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Effect of grape maturity on carbohydrate composition of red sparkling wines

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Red sparkling wine – grape maturity – polysaccharides – oligosaccharides

Introduction

Sparkling wines elaborated following the traditional method undergo a second fermentation in closed bottles of base wines, followed by aging of wines with lees for at least 9 months. The production of sparkling wines is lower compared to that of still wines, but the economic impact of this product is very important because of its high added value. For this reason winemakers are constantly looking for product improvements and new products. In fact, a new market strategy in the enological industry based on the diversification of wine production and on the exploitation of the characteristics and particularities of different varieties of grapes is emerging. In this sense, although most of the sparkling wines elaborated are white and rosé, the production of red sparkling wines is highly increasing. One of the initial problems in red sparkling wine processing is to obtain suitable base wines that should have moderate alcohol content. Therefore, grapes must be harvested at low maturity stage. This fact could affect the polysaccharide and oligosaccharide content of wines, which in turn could have implications for sparkling wine sensory properties. A previous study has analyzed the composition of polysaccharide families during the winemaking and aging of white and rosé sparkling wines [1], however, none has analyzed the evolution of oligosaccharides. Therefore, this paper aims to analyze the changes occurring in oligosaccharide and polysaccharide families during the red sparkling wine processing by the traditional method, as well as to study the effect of grape ripening stage on carbohydrate composition.

Materials and methods

Grapes from Tempranillo variety from the Cigales Denomination of Origin (D.O.) were harvested at two maturity levels: prematurity grapes (PM) and grapes at their optimum degree of maturity (M). Then, two red sparkling wines were manufactured using the traditional method champenoise in the enological station of Castilla y León (Valladolid, Spain). Samples for analyses were taken from the base wines and then after 3 months, 6 months and 9 months of aging on yeast lees. Isolation of polysaccharide and oligosaccharide fractions was made according to a previously described method [2]. The polysaccharide composition was estimated from the concentration of individual glycosyl residues determined by GC–MS after hydrolysis, reduction and acetylation as described elsewhere [3]. Oligosaccharide fraction was determined after solvolysis by GC of their per-O-trimethylsilyl methyl glycoside derivatives [4].

Results and discussion

Figure 1 gives the molecular weight distributions of polysaccharides and oligosaccharides of premature and mature red sparkling wines during their aging on yeast lees. The fraction eluted on Superdex 30-HR column between 40 and 53 min contained the polysaccharide fraction, while the oligosaccharide fraction was collected between 54 and 93 min. The first peak in the range 40–48 min corresponded to the

polysaccharide fraction of highest mass and rich in PRAGs (Polysaccharides Rich in Arabinose and Galactose) and mannoproteins (MPs). The second peak eluted between 49 and 53 min corresponded to the fraction containing mainly rhamnogalacturonan II (RG-II). Evident differences between the profiles of base wines were found. The polysaccharide and oligosaccharide fractions of red base wines elaborated with mature grapes were higher than the fractions in the other base wine due to a different ripening state at harvest. It should be noted the occurrence of peak tailing at 48 min in premature but no in mature red sparkling wines, probably due to a degradation of polysaccharides in mature grapes but no in premature grapes.

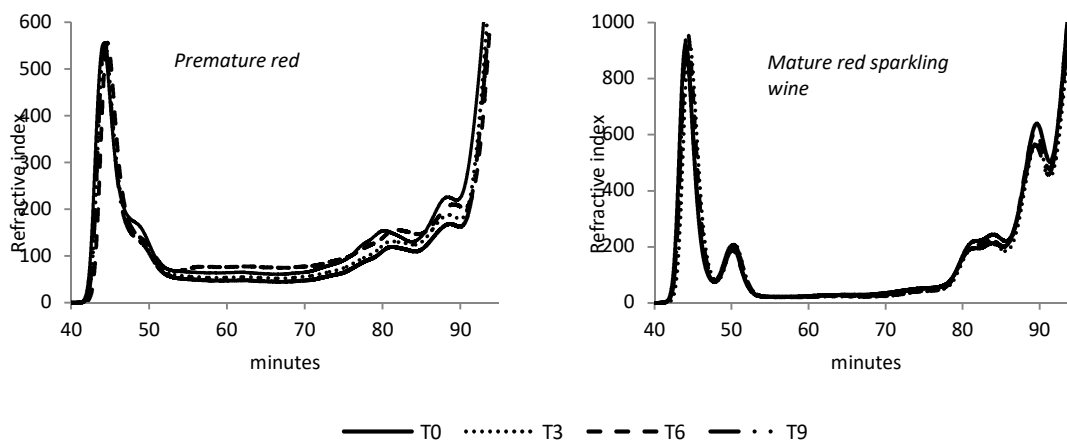


Fig. 1 - Purification by high-resolution size-exclusion chromatography of polysaccharide and oligosaccharide fractions isolated on Superdex 30-HR column from premature and mature red sparkling wines during different stages of sparkling wine production: base wines (T0), sparkling wines after 3 months (T3), 6 months (T6), and 9 months (T9) of aging on yeast lees (Refractive index versus Retention Time (Minutes)).

