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Effect of polyvinylpolypyrrolidone treatment on rosés wines during fermentation: impact on color, polyphenols and thiol aromas

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2 ABSTRACT

3 Fining treatment with polyvinylpolypyrrolidone (PVPP) is often used during winemaking of rosé wines. It can modulate the intensity and hue of their pink color and prevent some 4 organoleptic degradations. In this paper, the effect of PVPP treatments on rosé wine during 5 fermentation was investigated by measuring color, polyphenol content and thiol aromas. As 6 expected, colorimetry results showed a decrease in color, indicating some adsorption of 7 anthocyanins and other pigments. This was confirmed by UPLC-ESI-MS/MS analyses. 8 Specific adsorption of certain families of polyphenols was evidenced. Flavonols, flavanols 9 and anthocyanins, especially coumaroylated anthocyanins were preferentially adsorbed by 10 PVPP. Regarding the thiol content (3-mercaptohexyl acetate (3MHA) and 3-mercaptohexan-11 1-ol (3MH)), interestingly, their levels were usually higher after PVPP treatments, in a dose 12 dependent manner. A possible explanation is that the partial adsorption of some polyphenols 13 at an early stage of fermentation would later limit the amount of quinone compounds able to 14 trap thiol aromas. 15

- 17 Keywords:
- 18 Rosé wine

19 PVPP

- 20 Phenolic compounds
- 21 CIELAB
- 22 Multiple Reaction Monitoring MRM
- 23 Thiols
- 24

25 **1. Introduction**

In winemaking, fining is a process used to modulate and protect the organoleptic properties of 26 27 the wines and to ensure their physicochemical stability by preventing the formation of hazes and deposits (El Rayess et al., 2011). In practice, a fining agent is added to the wine and 28 29 adsorbs some molecules, like polyphenols, to create complexes that can be separated from the wine. Polyvinylpolypyrrolidone (PVPP) is regularly used to this purpose in alcoholic 30 beverage production like beer and wine (Doner, Bécard & Irwin, 1993; McMurrough, 31 32 Madigan & Smytht, 1995; Magalhães, Vieira, Goncalves, Pacheco, Guido & Barros, 2010). It is a partially cross-linked synthetic polymer of Polyvinylpyrrolidone PVP (Figure 1) known to 33 34 have polyphenol binding affinities.

Polyphenols are very important molecules in wines, responsible for quality and sensorial characteristics such as taste and color. However, in excess they may induce several problems regarding color and aroma. Anthocyanins, the red pigments extracted from grape are fragile molecules that can lose their color through oxidation (Lopez, Richard, Saucier, Teissedre, Monti & Glories, 2007). Chemical reactions of phenolic acids, flavanols and anthocyanins may form more stable orange pigments like xanthylium derivatives (Es-Safi, Guernevé,
Fulcrand, Cheynier & Moutounet, 2000; George, Clark, Prenzler & Scollary, 2006) or
pyranoanthocyanins (Sarni-Manchado, Fulcrand, Souquet, Cheynier & Moutounet, 1996; De
Freitas & Mateus, 2011; Vallverdú-Queralt et al., 2016).

In white or rosé wines, the oxidation of molecules, especially flavanols, may induce browning problems (Li, Guo & Wang, 2008). An excess of polyphenols can also negatively affect the aroma content of these wines. In fact, the oxidation of polyphenols leads to the formation of quinones that can irreversibly react with thiols, the varietal aromas, to form odorless adducts (Singleton 1987).

PVPP treatment is then often used to reduce the polyphenol content of wines in order to control these issues. It can be done at the grape must stage, during fermentation, or on finished wine. In practice, it is often done at the must or fermentation stage (Seabrook & van der Westhuizen, 2018). In fact, the oxidizable phenolics should be removed before any damage on aroma or color is caused, or at least as soon as possible to limit their negative impact.

