

## New Method for Reducing the Binding Power of Sweet White Wines

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Sulfur dioxide is now considered to be a toxic chemical by most world health authorities. However, it remains an irreplaceable additive in enology for wine conservation, combining antioxidant and antibacterial properties. Sweet white wines from botrytized grapes retain particularly high SO<sub>2</sub> levels due to their high sulfur dioxide binding power. This paper presents a new method for reducing this binding power by removing some of the carbonyl compounds responsible, which are naturally present in these wines. The main carbonyl compounds responsible for the SO<sub>2</sub> binding power of sweet wines were removed, that is, acetaldehyde, pyruvic acid, 2-oxoglutaric acid, and 5-oxofructose. The method retained was selective liquid–solid removal, using phenylsulfonylhydrazine as a scavenging agent. The scavenging function was grafted on different classes of porous polymer supports, and its efficiency was evaluated on sweet white wines under conditions intended to conserve their organoleptic qualities. The results obtained showed that the method was efficient for removing carbonyl compounds and significantly reduced the binding power of the wines. Sensory analysis revealed that this process did not deteriorate their organoleptic qualities.

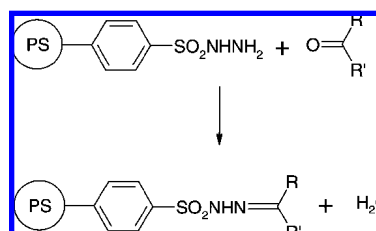
**KEYWORDS:** Carbonyl compound; sulfur dioxide; sweet wines; selective liquid–solid extraction.

### INTRODUCTION

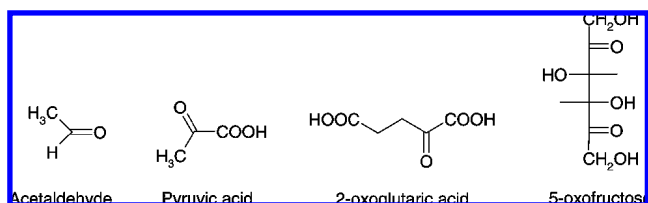
Sulfur dioxide, the most widely used additive in enology (1), is indispensable for wine conservation, thanks to a combination of antioxidant and antibacterial properties. Sulfur dioxide, either in its free form or as carbonyl bisulfites, presents a toxicity level that has led health authorities to regulate acceptable levels in wine. Nowadays, sweet white wines from botrytized grapes are among those with the highest SO<sub>2</sub> level. We developed a new methodology using model media, based on selective liquid–solid extraction, to reduce the binding power of wines (2, 3). Some of the carbonyl compounds responsible for SO<sub>2</sub> binding power (4) were removed using phenylsulfonylhydrazine grafted on an insoluble support, via a heterogeneous reaction preserving the wine's organoleptic properties (Scheme 1) (5–8). Good results were obtained by removing acetaldehyde, pyruvic acid, and 2-oxoglutaric acid under operating conditions similar to those

applied in winemaking (2). Wine is a very complex medium. It was necessary to prove the efficiency of this new method in wine before its implementation in the winemaking process could

**Scheme 1.** Polymer-Grafted Phenylsulfonylhydrazine Carbonyl Compound Removal Reaction



**Scheme 2.** Removed Carbonyl Compound Structures Support Functionalization Reactions



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Scheme 3. Support Functionalization Reactions

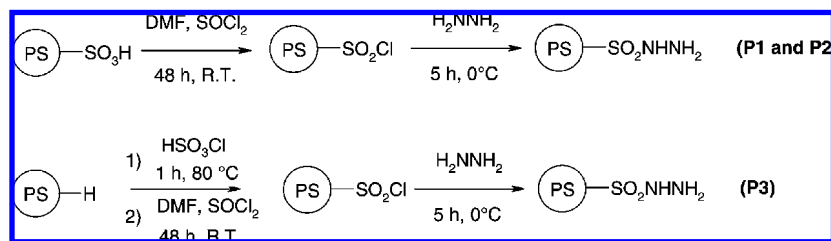


Table 1. Results of Grafting the Phenylsulfonylhydrazine Removal Function on Supports

final support	initial support commercial name	category	particle size <sup>a</sup> (mm)	specific surface area (BET) <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	phenylsulfonylhydrazine loading <sup>c</sup> (10 <sup>-3</sup> mol g <sup>-1</sup> )	swelling in wine (mL g <sup>-1</sup> )
P1	Dowex 50Wx2	gel type (2% cross-linking)	0.40–0.60		2.60	3.9
P2	Dowex 50Wx8	macroporous (8% cross-linking)	0.10–0.20	30	3.30	0.7
P3	Sepabead SP825	Macronet	0.25–0.60	875	1.66	0.8

<sup>a</sup> Supplier data. <sup>b</sup> Determined by N<sub>2</sub> adsorption–desorption experiments. <sup>c</sup> Determined from N elemental analysis.

