Effect of grape polysaccharides on the volatile composition of red wines

Diego Canalejo[1*], Feng Zhao[1], Leticia Martínez-Lapuente[1], Belén Ayestarán[1], Silvia Pérez-Magariño[2], Estela Cano-Mozo[2], María Curiel Fernández[2] , Zenaida Guadalupe[1]

[1]Instituto de Ciencias de la Vid y del Vino (Universidad de la Rioja, Gobierno de La Rioja y CSIC), Finca La Grajera, Ctra. De Burgos Km 6, 26007 Logroño, La Rioja

[2]Instituto Tecnológico Agrario de Castilla y León, Consejería de Agricultura y Ganadería, Ctra. Burgos Km 119, 47071 Valladolid

*diego.canalejo@unirioja.es

INTRODUCTION

Grapes

PRAG
RG-II
HG
GP

Yeast

MP GL

CELL WALL POLYSACCHARIDES

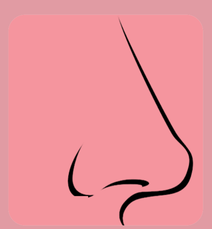
Commercially available

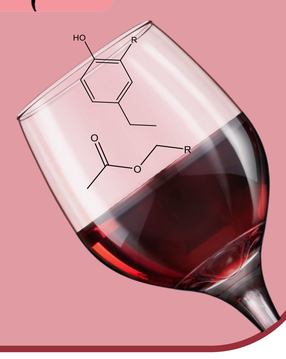
PRAG: polysaccharides rich in arabinose and galactose
RG-II : rhamnogalacturonans type II
HG: homogalacturonans
GP: glucosyl polysaccharides (cellulose y hemicellulose)
MP: mannoproteins or mannans
GL: glucans

WINE FINING

WINE QUALITY MODULATION

Increase the **volatility** of wine **aroma** compounds by interactions with **polysaccharides[1, 2]**.





OBJECTIVES

- In this study **polysaccharide extracts** obtained from **grape by-products** were used as **fining agents** at bottling in three wines from *Vitis vinifera* L. cv. Tempranillo (**TOB** and **UR**) and Graciano (**GRA**). Their effect on the volatile composition and profile was analyzed. Polysaccharides extracts were obtained from white pomace by-products (**WP**), red pomace by-products (**RP**), white must (**WM**), red must (**RM**), red wine (**RW**), and lees recovered after the winemaking (**RL**). Two more extracts with higher purification degrees were used: wine purified polysaccharides (**WPP**) and distilled washing residues (**DWRP**). The results were compared with a control (**C**) wine sample and with mannoproteins commercially available (**CM**).

MATERIAL AND METHODS

- The extracts were added in the wines as **fining agents** just **before bottling**. The **doses** used for the extracted fractions were defined by sensory analysis made by a group of **12 expert tasters**. The **doses selected** were **0.05 g L^{-1}** .
- The analysis of volatile compounds was performed using a **GC-MS** after **liquid-liquid extraction[3]**.
- A one-way analysis of variance (**ANOVA**) was performed to determine statistically significant differences among the wines treated with the different polysaccharide extracts.
- **Discriminant analyses** were performed to differentiate the red wines by the **fining extract** used.

RESULTS AND DISCUSSION

Table 1 shows the volatile concentration of **Graciano (GRA)** and **Tempranillo (TOB** and **UR)** wines and **Table 2** shows all the volatile compounds quantitated and grouped in their respective families. The extracts reduced the volatile concentration of most families in **TOB** and **UR** wines, except for **WM** in **UR** wines which concentration was higher than **C** wine. On the other hand, volatile composition in **GRA** wines did not show significant differences among the extracts and **C**, except for **RM** which concentration was the highest in most of the volatile families in this wine. Wines treated with **RL** and **CM** presented some of the highest concentrations after **C**. The wines treated with **WPP** and **DWRP** were those which presented the lowest concentrations on most of the volatile compounds detected in all wines. In the case of total terpenes and total phenols, the extracts showed different results. **RP**, **WP** and **WM** presented the highest concentration of phenols and terpenes in **GRA** and **RW** presented some of the highest concentration of these compounds in **TOB** and **UR**.