In a previous work, the effect of PVPP on rosé wine color and polyphenol content was 55 investigated (Gil et al. 2017). Color measurements, and targeted polyphenomics using Liquid 56 57 Chromatography - Electrospray Ionization - Mass Spectrometry (UPLC-ESI-MS/MS) in Multiple Reaction Monitoring (MRM) mode (Lambert et al., 2015) were used. A decrease in 58 wine color was observed, confirming the adsorption of pigments. MS analysis showed 59 adsorption differences among polyphenol families. Flavonols (42%) and flavanols (64%) 60 were the most affected. Anthocyanins were not strongly adsorbed on average (12%), but a 61 62 specific adsorption of coumaroylated anthocyanins was observed (37%). Using molecular dynamics simulations, intermolecular interactions were studied in order to explain these 63 specific affinities. 64



Superstart® and incubated at 20 °C. Fermentation activities were monitored by weight loss as 84 an estimate of CO₂ production, and fining agents were added at the end of the third of the 85 alcoholic fermentation. For all experiments, the kinetic of fermentation were the same after 13 86 days and the end of the fermentation was confirmed by measurement of glucose and fructose 87 concentrations using clinitest. At the end of the fermentation the wine was treated with 5 g/hL 88 of a 10% SO₂ solution, maintained at 5 °C for a day, and filtered through a 3 µm glass fiber 89 filter. Five fining modalities were tested, a control without fining and four different PVPP 90 concentrations: 20, 40, 60, and 80 g/hL, the maximum legal use. All micro-fermentations 91 were done in triplicates on 2 different musts obtained directly from the press without any 92 maceration, blends of Grenache Noir from Villevielle Cellar (Gard) Languedoc-Roussillon 93 and Merlot from Vignobles Ducourt Bordeaux in different proportions (Rosé A: 70/30 and 94 Rosé B: 50/50). At the end of the vinification process, all the classical oenological parameters 95 96 were measured by the SARCO Lab (alcohol, pH, TA, residual sugar, AV, SO2) and no significant differences were measured. 1.5 mL samples were prepared and kept in closed 97 plastic Eppendorf at -80°C for further UPLC-ESI-MS/MS analyses. Before analyses, the 98 99 samples were thawed to room temperature and centrifuged before injection.

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2.3 Spectrophotometric L*a*b* measurements

Color analysis were performed on a spectrophotometer CM-3600d from KONICA 102 MINOLTA with a 1.0 cm length glass cell, between 360-740 nm with 10 nm pitch, and 103 piloted with the SpectraMagic[™] NX software. The CIELAB coordinates L*, a*, b* were 104 obtained using the D65 illuminant and a 10° observer. The CIELAB is a color space defined 105 in 1976 (ISO 11664-4: 2008). In this three dimension system, the L* axis indicates the 106 lightness which value extends from 0 (black) to 100 (white), the a* and b* axes represent the 107 chromaticity. Coordinate a* has positive values for red colors and negative values for green 108 109 colors. Coordinate b* has positive values for yellow colors and negative values for blue colors. (Hernández, Sáenz, Alberdi, Alfonso & Diñeiro, 2011; Korifi, LeDréau, Antinelli, 110 111 Valls & Dupuy, 2013).

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2.4 UPLC-ESI-MS/MS parameters

114 Polyphenol analyses were performed with a Waters Acquity UPLC system connected to a triple quadrupole mass spectrometer equipped with an electrospray ionization source (ESI) 115 operating in switching positive and negative mode. The UPLC system included a binary 116 pump, a cooled autosampler maintained at 7 °C and equipped with a 5 µL sample loop, a 100 117 µL syringe and a 30 µL needle, a thermostated column department, and a DAD detector. 118 MassLynx software was used for instrument control and data acquisition and TargetLynx 119 software was used for data processing. Quantitative analyses were performed by UPLC-ESI-120 MS/MS using the Multiple Reaction Monitoring (MRM) detection mode under the conditions 121 (HPLC elution conditions, MS and MRM parameters, calibration standards) described in 122 Lambert et al (2015). 123

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125 **2.5 Thiol quantification**

