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Review

Recent advances in the knowledge of wine oligosaccharides

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ABSTRACT

Oligosaccharides are carbohydrates with a low polymerization degree containing between three and fifteen monosaccharide residues covalently linked through glycosidic bonds. Oligosaccharides are related to plant defense responses and possess beneficial attributes for human health. Research has focused in wine oligosaccharides only in the last decade. In this paper, a summary of these works is provided. They include: (i) wine oligosaccharides origins, (ii) techniques for isolating oligosaccharide fraction and determining their content, composition and structure, (iii) their dependence on the grape origin and cultivar and winemaking process, and (iv) the connection between oligosaccharides and wine sensorial attributes. Further research is required regarding the impact of agricultural aspects and winemaking techniques on wine oligosaccharides. The knowledge concerning their influence on sensorial and physicochemical properties of wines and on human health should also be improved. The implementation of laboratory methods will provide better understanding of these compounds and their performance within wine's matrix.

1. Introduction

Wine is a very complex matrix containing a wide range of components capable of influencing wine chemical properties and of inducing sensory/organoleptic perceptions. According to Cabanis, Cabanis, Cheynier and Teissedre (1998), wine is composed mainly of water (between 750 and 900 $g{\cdot}L^{-1}$), alcohols (69–121 $g{\cdot}L^{-1}$), polyols (5–20 $g{\cdot}L^{-1}$), organic acids (3–20 $g{\cdot}L^{-1}$), nitrogenous compounds (3–6 $g{\cdot}L^{-1}$) and polyphenolic compounds (2–6 $g{\cdot}L^{-1}$). In addition, there are also complex carbohydrate molecules, including polysaccharides and oligosaccharides coming from grapes, yeasts and bacteria during winemaking (Ballou, 1982; Ducasse, Williams, Meudec, Cheynier, & Doco, 2010; Apolinar-Valiente et al., 2013; Dols-Lafargue, 2018).

Oligosaccharides (from Greek ὀλίγοι, *olígoi* = few, little and σάκχαρον, *sákkharon* = sugar) are carbohydrates with low degree of polymerization which contain monosaccharide residues covalently linked through glycosidic bonds. Oligosaccharides present great biochemical diversity because the different anomeric configuration and glycosidic linkages they can perform. Although a strict definition of an oligosaccharide is yet to be agreed upon, it is generally accepted that an oligosaccharide is a carbohydrate consisting of three to fifteen monosaccharide residues with a defined structure. BeMiller (2019) also included disaccharides within the definition of oligosaccharide, and placed the demarcation between oligosaccharides and polysaccharides as 20 glycosyl units.

The relation between plant oligosaccharides and activation or inhibition of plant growth and development has been widely documented for a long time (Albersheim et al., 1992; Kollárova, Kamenická, Vatehová, & Liškova, 2018). Oligosaccharides are strongly related to plant protection against abiotic stress (ElSayed, Rafudeen, & Golldack, 2014). It is moreover recognized that these molecules act as elicitors of secondary metabolites involved in plant defense mechanisms against pathogens (Morkunas & Ratajczak, 2014). Recently, Zheng, Chen, Zhang, Zhou, Lu and Tian (2020) reviewed the mechanisms of carbohydrate elicitor perception and signaling in plants, including oligosaccharides. These authors summarized and discussed about the structure and activity of main oligosaccharides in order to control the plant diseases.

From a nutrition and health perspective, numerous applications have been associated with oligosaccharides (Mano, Neri-Numa, Bueno da Silva, Paulino, Pessoa, & Pastore, 2017), presenting significant physicochemical properties beneficial to consumers' health. According to Codex Alimentarius (2009), dietary fiber corresponds to carbohydrate polymers which are not hydrolyzed by the endogenous enzymes in the small intestine of humans, leaving to national authorities the

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decision to include short chain carbohydrates (from 3 to 9 degrees of polymerization) within this definition. Institutions from several countries such as Australia, Canada, China, the European Union and New Zealand have hence included oligosaccharides in their dietary fiber definitions (de Menezes, Giuntini, Dan, Sardá, & Lajolo, 2013; Westenbrink, Brunt, & van der Kamp, 2013). Positive relationships between dietary fiber and human health such as the prevention of diabetes, cardiovascular diseases and cancer of the colon have been stablished (Mudgil & Barak, 2013). Linked to dietary fiber, prebiotics are defined as "*non-digestible compounds that, through their metabolism by microorganisms in the gut, modulate the composition and/or activity of the gut microbiota, thus conferring a beneficial physiological effect on the host*" (Bindels, Delzenne, Cani, & Walter, 2015). Prebiotics compounds include a large number of oligosaccharides (namely arabinoxylan-, fructo-, *gluco*-, galacto-, isomalto-, mannan-, xylo-, soyo-oligosaccharides and others) (Mano et al., 2017; Mohanty, Misra, Mohapatra, & Sahu, 2018; Colantonio, Werner, & Brown, 2019). In this connection, some oligosaccharides are fermented selectively and stimulate the intestinal microbiota, which can result in beneficial impacts on the human health (Payling, Fraser, Loveday, Sims, Roy, & McNabb, 2020). Potential anticancer actions (Kapoor & Dharmesh, 2017) or antioxidant effects (Coelho, Rocha, Saraiva, & Coimbra, 2014; Kang, Ghani, Hassan, Rahmati, & Ramli, 2014) have been suggested in pectin-derived acidic oligosaccharides and arabinoxylooligosaccharides, which occur in fruits and vegetables. Numerous other prebiotic impacts of pectin oligosaccharides on human health have been largely reviewed by Gullón, Gómez, Martínez-Sabajanes, Yáñez, Parajó and Alonso (2013).

It has been demonstrated that the physiological properties of oligosaccharides change with their monosaccharide composition, molecular weight and glycosidic linkages (de Moura, Macagnan, & da Silva, 2015; Payling et al., 2020; Zheng et al., 2020). These parameters are directly related to their origin and the extraction process applied (Nabarlatz, Ebringerova, & Montane, 2007; Kang et al., 2014). Oligosaccharides are obtained by extraction from natural sources by chemical, enzymatic or biotechnological techniques (Nobre, Teixeira, & Rodrigues, 2015; Cho, Trinh, Song, Lee, & Bae, 2020). A recent and promising method to obtain oligosaccharides from natural products is subcritical water extraction (SWE), which moreover acts in an environmental friendly way (Zhang, Wen, Zhang, Duan, & Ma, 2020). The use of ultrasound-microwave-assisted extraction technology appears as a potential tool to improve the extraction of oligosaccharides under specific conditions (Guo, Zhao, Li, Miao, & Zheng, 2019).

Unlike wine polysaccharides, which have been the subject of many studies, information on wine oligosaccharide composition is still limited. This is due to the difficulty in separating and characterizing them, although their presence in wine has long been known. Sucrose and various disaccharides have been identified in wines (Pellerin & Cabanis, 1998), and a global fraction of oligomers of homo- and rhamnogalacturonan was described and shown to decrease during wine ageing (Doco, Quellec, Moutounet, & Pellerin, 1999). The structure and amount of oligosaccharides released into wine also depend on the grape variety and origin, as well as the winemaking process. The present review summarizes the origin of wine oligosaccharides, their main types, their structures, their analysis, their physicochemical and technological properties, and their potential wine applications. We would specify that, although wine oligosaccharide fraction is the particular focus of this review, we are often forced to incorporate detailed information regarding the polysaccharide fraction in wines. From our perspective, this appears inevitable as well as coherent: merely by looking closely at the origin and composition of each of both fractions, we can identify the intimate relationships which link them.

2. Oligosaccharides and grape berries

Oligosaccharides have been misidentified for a long time as sucrose and various disaccharides (Doco, Williams, Vidal, & Pellerin, 1997; Pellerin & Cabanis, 1998), although short chains of galacturonic acid (2–6 DP) have likewise been found. In grape, six oligosaccharides -two neutral and four acidic oligosaccharides- were evidenced after acid hydrolysis (Asensio, 1987) of a berry skin polysaccharide (Igartuburu, Pando, Rodríguez, & Gil-Serrano, 1997). Concerning the neutral oligosaccharides, methylation analysis and spectroscopic data showed them to be (β1 → 4) linked xylobiose and xylotriose. Besides, one of the acidic oligosaccharides corresponded to 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylopyranose (α-D-Glc*p*A(1 → 2)-D-Xyl*p*), an aldobiouronic acid (Igartuburu et al., 1997).

The majority of wine oligosaccharides come from grape polysaccharides, but only after cell wall degradation during (i) the grape ripening due to the action of endogenous (present in grapes) enzymatic activities, and (ii) the different winemaking steps.

The skin cell wall is a complex and heterogeneous structure. It consists of a network of polysaccharides, including cellulose, hemicelluloses and pectin (Carpita & Gibeaut, 1993), with phenolic compounds and structural proteins. The hydrolysis of cell wall polysaccharides from grape skin, specifically from pectin and hemicellulose (mainly xyloglucans, although this generic term also includes xylans and mannans, among others) (Pellerin & Cabanis, 1998; Nunan, Sims, Bacic, Robinson, & Fincher, 1997), causes the natural release of oligosaccharides to wine. Recently, Chong et al. (2019) exposed that the soluble cell wall carbohydrates (SCWCs) in Cabernet Sauvignon red wine were mainly formed by low molar weight oligosaccharides coming from the degradation of yeast and grape cell wall polysaccharides, including OligoGlucans, OligoMannans, OligoRhamnogalaturonans, OligoArabinogalactans, OligoArabinans and OligoXyloglucans. They analyzed the SCWCs by high-performance size-exclusion chromatography (HPSEC) and a DRI detector, estimating a DP about 5 from their molecular size.