Table 2. Results of Carbonyl Compound Removal: Percentage of Carbonyl Compound Left in Wine after 4 Weeks of Extraction

carbonyl compound removed	P1			P2			P3		
	4.4 g L <sup>-1</sup> (2 equiv)	13.2 g L <sup>-1</sup> (6 equiv)	22.0 g L <sup>-1</sup> (10 equiv)	3.3 g L <sup>-1</sup> (2 equiv)	9.9 g L <sup>-1</sup> (6 equiv)	16.6 g L <sup>-1</sup> (10 equiv)	2.7 g L <sup>-1</sup> (2 equiv)	8.0 g L <sup>-1</sup> (6 equiv)	13.3 g L <sup>-1</sup> (10 equiv)
acetaldehyde	60	75	92	62	78	85	29	53	60
pyruvic acid	82	90	90	74	86	86	63	89	92
2-oxoglutaric acid	100	100	100	100	100	100	100	100	100
5-oxofructose	60	75	82	70	74	70	12	21	23

be envisaged. In addition to the three carbonyl compounds previously studied, 5-oxofructose was selected as a new carbonyl compound to be removed from sweet white wines to obtain a significant reduction in binding power. 5-Oxofructose contributes significantly to the binding power of sweet white wines (12). Its formation is promoted by the action of *Botrytis cinerea* on the grapes. This compound is unaffected by the yeast metabolism, and concentrations may vary very significantly from one wine to another. Altogether, the four compounds mentioned are responsible for most of the SO<sub>2</sub> binding power of sweet wines made from botrytized grapes (4).

This paper presents the results obtained concerning the decrease in binding power of several sweet white wines by using the selective solid–liquid removal method. Its impact on the organoleptic properties of the wines was also studied.

## MATERIALS AND METHODS

**Reagents and Materials.** Dowex resins (Dow Chemical Co., Midland, MI), thionyl chloride (SOCl<sub>2</sub>), tartaric acid, chlorosulfonic acid, *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PF-BOA), lindane, D-fructose, 5-fructose dehydrogenase, 2,6-dichlorophenolindophenol, hydrazine monohydrate, and kits for enzymatic determination of pyruvic acid were obtained from Sigma-Aldrich (Saint-Quentin Fallavier, France). Ether and hexane were provided by SDS (Peypin, France). Tetrahydrofuran (THF), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), potassium metabisulfite, dimethylformamide (DMF), sodium phosphate dibasic dodecahydrate, monobasic potassium phosphate, monobasic ammonium phosphate, and ethylenediaminetetraacetic acid were purchased from VWR-Prolabo (Fontenay-sous-bois, France). Boehringer Mannheim kits for acetaldehyde enzymatic determination, glutamate dehydrogenase, and NADH were purchased from R-Biopharm (Saint Didier au Mont d'Or, France). Sepabead supports were kindly provided by Resindion SRL (Milano, Italia). Solvents were used without further purification.

**Preparing Supports.** *Gel Type and Macroporous Supports.* The as-received Dowex sulfonic acid resins were thoroughly washed with THF in a Soxhlet apparatus for 48 h. Then the SO<sub>3</sub>H upon loading was

estimated according to a reported method (2). The Dowex supports were modified as follows (2, 9, 10): Sulfonic resin (5 g) was placed in a 100 mL two-necked flask under magnetic stirring. DMF (30 mL) was then added, followed by thionyl chloride (54 mmol, 3 equiv/SO<sub>3</sub>H). The mixture was stirred for 48 h at room temperature. Then the supports were filtered and washed with dichloromethane (4 × 20 mL) and, finally, THF (4 × 20 mL). After drying under vacuum, supports were added to an aqueous hydrazine hydrate solution (72 mmol, 4 equiv/SO<sub>3</sub>H) in a water/ice bath. After 5 h of stirring at 0 °C, the beads were filtered and washed with aqueous HCl (3 mol L<sup>-1</sup>) and then water until pH 5.