Discriminant analyses (**Figure 1**) showed that the use of the polysaccharide extracts modified the volatile composition of the wines. According to discrimination analyses, **WM**, **RM** and **CM** wines were characterized by **high** contents of **alcohols**, **C6 alcohols**, some esters as **ethyl isovalerate**, **acetates** and **acids**. On the other hand, **RW**, **RP**, and **RL** wines were characterized by **high** contents of ethyl esters as **ethyl lactate**, **ethyl hexanoate** and **ethyl octanoate** and volatile phenols, specially **4-vinylguaiacol** and **4-ethylguaiacol**. **Figure 1** shows three differentiated groups: **CM** and **RL**; **RW**, **WPP** and **DWRP**; and **WP**, **RP** and **WM**. The volatile profile of **RM** wines were the most similar to **C** wines.

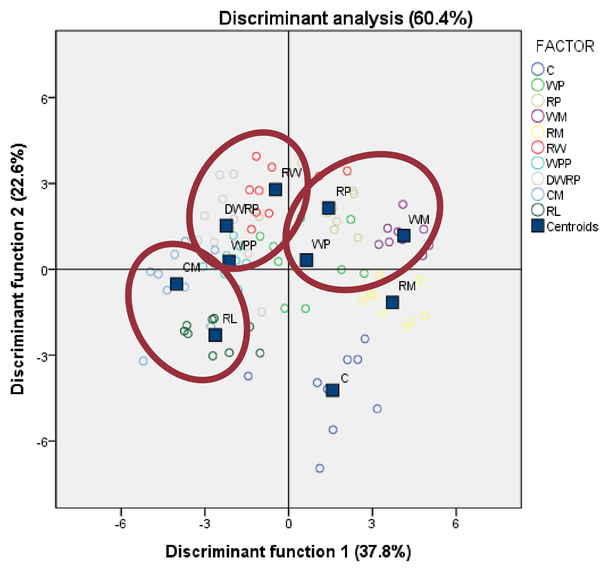


Figure 1: Discriminant analysis of the Tempranillo and Graciano volatile profiles

Table 1: Total volatile concentration (mg/L)[a] of Graciano (GRA) and Tempranillo (TOB and UR) wines treated with polysaccharides extracts as fining agents.