Cell walls polysaccharides are strongly disassembled during fruit ripening by the action of different endogenous enzymatic activities. Pectins are hydrolysed by the enzyme group called pectinases, including polygalacturonase (PG) pectin methylesterase (PME) and β-galactosidase. PG activity catalyzes the degradation of polygalacturonic acid. This activity has been proposed to be interconnected with PME activity because a decrease in pectin methyl-esterification generates accessible hydrolysis sites for PG activity (Van Dyk & Pletschke, 2012). Likewise, β-galactosidase activity removes non-reducing terminal galactosyl residues from side chains of pectic polysaccharides. On the other hand, a large number of enzymatic activities is necessary to hydrolyse hemicellulose (Van Dyk & Pletschke, 2012). Hemicellulose removal facilitates hydrolysis of the cellulose, improving cellulase accessibility. Regarding the presence of endogenous enzymatic activities in grapes, several works present opposite results. James, Dixon and Lamikanra (1999) reported low levels of cellulase activity in muscadine grapes. During grape ripeness, Nunan, Davies, Robinson and Fincher (2001) detected α-galactosidase, β-galactosidase and pectin methylesterase activities, but no polygalacturonase or activities. Ortega-Regules, Ros-García, Bautista-Ortín, López-Roca and Gómez-Plaza (2008) observed that endogenous enzymatic activities were influenced by the cultivar. These authors found no polygalacturonase or cellulase activity in Cabernet Sauvignon, Merlot, Monastrell and Syrah grapes. However, they observed that α- and β-galactosidases presented higher activity than pectinmethylesterase, especially in Cabernet Sauvignon grapes, whereas these two galactosidase activities were low in Monastrell grapes. Linked to this, Zietsman, Moore, Fangel, Willats, Trygg and Vivier (2015) observed that the ripeness of Pinotage berries showed a significant influence on the grape cell walls and hence in the action of the endogenous and exogenous enzymatic activities. Likewise, Gao, Fangel, Willats, Vivier and Moore (2016) reported that more ripe Cabernet Sauvignon berries with higher cell wall degradation presented obvious evidence of de-pectination from the fermentation itself. Noting the natural ripening process, it seems logical to deduce that commercial enzyme treatments based on the endogenous enzymatic activities

promote the cell wall polysaccharides degradation during winemaking and, hence, the oligosaccharide release.

Certain vineyard treatments, such as the direct application of elicitors and/or oligosaccharides to berries, induce a reinforcement of cell walls from grape skin (Apolinar-Valiente, Ruiz-García, Williams, Gil-Muñoz, Gómez-Plaza, & Doco, 2018). This would hinder their degradation, stunting hence the oligosaccharides release from berry and affecting the characteristics of the corresponding elaborated wine. However, the release of cell wall components from berry to wine can be increased by the addition of commercial enzymes to grapes at the beginning of wine elaboration. This treatment will favour a progressive cell wall disassembly during winemaking, improving the release of berry skin compounds. In this sense, Apolinar-Valiente, Romero-Cascales, Gómez-Plaza and Ros-García (2016) and Apolinar-Valiente et al. (2017) reported that separate addition of polygalacturonase and cellulase activities degraded cell wall materials from Cabernet Sauvignon, Syrah and Monastrell berry skins. By contrast, the addition of pectin methylesterase did not present any impact on Monastrell grape skins. Besides, these authors deduced an interesting synergy between polygalacturonase and cellulase activities which caused a higher degradation of Monastrell grape skins (Apolinar-Valiente et al., 2017). Similarly, the combined addition of polygalacturonase and pectin methylesterase caused a synergistic effect on Monastrell grape skins, although much lesser. Moreover, enzymatic treatments have been identified as a factor decreasing total sugars content in cell walls from grape marc skins compared to those from non-treated elaborations (Apolinar-Valiente, Romero-Cascales, Gómez-Plaza, López-Roca, & Ros-García, 2015). The enzymatic treatments can therefore improve oligosaccharide release, thus enhancing their final amount in wine (Ducasse, Williams, Canal-Llauberes, Mazerolles, Cheynier, & Doco, 2011; Apolinar-Valiente et al., 2014). Other oenological treatments and procedures could also influence on the degradation of grape skin and, therefore, on the oligosaccharides release. For example, significant changes in oligosaccharides concentration and composition of base wines during the pressing cycle have been observed (Jégou et al., 2017).

3. Analysis of oligosaccharides in wines

3.1. Isolation methods of oligosaccharide fractions from wines

Information about composition and structure of wine oligosaccharides is still limited, and has been the subject of research only recently. A total oligosaccharide fraction in wines was isolated for the first time by Ducasse et al. (2010) using high resolution size-exclusion chromatography (HR-SEC). More recently, neutral oligosaccharide fractions from Carignan wine were characterized (Doco, Williams, Meudec, Cheynier, & Sommerer, 2015). Wine was partially depigmented through discoloration using a MN Polyamide SC6 column. Wine oligosaccharides, as well as polysaccharides, were not retained by the polyamide column, being then eluted with 1 M NaCl. To separate oligosaccharides from polysaccharides, HR-SEC was performed on a Superdex 30-HR column with a pre-column. Furthermore, Bordiga et al. (2012) isolated complex free oligosaccharides in Grignolino and Chardonnay wines (red and white respectively) using different methodology. They characterized them by gas chromatography (GC) and high resolution and high mass accuracy matrix-assisted laser desorption ionization (MALDI)–Fourier transform ion cyclotron resonance (FTICR)–mass spectrometry (MS) analysis. The concentrated wine samples were purified through a SPE C-18 cartridge to eliminate possible interfering compounds, such as proanthocyanidins and anthocyanins, and consequently a SPE carbograph was applied to remove residual salts and also monosaccharides which could alter MS detection. Doco et al. (2015) prepared oligosaccharide fractions after removal of phenolic compounds and polysaccharides by polyamide chromatography and alcohol precipitation, respectively. Oligosaccharides were then fractionated by anion exchange and size-exclusion chromatography to separate neutral and acidic oligosaccharides. The methodology described above constitutes a simple and rapid procedure to obtain wine oligosaccharides and has shown very good reproducibility in wine samples.

3.2. Methods to determinate the composition and structure of wine oligosaccharides

Analyses of monosaccharides/oligosaccharides have been made by high-performance anion exchange chromatography (HPAEC) coupled with reflective index (RI) detection (Chávez-Servín, Castellote, & López-Sabater, 2004; Giannoccaro, Wang, & Chen, 2008). However, this detector is not compatible with gradient elution. High-performance liquid chromatography (HPLC) with gradient elution is advisable for fine analysis of the complex carbohydrates from fermented products, such as beer or wine. In beer, Nogueira, Silva, Ferreira and Trugo (2005) detected carbohydrates with gradient elution by HPLC coupled to an evaporative light scattering detection (ELSD), whereas Arfelli and Sartini (2014) used pulsed amperometric detection (PAD) to detect beer oligosaccharides. Similarly, Hayakawa et al. (2000) analyzed oligosaccharides from sake using HPLC coupled with a polarized photometric detector (PPD).

Nakanishi and Yokotsuka (1989) examined the composition of oligosaccharides in four varieties of Japanese white wines by two separation methods: charcoal column chromatography and paper chromatography. They isolated laminaribiose and gentiobiose as the principal constituents of the wine oligosaccharide fraction, the content of either sugar ranging from 15 to 25 $mg{\cdot}L^{-1}$. These authors suggested that both sugars were released from yeast cell walls into wine during fermentation, being the amounts of released sugars independent of the yeast strain. According to these same authors, different kinds of β-glucanase action on the β(1–3)- and β(1–6)-linked glucan from the yeast cell wall could be strongly associated with release of laminaribiose and gentiobiose. Similarly, Ruiz-Matute, Sanz, Moreno-Arribas and Martínez-Castro (2009) also found laminaribiose, as well as cellobiose and sophorose, using trimethylsilyl ethers (TMS) (Bertrand, Dubernet, & Ribéreau-Gayon, 1975; De Smedt, Liddle, Cresto, & Bossard, 1979) and TMS oximes (TMSO) (Liu & Davis, 1994) as derivatives for GC analysis. These three β-linked disaccharides were formed by transglycosidation action of a β-glucosidase from glucose (Ruiz-Matute et al., 2009). In this regard, it should be added that yeast extracellular glycolipids contains sophorolipids which comprise a residue of sophorose, as well as cellobiose could be formed from cellulase activity on cellulose. In Carignan and Merlot wines, Ducasse et al. (2010) and Doco et al. (2015) determined the neutral and acidic sugar composition of oligosaccharide fractions after solvolysis with MeOH/HCl of their per-*O*-trimethylsilylated methyl glycoside derivatives by GC (Doco, O'Neill, & Pellerin, 2001). The glycosyl residue analysis of wine oligosaccharide composition (Ducasse et al., 2010, 2011; Bordiga et al., 2012; Apolinar-Valiente et al., 2014, 2018; Apolinar-Valiente, Romero-Cascales et al., 2015; Quijada-Morín, Williams, Rivas-Gonzalo, Doco, & Escribano-Bailón, 2014; Doco et al., 2015; Martínez-Lapuente et al., 2016, 2018; Jégou et al., 2017) shows that they present most of the sugars known to be part of wine carbohydrates (Vidal et al., 2003; Aguirre, Isaacs, Matsuhiro, Mendoza, & Zúñiga, 2009; Guadalupe, Martínez-Pinilla, Garrido, Carrillo, & Ayestarán, 2012; Gao et al., 2016; Kassara, Li, Smith, Blando, & Bindon, 2019). They include sugars that arise from the pectic polysaccharides from cell walls of grape berries, such as rhamnose, arabinose, galactose, xylose and galacturonic and glucuronic acids, but also mannose and glucose released from yeast and/or bacteria polysaccharides (Ballou, 1982; Dols-Lafargue, 2018). Moreover, identification of xylose, glucuronic and 4-*O*-Me glucuronic acid residues indicates that traces of hemicelluloses might be solubilized from grape cell walls (Carpita & Gibeaut, 1993; Doco, Williams, Pauly, O'Neill, & Pellerin, 2003) and recovered as oligosaccharide