**Hyper-Cross-Linked (Macronet) Supports.** The as-received Sepabead supports were thoroughly washed with THF in a Soxhlet apparatus for 48 h. The supports were modified as follows (2, 9, 10): Macronet supports (5 g) were placed in a 100 mL two-necked flask under magnetic stirring, and chlorosulfonic acid (24 mL) was then added. The mixture was stirred for 1 h at 80 °C. Then the supports were filtered and washed successively with CH<sub>2</sub>Cl<sub>2</sub> (4 × 20 mL), CH<sub>2</sub>Cl<sub>2</sub>/THF (4:1) (3 × 20 mL), CH<sub>2</sub>Cl<sub>2</sub>/THF (2:1) (20 mL), and finally THF (12 mL). Sulfonated resin (5 g) was placed in a 100 mL two-necked flask under magnetic stirring. DMF (30 mL) was then added, followed by thionyl chloride (54 mmol, 3 equiv/SO<sub>3</sub>H). The mixture was stirred for 48 h at room temperature. Then the supports were filtered and washed with dichloromethane (4 × 20 mL) and, finally, THF (4 × 20 mL). After drying under vacuum, supports were added to an aqueous hydrazine hydrate solution (150 mmol, 4 equiv/SO<sub>3</sub>H), in a water/ice bath. After 5 h of stirring at 0 °C, the beads were filtered and washed with aqueous HCl (3 mol L<sup>-1</sup>) and then water until pH 5. After drying under vacuum, elemental N was assayed for loading determination. Solvent swelling of the supports was measured using a water/ethanol mixture (88:12, v/v) in a fritted graduated burette.

**Removal of Carbonyl Compounds from Wines.** Wines studied were sweet white Sauternes (Bordeaux area, France). Wines from the 1999 vintage were used for tests with supports P1 and P2 and the 2001 vintage for tests with support P3. Before any experiment, total SO<sub>2</sub> levels were adjusted to 400 mg L<sup>-1</sup> by adding potassium metabisulfite, if necessary. Reactions took place at room temperature without any agitation. Experiments using different amounts of supports were performed with an 80 mL wine sample and a contact

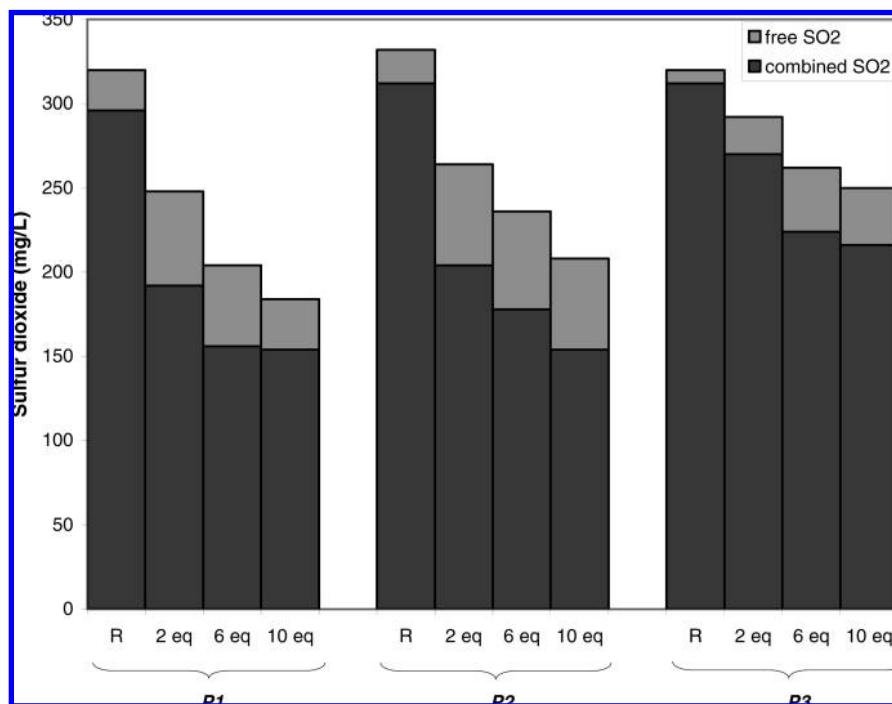
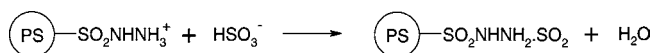


Figure 1. Variations in sulfur dioxide concentrations in wine according to the amount of extractive agent used (4 weeks of reaction time).