Grape ripening stage affected the content and evolution of polysaccharides and oligosaccharides. Figure 2 shows the concentration of MPs, glucans (GLs), PRAGs and RG-II in premature and mature red sparkling wines during different stages of sparkling wine production. In both wines and in all vinification stages, PRAGs were the most prevalent polysaccharide family detected. However in all vinification stages mature sparkling wines showed higher content of MPs, PRAGs and RG-II than premature ones. The higher MPs content could be caused by changes in yeast conditions, such as the different alcohol content of base wines, during alcoholic fermentation, which could influence the kinetics of the release of mannose. The higher content of polysaccharides from grapes in mature red base wines could be due to an easier degradation of cell walls in mature grapes that could ease the extraction of wine components during the early steps of their processing to base wine. The evolution of polysaccharide families was different during the stages of the sparkling wine processing. In mature red sparkling wines, MPs increased from 3 to 6 months of aging, GLs increased from base wine to 3 months of aging, while PRAGs and RG-II slightly decreased at 9 months. However, in premature red sparkling wines, MPs increased at 6 months of aging, GLs and PRAGs remained and RG-II decreased. As observed with polysaccharide families, grape maturity also affected the arabinose/galactose ratio of the wine PRAGs composition. Mature red sparkling wines showed higher arabinose/galactose ratio than premature ones, which suggests higher release of arabinose. In both wines the ratio remained constant during the aging, which suggests that aging did not change the PRAGs composition (date not shown).

Table 1 shows the glycosyl composition (mg/L) of oligosaccharides from red sparkling wines during aging on yeast lees. In all wines and together with PRAGs, oligosaccharides were the two most prevalent carbohydrates detected in all vinification stages. Oligosaccharides of all wines included sugars such as rhamnose, arabinose, galactose, xylose and galacturonic and glucuronic acids coming from the pectocellulosic cell walls of grape berries but also mannose and glucose released from yeast polysaccharides. Galacturonic acid, arabinose, xylose, mannose and glucose presented the highest contents in both wines during all vinification stages.

