New Methodology for Removing Carbonyl Compounds from Sweet Wines

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Sweet white wines from botrytized grapes present high SO_2 levels because of their high sulfur dioxide binding power. The objective of this work was to develop a new method for reducing this binding power by partially eliminating the carbonyl compounds naturally present in these wines that are responsible for this phenomenon. A selective liquid–solid removal technique was developed. Phenylsulfonylhydrazine was selected as the best candidate for removing carbonyl compounds. Its reactivity in the presence or absence of sulfur dioxide was verified in model media containing acetaldehyde, pyruvic acid, and 2-oxoglutaric acid, some of the main carbonyl compounds responsible for the SO_2 binding power of sweet wines. The scavenging function was grafted on porous polymer supports, and its efficiency was evaluated in model wines. Dependent upon the supports used, different quantities of carbonyl compounds (over 90% in some cases) were removed in a few days. The presence of sulfur dioxide delayed removal without changing its quality. The results obtained showed that the method removed carbonyl compounds efficiently and was applicable to wines at any stage in winemaking.

KEYWORDS: Carbonyl compound; sulfur dioxide; sweet wines; selective liquid–solid removal

INTRODUCTION

Sulfur dioxide is an indispensable winemaking additive, combining antioxidant and antibacterial properties (*1, 2*). Sulfur dioxide is added to sweet white wines made from grapes infected with *Botrytis cinerea* (known as noble rot) to stop alcoholic fermentation; this step is called "mutage". When sulfur dioxide is added to wine, a balance is established between the various forms of this compound (*3*). The SO_2 that reacts with carbonyl compounds in the wine to produce carbonyl bisulfite is known as "bound" SO_2. At wine pH values, most of the free SO_2 is present in the bisulfite (HSO_3^-) form, whereas in active or molecular SO_2, the H_2SO_3 form is present at low levels, mainly depending upon the pH and ethanol content of the medium, as well as temperature. Generally, in wines from botrytized grapes, at temperatures around 20 °C, the H_2SO_3 content is about 1–2%

that of "free" SO_2, whereas the sulfite form, SO_3^{2-}, is negligible. Thus, to obtain 1 mg L^{-1} active SO_2 (the concentration required to avoid any further fermentation), a few hundred milligrams per liter total SO_2 are required, resulting in about 50 mg L^{-1} free SO_2 (*4*).

The toxicity of sulfur dioxide and carbonyl bisulfite has been studied since the early 20th century (*5–12*), leading authorities to regulate the quantity of sulfur dioxide permitted in wine for health reasons (OIV oeno resolution 7/2003 and EC rule number 1493/1999). Reducing the total quantity of sulfur dioxide in wine is a challenge, and several recent publications have explored physical and chemical methods for doing so (*13*). However, sulfur dioxide remains an indispensable additive in winemaking.

The goal of a winemaker is to achieve a satisfactory active SO_2 level in wine with the lowest possible total SO_2 content. To reduce the total quantity of sulfur dioxide, it was necessary to focus on reducing the quantity of the bound form. This quantity is correlated to carbonyl concentrations in wine, and a decrease in these compounds reduces the binding power of the wine, thus decreasing the total SO_2 level necessary to stabilize it.

The objective of this research was to find a new way of reducing the amounts of sulfur dioxide added to wines using a new methodology based on selective liquid–solid removal (*14–17*).

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Scheme 1. Derivatization of Supports

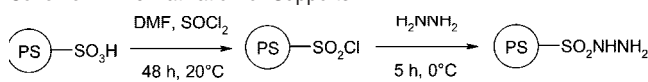**Table 1.** Quantities of Support (in g/100 mL) Added to Media

	acetaldehyde medium	pyruvic acid medium	2-oxoglutaric acid medium
support P1	0.394	0.480	0.288
support P2	0.146	0.177	0.107
support P3	0.148	0.180	0.108

More specifically, the aim of the study was to remove some of the natural carbonyls responsible for the high binding power of sweet wines (*18*). The technique made use of a selective scavenging molecule, grafted onto an insoluble support, in a heterogeneous reaction that preserves all of the organoleptic properties of the wine (*19*). This paper describes the methodology developed and results obtained using model solutions.

MATERIALS AND METHODS

Reagents and Material. Acetaldehyde, pyruvic acid, 2-oxoglutaric acid, Dowex resins (Dow Chemical Co., Midland, MI), thionylchloride (SOCl₂), L-(+)-tartaric acid, hydrazine monohydrate, and analytical kits for pyruvic acid determination were purchase from Sigma-Aldrich (Saint-Quentin Fallavier, France). Tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), dimethylformamide (DMF), ethanol, D-(+)-glucose, D-(−)-fructose, dibasic sodium phosphate dodecahydrate, monobasic potassium phosphate, ammonium phosphate monobasic, and ethylenediaminetetraacetic acid were purchased from VWR-Prolabo (Fontenay-sous-bois, France). Boerhinger-Mannheim kits for acetaldehyde determination, glutamate dehydrogenase, and reduced nicotinamide adenine dinucleotide (NADH) were purchased from R-Biopharm (Saint Didier au Mont d'Or, France). Solvents were used without further purification.