Table 1
Glycosyl composition (mg·L^{-1}) of oligosaccharides isolated from wine.

Cultivar	Rha [h]	Fuc	Ara	Xyl	Man	Gal	Glc	Gal A	Glc A	Xylitol	4-OMeGlc A	Total
Cabernet Sauvignon [a]	9.9	2.0	24.9	13.3	34.4	21.2	34.0	21.6	5.6	1.6	5.9	174
Syrah [a]	58.0	6.6	109.9	18.1	55.9	56.7	72.4	79.9	11.1	3.5	7.5	479
Monastrell [a]	16.4	2.5	50.8	9.6	39.7	32.8	58.5	24.7	4.4	0.8	3.7	244
Carignan 2004[b]	44.9	1.6	88.1	40.5	45.2	33.6	20.2	46.2	4.9	4.9	2.3	332
Merlot 2004[b]	23.6	1.2	54.4	19.1	33.0	23.6	24.6	57.9	3.7	7.3	3.0	251
Monastrell *Cañada Judío* [c]	11.8	2.6	21.7	14.7	37.0	27.6	28.0	89.7	7.5	1.7	8.8	251
Monastrell *Albatana* [c]	11.7	2.4	19.1	15.5	31.2	22.4	37.5	42.0	4.0	2.0	6.8	194
Monastrell *Bullas* [c]	5.6	2.5	22.9	14.5	33.3	19.1	33.3	56.7	7.1	1.3	6.9	203
Monastrell *Montealegre* [c]	34.0	3.9	73.6	18.4	32.5	40.7	37.1	31.3	7.5	1.1	7.7	288
Merlot 2006 [d]	21.8	1.1	46.6	20.7	24.0	19.3	33.1	62.2	4.1	2.6	8.6	244
Chardonnay (*fraction 20% Acetonitrile*) [e]	1.1	0.6	4.8	7.8	3.1	3.7	25.1	3.4	0.8	–	–	50
Tempranillo (*from under ripe grape*) [f]	4.3	3.3	11.6	17.9	26.0	7.5	41.1	176.8	3.1	1.8	5.6	299
Tempranillo (*from fully ripe grape*) [f]	3.2	2.7	18.0	20.9	24.2	11.0	42.2	174.2	3.9	3.3	7.6	311
Verdejo (*white base wine*) [g]	2.0	0.7	4.2	11.4	9.5	7.1	32.7	6.6	2.4	1.8	4.9	88
Tempranillo (*rosé base wine*) [g]	6.5	1.8	4.9	11.1	17.1	14.7	38.1	9.3	2.1	1.5	3.9	112

[a] Apolinar-Valiente, Romero-Cascales et al., 2015. [b]Ducasse et al., 2010. [c]Apolinar-Valiente et al., 2014. [d]Ducasse et al., 2011. [e]Bordiga et al., 2012. [f]Martínez-Lapuente et al., 2016. [g]Martínez-Lapuente et al., 2018. [h]Rha, Rhamnose; Fuc, Fucose; Ara, Arabinose; Gal, Galactose; Glc, Glucose; Man, Mannose; Xyl, Xylose; Gal A, Galacturonic acid; Glc A, Glucuronic acid; 4-OMeGlc A, 4-*O*-methyl Glucuronic acid.

structures in wines (Ducasse et al., 2010; Doco et al., 2015). Table 1 gives the glycosyl composition (mg·L^{-1}) of wine oligosaccharides from results obtained by several authors. As previously mentioned, the sum of the individual monosaccharide contents enables to calculate the amount of total oligosaccharides. The literature indicates that this value varies greatly and can range from 50 (Bordiga et al., 2012) to 550 mg·L^{-1} (Boulet et al., 2016) depending on several factors.

To elucidate the structural characteristics of oligosaccharides, they had been analyzed by several techniques, such as glycosyl and linkage analysis, nuclear magnetic resonance (NMR) (Abe et al., 2016) or infrared spectroscopic techniques (Romano, Santos, Mobili, Vega, & Gómez-Zavaglia, 2016). Ducasse et al. (2010) and Doco et al. (2015) determined the glycosyl linkage composition in Carignan and Merlot wines by GC–MS of the partially methylated alditol acetates, in an attempt to determine the structure of oligosaccharides released. Thanks to the identification of the corresponding glycosidic linkages, the presence of mannan-, arabinan-, arabinogalactan-, xylan-, glucuronoxylan-, homogalacturonan- and rhamnogalacturonan-like structures in red wine oligosaccharides could be confirmed (Ducasse et al., 2010, 2011; Apolinar-Valiente, Romero-Cascales et al., 2015; Doco et al., 2015). Great differences have been found in the glycosidic linkage composition of wine oligosaccharides from different oligosaccharide fractions (Doco et al., 2015) and from different cultivars (Ducasse et al., 2010; Apolinar-Valiente, Romero-Cascales et al., 2015). Fig. 1 shows the variations in major oligosaccharide families from Cabernet Sauvignon, Syrah and Monastrell wines, which result from their different glycosyl linkage composition (adapted from Apolinar-Valiente, Romero-Cascales et al., 2015). The oligosaccharide families from yeasts (mannans and glucans) and grapes (xylans, rhamnogalacturonans, arabinans and arabinogalactans) can be calculated from the glycosyl linkage composition. The sum of mannose linked in → 2,6 and terminal mannose is attributed to OligoMannans (Ducasse et al., 2011), whereas OligoGlucans were calculated as the sum of glucose linked in → 6 and terminal glucose (Ballou, 1982). The sum of rhamnose linked in → 2 and linked in → 2,4 corresponded to OligoRhamnogalacturonans (Ducasse et al., 2011). OligoArabinogalactans type I were estimated as the sum of galactose linked in → 4 and linked in → 3,4 Gal plus terminal galactose whereas OligoArabinogalactan type II as the sum of galactose linked in → 3 and galactose linked in → 3,6 and equivalent in terminal arabinose to the value for galactose linked in → 3,6 (Ducasse et al., 2011). The sum of arabinose linked in → 5 and linked in → 3,5 corresponded to OligoArabinans (Ducasse et al., 2011). OligoXyloglucans were calculated as the sum of terminal xylose, terminal fucose, and glucose linked in → 4,6 and of one third of its proportion in glucose linked in → 4 (Fry et al., 1993).

Another method to determine the oligosaccharide structure is mass spectrometry (MS), due to its potential in elucidating molecular species based on the *m/z* value of the detected ion. The development of soft ionization techniques such as electrospray ionization (ESI) and MALDI has enabled MS analysis of oligosaccharides. ESI is normally preferred

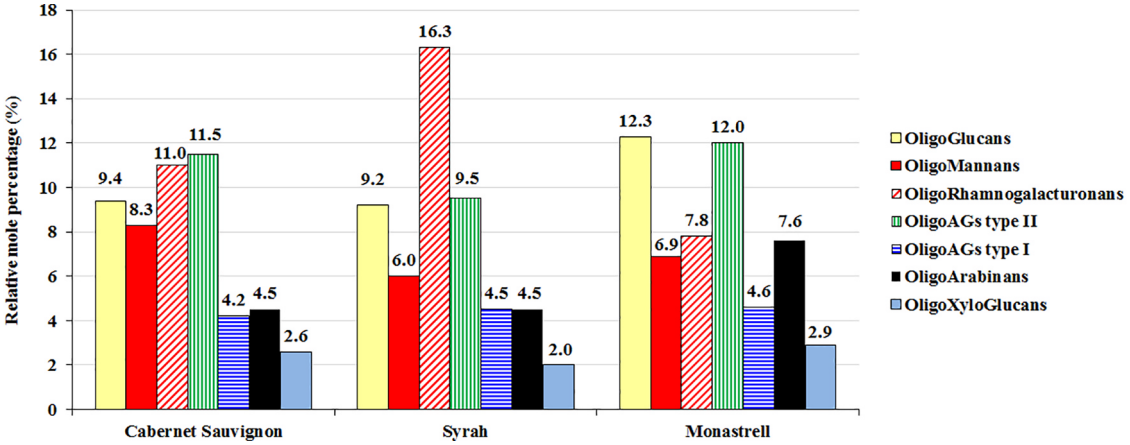

Fig. 1. Major families (relative mole percentage) of released oligosaccharides isolated from Cabernet Sauvignon, Syrah and Monastrell wines. Adapted from Apolinar-Valiente, Romero-Cascales et al. (2015).