**Scheme 4.** Reaction between Grafted Phenylsulfonylhydrazine and Sulfur Dioxide



time of 4 weeks. For experiments on variable volumes, support P1 was added to a  $5 \text{ g L}^{-1}$  concentration for a contact time of 2 weeks. For sensory analysis, support P1 was added to wine at a concentration of  $5.6 \text{ g L}^{-1}$  for a contact time of 2 weeks.

**Carbonyl Compound Analysis.** Acetaldehyde and pyruvic acid concentrations in wine were determined enzymatically, using commercial kits. The enzymatic method described by Blouin was used for 2-oxoglutaric acid (11). Absorbances for enzymatic determination were carried out at  $\lambda = 340 \text{ nm}$  on a Spectronic 20 Genesys spectrophotometer. Values are  $\pm 3\%$ . Standard 5-oxofructose solutions were prepared from D-fructose and 5-fructose dehydrogenase in the presence of 2,6-dichlorophenolindophenol, according to a published method (12). Concentrations of this carbonyl compound in wine were assayed after oxime derivatization with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFOA), using a Hewlett-Packard HP 6890 gas chromatograph coupled with a Hewlett-Packard HP 5973i mass spectrometer, as reported by Barbe et al. (12). Intralaboratory repeatability was determined by 10 successive analyses of the same sample containing  $94 \text{ mg L}^{-1}$  5-oxofructose, and the variation coefficient was 7.2%. Method linearity was studied by adding 5-oxofructose (50, 100, 200, 400, or  $800 \text{ mg L}^{-1}$ ) to a must that had no detectable level. The correlation coefficient between measured and added levels was 0.995.

**SO<sub>2</sub> Level Determination.** Free and total SO<sub>2</sub> levels were determined by iodometry, as described by Ribéreau-Gayon et al. (20).

**Centesimal Analysis.** Centesimal analyses were carried out by the Central Service of Elemental Analysis of the CNRS (Vernaison, France). Values are given at  $\pm 0.3\%$  on N.

**Sensory Analysis.** Sensory triangular tests were performed to evaluate the organoleptic impact of the process and look for exogenous notes. The sensory panel was composed of 18 persons who attended a weekly training session. The test was performed in individual booths, at controlled room temperature of  $20 \text{ }^\circ\text{C}$ , using covered AFNOR (French Standard Association) glasses, containing 40 mL of wine. Just after heterogeneous extraction, free SO<sub>2</sub> concentrations were adjusted by sodium metabisulfite addition to obtain a value of  $40 \text{ mg L}^{-1}$  in all samples. Two triangular tests were performed: in the first round, one

glass contained the treated wine and the two others the original wine, and the presentation was reversed in the second round.

## RESULTS AND DISCUSSION

### Selecting the Carbonyl Compounds To Be Removed.

Acetaldehyde, pyruvic acid, 2-oxoglutaric acid, and 5-oxofructose were selected as the carbonyl compounds to be removed from sweet wines, to achieve a significant reduction in their binding power (Scheme 2). The choice of the first three compounds was previously reported (2). 5-Oxofructose is another carbonyl compound that plays a significant role in the binding power of sweet white wines (12). This compound is produced by the action of *Gluconobacter oxidans* on botrytized grapes (12). 5-Oxofructose was synthesized according to the best available enzymatic method (4). However, the difficulty of purifying 5-oxofructose from its preparation media prevented us from studying its removal from model media in our preliminary study (2). Therefore, we decided to study its removal from wine directly.

**Removing Carbonyl Compounds from Wine.** Supports from three different origins were selected to evaluate the best category of support to be used in the process. Dowex 50Wx2 is a gel-type support characterized by a low cross-linking level (2%) that does not induce any apparent porosity in the dry state and a large swelling capacity in solvents compatible with its chemical nature (13). Dowex 50Wx8 is a macroporous support characterized by a permanent porosity and a measurable specific surface area. Its rather high cross-linking level (8%) is responsible for a lower swelling capacity than gel-type supports, at least in dilute-alcohol media (14). Hyper-cross-linked or Macronet support Sepabead SP825 is produced by postreticulation of a linear or gel-type polymer (15). It is characterized by a permanent porosity and a large specific surface area (16). This kind of support is usually compatible with aqueous solutions and has given good results in aqueous effluent treatment (17, 18). Dowex 50Wx2 and Dowex 50Wx8 are sulfonic acid resins, whereas Sepabead SP825 is a nonfunctionalized support. These initial supports were derivatized in a two-step procedure (except