Working Solutions. For tests in homogeneous solution to evaluate the efficiency of the removal agent, model medium A (500 mL) consisted of acetaldehyde (0.05 g/L), pyruvic acid (0.1 g/L), 2-oxoglutaric acid (0.1 g/L), and tartaric acid (4 g/L) in a water/ethanol mixture (88:12, v/v), adjusted to pH 3.5 (NaOH, 2 mol/L). For carbonyl removal in the presence of sugars, model medium B (250 mL) consisted of acetaldehyde (0.05 g/L), pyruvic acid (0.1 g/L), 2-oxoglutaric acid (0.1 g/L), tartaric acid (4 g/L), fructose (75 g/L), and glucose (25 g/L) in a water/ethanol mixture (88:12, v/v), adjusted to pH 3.5 (NaOH, 2 mol/L). For carbonyl removal after the addition of sugars, model medium C (250 mL) consisted of fructose (75 g/L) and glucose (25 g/L) in a water/ethanol mixture (88:12, v/v), adjusted to pH 3.5 (NaOH, 2 mol/L). For tests in homo- and heterogeneous media using single carbonyl compounds, model solution D (1 L) contained acetaldehyde (0.041 g/L), pyruvic acid (0.108 g/L), or 2-oxoglutaric acid (0.103 g/L) together with tartaric acid (4 g/L) in a water/ethanol mixture (88:12, v/v), adjusted to pH 3.5 (NaOH, 2 mol/L). For experiments after the addition of sulfur dioxide, 600 μL of 5% aqueous solution of sulfur dioxide was added to 300 mL of each solution, to obtain a total SO₂ content of 100 mg/L. Media were left for 72 h at room temperature to homogenize.

Preparing Supports (Scheme 1). The as-received Dowex sulfonic acid resins were thoroughly washed with THF in a Soxhlet apparatus for 48 h. Then, the SO₃H upon loading was estimated according to a reported method (*20*). The Dowex supports were modified as follows (*21–23*): sulfonic resin (5 g) was placed in a 100 mL two-necked flask under magnetic stirring. DMF (30 mL) was then added, followed by thionylchloride (54 mmol, 3 equiv/SO₃H). 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/SO₃H) in a water/ice bath. After 5 h of stirring at 0 °C, the beads were filtered

Scheme 2. Carbonyl Compounds Selected

Acetaldehyde   Pyruvic acid   2-oxoglutaric acid
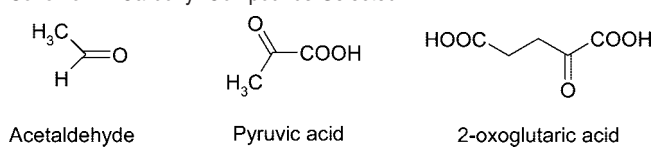
Scheme 3. Reaction between a Carbonyl Compound and Phenylsulfonylhydrazine
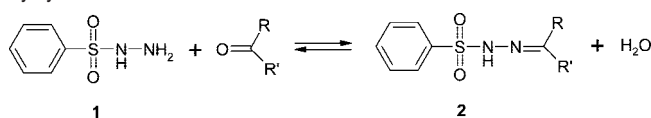
and washed with aqueous HCl (3 mol/L) and then water until pH = 5. After drying under a vacuum, elemental N was assayed for loading determination. Solvent swelling of the supports was measured using a water/ethanol mixture (88:12, v/v) in a fritted graduated burette.

Phenylsulfonylhydrazine Experiments. Reactions took place at room temperature in 500 mL bottles placed on a tumbling rotary agitator at 9 rd min⁻¹. The efficiency of removal was monitored by regular withdrawal of 1 mL aliquot to assay the carbonyl compound concentrations. For tests in homogeneous media without (model medium A) and with (model medium B) sugars, 0.172 g of phenylsulfonylhydrazine was added to 100 mL samples. For tests in homogeneous media after the addition of sugars (model medium C), 0.199 g of phenylsulfonylhydrazine was added to 100 mL samples. After 48 h of agitation, 0.025 g of pyruvic acid was added to the solution. For tests in homogeneous single carbonyl compound media, 0.048 g of phenylsulfonylhydrazine was added to 100 mL of aldehyde solution, 0.063 g of phenylsulfonylhydrazine was added to 100 mL of pyruvic acid solution, and 0.036 g of phenylsulfonylhydrazine was added to 100 mL of 2-oxoglutaric acid solution. For tests in heterogeneous media, quantities of support were added to 100 mL of solution as reported in **Table 1**.