Wine	Extract [b]	TOTAL ALCOHOLS	TOTAL C6 ALCOHOLS	TOTAL ESTHERS	TOTAL ACETATES [c]	TOTAL ACIDS	TOTAL TERPENES [c]	TOTAL PHENOLS [c]
GRA	C	161.9 (17.1)**ab**	2.2 (0.5)**ab**	9.6 (1.8)**ab**	647.1 (227.0)**ab**	1.0 (0.5)**ab**	30.8 (1.5)**b**	208.8 (1.4)**c**
GRA	WP	169.1 (13.9)**ab**	2.6 (0.5)**ab**	10.12 (1.6)**ab**	810.6 (190.0)**ab**	1.4 (0.4)**ab**	31.8 (1.5)**bc**	235.9 (1.5)**f**
GRA	RP	145.4 (24.1)**a**	1.7 (0.5)**a**	7.6 (2.1)**a**	477.9 (166.5)**a**	0.9 (0.3)**a**	32.7 (0.4)**bc**	228.7 (6.9)**e**
GRA	WM	183.1 (18.7)**ab**	2.8 (0.7)**ab**	11.1 (3.4)**ab**	801.0 (183.8)**a**	1.4 (0.3)**a**	33.7 (0.1)**d**	217.5 (0.4)**d**
GRA	RM	257.9 (42.3)**c**	4.6 (1.6)**c**	17.9 (4.7)**c**	1464.4 (553.9)**c**	2.6 (0.9)**c**	32.5 (0.7)**bc**	190.4 (5.4)**b**
GRA	RW	182.9 (8.1)**ab**	2.9 (0.2)**ab**	11.4 (0.7)**ab**	848.6 (49.2)**ab**	1.57 (0.2)**ab**	33.0 (1.4)**cd**	170.1 (3.2)**a**
GRA	WPP	165.6 (20.7)**ab**	2.4 (0.4)**ab**	9.9 (1.5)**ab**	712.3 (114.8)**a**	1.3 (0.3)**a**	27.2 (1.4)**a**	165.2 (1.8)**a**
GRA	DWRP	149.1 (6.9)**a**	2.1 (0.3)**ab**	8.2 (0.6)**a**	672.7 (135.4)**a**	1.1 (0.3)**a**	28.3 (1.1)**a**	210.6 (3.2)**c**
GRA	CM	198.1 (24.8)**b**	3.2 (0.7)**b**	13.6 (2.5)**b**	1052.9 (128.4)**ab**	1.8 (0.3)**ab**	31.5 (0.2)**bc**	215.6 (2.8)**cd**
GRA	RL	169.8 (9.9)**ab**	2.5 (0.4)**ab**	10.5 (1.4)**ab**	789.3 (102.3)**ab**	1.36 (0.2)**ab**	31.3 (1.2)**bc**	236.9 (2.8)**f**
TOB	C	322.8 (30.0)**e**	6.3 (1.1)**c**	44.7 (9.6)**d**	1619.9 (230.1)**d**	6.1 (1.3)**c**	29.3 (0.1)**bc**	72.1 (0.9)**a**
TOB	WP	291.2 (8.5)**de**	4.8 (0.5)**ab**	37.3 (2.7)**bc**	1143.4 (80.6)**bc**	4.6 (0.3)**bc**	30.8 (0.1)**cd**	75.9 (1.0)**ab**
TOB	RP	238.5 (32.2)**ab**	4.2 (1.4)**ab**	31.8 (9.8)**ab**	868.3 (230.7)**ab**	3.6 (1.2)**ab**	33.2 (0.3)**d**	77.8 (0.3)**ab**
TOB	WM	253.9 (9.7)**abc**	2.6 (0.1)**a**	25.9 (0.8)**a**	760.9 (130.6)**a**	3.3 (0.6)**a**	27.3 (0.7)**b**	86.5 (3.9)**b**
TOB	RM	268.2 (23.4)**bcd**	4.3 (0.81)**ab**	33.3 (6.6)**ab**	870.0 (136.2)**ab**	3.7 (0.6)**a**	26.8 (0.3)**b**	86.9 (2.8)**b**
TOB	RW	269.5 (1.9)**bcd**	4.8 (0.4)**ab**	37.1 (5.6)**bc**	1101.2 (336.2)**bc**	4.2 (1.0)**ab**	31.4 (5.3)**cd**	100.5 (13.3)**cd**
TOB	WPP	228.1 (3.8)**a**	3.2 (0.1)**a**	26.7 (1.8)**a**	772.2 (41.2)**a**	3.2 (0.2)**a**	28.2 (1.4)**bc**	89.3 (2.6)**bc**
TOB	DWRP	278.2 (8.3)**cd**	4.2 (0.1)**ab**	35.0 (5.2)**ab**	964.7 (115.4)**ab**	4.1 (0.5)**ab**	27.2 (0.2)**b**	85.1 (3.5)**ab**
TOB	CM	302.5 (22.5)**de**	5.2 (0.9)**bc**	42.3 (5.9)**cd**	1224.6 (233.1)**c**	4.9 (0.9)**bc**	32.6 (5.1)**cd**	103.6 (16.6)**d**
TOB	RL	284.7 (17.4)**cd**	5.0 (0.9)**bc**	40.3 (9.7)**cd**	1026.6 (138.4)**bc**	4.2 (0.6)**ab**	22.2 (1.7)**a**	83.7 (3.8)**ab**
UR	C	411.5 (69.1)**cd**	4.3 (1.1)**cd**	24.2 (5.5)**de**	1823.9 (395.8)**de**	3.9 (1.2)**de**	20.3 (0.9)**a**	40.3 (1.1)**a**
UR	WP	240.2 (40.3)**ab**	2.2 (0.5)**a**	12.1 (2.6)**ab**	910.0 (211.7)**a**	1.91 (0.5)**a**	22.5 (0.1)**bc**	46.0 (0.5)**cd**
UR	RP	251.8 (35.1)**ab**	2.0 (0.5)**a**	10.5 (2.4)**ab**	786.6 (101.1)**a**	1.9 (0.5)**a**	22.5 (1.0)**bc**	44.8 (1.2)**c**
UR	WM	464.4 (101.7)**d**	5.3 (1.3)**d**	27.0 (6.6)**e**	2352.3 (492.5)**e**	4.9 (1.2)**e**	23.8 (0.7)**cd**	45.5 (0.1)**cd**
UR	RM	318.9 (52.6)**b**	2.8 (0.7)**ab**	14.7 (4.0)**cd**	1261.9 (234.0)**bc**	2.9 (0.7)**bc**	22.1 (0.5)**bc**	44.5 (0.5)**c**
UR	RW	266.3 (34.6)**ab**	2.5 (0.3)**a**	12.8 (2.5)**bc**	1073.4 (166.7)**ab**	2.2 (0.2)**ab**	25.3 (0.8)**e**	48.2 (1.0)**e**
UR	WPP	205.3 (21.4)**a**	1.7 (0.2)**a**	9.0 (1.6)**a**	697.6 (55.9)**a**	1.4 (0.1)**a**	22.9 (2.0)**c**	42.9 (0.8)**b**
UR	DWRP	185.5 (27.2)**a**	1.3 (0.3)**a**	6.9 (1.4)**a**	558.2 (149.7)**a**	1.2 (0.4)**a**	24.4 (0.8)**de**	45.0 (0.3)**c**
UR	CM	304.0 (24.3)**b**	2.8 (0.2)**ab**	15.9 (0.4)**bc**	1187.5 (150.1)**bc**	2.6 (0.3)**bc**	22.6 (0.8)**c**	46.5 (1.0)**d**
UR	RL	329.7 (5.5)**bc**	3.74 (0.4)**bc**	18.6 (1.6)**cd**	1622.2 (285.7)**cd**	3.4 (0.5)**cd**	20.7 (0.9)**ab**	43.1 (0.4)**b**