**Table 3.** Carbonyl Compound Removal Efficiency in Sweet White Wine: Extractions Using 80 mL of Wine

	P1			P2			P3		
	4.4 g L <sup>-1</sup> (2 equiv)	13.2 g L <sup>-1</sup> (6 equiv)	22.0 g L <sup>-1</sup> (10 equiv)	3.3 g L <sup>-1</sup> (2 equiv)	9.9 g L <sup>-1</sup> (6 equiv)	16.6 g L <sup>-1</sup> (10 equiv)	2.7 g L <sup>-1</sup> (2 equiv)	8.0 g L <sup>-1</sup> (6 equiv)	13.3 g L <sup>-1</sup> (10 equiv)
carbonyl <sup>a</sup> compound removed (mmol)	0.35	0.44	0.46	0.38	0.45	0.47	0.275	0.419	0.454
SO <sub>2</sub> <sup>b</sup> removed (mmol)	0.09	0.15	0.17	0.08	0.12	0.15	0.04	0.07	0.09
support functions available <sup>c</sup> (mmol)	1.0	3.0	5.0	1.0	3.0	5.0	1.4	4.4	7.0
support functions used (mmol)	0.44	0.59	0.63	0.46	0.57	0.62	0.32	0.49	0.54
percentage of function used	44	20	12	46	19	12	23	12	8

<sup>a</sup>Initial amount of carbonyl compound = 0.70 mmol. <sup>b</sup>Calculated from total and free SO<sub>2</sub> determination before and after processing. <sup>c</sup>Determined by N<sub>2</sub> adsorption–desorption experiments.

the unsulfonated one, which required an additional chlorosulfonation step) to produce phenylsulfonylhydrazine-grafted supports P1, P2, and P3 (**Scheme 3**). The characteristics of the initial resin and final grafted supports are described in **Table 1**. Swelling measurements indicated that the supports absorbed only a small quantity of wine. This is an important parameter for winemaking applications: the wine absorbed by the support will be lost to the winemaker. The efficiency of carbonyl removal from wine, using these supports, is shown in **Table 2**. It is interesting to note that, according to the support and the amount used, very large quantities of some carbonyl compounds were removed (often between 80 and 100%). This suggests that, when free carbonyl compounds react with grafted phenylsulfonylhydrazine and are extracted from the solution (wine), some of the corresponding carbonyl bisulfite dissociates to form free carbonyl, carbonyl bisulfite, and HSO<sub>3</sub><sup>-</sup>, in agreement with the mass action law. Three different quantities of scavenging agent were used in this study: 2, 6, and 10 equiv; “2 equiv” means a molar ratio of 2 between the quantity of grafted phenylsulfonylhydrazine added and the estimated total amount of acetaldehyde, pyruvic acid, 2-oxoglutaric acid, and 5-oxofructose present in the wine. The first observation was that carbonyl compound removal was possible in wine. For all supports tested, a clear improvement in the acetaldehyde removal efficiency was observed when the scavenging agent increased from 2 to 10 equiv. The improvement in performance was less obvious in the case of pyruvic acid with supports P1 and P2, but still significant when support P3 was used. All of the 2-oxoglutaric acid was removed with 2 equiv of extractive agent on all supports. 5-Oxofructose was efficiently removed using supports P1 and P2, even with only 2 equiv of phenylsulfonylhydrazine. Support P3 was much less efficient in eliminating this carbonyl. The removal of carbonyl compounds by grafted phenylsulfonylhydrazine corresponded to an equilibrium. The use of an excess of one of the reagents is frequently used in chemistry to improve an equilibrium displacement in the desired direction. In this case, the results obtained indicated that the use of large excesses of the removal agent was not necessary to displace the heterogeneous equilibrium significantly toward efficient carbonyl compound removal. The results presented in **Table 2** were obtained without stirring. The same experiments were carried out with stirring, using a rotary agitator at 9 rpm (results not reported). Similar removal efficiency was obtained in both cases. Therefore, stirring did not enhance the process. This observation is useful for winemakers if this method is to be applied to large quantities of wine.