over atmospheric pressure chemical ionization (APCI) because of the high polarity and low volatility of carbohydrates. By contrast, these molecules usually present low sensitivity in ESI, but this can be improved by cationization. Then, the addition of a low concentration of lithium salts (for example) to the eluent further increases sensitivity (Di Stefano et al., 2012). Several authors (Ducasse et al., 2010; Bordiga et al., 2012; Doco et al., 2015) used this technique to characterize wine oligosaccharide fractions. Ducasse et al. (2010) reported for the first time high resolution MS spectra of wine oligosaccharides. For this purpose, they used an AccuTOF mass spectrometer equipped with an ESI source and a time-of-flight (TOF) mass analyzer in negative ion modes. The MS spectra in negative mode showed all the oligosaccharide molecules to be deprotonated $[M-H]^-$ ions. The profiles obtained were highly reproducible and showed important differences between samples, which allowed their meaningful comparison.

In any case, it is appropriate to note that MS cannot be considered a suitable method for oligosaccharide species quantification due to the fact that these species may exhibit different desorption capacities depending on their structure. Ducasse et al. (2010) performed further MS experiments in the positive/negative ion mode and MS^n fragmentation analysis on a mass spectrometer equipped with an ESI source and an ion trap mass analyzer. MS is a powerful technique to identify and determine the structure of wine oligosaccharides, but glycosyl composition and glycosidic linkage analyses are necessary complementary methods to quantify and validate the results.

Bordiga et al. (2012) successfully characterized oligosaccharides from red and white wines by MALDI-FTICR-MS analysis, following the instrumental conditions for oligosaccharide analysis previously described by Penn, Cancilla, Green and Lebrilla (1997).

The neutral oligosaccharides of Carignan red wines have been characterized by high resolution MS spectra after separation by Hydrophilic Interaction liquid Chromatography on a Nucleodur HILIC column (zwitterionic sulfoalkyl betaine stationary phase) coupled to a mass spectrometer equipped with an ESI source and an ion trap mass analyzer (Doco et al., 2015). Oligosaccharides display an extreme diversity, as evidenced by the fact that approximately 100 peaks in HPLC-ESI-TOF spectra have been identified, corresponding each of them to at least one oligosaccharidic structure (Doco et al., 2015). The MS spectra of the neutral oligosaccharide fractions showed a high variety of oligosaccharides (detected as $[M-H]^-$, $[M-2H]^{2-}$, and $[M-3H]^{3-}$ ions). They corresponded to (i) *arabino*-oligosaccharides, (ii) rhamnose substituted with *arabino*-oligosaccharides, and (iii) different rhamnogalacturonan *arabino*-oligosaccharides composed of one or two rhamnose residues, one galacturonic acid residue and lateral side chains of arabinose residues.

3.3. Determination of the degree of polymerization

The degree of polymerization (DP) of hexose (glucose-galactose) and other free oligosaccharides from red and white wines was determined by tandem MS by Bordiga et al. (2012). These authors used the exact molecular mass measurement, and assigned the quasi-molecular ions with < 5 ppm difference between the theoretical and the calculated molecular masses. In order to detect oligosaccharides with higher masses, the ion guide of the MALDI-FTICR was increased. The collision induced dissociation (CID) method was employed to carry out the analysis of selected oligosaccharide peaks by Tandem MS analysis.

The oligosaccharides identified by MS spectra after separation on a Nucleodur HILIC column showed a wide variety of oligosaccharides. They corresponded to (i) *arabino*-oligosaccharides with DP ranging from 8 to 49 arabinose residues (Fig. 2, adapted from Doco et al., 2015), (ii) rhamnose substituted with *arabino*-oligosaccharides with a DP between 5 and 21, and (iii) different rhamnogalacturonan *arabino*-oligosaccharides composed of one or two rhamnose residues, one galacturonic acid residue and side chains of 13 to 30 arabinose residues (adapted from Table 3 in Doco et al., 2015). In short, MS analysis appears as an ideal tool to obtain wine oligosaccharides spectra, which allows comparing their widely varied structures. Therefore, further studies to explore the potential impact of many factors on these molecules must inevitably consider this powerful and highly reproducible method.

3.4. Molar mass and distribution analysis methods

Apolinar-Valiente, Romero-Cascales et al. (2015) determined the molar mass distributions of oligosaccharides by coupling size exclusion chromatography with a multi-angle light scattering device (SEC-MALLS) and a differential refractive index (DRI) detector. SEC-MALLS is a powerful technique that enables determining accurately the absolute molar weight while covering a wide range of molecular weights (Xie, Penelle, & Verraver, 2002). SEC elution was performed on OHPAK guard column followed by four serial Shodex Ohpak KB-803, KB-804, KB-805 and KB-806 columns (0.8 × 30 cm; Shodex Showa Denko, Japan) at 1 $mL{\cdot}min^{-1}$ flow rate in 0.1 M $LiNO_3$ filtrated through 0.1 μm filter unit. Oligosaccharide concentration was established using a DRI detector (Apolinar-Valiente, Romero-Cascales et al., 2015).

4. Wine oligosaccharides

Wine appear as a complex mixture of hundreds of molecules that present valuable biological and/or organoleptic properties (Davies et al., 2004; Quijada-Morín et al., 2014; Boulet et al., 2016; De Santis, Frangipane, Brunori, Cirigliano, & Biasi, 2017; Ployon et al., 2018). Numerous different factors (e.g. viticultural, genetic –cultivar and/or yeast strain–, technological, storage conditions, etc.) related by multifactorial aspects, affect both the content and profiles of such compounds, either in grape or in wine. Several wine molecules, such as polyphenols, aroma compounds, polysaccharides or biogenic amines, and their link with the aforementioned factors have been deeply investigated. However, information about the effect of terroir, grape cultivar or winemaking conditions on the amount, composition and performance of oligosaccharides in wine is rather scarce. While an increasing number of works show the importance of oligosaccharides in wine, an in-depth knowledge of these molecules is clearly yet to be achieved. We will present in this section the most relevant studies connecting oligosaccharides with viticultural (terroir and cultivar) and technological (winemaking procedures) factors.

4.1. Viticultural factors affecting wine oligosaccharide fraction: Terroir and grape cultivar

4.1.1. Terroir

The French term “terroir” denotes a usually rather small area whose soil and microclimate impart distinctive quality characteristics to food products. This concept is particularly associated with the production of wine in a specific area (Barham, 2003), which builds an intimate link between the wine and its particular production zone. According to the definition of the International Organization of Vine and Wine (OIV), “*Vitivinicultural ‘terroir’ is a concept that refers to an area in which collective knowledge of the interactions between the identifiable physical and biological environment and applied vitivinicultural practices develops, providing distinctive characteristics to the products originating from this area*” (OIV, 2010). The vineyard and, consequently, the quality of berries and wines are influenced, among other factors, by the climate (Bonada, Jeffery, Petrie, Moran, & Sadras, 2015; Jones, 2018) as well as by the soil characteristics and topography (van Leeuwen, Roby, & de Rességuier, 2018; Ferretti, 2020). These parameters are therefore key elements of the “terroir” impact (Roullier-Gall, Lucio, Noret, Schmitt-Kopplin, & Gougeon, 2014; Blotevogel et al., 2019). If we focus on the strictest definition of terroir, grapes of the same cultivar but from different terroirs would express significantly different characteristics (Frost, Quiñones, Veldhuizen, Alava, Small, & Carreiras, 2015). It is

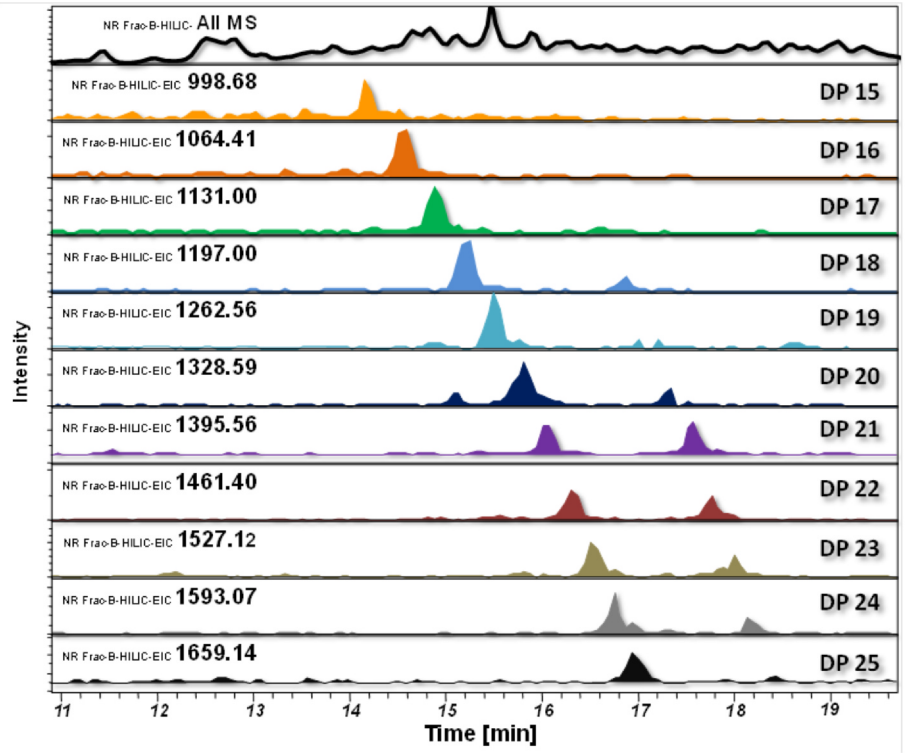

Fig. 2. Ions Spectra and degrees of polymerization (DP; at right) of oligo-arabinans, one oligosaccharide sequence from Non-retained Fraction C (adapted from Table 3 given by Doco et al. 2015).

