *veraison*, thus activating pectin depolymerisation and increasing the availability of pectic polysaccharides in berries with greater maturity, explaining the increased content of PRAG and RG-II observed in wine produced from riper grapes (Cabanne & Donèche, 2001). Martínez-Lapuente et al. noticed that the MP concentration was also lower in the wines produced using berries that were less ripe when compared to wines made with ripe berries; however, as all yeast strains were identical and all MP were claimed to have originated from yeasts, the higher MP content of the mature sparkling wines were thought to be the result of different alcohol concentrations of the wines. MP release can be influenced by several factors and this will be discussed later in this section. Overall, Martínez-Lapuente et al. concluded that the concentrations of PRAGs, MP and RG-II were all higher in grapes with greater ripeness, which agrees with findings reported by other research groups who focused on same topic, despite differences in finished wine types (Gil et al., 2015; Vicens et al., 2009).

A classical ideology of viticulture claims that small grape berries produce the best red wines (Cortiella, Úbeda, Barrio-Galán, & Peña-Neira, 2020). Cortiella et al. investigated this claim and reported that larger berries have a lower surface-to-volume ratio and tend to have thicker skins, thus contain a greater proportion of skin material compared to smaller grapes (Cortiella, Úbeda, Barrio-Galán, & Peña-Neira, 2020; Vidal et al., 2001). Cortiella et al. concluded that wines produced with grapes with a greater portion of skins (*i.e.* larger berries) contained a higher content of phenolic compounds and polysaccharides as these are found in larger quantities in this part of the berry (Vidal et al., 2001). Previous studies indicated that many factors influence berry size at harvest, including pruning treatments (Holt, Francis, Field, Herderich, & Iland, 2008), crop yield (Bravdo, Hepner, Loinger, Cohen, & Tabacman, 1985), cluster light exposure (Dokoozlian & Kliewer,

1996), partial defoliation (Hunter, Villiers, & Watts, 1991) and water deficit (Chacón, García, Martínez, Romero, & Gómez, 2009), and it has been demonstrated that all of these factors do alter the molecular composition of the grape (Cortiella et al., 2020; Moreno & Peinado, 2012). Cortiella et al. concluded that it can be ascertained that a higher proportion of grape skin (larger berries) and thicker skins can influence the polysaccharide profile in grape berries and therefore produce wines with a higher polysaccharide content, concluding that skin thickness is a more influential factor affecting the final wine composition than the size of the berry itself.

Vidal et al. investigated the isolation and characterisation of grape berry polysaccharides from different tissues (skin and pulp), identifying that 80% of AGPs found in grape originate from the pulp tissue (Vidal et al., 2001). The detection of the rare RG-II diagnostic saccharides 2-*O*-methyl fucose, 2-*O*-methyl xylose, apiose, aceric acid, Kda and Dha, allowed Vidal et al. to conclude that RG-II is present in grape must and may be responsible for $<5\%$ of the soluble polysaccharides such as PRAGs, which is consistent with previously reported results from pectin solubilisation without enzymatic digestion (Vicens et al., 2009; Vidal et al., 2001). However, after enzymatic treatment the results indicated that HG, RG-I and RG-II accounted for 80%, 15% and 5% of the pectic polysaccharides present the skin and pulp cell wall material, respectively. These results showed that the RG-I content was three-fold higher than that of RG-II (Vidal et al., 2001). However, in a later publication, Vidal et al. reported the concentration of RG-I and RG-II in a red wine sample to be 4% and 19% of the total polysaccharides, respectively (Vidal et al., 2003). Also, the results from the skin tissue alone accounted for 75% of the total HG, RG-I and RG-II content in the whole berry, and thus it could be concluded that the skin is the primary source of pectic polysaccharides in grapes (Cortiella et al., 2020; Vidal et al., 2001). Furthermore, while being the primary pectic source, it was suggested that these polysaccharides were also more tightly held in the skin cell wall matrix, as opposed to the pulp cell wall tissue (Vidal et al., 2001), supporting the need for enzymatic treatment to increase the extractability of cellular contents during the winemaking process. Further investigations have led to the conclusion that red wines are richer in grape-derived polysaccharides than white wines (Pellerin & Cabanis, 1998; Vidal et al., 2001), a conclusion that is well-supported by the fact that white wines exhibit roughly half of the amount of polysaccharides found in red wines (Doco et al., 1996). Differences in the winemaking procedures between red and white wines (see Fig. 1), and especially to the maceration step required to produce red wines is one of the key explanations supporting these observations.