Volatile thiol quantifications were performed by the wine analysis laboratory Sarco 126 (Bordeaux, France) with this protocol: From 50 mL of the previously described wine, as 127 described by Tominaga & Dubourdieu (2006), 4-methyl-4-sulfanylpentan-2-one (4MSP), 3-128 sulfanylhexan-1-ol (3SH), and 3-sulfanylhexyl acetate (3SHA) were specifically extracted by 129 reversible combination of the thiols with sodium-p-hydroxymercuribenzoate. They were then 130 quantified by gas chromatography-mass spectrometry using methods described by Tominaga, 131 Furrer, Henry & Dubourdieu (1998a), and Tominaga & Dubourdieu (2000). The aromatic 132 indexes are then calculated by dividing the concentration by the perception threshold. For 133 3MH and 3MHA, the perception threshold values are 60 ng/L and 4 ng/L respectively. 134

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2.6 Statistical analyses

All the experiments were carried out in triplicate (biological replicates). Statistical analyses, 137 138 including means, standard deviations, variance analysis (ANOVA), were performed using Excel (Microsoft, Redmond, WA, USA). 139

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3. Results and discussions

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3.1 Effect of PVPP on rosé wine colors

As expected, the CIELAB coordinates of the studied wines were modified by the PVPP 143 treatments. The average values of the different color coordinates measured on the control 144 wines and after all treatments are reported in Table 1. 145

		Control	PVPP	PVPP	PVPP	PVPP
		Control	20 g/hL	40 g/hL	60 g/hL	80 g/hL
L*	Rosé A	91.2 ± 0.1	92.7 ± 0.1	93.5 ± 0.01	93.7 ± 0.1	94.1 ± 0.1
		d	с	b	b	а
	Rosé B	90.1 ± 0.03	91.8 ± 0.04	92.7 ± 0.04	93.0 ± 0.1	93.3 ± 0.1
		e'	d'	c'	b'	a'
a*	Rosé A	5.06 ± 0.12	3.95 ± 0.17	3.15 ± 0.02	3.00 ± 0.14	2.64 ± 0.06
		а	b	с	cd	d
	Rosé B	6.29 ± 0.08	4.99 ± 0.10	4.26 ± 0.13	3.97 ± 0.11	3.70 ± 0.06
		a'	b'	c'	c'd'	d'

b*	Rosé A	7.16 ± 0.17	5.07 ± 0.06	4.20 ± 0.06	3.86 ± 0.16	3.58 ± 0.09
		a	b	с	cd	d
	Rosé B	8.43 ± 0.08	6.00 ± 0.17	4.92 ± 0.09	4.41 ± 0.08	4.09 ± 0.12
		a'	b'	C'	ď	d'
ΔE with Control	Rosé A		2.79	4.22	4.64	5.19
	Rosé B		3.21	4.78	5.46	5.96

146Table 1. Average CIELAB coordinates measured in the wines after PVPP treatment. Within each line,

147 *a to e represent the groups identified in an ANOVA statistical test with a confidence interval of 99%.*

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In all treatments, the lightness L* have increased. On the contrary, both a* and b* coordinates 149 decreased, implying a reduction of red and yellow color components respectively. This 150 reflects adsorption of color active polyphenol, such as anthocyanins and their derivatives and 151 flavonols, as described earlier (Gil et al. 2017). Besides pigment adsorption, the color drop 152 153 can also be related to the reduction of the copigmentation effect by adsorption of copigments (Boulton, 2001; Gutiérrez, Lorenzo & Espinosa, 2005). Regarding b* values, an adsorption of 154 orange aging pigments (Guyot, Vercauteren & Chevnier, 1996; Simpson, 1982; Chevnier, 155 Rigaud, Souquet, Barillere, & Moutounet, 1989; Oliveira, Silva Ferreira, De Freitas, & Silva, 156 2011; Es-Safi et al., 2000; Sarni-Manchado et al., 1996; De Freitas et al., 2011; Vallverdú-157 Queralt et al., 2016) by PVPP may also explain the decrease observed. 158

159 Regarding the efficiency of the treatment, the discoloration effect increased with the PVPP160 dose used.

In the CIELAB color space, ΔE is a parameter illustrating the difference of colors between two samples. It is calculated as $\sqrt{[(L_1*-L_2)^2+(a_1*-a_2*)^2+(b_1*-b_2*)^2]}$, if this value is greater than 1, a color difference can be perceived by the human eye, and the higher the ΔE value, the easier it is to notice the color difference (Wojciech & Maciej, 2011).