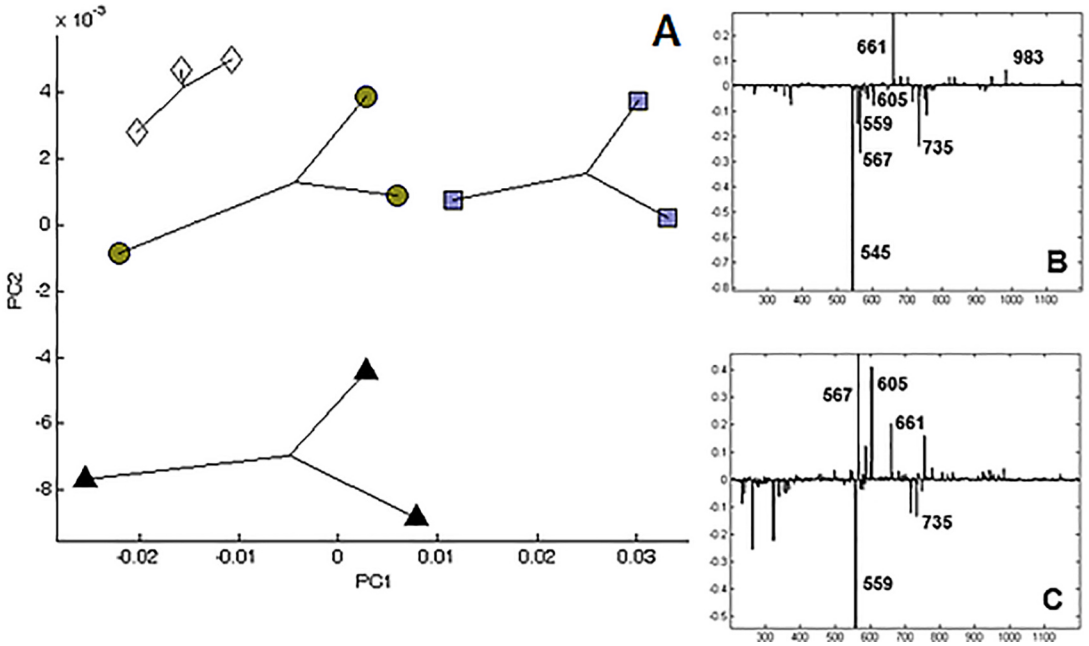

Fig. 3. Principal Components Analysis (PCA) of negative $[M-H]^-$ oligosaccharide ions mass spectra of Monastrell red wines originating from four different terroirs: Cañada Judío (◊), Albatana (▲), Chaparral-Bullas (●) and Montealegre wines (■). **A**: The wine projections on the first axis (PC1) show clear separation of Montealegre wines with regards to the other three wines. The wine projections on the second axis (PC2) show clear separation of Albatana wines from the other three wines (from Apolinar-Valiente et al., 2014). The contributions of the variable to principal component are shown in Fig. 3B (PC1) and **3C** (PC2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

well known that terroir seriously affects wine metabolites (Roullier-Gall et al., 2014), such as phenolics (Belmiro, Pereira, & Paim, 2017), volatile compounds (De Santis et al., 2017) or polysaccharides (Apolinar-Valiente et al., 2013). With the objective of studying a possible "terroir" effect on oligosaccharides in red wines, Apolinar-Valiente et al. (2014) compared the amount of oligosaccharides in isolated fractions of wines elaborated with the same grape cultivar (Monastrell) originating from four plots clearly differentiable from a "terroir" point of view. However, these authors observed that total oligosaccharide concentrations were not significantly different between the four terroir studied, presenting values ranging between 195 and 288 $mg{\cdot}L^{-1}$. By contrast, they detected that one of the specific terroirs presented significantly higher amounts

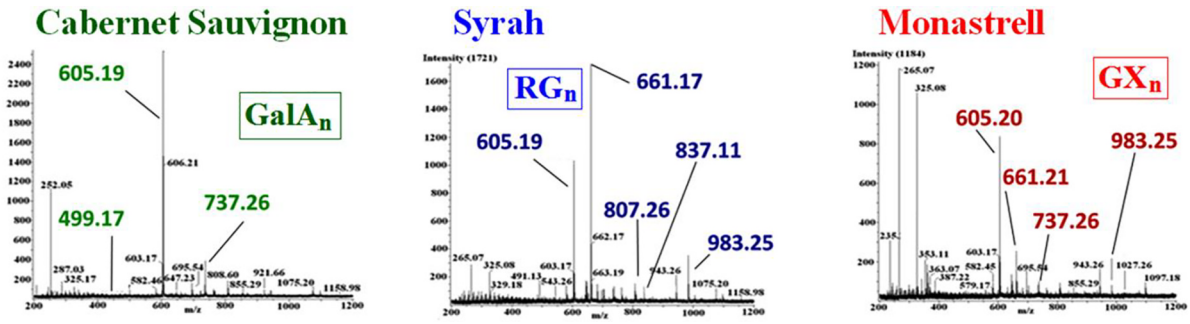

Fig. 4. Negative ESI-TOF mass spectrometry of deprotonated molecule $[M-H]^-$ ions of released oligosaccharides isolated from Cabernet Sauvignon, Syrah and Monastrell wines. Adapted from Apolinar-Valiente, Romero-Cascales et al. (2015). $GalA_n$: galacturono-oligosaccharides; RG_n: rhamnogalacturono-oligosccharides; GX_n: xylano-oligosaccharides.

of several monosaccharides (rhamnose, arabinose and galactose) in the oligosaccharide fraction compared to the other three. Similarly, another terroir showed a higher galacturonic acid concentration in comparison with the others. Therefore, they concluded that the glycosyl residue composition of the wine oligosaccharides could be affected by grape origin. Furthermore, the data set corresponding to whole ESI-TOF mass spectra of oligosaccharides isolated from Monastrell wines (Fig. 3, from Apolinar-Valiente et al., 2014) revealed that the composition of these molecules is indeed influenced by a terroir effect. The variability which can be attributed to the variation of the different terroir average spectra was found equal to 26.2%. It must be noted that the mass spectrometry is not a quantitative method but allows a good comparison among samples. Taken as a whole, these data illustrate terroir impact on wine oligosaccharide concentration, composition and structure, even for the same grape variety.

4.1.2. Grape cultivar

It has been extensively demonstrated that the cultivar has a large influence on grape composition and morphology and, hence, on its performance during the winemaking process as well as on the characteristics of the resulting wine. Thus, whereas other grape and wine compounds have been largely studied, information about cultivar influence on the wine oligosaccharide fraction is essentially limited to very few works. Ducasse et al. (2010) found remarkable differences in total oligosaccharide amounts between Carignan and Merlot wines, with values of 332 and 252 $mg{\cdot}L^{-1}$ respectively (Table 1). They also detected some variations regarding their glycosyl composition of oligosaccharides isolated from wines elaborated with these two varieties: rhamnose and galactose content was higher in Carignan wine, whereas xylose, galacturonic acid, 4-*O*-methyl glucuronic acid and xylitol were in higher amount in Merlot wine. These discrepancies can be explained by differences in maturity stages between cultivars at harvest time (Vicens, Fournand, Williams, Sidhoum, Moutounet, & Doco, 2009; Hernández-Hierro et al., 2014). Martínez-Lapuente et al. (2016) suggested that sparkling wine oligosaccharides from fully ripe Tempranillo grapes presented more solubility and stability, also reporting differences in the oligosaccharides composition related to grape maturity (Table 1). Zietsman et al. (2015) reported the impact of the ripeness on the grape cell wall degradation of Pinotage grapes by endogenous enzymatic activities, and Gao et al. (2016) observed higher cell wall degradation in more ripe Cabernet Sauvignon grapes. In the same way, factors linked to grape cultivar, winemaking procedure, origin or variations in berry maturity could explain the differences detected by Bordiga et al. (2012), who identified lower oligosaccharides amounts for Chardonnay (102 $mg{\cdot}L^{-1}$) and Grignolino wines (127 $mg{\cdot}L^{-1}$) (Table 1). Trying to combine all the other factors excepting grape cultivar, Apolinar-Valiente, Romero-Cascales et al. (2015) compared oligosaccharide concentrations in three varieties of wines: Cabernet Sauvignon, Syrah and Monastrell. Grapes came from the same experimental plot, and hence, the vineyard conditions and winemaking procedures were similar in the three cases. These authors observed that oligosaccharide amount from Syrah wine was significantly higher (480 $mg{\cdot}L^{-1}$) compared with Cabernet Sauvignon (174 $mg{\cdot}L^{-1}$) and Monastrell (244 $mg{\cdot}L^{-1}$) wines. Besides, they determined that Syrah wine oligosaccharides presented a higher concentration in most of the sugars compared with those from Cabernet Sauvignon and Monastrell wines, whereas Cabernet Sauvignon wines showed the lowest arabinose and glucose concentration and Monastrell oligosaccharides presented the lowest xylose and xylitol contents (Table 1). As previously described, Apolinar-Valiente, Romero-Cascales et al. (2015) evidenced significant differences between proportions of several families of oligosaccharides in wines from different varieties (Fig. 1). Syrah showed the lowest value for cell wall oligosaccharides from yeasts (the sum of OligoGlucans and OligoMannans) and also for OligoArabinogalactans type II, but the highest release of OligoRhamnogalacturonans. By contrast, they detected that Monastrell presented the highest quantity for OligoArabinans and OligoXyloglucans. Besides, Apolinar-Valiente, Romero-Cascales et al. (2015) disclosed ESI-TOF spectra of Cabernet Sauvignon, Syrah and Monastrell wine oligosaccharides, which also showed clear differences (Fig. 4). The ions identified in Cabernet Sauvignon wine corresponded to galacturonan (smooth regions) and glucuronoxylan structures. Regarding Syrah and Monastrell wines, the ions observed displayed rhamnogalacturonan (hairy regions) as well as glucuronoxylan-like structures.