Investigations by Apolinar-Valiente et al. (Apolinar-Valiente et al., 2016) into the grape skin cell wall material from different grape varieties identified variation in skin thickness, which could explain differences in grape skin degradation and consequently the extraction of cellular components such as polysaccharides, proteins (Tian, Harrison, Morton, & Jaspers, 2020) and tannins for different grape varieties Ortega-Regules et al., 2006. Similar conclusions were drawn by Ortega-Regules et al. (Ortega-Regules et al., 2008) who also observed differences in skin thickness between different grape varieties. Optical microscopy techniques were used to visualise and confirm differences in skin thickness between Merlot, Syrah, Apolinar-Valiente et al. (Apolinar-Valiente et al., 2013) and Cejudo-Bastante et al. (Cejudo-Bastante, del Barrio-Galán, Heredia, Medel-Marabolí, & Peña-Neira, 2018) performed further studies which examined differences arising from potential locational effects ("*terroir effect*") of cultivar grapes and their influence on the polysaccharide content of the resulting wines. Cejudo-Bastante et al. investigated wines from the Chilean Maule region; a fertile area located between the Andes Mountains of South America and the Pacific Ocean, and discovered that grapes grown closer to the mountain ranges produced wines with greater individual variations within samples, and higher polysaccharide content compared to other regions (Cejudo-Bastante et al., 2018). Apolinar-Valiente et al. confirmed that the RG-II contents present in finished wines are not only influenced by grape variety during must processing, but also by grape origin, suggesting that climate is a potential factor contributing to the differences observed between polysaccharide profiles of grapes and wine.

2.2. Changes in polysaccharide profiles of grape and wine during vinification

Cell wall composition and stability is crucial for winemaking as the final concentration of cell wall proteins and polysaccharides that are extracted during maceration and fermentation are important for the colloidal properties and stability of a wine (Garrido-Bañuelos et al., 2019b). Cell wall polysaccharides have been reported to have an impact on the adsorption of polyphenol to cell walls and thus their extraction from grape tissue during winemaking. Ruiz-Garcia et al. (Ruiz-Garcia, Smith, & Bindon, 2014) identified that the bulk of cell wall-tannins are bound to a relatively minor component of the cell wall. Their model experiments with purified grape skin showed that removal of pectic polysaccharides from the cell wall network significantly lowered the adsorption of tannins. Furthermore, Ruiz-Garcia et al. noted that more than 54% of tannins were localised with pectic polysaccharides, suggesting a strong relationship between pectic cell wall and tannin-cell wall affinity. As mentioned earlier, understanding the degree of pectin modification and factors that can affect this is essential as this can influence the binding affinity between polysaccharides and tannins, influencing extraction efficiency and the skin cell wall porosity (Watrelot, Le Bourvellec, Imberty, & Renard, 2013). Medina-Plaza et al. (Medina-Plaza et al., 2019) identified that alongside cell wall composition and properties, temperature and ethanol content during winemaking are key factors influencing polysaccharide and tannin extraction. Medina-Plaza et al. observed that a higher alcohol content and increased temperatures resulted in better extraction during winemaking. This was exacerbated further in grape cell walls that presented with reduced interwoven macromolecular networks, which decreased stability, and increased porosity.

Garrido-Bañuelos et al. (Garrido-Bañuelos et al., 2019b) found that temperature during berry development can alter the cell wall polysaccharide structure, with higher temperatures shown to influence cell wall polysaccharide composition, through a notable decrease in pectic polysaccharides and an increase in arabinose and galactose content (Lima et al., 2013). Garrido-Bañuelos et al. found that grape of the same variety (but different vintage) grown in warmer, draught-like conditions had less intact berry cell wall structures than those grown in cooler, moist conditions. This suggests a possible relationship between heat stress and pectin depolymerisation, and subsequently a relationship between cell wall integrity and extractability (Garrido-Bañuelos et al, 2019a, 2019b). This finding establishes further questions involving the impact of increasing global temperatures on berry composition, and what influence this could have on vineyards, winemaking, and the final chemical composition and characteristics of a finished wine.

Grape must is the complex mixture obtained during the initial stages of the winemaking process (Jackson, 2008). The grape juice/must matrix contains several chemical families, arguably the most important of these being water, polyphenols, organic acids, aromatics, proteins and polysaccharides (Jackson, 2008; Moreno & Peinado, 2012). Several studies have been performed to examine the polysaccharide profile of grape juice, must and/or wine (Doco et al., 1996; Doco et al., 1999; Doco, Williams, et al., 2003; Gil et al., 2015; Guadalupe & Ayestarán, 2007; Martínez-Lapuente et al., 2018Martínez-Lapuente et al., 2018; Vidal et al., 2001; Vidal, Doco, Moutounet, & Pellerin, 2000).Vidal et al. (Vidal et al., 2000) conducted a study aimed at profiling the polysaccharide content of grape juice immediately after the crushing and pressing of Sauvignon and Ugni blanc grapes. Several types of polysaccharides were found to be solubilised in the juice, primarily arabino-

galactans, arabinans and galacturonans. It was reported that AGPs were the main polysaccharides released from berries after crushing and pressing, and it was concluded that these compounds are soluble in plant tissues, requiring less intensive techniques for extraction (Vidal et al., 2001). Vidal et al. also discovered that RG-II was present in small amounts in the grape juice (30–50 mg L^{-1}) (Vidal et al., 2000, 2001), indicating this compound is also partially soluble during these initial vinification stages as alluded to earlier.