165 In our study, in all cases, the ΔE value between the colors of the control and the treated wine 166 is greater than 1 (Table 1) meaning that a standard observer can see a difference in color. At

167	20 g/hL, 2 < ΔE < 3,5, all observers can see the difference, experienced or not. For medium
168	PVPP concentrations, $3,5 \le \Delta E \le 5$, a clear difference in color is noticed. For the highest
169	concentrations, $\Delta E > 5$, the observers will see two different colors.
170	
171	3.2 Effect of PVPP on the polyphenol composition of rosé wines
172	
173	The polyphenol composition of the wines was determined by UPLC-ESI-MS/MS using the
174	MRM detection mode under the conditions described in Lambert et al (2015). The
175	concentrations of the different families and associated statistics are available in Appendix 1.
176	Among the seven studied polyphenol families (benzoic acids, hydroxycinnamic acids,
177	stilbenes, flavonols, flavanols, dihydroflavonols, anthocyanins), mainly three were affected by
178	PVPP fining: flavonols, flavanols (especially dimers and trimmers) and anthocyanins
179	(especially coumaroylated anthocyanins).



Figure 2. Concentration before and after fining of flavonols (A), flavanols (B), anthocyanins (C) and
coumaroylated anthocyanins (D). Within each line, a to e represent the groups identified in an
ANOVA statistical test with a confidence interval of 99%.

These concentrations drops can be related to the diminution of the CIELAB a* and b* 184 185 components. Actually, these three families are known to play a major role in wine color. Anthocyanins are the major red grape pigments in young red or rosé wines and flavonols are 186 yellow grape pigments (Jeffery, Parker & Smith, 2008) that can favor the copigmentation 187 effect by enhancing the redness of anthocyanins (Boulton, 2001). Flavanols are easily 188 oxidized compounds inducing browning and appearance of orange pigments (Es-Safi et al., 189 2000; George et al., 2006). For all those reasons, the diminution of these compounds is 190 immediately leading to a yellow and red color decrease. 191

These results are similar to those found in our previous published work (Gil et al. 2017) where the PVPP treatments were done on commercial rosé wines. The selectivity of PVPP towards polyphenols seems to be similar whether the fining treatment occurs during fermentation or after fermentation on finished wines.

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3.3 Effect of PVPP on the thiol composition of rosé wines

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Grapes used to make rosé wines possess some odorless molecules, called varietal precursors which are able to generate odoriferous compounds during winemaking: the varietal aromas (Roland, Schneider, Razungles & Cavelier, 2011; Murat, Tominaga, & Dubourdieu, 2001).Some of the main varietal aromas are 4-mercapto-4-methylpentan-2-one (4MMP), 3mercaptohexyl acetate (3MHA), and 3-mercaptohexan-1-ol (3MH). These varietal thiols are released during alcoholic fermentation from the cleavage of odorless precursors identified in grapes and musts (Ribéreau-Gayon, Glories, Maujean & Dubourdieu, 2006).

Three important varietal thiols were quantified and the detailed aromatic indexes and associated statistics are available in Appendix 1. 4MMP was not detected in our wines. The

208 PVPP treatments had a clear impact on 3MHA and 3MH, as shown in Figure 2 and detailed in



Appendixes 1 and 2.

Figure 3. Evolution of the aromatic indexes before and after PVPP fining. Within each line, a to c
represent the groups identified in an ANOVA statistical test with a confidence interval of 99%.