Studying the connection between grape cultivar and wine oligosaccharides, Jégou et al. (2017) examined these molecules in Pinot meunier and Chardonnay base wines, noting a remarkable effect of grape variety on oligosaccharides composition and content. Nevertheless, it seems essential to remark that Quijada-Morín et al. (2014) observed a significant variability of total oligosaccharides content in wines from the same grape variety. These authors observed that commercial red wines elaborated with the cultivar Tempranillo showed total oligosaccharides concentrations ranging from 75 to 325 $mg{\cdot}L^{-1}$. However, this variability cannot be easily explained because no data concerning yeasts used or winemaking procedures was provided although these latter can, as we shall see below, play an important role. Moreover, the Tempranillo grapes used had different origins, so neither can we reject here a possible terroir effect.

4.2. Influence of winemaking techniques on wine oligosaccharides

Winemaking relates to the transformation of grapes into wine, involving a variable set of elements which play a key role. Two of the most important and influencing factors generally considered by winemakers are grape quality and winemaking practices (*e.g.* maceration time, temperature, classical –cold pre-fermentative maceration, enzymatic treatments–and emerging –application of ultrasounds, microwaves and pulsed electric field– technologies, yeast used, fining agents, ageing) (Apolinar-Valiente et al., 2014; Clodoveo, Dipalmo, Rizzello, Corbo, & Crupi, 2016; Martínez-Lapuente et al., 2016; Aleixandre-Tudó

& du Toit, 2018; Frost, Blackman, Hjelmeland, Ebeler, & Heymann, 2018; Minnaar, Nyobo, Jolly, Ntushelo, & Meiring, 2018; Jiménez-Martínez, Bautista-Ortín, Gil-Muñoz, & Gómez-Plaza, 2019; Miller & Block, 2019).

4.2.1. Red and white winemaking processes

Bordiga et al. (2012) identified and characterized oligosaccharides in Chardonnay white and Grignolino red wines. Slight differences only in the total oligosaccharide concentration could be observed between Grignolino (127 mg·L^{-1}) and Chardonnay (107 mg·L^{-1}). These variations could be linked to the different winemaking techniques employed for red and white wines: the longer contact period between skins and must during the vinification of red wine in comparison with white wine might account for the higher amount of oligosaccharides observed in Grignolino red wine. Moreover, they concluded that differences in maturity stages at harvest could explain the varying performance between grape cultivars. This conclusion is in accordance with observations reported by Zietsman et al. (2015) and Gao et al. (2016) concerning the ripeness influence on the grape cell walls on account of the action of the endogenous enzymes. It is well-known that the integrity of skin cell walls and their possible degradation affect the extraction of several compounds, including polysaccharides and oligosaccharides, during winemaking. Red wine can notably change over time in the bottle, which can affect sensorial aspects. These variations can be linked to several aspects, such as the temperature of storage (Hopfer, Buffon, Ebeler, & Heymann, 2013), the composition of the wine before its bottling (Avizcuri, Sáenz-Navajas, Echávarri, Ferreira, & Fernández-Zurbano, 2016) and the time in the bottle. Notably, Doco et al. (1999) reported that the global fraction of homo- and rhamnogalacturonan oligomers decreased with ageing in red Carignan noir wines (approximately 15 years of storage).

The red winemaking procedure is characterized by the simultaneous progress of alcoholic fermentation and maceration. In order to improve the extraction of different valuable grape components, alternative maceration conditions processes have been developed to enhance or substitute conventional winemaking techniques, such as the technique of cold pre-fermentative maceration. In this technique, the onset of fermentation is delayed because of the low temperatures used (lower than 4-8° C) and, several water-soluble grape components, such as aroma precursors, glycosylated phenols and polysaccharides are preferentially extracted during this process (Aleixandre-Tudó & du Toit, 2018; Casassa et al., 2019). As dry ice is the most broadly used freezing agent, Apolinar-Valiente et al. (2010) determined the glycosyl residue composition of oligosaccharides after treatment with dry ice in Syrah and Monastrell wines. When dry ice was added, oligosaccharides from Syrah wine showed statistically lower amounts of rhamnose and galacturonic acid than the control wine. However, no differences were found between the dry ice-treated wine and control wine in the case of Monastrell wine. Dry ice-treated Syrah wine displayed a lower total oligosaccharide amount (215 mg·L^{-1}) than the control sample (480 mg·L^{-1}). On the contrary, in the case of Monastrell, no differences between the dry ice-treated wine (277 mg·L^{-1}) and control wine (244 mg·L^{-1}) were detected. In Syrah wine treated with dry ice, the (Ara + Gal)/Rha ratio pointed to a greater release of rhamnogalacturan type oligosaccharides carrying side chains of arabinans (AG-I) and arabinogalactans from the hairy zones or by the presence of *arabino*-oligosaccharides. All these data confirmed that dry ice addition had an obvious effect on Syrah wine oligosaccharide concentration and composition, but had no such influence in Monastrell wine. This can be explained by differences between cultivars in berry skin thickness or composition.

4.2.2. Addition of enzymes during the winemaking process

The use of enzymes during the winemaking procedure has also been established as a possible technique to improve red wine quality. The maceration process during red winemaking involves fermenting berry skins with must. Although how enzymes act on grape berries is far from being clearly understood, commercial enzyme preparations are added at this stage. Thus, they promote cell wall breakdown and the subsequent release of compounds of interest from grape skin. Among them are phenolic (Río-Segade, Pace, Torchio, Giacosa, Gerbi, & Rolle, 2015) or desirable aroma compounds (Sun, Hu, Zhang, Zhu, & Tao, 2018), but also polysaccharides and oligosaccharides due to the pectinolytic nature of enzymes used (Apolinar-Valiente et al., 2013, 2014). Ducasse et al. (2011) studied the effect of different commercial enzyme preparations on Merlot red wine oligosaccharide composition and structure. They observed that eight out of the ten enzyme-treated wines presented lower amounts of oligosaccharides than the control. These authors explained their results by varying enzyme activities, resulting in different release and/or degradation of oligosaccharides. They concluded that the lower amounts of oligosaccharides could be linked to the different concentrations of polysaccharide families from enzyme-treated wines: more rhamnogalacturonan type II (RG-II) and less polysaccharides rich in arabinose and galactose (PRAGs). This would mean that homogalacturonans and arabinans were highly degraded by pectinases and, therefore, not recovered in the oligosaccharide fraction. However, these results seem to contrast with later works, which showed significantly higher total concentrations of oligosaccharides when commercial enzymes were added to grapes from different origins (Apolinar-Valiente et al. 2014). Yet, the oligosaccharide concentration in treated Monastrell wine was similar to that found in the control indicating that oligosaccharides did accumulate and were either less degraded or not at all. The apparent discrepancies between these two works could be explained by the combination of complex key factors such as grape cultivar and origin, the commercial enzymatic treatments and the moment at which they were applied. It should also be emphasized that the commercial enzyme formulations used in these works was not always identical. Concerning oligosaccharide fractions composition, Ducasse et al. (2011) reported that the concentrations of arabinose residues from nine out of the ten enzyme-treated Merlot wines were lower than that of the control. In the case of the sample that was much enriched in this residue, they concluded it probably originated from pectin side chains (hairy regions of pectins, according to Carpita and Gibeaut (1993)). These authors also evidenced an increase in rhamnose except for one treated wine, suggesting a synergistic effect between some enzymatic preparations. Later work showed statistically different amounts of several sugar residues when Monastrell red wines were elaborated using commercial enzymes (Apolinar-Valiente et al., 2014), although these differences seemed to be also influenced by grape origin.

