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

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1

2 **ABSTRACT**

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

16

17 Keywords:
18 Rosé wine
19 PVPP
20 Phenolic compounds
21 CIELAB
22 Multiple Reaction Monitoring - MRM
23 Thiols

24

25 **1. Introduction**

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

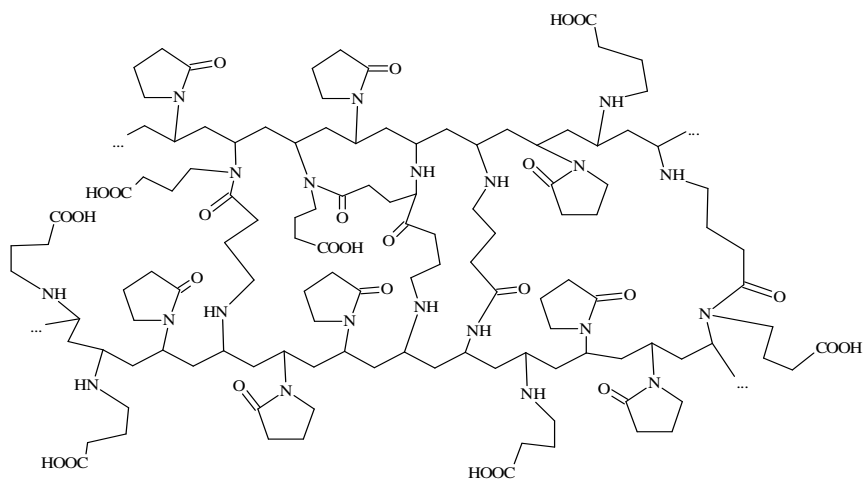
35 Polyphenols are very important molecules in wines, responsible for quality and sensorial
36 characteristics such as taste and color. However, in excess they may induce several problems
37 regarding color and aroma. Anthocyanins, the red pigments extracted from grape are fragile
38 molecules that can lose their color through oxidation (Lopez, Richard, Saucier, Teissedre,
39 Monti & Glories, 2007). Chemical reactions of phenolic acids, flavanols and anthocyanins

40 may form more stable orange pigments like xanthylium derivatives (Es-Safi, Guernevé,
41 Fulcrand, Cheynier & Moutounet, 2000; George, Clark, Prenzler & Scollary, 2006) or
42 pyranoanthocyanins (Sarni-Manchado, Fulcrand, Souquet, Cheynier & Moutounet, 1996; De
43 Freitas & Mateus, 2011; Vallverdú-Queralt et al., 2016).

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

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

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



65

66

Figure 1. Structure of PVPP

67

68 This initial work was done on commercial rosé wines, while in practice the fining process is
 69 often realised during fermentation. The goal of the present paper was to study the effect of
 70 PVPP on color, polyphenol content and thiol aroma compounds, when the treatment is
 71 performed at the early fermentation stage for rosé wines.

72

73 2. Material and methods

74

2.1 Chemicals

75 All chemicals were of analytical reagent grade. HPLC grade methanol and formic acid were
 76 obtained from Sigma-Aldrich (Saint-Quentin Fallavier, France). Deionized water was
 77 obtained from a Milli-Q Advantage A10 purification system from Millipore (Fontenay sous
 78 Bois, France). Zymaflore® X5, Superstart® and PVPP samples were obtained from Laffort
 79 (Bordeaux, France).

80

81 2.2 Wines and sample preparation

82 300 mL of must from free run juice conserved by congelation with a level of turbidity of 200
 83 NTU were inoculated using Zymaflore® X5 at 20 g/hL (equivalent to 200 mg/L) and 30 g/hL

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

100

101

2.3 Spectrophotometric L*a*b* measurements

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

112

113 **2.4 UPLC-ESI-MS/MS parameters**

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

124

125 **2.5 Thiol quantification**

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

135

136 **2.6 Statistical analyses**

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

140

141 **3. Results and discussions**

142 **3.1 Effect of PVPP on rosé wine colors**

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

| | | Control | PVPP 20 g/hL | PVPP 40 g/hL | PVPP 60 g/hL | PVPP 80 g/hL |
|----|--------|--------------------------|--------------------------|--------------------------|----------------------------|--------------------------|
| L* | Rosé A | 91.2 ± 0.1 d | 92.7 ± 0.1 c | 93.5 ± 0.01 b | 93.7 ± 0.1 b | 94.1 ± 0.1 a |
| | Rosé B | 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* | Rosé A | 5.06 ± 0.12 a | 3.95 ± 0.17 b | 3.15 ± 0.02 c | 3.00 ± 0.14 cd | 2.64 ± 0.06 d |
| | Rosé B | 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* | Rosé A | 7.16 ± 0.17 a | 5.07 ± 0.06 b | 4.20 ± 0.06 c | 3.86 ± 0.16 cd | 3.58 ± 0.09 d |
| | Rosé 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' |
| ΔE with Control | Rosé A | | 2.79 | 4.22 | 4.64 | 5.19 |
| | Rosé B | | 3.21 | 4.78 | 5.46 | 5.96 |

146 *Table 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%.*

148

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

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

161 In the CIELAB color space, ΔE is a parameter illustrating the difference of colors between
162 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
163 1, a color difference can be perceived by the human eye, and the higher the ΔE value, the
164 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, $2 < \Delta E < 3,5$, all observers can see the difference, experienced or not. For medium
168 PVPP concentrations, $3,5 < \Delta E < 5$, a clear difference in color is noticed. For the highest
169 concentrations, $\Delta E > 5$, the observers will see two different colors.