In a previous paper, we reported the removal of acetaldehyde, pyruvic acid, and 2-oxoglutaric acid from single-compound model solutions using grafted phenylsulfonylhydrazine (2). These results indicated that the carbonyl compounds removal

behavior was different in wine and single model solutions. The process was more efficient in wine than single model media, but also slower. Wine is a complex medium, so equilibria in wine not considered in the model medium affected removal efficiency and the kinetics. The bound and free SO<sub>2</sub> concentrations measured after carbonyl compound removal using the various supports are presented in **Figure 1**. After 4 weeks of storage at room temperature, untreated wine samples had a total SO<sub>2</sub> content of <350 mg L<sup>-1</sup> (initial concentration = 400 mg L<sup>-1</sup>). This is indicative of oxidation of the wine (20). The total and free SO<sub>2</sub> concentrations measured before and after processing showed that carbonyl compound removal was accompanied by a decrease in total SO<sub>2</sub> concentrations, associated with an increase in free SO<sub>2</sub>. This confirmed that the bound SO<sub>2</sub> concentration decreased, which was the aim of this technique. An increase in the amount of scavenging agent used during the process had a rather limited effect on the free SO<sub>2</sub> concentration. This can be explained by a limited use of the available phenylsulfonylhydrazine moieties for carbonyl compound removal. Conversely, for all supports tested, total SO<sub>2</sub> concentrations decreased as the amount of scavenging agent increased. Part of this SO<sub>2</sub> elimination may be attributed to wine oxidation, but a large part must be due to another mechanism. There are two possible hypotheses. The first is that the bisulfite form reacts with phenylsulfonylhydrazine. The other is that sulfur dioxide itself reacts with phenylsulfonylhydrazine. The fact that the total SO<sub>2</sub> content decreased even when the carbonyl compound concentration remained stable (i.e., a steady combined SO<sub>2</sub> concentration) tends to indicate the free sulfur dioxide reacts with phenylsulfonylhydrazine. The reactivity of sulfur dioxide with hydrazine has scarcely been studied (20, 21). The formation of adducts between sulfur dioxide and bisubstituted hydrazines has been reported, but under different experimental conditions (22). However, a fraction of the grafted functions may be protonated in the acid wine medium, reacting with the HSO<sub>3</sub><sup>-</sup> ion, forming a neutral adduct (**Scheme 4**). The function obtained may be correlated with a grafted sulfinamic acid R–NH–SO<sub>2</sub>H. This compound was previously synthesized by direct condensation of an amine and sulfur dioxide (23, 24). In the presence of water, this relatively unstable compound is probably transformed into an amine and sulfurous anhydride. Nevertheless, the heterogeneous nature of the medium may be assumed to improve its stability in this case.

The process balance sheet is presented in **Table 3**. Results revealed that carbonyl compound and sulfur dioxide removal efficiencies were not proportional to the increase in scavenging agent involved: a removal efficiency limit was reached in both cases, for all of the supports tested. This limit was between 2 and 6 equiv of scavenging agent. It is, therefore, undesirable to use large quantities of scavenging agent. In most cases, the use

of 2 equiv of scavenging agent is sufficient to cause a significant decrease in the wine's binding power. The supports were not equally efficient at this ratio: only 23% of the functions grafted on P3 were used, compared to about 45% on P1 and P2.

**Sensory Impact.** Sensory analysis showed that the use of support P2 gave an exogenous odor to the treated wine, whereas support P1 did not modify their aromatic qualities. Support P3 did not give any exogenous odor to wine, but it was discarded due to its lower efficiency. Triangular tests to evaluate the organoleptic impact of extraction with support P1 showed that it was difficult for the panel to recognize the treated wine. In the two-sample presentation, only 6 persons identified the different glass, whereas 12 failed. According to the null hypothesis, the number of correct assessments was binomial with parameters  $n = 18$  and  $p = 1/3$ . There was no significant difference at the threshold of 0.1% between treated and sample wines (25–26).

**Influence of the Removal Time and Volume Treated.** Intermediate measures (not shown) showed that 2 weeks was sufficient to reduce the binding power significantly. Removal experiments were carried out on different volumes of wine using support P1. After a contact time of 2 weeks, the removal efficiencies of acetaldehyde, pyruvic acid, 2-oxoglutaric acid, and 5-oxofructose were comparable, irrespective of the volume of wine (80, 750, or 5000 mL) (not shown). These results indicated that, very probably, this technique could be directly transposed to large-scale production.

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