The characteristic arabinose to galactose (Ara/Gal) ratio obtained for Merlot oligosaccharide fractions by Ducasse et al. (2011) was strongly modified by the use of pectinolytic enzymes. It decreased from 2.42 for the control to < 1 for six out of the ten treated wines, whereas only one treated wine presented a higher ratio (2.87). This exception coincides with the data reported by Apolinar-Valiente et al. (2014) who, using commercial enzymes on three Monastrell wines, found significantly higher values for this ratio (1.26 and 1.54) for two enzyme-treated wines in comparison with their control samples (0.77 and 0.84, respectively), whereas a third enzyme-treated wine showed no statistically significant difference. The increase of Ara/Gal ratio in treated wines would indicate a release of arabinose or arabinose-rich oligosaccharides arising from the pectic framework (Carpita & Gibeaut. 1993). Ducasse et al. (2011) observed a lower value for the rhamnose to galacturonic acid (Rha/GalA) ratio in oligosaccharides from Merlot control wines (0.35), which would indicate a predominance of homogalacturonans. The higher (Rha/GalA) ratio (from 0.5 to 0.8) observed in most treated wines would suggest a majority of rhamnogalacturonan structures. This suggests that that enzyme preparation released rhamnogalacturonan-based oligosaccharides. Moreover, some homogalacturonan degradation by the polygalacturonase activities present in the enzyme preparations might also take place, resulting in increased

Rha/GalA ratios. But these authors also found that this ratio was lower in two out of ten treated-wines, explaining this behavior by a possible synergistic effect. Apolinar-Valiente et al. (2014) also found that this ratio presented lower values in commercial enzyme-treated Monastrell wines from two different origins (0.06 and 0.17) compared to control wines (0.13 and 0.28, respectively). This would suggest instead an increase of homogalacturonan-oligosaccharide predominance over rhamnogalacturonan-oligosaccharides when commercial enzyme was added to Monastrell wines. The ratio of (Ara + Gal)/Rha showed lower values in Merlot (Ducasse et al., 2011) and Monastrell (Apolinar-Valiente et al., 2014) commercial enzyme-treated wines, compared to control wines. The authors suggested that rhamnogalacturonan oligomers released in wines carried less neutral lateral chains when commercial enzymes were added. The different behaviors depending on the grape cultivar and the harvesting year in relation with all these ratios could be explained by possible variations in pectin composition of grape skin cell walls. It seems coherent to think that methyl esterification of the pectin would play an important role in the mentioned variations.

With the aim to compare oligosaccharide structures in control and enzyme-treated Merlot wines, Ducasse et al. (2011) analyzed glycosidic linkages after permethylation and acidic hydrolysis. They observed that oligosaccharides of the enzyme-treated wines were mainly rhamnogalacturonans from hairy region. Besides, the arabinose degradation from PRAGs or arabinans of the rhamnogalacturonan side chain caused by the enzymatic treatments also released oligosaccharides. They concluded that the addition of enzymes with varying formulations could differently affect oligosaccharide releases, thus influencing wine properties. Besides, they analyzed the oligosaccharides mass spectra obtained by principal component analysis (PCA). The nature of the oligosaccharides associated with the discrimination along axis 1 (Fig. 5A) indicates that pectin-methyl esterase and polygalacturonase activities (present in the enzymatic preparations) demethylate and degrade oligosaccharides released from the smooth zones of berry cell walls during winemaking. Fig. 5B shows that the ions corresponding to methylated galacturonic acids (*m/z* 545, 559, and 749) are more abundant in control wines. Furthermore, ions corresponding to rhamnogalacturonans fragments (*m/z* 661, 837, and 983) are associated with the oligosaccharides from enzyme-treated wines (Fig. 5A). The different actions of several enzymatic activities, such as those previously mentioned, on the oligosaccharide release from smooth or hairy pectin regions were deduced from the data obtained by MS fragmentation analysis.

The results obtained by Kassara et al. (2019) did not determined the strict oligosaccharide fraction, but they observed a release of free monosaccharides after pectolytic enzyme treatment in rosé and red wines. This phenomenon, in accordance with the broadly demonstrated action of enzymatic activities on the grape cell wall, could be linked to an extreme enzymatic hydrolysis, as suggested by Gao, Zietsman, Vivier and Moore (2019).

Given the demonstrated relevance of the subject, future and deeper studies regarding the characteristics of grape skin and the action of different enzymatic activities seem essential. These further works would deepen and extend our knowledge about the impact of commercial enzyme formulates on wine oligosaccharide fractions.

4.2.3. *Elaboration of sparkling wines*

Sparkling wines are characterized by the production of effervescence originating from the release of carbon dioxide of exclusively endogenous origin (OIV, 2020). This type of wines undergoes two sequential fermentations: during the first period, grape must is transformed into wine, which is termed base wine. After bottling, there is a second fermentation inside the bottle due to the addition of sugar and yeasts to base wine. Subsequently, a period of ageing is carried out, during which sparkling wines are in contact with yeasts under anaerobic conditions. It seems logical to think that base wine characteristics as well as the later procedures are really important factors impacting the properties of these wines. When base wine is elaborated, the pressing cycle is considered as one of the most important procedures. In this phase there is a fractionation of different grape juices with different qualities and characteristics. When we speak about sparkling wines, a

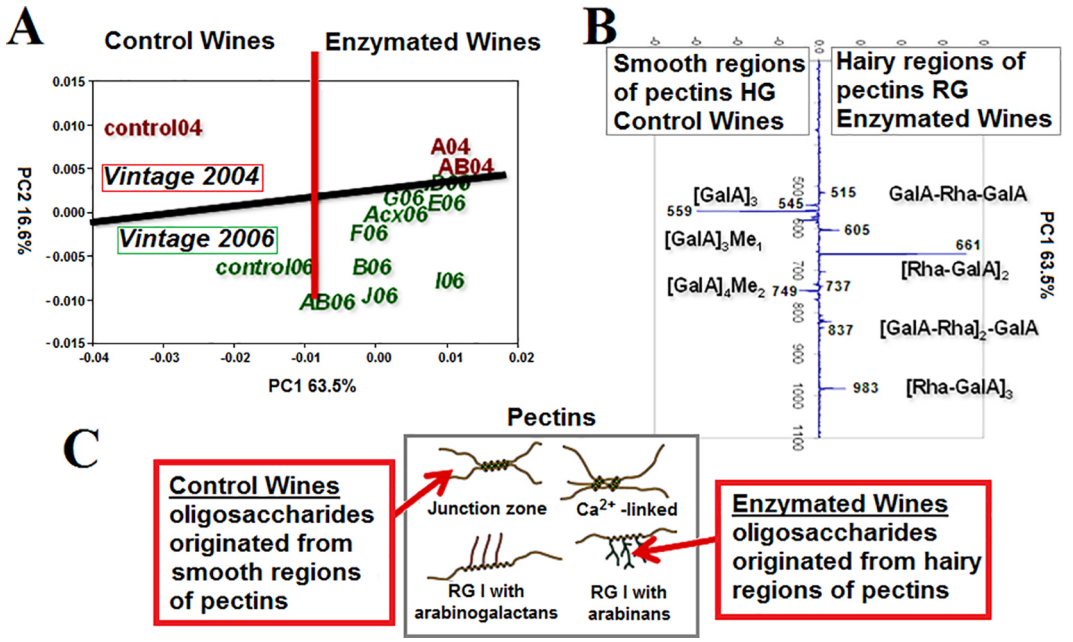

Fig. 5. A: Principal component analysis of negative $[M-H]^-$ oligosaccharide ions mass spectra in Merlot wines (vintages 2004 and 2006). The first two major components (PC1 and PC2) account for 80.1% of the variability of all spectra. Axis 2 (PC2), representing 16.6% of the variability, differentiates 2004 and 2006 vintages. Axis 1 (PC1) separates the control wines from enzymated wines and represents 63.5% of the variability. **B**: The ions corresponding to methylated galacturonic acids (*m/z* 545, 559, and 749) are more abundant in control wines whereas the ions corresponding to fragments of rhamnogalacturonans (*m/z* 661, 837, and 983) are associated with oligosaccharides from enzyme-treated wines. **C**: It is positively defined by masses representing rhamnogalacturonic zones (RG zones) and negatively by masses representing homogalacturonic zones (HG zones). **A** and **B**: Adapted from Ducasse et al. (2011). **C**: Adapted from Carpita and Gibeaut (1993).