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At low PVPP concentrations (20 to 40 g/hL), there was a significant gain in thiol compounds 214 and their aromatic indexes. A possible explanation is that the removal of some polyphenols at 215 216 the early stage of fermentation would reduce the amount of quinones generated by oxidation during later stages of fermentation. A similar amount of thiol aroma from precursors would be 217 218 released but less would be trapped by quinones to form adducts (Nikolantonaki, Chichuc, Teissedre & Darriet, 2010). At higher concentration, the gain in thiol was more limited, 219 suggesting that another phenomenon is taking place. A possible explanation is that PVPP 220 221 would adsorb glutathione-S-conjugates aroma precursors, thus reducing the aroma content on the finished wine. The optimum dose for the PVPP treatment observed in our experiments 222 would then be the balance between two specific adsorption phenomena (quinones on one side 223 224 and glutathione-S-conjugates on the other side).

226

4. Conclusions

The effect of PVPP treatments on rosé wines during early stages of fermentation was 227 investigated. A clear effect on color and polyphenol adsorption was observed and increased 228 with the PVPP concentration used. Some polyphenol families or sub-families had specific 229 affinities for PVPP. A clear effect on thiol aroma in the corresponding finished wines was 230 evidenced for the first time in our study. The gain in thiol compounds observed was PVPP 231 dose dependent. An optimum dose, non-correlated with the color removal effect was 232 233 measured. Further research is needed to explain this dose-dependent effect of PVPP treatment during fermentation on thiol release in the corresponding finished wines. 234

235

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240 Declarations of interest: none.

Appendix

			Rosé A			
		Control	PVPP 20 g/hL	PVPP 40 g/hL	PVPP 60 g/hL	PVPP 80 g/hL
	Analyses	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
	Hydroxycinnamic acids	29.09 ± 0.91 ab	30.30 ± 1.16 a	28.50 ± 1.04 ab	28.53 ± 1.02 ab	26.03 ± 0.12 b