[a] All parameters are given with their standard deviation (n=3). Different letters in the same column indicate statistically significant differences ($p < 0.05$). A one-way analysis of variance (ANOVA) with the Duncan post-hoc test was used.
[b] Extracts obtained from the different matrix. WP: White Pomace; RP: Red Pomace; WM: White Must; RM: Red Must; RW: Red Wine; WPP: Wine Purified Polysaccharides; DWRP: Distilled Washing Residues; RL: Red Lees; CM: Commercial Mannoproteins.
[c] Total acetates, total terpenes and total phenols concentration expressed in µg/L.

Table 2: Volatile compounds of each family quantitated in every analyzed wine.

TOTAL ALCOHOLS	1-propanol
	Isobutanol
	2-methyl-1-butanol
	3-methyl-1-butanol
	Phenylethanol
TOTAL C6 ALCOHOLS	Hexanol
	(Z)-3-Hexenol
	(E)-3-Hexenol
	Benzyl-alcohol
TOTAL ETHYL ESTERS	Ethly-butyrate
	Ethyl-hexanoate
	Ethyl-octanoate
	Ethyl-decanoate
	Ethyl-2-methylbutyrate
	Ethyl-isovalerate
	Ethyl-lactate
TOTAL ACETATES	Propyl-acetate
	Isobutyl-acetate
	Isoamyl-acetate
	Hexyl-acetate
	Phenylethyl-acetate
TOTAL ACIDS	Methylbutanoic-acids
	Hexanoic-acid
	Octanoic-acid
	Decanoic-acid
TOTAL TERPENES	Linalool
	Terpineol
TOTAL PHENOLS	Citronellol
	Guaiacol
	4-vinylguaiacol
	4-ethylguaiacol
	4-vinylphenol
	4-ethylphenol
	Eugenol
	cis-Isoeugenol
	Dimethoxyphenol

CONCLUSIONS

Polysaccharide extracts obtained from grape by-products as fining agent could decrease the concentration of some undesirable volatile compounds such as acids in Tempranillo wines. The most purified polysaccharide extracts (WPP and DWRP) reduced the concentration of most of the volatile compounds, while RM, WM and RL wines presented similar or higher concentrations than wines treated with the commercial mannoproteins (CM). However, the effect of the extracts on Graciano wine were not as clear as Tempranillo wines. The results of the discriminant analyses showed that the wines treated with the extracts presented different volatile profile compared to C wines, so polysaccharide extracts modified the volatility of Tempranillo and Graciano wines.

Fining agent are commonly used in wine to reduce the concentration of undesirable compounds and to increase the concentration of desirable compounds. According to our results future studies will determine the proper polysaccharide purity and concentration to obtain the best fining results.

REFERENCES

1. Rinaldi, A., Gonzalez, A., Moio, L., & Gambuti, A. (2021). Commercial mannoproteins improve the mouthfeel and colour of wines obtained by excessive tannin extraction. Molecules, 26, 4133, https://doi.org/10.3390/molecules26144133.
2. Ribeiro, T., Fernandes, C., Nunes, F. M., Filipe-Ribeiro, L., & Cosme, F. (2014). Influence of the structural features of commercial mannoproteins in white wine protein stabilization and chemical and sensory properties. Food Chemistry, 159, 47–54. https://doi.org/10.1016/j.foodchem.2014.02.149.
3. Oliveira, J. M., Faria, M., Sá, F., Barros, F., & Araújo, I. M. (2006). C6-alcohols as varietal markers for assessment of wine origin. Analytica Chimica Acta, 563, 300–309. https://doi.org/10.1016/j.aca.2005.12.029.

ACKNOWLEDGEMENTS

The authors would like to thank the Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA) and the Ministerio de Ciencia e Innovación for the funding provided for this study through the project RTA2017-00005-C02-02.