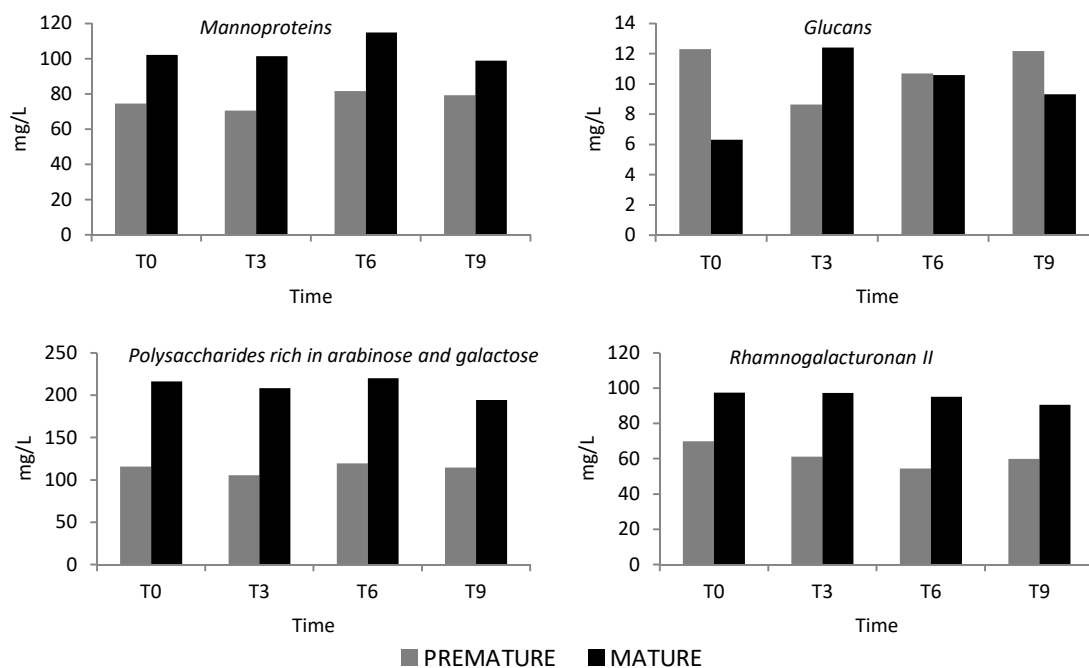


Fig. 2 - Concentration of mannoproteins (MPs), glucans (GLs), polysaccharides rich in arabinose and galactose (PRAGs), and rhamnogalacturonan II (RG-II) in premature and mature red sparkling wines during different stages of sparkling wine production: base wines (T0), sparkling wines after 3 months (T3), 6 months (T6), and 9 months (T9) of aging on yeast lees.

Table 1 - Glycosyl composition (mg/L) of oligosaccharides from red sparkling wines during different stages of sparkling wine production: base wines (BW), sparkling wines after 3 months (T3), 6 months (T6), and 9 months (T9) of aging on yeast lees.

	Rha ^a	Fuc ^a	Ara ^a	Xyl ^a	Man ^a	Gal ^a	Glc ^a	Gal A ^a	Glc A ^a	Xylitol	4-OMeGlc A ^a	Total
PM^b												
T0	4.3	3.3	11.6	17.9	26.0	7.5	41.1	176.8	3.1	1.8	5.6	299.0
T3	3.4	2.2	10.3	15.1	21.6	7.3	34.5	144.0	2.6	2.0	4.9	247.9
T6	4.1	2.6	12.5	17.0	24.4	7.9	50.0	172.9	3.1	2.1	5.3	301.9
T9	2.6	2.1	6.7	10.8	18.1	6.2	36.2	91.8	1.7	1.3	3.0	180.5
M^b												
T0	3.2	2.7	18.0	20.9	24.2	11.0	42.2	174.2	3.9	3.3	7.6	311.2
T3	3.0	3.0	16.8	21.1	26.0	9.3	54.7	172.8	3.6	3.2	7.2	320.7
T6	2.5	2.5	13.7	16.4	20.6	6.9	44.4	160.2	3.7	2.0	6.0	278.9
T9	2.5	2.5	15.0	18.8	21.6	7.0	56.8	147.0	3.3	2.8	6.0	283.3

^aRha, Rhamnose; Fuc, Fucose; Ara, Arabinose; Xyl, Xylose; Man, Mannose; Gal, Galactose; Glc, Glucose; Gal A, Galacturonic acid; Glc A, Glucuronic acid; 4-OMeGlc A, 4-O methyl Glucuronic acid. ^bPM, premature grapes; M, mature grapes.

Several characteristic ratios were calculated from oligosaccharide sugar composition: Arabinose/Galactose, Rhamnose/Galacturonic acid, and (Arabinose + Galactose)/Rhamnose (Table 2). Red mature sparkling wines showed higher arabinose/galactose ratio than premature ones, which suggests a greater release of arabinose or oligosaccharides rich in arabinose arising from the pectic framework into this wine. The lower value calculated for Rha/Gal A suggests an homogalacturonan structure predominance. (Arabinose + Galactose) to Rhamnose ratio was lower in premature red sparkling wines than mature wines. It could indicate that the rhamnogalacturonan oligomers present in mature red sparkling wines carry more neutral lateral chain.

Table 2 - Glycosyl composition (mg/L) of oligosaccharides from red sparkling wines during different stages of sparkling wine production: base wines (BW), sparkling wines after 3 months (T3), 6 months (T6), and 9 months (T9) of aging on yeast lees.

	Ara/Gal ^a	Rha/Gal A ^a	(Ara+Gal)/Rha ^a
Premature			
T0	1.87	0.03	4.49
T3	1.68	0.03	5.27
T6	1.89	0.03	5.03
T9	1.30	0.03	4.98
Mature			
T0	1.96	0.02	9.24
T3	2.17	0.02	8.89
T6	2.37	0.02	8.51
T9	2.56	0.02	9.27

^a Ara, Arabinose; Gal, Galactose; Gal A, Galacturonic acid; Rha, Rhamnose.

Conclusion

The results of this study highlight grape ripening stage affected the concentration, composition and evolution of polysaccharides and oligosaccharide during the aging on lees of sparkling wines. Polysaccharides rich in arabinose and galactose and oligosaccharides were the two most prevalent carbohydrates detected in all vinification stages. More studies should be carried out to further investigate the possible influence that different polysaccharides and oligosaccharides from different grape maturity could have on the physico-chemical and sensory properties of sparkling wines.

Acknowledgements

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