The transformation of grape juice/must to wine imparts many changes on the polysaccharide profile (Guadalupe & Ayestarán, 2007). Vidal et al. suggested that the some of the major factors affecting the polysaccharide content of wines include the type of grape tissue used and the polysaccharides respective solubility and stability towards enzymatic activity and ethanol content (Vidal et al., 2001). However, it is evident that there are many factors contributing to changes in polysaccharide content during the winemaking process (Apolinar-Valiente et al., 2013; Cejudo-Bastante et al., 2018). Common consensus dictates that AGPs and RG-II are the most important grape-derived polysaccharides (Ayestarán et al., 2004; Guadalupe & Ayestarán, 2007; Vidal et al., 2003), with AGPs in high abundance in both grape berry tissue (Saulnier & Thibault, 1987; Vidal et al., 2000, 2001) and in the final wine (> 40%) (Guadalupe & Ayestarán, 2007; Vidal et al., 2003), making it the most abundant grape-derived polysaccharide (Guadalupe & Ayestarán, 2007; Pellerin et al., 1996). This is in stark contrast to RG-II, which accounts for less than 5% of skin and pulp cell wall polysaccharides in grape material, yet is a major component (20%) of red wines (Ayestarán et al., 2004; Vidal et al., 2003) (Vidal et al., 2001). Interestingly, despite a three-fold higher presence in grapes than RG-II, RG-I is only a minor polysaccharide component of wine, (4% (Vidal et al., 2003), < 20 mg L^{-1} (Pellerin & Cabanis, 1998)). This observation can be explained either through incomplete solubilisation of the cell wall, or through weak intrinsic resistance of RG-Is to enzyme activity (Vidal et al., 2001).

During the compositional monitoring of the wine matrix throughout the winemaking process, Guadalupe et al. (Guadalupe & Ayestarán, 2007) discovered changes in the profile of grape derived saccharides. In wines at the beginning of maceration and wines with short macerations times, AGP was the dominant polysaccharide and RG-II was identified in very low quantities. Guadalupe et al. indicated that RG-II is more tightly bound to cell walls than AGPs and therefore needs a longer period of maceration to solubilise (Guadalupe & Ayestarán, 2007), which is in agreement with results from Vidal et al. (Vidal et al., 2000, 2001). Thus an increase in RG-II during maceration can be observed, as this is released from insoluble cell wall material (Doco et al., 1996).

Fermentation has a significant impact on the polysaccharide profile of wines (Guadalupe & Ayestarán, 2007), and the evolution of polysaccharides during alcoholic fermentation can be described as a continuous and progressive release of carbohydrate polymers from grape materials, as well as a liberation of mannoproteins from yeast material (Doco et al., 1996). Changes in the polysaccharide profile during the winemaking process can be visualised in Fig. 7 which has been constructed using the results reported by Guadalupe et al. (Guadalupe & Ayestarán, 2007). The concentration of all the measured saccharides increased during fermentation, by more than two-fold in most cases; however, mannoproteins saw that most dramatic change with Guadalupe et al. reporting a 6-fold increase. This finding was supported by results from Doco et al. who also observed a dramatic increase in mannoprotein concentration from 28 mg L^{-1} to 162 mg L^{-1} from pressing until the end of fermentation (Doco et al., 1996). Gill et al. (Gil et al., 2015) also performed studies which focused on maceration length and the polysaccharide content of final wines, discovering that increased maceration length resulted in increased polysaccharide content across all molecular weights.

One final discovery by Doco et al. and Guadalupe et al. was that there was no additional release of grape derived polysaccharides into the matrix following the completion of alcoholic fermentation, with Guadalupe et al. further concluding that during malolactic fermentation, AGP content decreased while other polysaccharides remained relatively stable. Post-maceration saw an overall decrease of 8% in polysaccharide content, agreeing with findings from Doco et al. (Doco, Vuchot, Cheynier, & Moutounet, 2003) and Martínez-Lapuente et al. (Martínez-Lapuente et al., 2016), whereas in general, post-maceration steps, such as ageing yeast on lees, yielded a significant reduction in PRAG and RG-II concentrations in wines (Martínez-Lapuente et al., 2016).