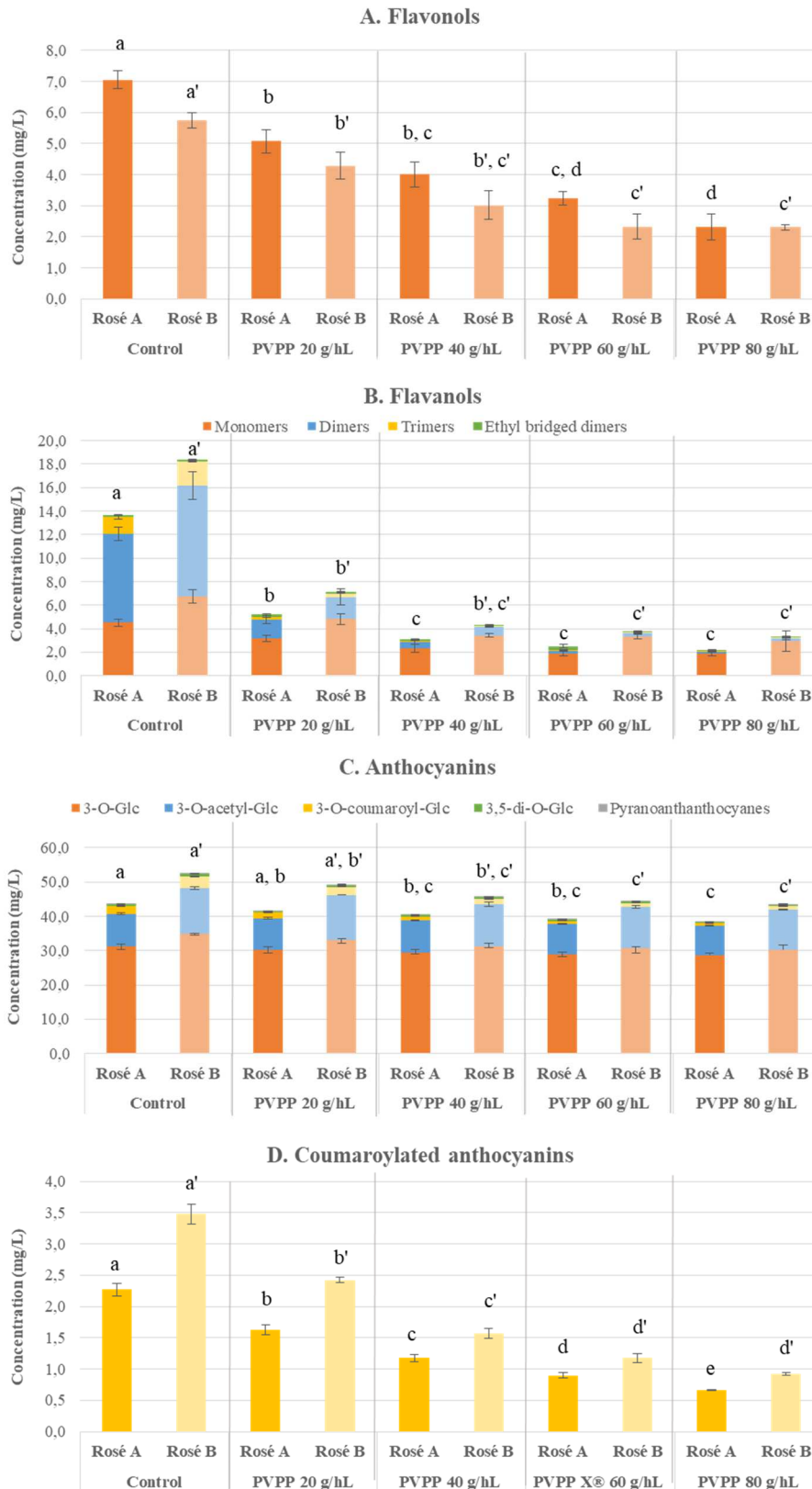
170

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).