complete pressing cycle means a series of pressure increases/decreases as well as pomace breakdown, which leads to a remarkable variation in juice composition depending on the pressing cycle (Marchal et al., 2012). Regarding "*Méthode Champenoise*", Jégou et al. (2017) studied oligosaccharides from Pinot meunier and Chardonnay base wines from Champagne. They reported significant variations in base wine oligosaccharides as the pressing cycle progressed, during which oligosaccharide content varied between 97 and 139 $mg{\cdot}L^{-1}$. In terms of oligosaccharide composition, the Ara/Gal ratio showed significant differences among five Chardonnay (ranging from 1.2 to 2.7) and six Pinot meunier (ranging from 1.2 to 3.5) base wines. The Rha/Gal ratio varied between 0.06 and 0.16 for Chardonnay and between 0.53 and 0.72 for Pinot meunier, these low values in this ratio reflecting a majority of homogalacturonan-like structures. Finally, the (Ara + Gal)/Rha ratio differed between the Pinot meunier and Chardonnay base wines with values ranging from 5.7 to 11.3 and from 4.5 to 6.9, respectively. Thus, these authors demonstrated that oligosaccharide composition and content in Champagne base wines are notably influenced by press fractioning and grape variety. Martínez-Lapuente et al. (2016) studied how the ageing of red Tempranillo sparkling wine on yeast lees could affect oligosaccharides. They found significantly greater amounts of galacturonic acid in red sparkling wines than those previously observed for still wines, which was explained by differences in pectin composition and natural pectinase activities from grape skins. These authors concluded that the total glycosyl content of oligosaccharides decreased during the whole period of ageing. Concerning the characteristic compositional ratios, the Ara/Gal ratio was 2-fold higher than that of still red wine polysaccharides. Moreover, this ratio increased or decreased during ageing depending on grape maturity. In addition, they observed lower values for the Rha/GalA ratio than those obtained for still red wines, while the mannose to glucose (Man/Glc) ratio in oligosaccharides decreased throughout ageing. This could be explained either by (i) a reduction of the hydrolytic enzyme activity involved in the autolytic process, and/or by (ii) a higher precipitation or combination rate of oligomannans than their solubilisation into the wine. Apolinar-Valiente et al. (2020) reported that the variation of total oligosaccharides content depending on the origin of the sparkling base wine. This parameter ranged between 138 and 148 $mg{\cdot}L^{-1}$ in Spanish base wines, whereas French base wines showed values between 78 and 98 $mg{\cdot}L^{-1}$. However, other factors such as the maturity, the enological techniques or the cultivar grape could also be considered (Martínez-Lapuente et al., 2016; Jégou et al., 2017).

5. Sensorial and chemical wine properties relating to the oligosaccharides

The determination of the links between oligosaccharide fractions and wine sensory perceptions appears as an interesting and new goal in oenology research. But the influence of the oligosaccharide fraction from red wines on sensory perceptions has been very little studied. This challenge seems closely related, as shown below, to the mechanisms involved in astringency perception. This parameter has been defined as "*the complex of tactile sensations due to shrinking, drawing or puckering of the mucosal of the oral cavity because of exposure to certain substances*" (Lei, et al., 2019). Astringency is an important sensory attribute for wine, affecting its quality (Ployon et al., 2018). This sensorial perception is caused by the capacity of phenolic compounds (especially tannins) to bind salivary proteins such as mucins, forming aggregates and precipitates with the subsequent reduction of mouth lubrication (Davies et al., 2004; Ployon et al., 2018). Astringency has been shown to be a complex perceptual phenomenon which can be impacted by several factors such as the polysaccharide presence in wine, among others (Brandão et al., 2017; Lei, et al., 2019). But until now, there are few works which research the relationship between wine oligosaccharides and astringency. Quijada-Morín et al. (2014) showed the effect of the composition in certain compounds, including oligosaccharides, on perceived astringency in Tempranillo red wines. They revealed that structure and size of carbohydrates are important for astringency perception, which was positively related to the presence of mannose and galactose residues in the oligosaccharide fraction. However, they concluded that this event was probably connected with the decrease in mannoproteins and PRAGs contents and not with a direct effect of these glycoside residues on astringency perception. Likewise, Boulet et al. (2016) reported that astringency intensities correlated positively with oligosaccharides content in all their selected models. Therefore, the oligosaccharide fraction had a direct effect on astringency, although a competition with astringency-tempering polysaccharides was also considered. Astringency perception in wine is included, among others, in mouthfeel sensation (Jackson, 2009). Different from taste and aroma, wine 'mouthfeel' arises from a group of oral tactile stimulations. Mouthfeel represents therefore a major contributor to the organoleptic perception of wine and is predominated understood as "*a holistic multisensory perception of flavour*" by consumers (Laguna, Bartolomé, & Moreno-Arribas, 2017). Chong et al. (2019) exposed that the soluble cell wall carbohydrates (SCWCs) of Cabernet Sauvignon red wine play a key role in wine mouthfeel. These authors suggested that due to the relatively small molar weight and the low concentration observed in SCWCs, the contribution of these compounds to viscosity could be questioned. They hypothesized that the SCWCs influenced on mouthfeel attributes through specialized taste receptors cells in the mouth. In the light of these few yet valuable findings, a more in-depth knowledge about the relationship between oligosaccharides, wine sensorial properties and even mouth physiological aspects seems essential to us.

6. Summary and perspectives

Oligosaccharides are complex carbohydrates related to growth, development and defensive strategies of plants. Besides, these molecules have been broadly evidenced as beneficial to human health.

In wine, oligosaccharides have been largely demonstrated to be degraded polysaccharide structures coming mainly from the grape berry cell wall, through the action of endogenous (present in grapes) or exogenous (added by the winemakers) enzyme activities during the various stages of wine elaboration. Consequently, oligosaccharides present in wines are mainly branched structures which these enzymes were not able to degrade them.

From an oenological point of view, further and deeper work should be performed to clarify the composition and structure of the wine oligosaccharide fraction. We know that this fraction is affected by several agricultural aspects, such as different grape cultivars and origins or the use of various elicitor treatments in vineyards. We could likewise suppose the influence of other factors such as the use of intraspecific hybrid grapes or the climate change issues on wine oligosaccharides. The impact of all these agricultural, genetic or climatic points on the endogenous enzymes expression both hydrolases and synthases should be deepened. But these aspects may also interact with several old and new winemaking techniques. For example, as previously mentioned, ultrasound technology has been referenced as a procedure to increase the extraction of oligosaccharides (Guo et al., 2019). It is coherent to think that sonication would promote the hydrolysis of polysaccharides, improving the oligosaccharides release. Similarly, this technology appears in oenology as an emerging technique to increase the phenolic compounds extraction from grape to must (Clodoveo et al., 2016; Gambacorta et al., 2017). Furthermore, extended maceration has been strongly related to pH (Frost et al., 2018), suggesting an obvious effect of grape skin degradation due to the exchange of skin bound potassium for hydronium. Would the extended maceration also influence on the oligosaccharide fraction as a result of the higher cell wall disruption? Further research should thus definitely focus on these multiple and complex interactions, together with other subjects such as the use of non-*Saccharomyces* yeast strains, co-winemaking techniques or cold pre-fermentative, the use of varying enzymatic activities or the direct

relationship between endogenous enzymatic activities in different varieties and oligosaccharides release. The implementation of improved purification and identification methodologies will therefore enhance our understanding of oligosaccharide composition, structures and potential interactions with other molecules (polyphenols, proteins and aroma compounds). The effect of each particular and well-characterized oligosaccharide fraction on the sensorial and physicochemical features of wine should be studied in depth, especially their involvement in certain aspects such as haze development, wine bitterness sensations or their interaction with other compounds. For instance, as arabinans are known to participate in haze formation when they have a low degree of branching (Belleville, Williams, & Brillouet, 1993), it seems coherent to carry out further studies about oligosaccharide involvement in wine haze development, focusing particularly on their DP. On the other hand, we have no found studies linking bitterness to wine oligosaccharides content, composition and/or structure. As an example, in *koji amazake* (traditional Japanese sweet beverage) gentiobiose has been demonstrated as a disaccharide giving bitterness (Oguro, Nakamura, & Kurahashi, 2018). However, Côté (2009) reported that the glucosylation of gentiobiose produced novel oligosaccharides decreasing or removing its bitter taste, which could allow its adoption as food ingredient. Could then oligosaccharides in some particular wine somewhat be related to bitterness? Regarding the astringency, the research about the demonstrated direct effect of oligosaccharides reported for the first time by Boulet et al. (2016) should be continued, deepening in the potential oligosaccharide-tannin-protein interactions.

We also must not forget the demonstrated strong ties between nutrition and health and oligosaccharides. These molecules have been demonstrated as owning antioxidant properties (Coelho et al., 2014; Kang et al., 2014). Similarly, antioxidant features has been found in wine polysaccharides by Aguirre et al (2009), suggesting that they could play a significant role in the antioxidant features of red wine. The logical question here is whether the wine oligosaccharides could also present antioxidant activities. Moreover, would wine oligosaccharides always display these properties? Coelho et al. (2014) suggested different applications and uses of arabinoxylans or arabinoxylo-oligosaccharides from brewers' spent grain depending, among others, on their DP. Connecting this with prebiotics aspects, Sanchez, Marzorati, Grootaert, Baran, Van Craeyveld and Courtin (2009) reported that shorter-chain-length oligosaccharides were primarily fermented in the proximal colon, whereas longer molecules (DP: 29) reached the distal colon. It is reasonably safe to conclude that the study of the possible beneficial impact of wine oligosaccharides on human health as prebiotic could be an opportunity to open a new research field.

To sum up, wine oligosaccharide fraction appears as an exciting challenge showing still a long way to go here. More research concerning the field of wine oligosaccharides should be carried out and some points need to be addressed in order to gain theoretical and practical knowledge of these valuable molecules and of their entire environment.

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.

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