As alluded to earlier, yeast provides an alternative introductory source of polysaccharides to wine in the form of mannoproteins, which quantitatively are the second most abundant polysaccharide (~35% (Vidal et al., 2003)) (Ayestarán et al., 2004; Marangon et al., 2018; Vidal et al., 2003). These polysaccharides can be introduced into the wine matrix either through direct secretion from yeast cells during fermentation, or indirectly through autolysis while ageing wine on lees (Ayestarán et al., 2004; Dufour & Bayonove, 1999; Escot et al., 2001; Guadalupe & Ayestarán, 2007; Marangon et al., 2018; Unterkofler et al., 2020). These complicated macromolecules are present in yeast cell walls as proteoglycans and contain high levels of mannose, (upwards of 80%) and some glucose (6–11%), and exist as covalent complexes with proteins (10–15%) (Escot et al., 2001; Vidal et al., 2003). It has been reported and corroborated by many authors (Doco, Vuchot, et al., 2003; Guadalupe & Ayestarán, 2007; Martínez-Lapuente et al., 2016; Pati, Liberatore, Lamacchia, & La Notte, 2010) that the process of ageing on lees enriches wine with yeast derived polysaccharides, primarily mannoproteins and mannans. Escot et al. (Escot et al., 2001) suggested the release of mannoproteins into the wine matrix was dependent on the type of yeast strain used and the turbidity of the grape juice/must during fermentation. Corroborating these findings, Rosi et al. (Rosi, Gheri, Domizio, & Fia, 2000, pp. 18–20) showed that the degree of polysaccharide release is also dependent on the metabolic phase of the yeast (growth phase) and the lytic susceptibility of the strain, noting that the greatest release of MP occurred during high yeast mortality. Additionally, Martínez-Lapuente et al. (Martínez-Lapuente et al., 2018) claimed that the winemaking conditions, the initial colloid content of the grape juice/must and the ripeness of the grape at harvest may also influence the release of mannoproteins by yeast. Gil et al. (Gil et al., 2015) reported that yeast mannoproteins were mainly released during the first week of maceration, while alcoholic fermentation is occurring, and as mentioned earlier, mannoproteins are absent in the grape juice/must, but begin to steadily increase in concentration and follow continuous liberation into the medium during fermentation and ageing processes to become one of the most prevalent polysaccharides in wine (Doco et al., 1999; Escot et al., 2001; Guadalupe & Ayestarán, 2007). Guadalupe et al. discovered that during post maceration, MPs are the only reported polysaccharide to increase in concentration; a 20% increase was reported (Guadalupe & Ayestarán, 2007). An investigation by Doco et al. (Doco et al., 1999) following the polysaccharide profile of ageing Carignan noir wines over a 23 year period revealed that mannans were stable in the matrix throughout this time period. Furthermore, mannans and MPs were identified to have concentrations ranging between 120 and 150 mg L^{-1}; however, they exhibited a gradual evolution to lower molecular weight fractions. Doco et al. claimed that the grape derived polysaccharides present in the wines were stable for up to 10 years after their production, but began to slowly decrease in concentration with further ageing (Doco et al., 1999), a finding in alignment with Gil et al. (Gil et al., 2015). This decline was suggested to be attributed to the inevitable hydrolysis of AGPs and RG-II during storage, which may modify the stability and ionic charge balance of older wines (Doco et al., 1999), and hence facilitate further changes in organoleptic properties.

3. Conclusion

Polysaccharides are important macromolecules within the wine matrix and their concentration and composition can vary depending on the wine variety. Tremendous alterations in the polysaccharide profile throughout the journey from grape to wine can be observed, with the most significant changes occurring during alcoholic fermentation. Many analytical techniques and instrumentation have been utilised and adapted to analyse, quantify and characterise these macromolecules, with the most important of these macromolecules being arabinogalactan proteins (AGP), rhamnogalacturonans (RG-I and RG-II) and mannoproteins (MP). AGPs are the most abundant grape derived polysaccharides and are present in high quantities in both the grape must and in the resulting wine. RG-II is present in low amounts in grape must, with maceration and fermentation increasing its availability and thus concentration. MPs are the most prevalent yeast derived polysaccharides and are introduced into the matrix during fermentation and the ageing process. Many factors can impart changes on the polysaccharide profile of the grape berry, with grape maturity, grape variety, vintage and environmental impacts (such as weather, climate and soil) being key examples. The transformation of grape to wine elicits several major changes in the polysaccharide composition and content, with steps such as maceration, fermentation and ageing highlighting how different processing techniques can create further variations in the presence of polysaccharides of wine. These differences can allow for variations in stylistic design, characteristics and organoleptic properties of the final wine. An understanding of the polysaccharide profile at different stages of vinification is crucial for oenologists as it allows for a fundamental understanding of the wine matrix and how the addition of various components may alter the chemical composition, properties and thus quality of their wines. Such an understanding can assist in tailoring their beverages and improving quality to meet the consumer desires.

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