	Benzoic acids	3.29 ± 0.05 a	3.31 ± 0.17 a	3.00 ± 0.15 ab	2.88 ± 0.16 ab	2.79 ± 0.10 b
	All anthocyanins	43.65 ± 1.11 a	41.60 ± 1.13 ab	40.43 ± 1.08 bc	39.15 ± 0.52 bc	38.38 ± 0.43 c
Р	Anthocyanins 3-O-Glc	31.16 ± 0.74 a	30.20 ± 0.83 a	29.52 ± 0.88 a	28.79 ± 0.62 a	28.64 ± 0.56 a
0	Anthocyanins 3-O-acetyl Glc	9.58 ± 0.27 a	9.22 ± 0.28 ab	9.22 ± 0.11 ab	8.92 ± 0.15 ab	8.59 ± 0.12 b
L Y	Anthocyanins 3-O-coumaroyl Glc	2.27 ± 0.10 a	1.63 ± 0.07 b	1.18 ± 0.06 c	$0.90 \pm 0.04 \text{ d}$	$0.66 \pm 0.01 \text{ e}$
P	Anthocyanins 3,5-di-O-Glc	$0.43 \pm 0.05 \text{ a}$	0.37 ± 0.06 a	0.37 ± 0.09 a	0.39 ± 0.08 a	0.31 ± 0.13 a
H	Pyranoanthanthocyanins	0.21 ± 0.03 a	0.18 ± 0.03 a	0.14 ± 0.02 a	0.15 ± 0.04 a	0.18 ± 0.06 a
E N	Dihydroflavonols	0.46 ± 0.06 a	0.33 ± 0.06 a	0.46 ± 0.20 a	$0.35 \pm 0.06 \text{ a}$	0.28 ± 0.02 a
	Flavonols	7.05 ± 0.29 a	5.07 ± 0.37 b	4.00 ± 0.40 bc	3.25 ± 0.21 cd	$2.31 \pm 0.43 \text{ d}$
L	Stilbenes	1.82 ± 0.03 a	1.48 ± 4.00 a	1.85 ± 0.46 a	2.01 ± 0.02 a	1.52 ± 0.30 a
S	Flavanols	13.63 ± 1.05 a	5.18 ± 3.07 b	3.07 ± 0.23 c	$2.52 \pm 0.40 \text{ c}$	$2.18 \pm 0.21 \text{ c}$
(mg/L)	Flavanols: monomers	4.51 ± 0.29 a	3.16 ± 2.35 b	2.35 ± 0.35 bc	1.91 ± 0.20 c	1.90 ± 0.19 c
	Flavanols: dimers	7.54 ± 0.58 a	$1.58 \pm 0.50 \text{ b}$	0.50 ± 0.18 bc	$0.21 \pm 0.08 \ c$	$0.10 \pm 0.04 \text{ c}$
	Flavanols: trimers	1.41 ± 0.19 a	$0.27 \pm 0.10 \ \mathbf{b}$	$0.10 \pm 0.01 \ \mathbf{b}$	$0.10 \pm 0.01 \ \mathbf{b}$	$0.08 \pm 0.01 \ \mathbf{b}$
	Ethyl bridged tannins	0.16 ± 0.02 a	0.17 ± 0.12 a	$0.12 \pm 0.03 \ a$	0.30 ± 0.18 a	0.11 ± 0.04 a
CIELAB	L*	$91.2 \pm 0.1 \text{ d}$	92.7 ± 0.1 c	93.5 ± 0.01 b	93.7 ± 0.1 b	94.1 ± 0.1 a
	a*	5.06 ± 0.12 a	3.95 ± 0.17 b	$3.15 \pm 0.02 \text{ c}$	3.00 ± 0.14 c, d	$2.64 \pm 0.06 \text{ d}$
	b*	7.16 ± 0.17 a	5.07 ± 4.20 b	4.20 ± 0.06 c	3.86 ± 0.16 c , d	$3.58 \pm 0.09 \text{ d}$
Thiols (Aromatic	3MH	$2.77 \pm 0.21 \text{ c}$	4.97 ± 0.15 a	5.10 ± 0.10 a	3.57 ± 0.15 b	3.50 ± 0.10 b
index)	3MHA	0.60 ± 0.17 b	1.10 ± 0.17 a	1.00 ± 0.00 a , b	0.87 ± 0.12 a , b	0.80 ± 0.00 a , b