180

181 *Figure 2. Concentration before and after fining of flavonols (A), flavanols (B), anthocyanins (C) and*

182 *coumaroylated anthocyanins (D). Within each line, a to e represent the groups identified in an*

183 *ANOVA statistical test with a confidence interval of 99%.*

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

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

196

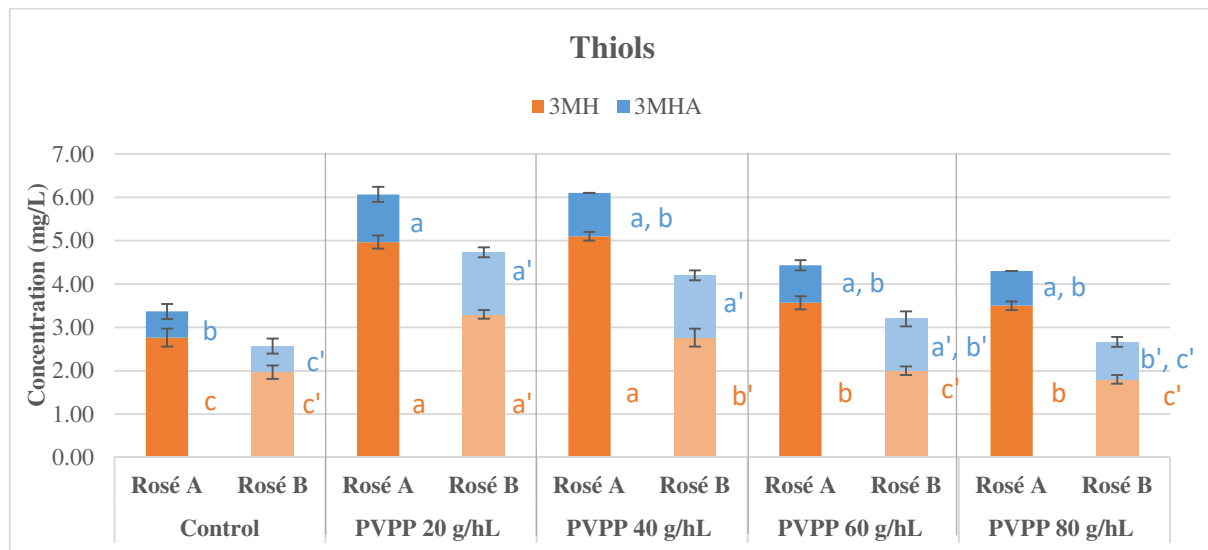
197 **3.3 Effect of PVPP on the thiol composition of rosé wines**

198

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

206 Three important varietal thiols were quantified and the detailed aromatic indexes and
207 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
 209 Appendixes 1 and 2.



210

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

213

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

225

226 **4. Conclusions**

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

235

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238 ESI-MS/MS analysis at the Plateforme Polyphenol (PFP) of our unit.

239 The authors would like to thank the Biolaffort Company for funding.

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 |
| P O L Y P H E N O L S (mg/L) | 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 |
| | 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 |
| | 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 |
| | Anthocyanins 3-O-coumaroyl Glc | 2.27 ± 0.10 a | 1.63 ± 0.07 b | 1.18 ± 0.06 c | 0.90 ± 0.04 d | 0.66 ± 0.01 e |
| | Anthocyanins 3,5-di-O-Glc | 0.43 ± 0.05 a | 0.37 ± 0.06 a | 0.37 ± 0.09 a | 0.39 ± 0.08 a | 0.31 ± 0.13 a |
| | Pyranoanthocyanins | 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 |
| | Dihydroflavonols | 0.46 ± 0.06 a | 0.33 ± 0.06 a | 0.46 ± 0.20 a | 0.35 ± 0.06 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 ± 0.43 d |
| | 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 |
| | Flavanols | 13.63 ± 1.05 a | 5.18 ± 3.07 b | 3.07 ± 0.23 c | 2.52 ± 0.40 c | 2.18 ± 0.21 c |
| | 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 ± 0.50 b | 0.50 ± 0.18 bc | 0.21 ± 0.08 c | 0.10 ± 0.04 c |
| Flavanols: trimers | 1.41 ± 0.19 a | 0.27 ± 0.10 b | 0.10 ± 0.01 b | 0.10 ± 0.01 b | 0.08 ± 0.01 b | |
| Ethyl bridged tannins | 0.16 ± 0.02 a | 0.17 ± 0.12 a | 0.12 ± 0.03 a | 0.30 ± 0.18 a | 0.11 ± 0.04 a | |
| CIELAB | L* | 91.2 ± 0.1 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 ± 0.02 c | 3.00 ± 0.14 c, d | 2.64 ± 0.06 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 ± 0.09 d |
| Thiols (Aromatic index) | 3MH | 2.77 ± 0.21 c | 4.97 ± 0.15 a | 5.10 ± 0.10 a | 3.57 ± 0.15 b | 3.50 ± 0.10 b |
| | 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 I. 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 |
| P O L Y P H E N O L S (mg/L) | 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' |
| | 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' |
| | 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' |
| | 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 ± 0.02 d' |
| | 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' |
| | Pyranoanthocyanins | 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' |
| | 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' |
| | 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' |
| | 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' |
| | 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' |
| | 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' |
| | 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 | 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' |
| Thiols (Aromatic index) | 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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334

335 **Figure captions**

336 Figure 1. Structure of PVPP

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

340 Figure 3. Evolution of the aromatic indexes before and after PVPP fining. Within each line, a to
341 c represent the groups identified in an ANOVA statistical test with a confidence interval of
342 99%.

343 Table 1. Average CIELAB coordinates measured in the wines after PVPP treatment. Within
344 each line, a to e represent the groups identified in an ANOVA statistical test with a confidence
345 interval of 99%.

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

350

351