241 Appendix 1. Analytical results and statistics for Rosé A. a to e represent the groups identified in an ANOVA statistical test with a confidence interval of 99%.

			Rosé B			
		Control	PVPP 20 g/hL	PVPP 40 g/hL	PVPP 60 g/hL	PVPP 80 g/hL
	Analyses	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
_	Hydroxycinnamic acids	28.21 ± 2.27 a'	26.25 ± 1.02 a'	26.30 ± 1.29 a'	25.36 ± 0.53 a'	25.92 ± 1.61 a'
	Benzoic acids	3.25 ± 0.08 a'	2.91 ± 0.27 ab'	2.65 ± 0.14 b'	2.68 ± 0.03 ab'	2.34 ± 0.19 b'
	All anthocyanins	52.55 ± 0.98 a'	49.24 ± 0.47 ab'	45.75 ± 1.76 bc'	44.46 ± 0.92 c'	43.52 ± 1.60 c'
P	Anthocyanins 3G	34.80 ± 0.34 a'	33.10 ± 0.38 ab'	31.21 ± 0.93 bc'	30.72 ± 0.49 c'	30.19 ± 1.36 c'
U I	Anthocyanins 3G acétyl	13.36 ± 0.41 a'	13.06 ± 0.05 ab'	12.29 ± 0.58 ab'	11.96 ± 0.43 b'	11.79 ± 0.15 b'
Y L Y	Anthocyanins 3G coumaroyl	3.48 ± 0.16 a'	2.42 ± 0.04 b'	1.57 ± 0.08 c'	1.18 ± 0.07 d'	$0.92 \pm 0.02 \text{ d'}$
P	Anthocyanins diGlc	0.64 ± 0.07 a'	0.37 ± 0.06 a'	0.47 ± 0.16 a'	0.40 ± 0.07 a'	0.37 ± 0.09 a'
Н	Pyranoanthanthocyanins	0.26 ± 0.03 a'	0.28 ± 0.03 a'	0.20 ± 0.04 a'	0.21 ± 0.05 a'	0.24 ± 0.02 a'
E	Dihydroflavonols	0.32 ± 0.06 a'	0.39 ± 0.09 a'	0.31 ± 0.05 a'	0.30 ± 0.15 a'	0.40 ± 0.05 a'
Ν	Flavonols	5.74 ± 0.25 a'	4.28 ± 0.44 ab'	3.01 ± 0.46 bc'	2.32 ± 0.40 c'	2.30 ± 0.10 c'
O	Stilbenes	2.53 ± 0.36 a'	2.41 ± 0.37 a'	2.55 ± 0.30 a'	2.25 ± 0.31 a'	1.99 ± 0.34 a'
L	All flavanols	18.34 ± 1.53 a'	7.11 ± 0.29 b'	4.32 ± 0.21 bc'	3.79 ± 0.23 c'	3.33 ± 0.92 c'
S (mg/L)	Flavanols: monomers	6.74 ± 0.54 a'	4.82 ± 0.45 b'	3.43 ± 0.18 bc'	3.35 ± 0.19 bc'	2.94 ± 0.89 c'
(IIIg/L)	Flavanols: dimers	9.44 ± 1.18 a'	1.86 ± 0.68 b'	0.73 ± 0.07 b'	0.24 ± 0.03 b'	0.19 ± 0.07 b'
	Flavanols: trimers	2.02 ± 0.05 a'	0.31 ± 0.02 b'	0.09 ± 0.02 c'	0.10 ± 0.04 c'	0.09 ± 0.01 c'
	Ethyl bridged tannins	0.14 ± 0.03 a'	0.13 ± 0.03 a'	0.09 ± 0.02 a'	0.10 ± 0.04 a'	0.10 ± 0.03 a'
CIELAB Thiols (Aromatic index)	L*	90.1 ± 0.03 e'	91.8 ± 0.04 d'	92.7 ± 0.04 c'	93.0 ± 0.1 b'	93.3 ± 0.1 a'
	a*	6.29 ± 0.08 a'	4.99 ± 0.10 b'	4.26 ± 0.13 c'	3.97 ± 0.11 c, d'	3.70 ± 0.06 d'
	b*	8.43 ± 0.08 a'	6.00 ± 0.17 b'	4.92 ± 0.09 c'	4.41 ± 0.08 d'	4.09 ± 0.12 d'
	3MH	1.97 ± 0.15 c'	3.30 ± 0.10 a'	2.77 ± 0.21 b'	2.00 ± 0.10 c'	1.80 ± 0.10 c'
	3MHA	0.60 ± 0.17 c'	1.43 ± 0.12 a'	1.43 ± 0.12 a'	1.20 ± 0.17 a', b'	0.87 ± 0.12 b', c'

243 Appendix 2. Analytical results and statistics for Rosé B. a' to e' represent the groups identified in an ANOVA statistical test with a confidence interval of 99%.

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335 Figure captions

336 Figure 1. Structure of PVPP

Figure 2. Concentration before and after fining of flavonols (A), flavanols (B), anthocyanins
(C) and coumaroylated anthocyanins (D). Within each line, a to e represent the groups
identified in an ANOVA statistical test with a confidence interval of 99%.

- Figure 3. Evolution of the aromatic indexes before and after PVPP fining. Within each line, a to
 c represent the groups identified in an ANOVA statistical test with a confidence interval of
 99%.
- 343 Table 1. Average CIELAB coordinates measured in the wines after PVPP treatment. Within
- each line, a to e represent the groups identified in an ANOVA statistical test with a confidenceinterval of 99%.
- Appendix 1. Analytical results and statistics for Rosé A. a to e represent the groups identifiedin an ANOVA statistical test with a confidence interval of 99%.
- 348 Appendix 2. Analytical results and statistics for Rosé B. a to e represent the groups identified
- in an ANOVA statistical test with a confidence interval of 99%.

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