Carbonyl Compound Analysis. Acetaldehyde and pyruvic acid concentrations in model solutions were determined enzymatically, using commercial kits. The enzymatic method described by Blouin was used for 2-oxoglutaric acid (*24*). Absorbances for enzymatic determination were carried out at $\lambda = 340$ nm on a Spectronic 20 Genesys spectrophotometer. Values are ±3%.

Centesimal Analysis. Centesimal analyses were carried out by the Central Service of Elemental Analysis of the CNRS (Vernaison, France). Values are ±0.3% on N.

RESULTS AND DISCUSSION

Carbonyl Compound Selection. Acetaldehyde, pyruvic acid, and 2-oxoglutaric acid were selected as carbonyl compounds
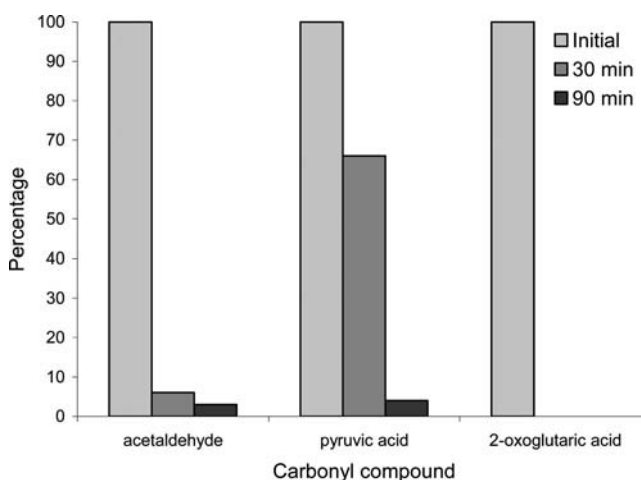

Figure 1. Changes in the carbonyl compound concentration over time in a homogeneous solution in the presence of glucose and fructose with 3 equiv of phenylsulfonylhydrazine.

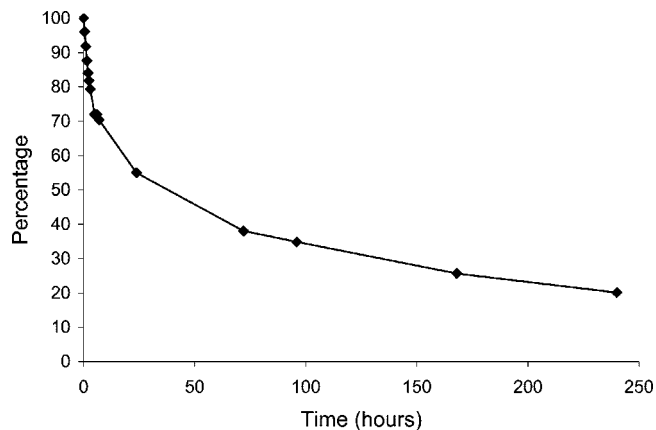**10384** *J. Agric. Food Chem.,* Vol. 55, No. 25, 2007

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Figure 2. Changes in the pyruvic acid concentration over time in a homogeneous solution in the presence of glucose and fructose, when pyruvic acid was added after the for sugars.
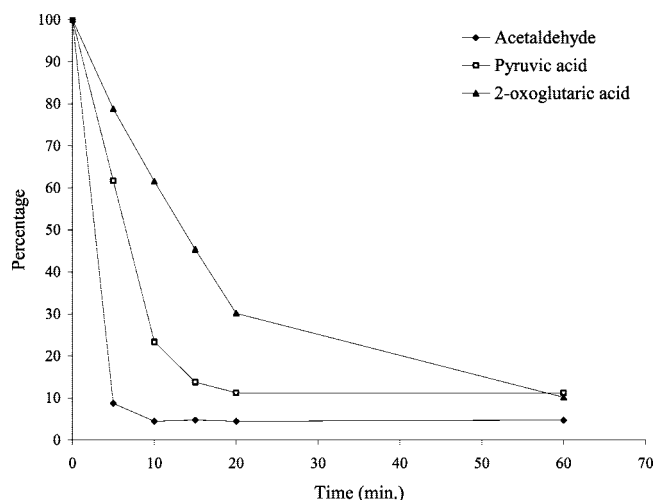

Figure 3. Changes in the carbonyl concentration over time in a homogeneous solution in the absence of SO$_2$ for single carbonyl solutions.

Figure 4. Changes in the carbonyl concentration with time in a homogeneous solution in the presence of SO$_2$ for single carbonyl solutions.

Table 2. K_d Values and Removal Time in Homogeneous Media Using Single Carbonyl Solutions

	carbonyl bisulfite K_d (M)	time to reach a balance in the medium without SO$_2$ (min)	time to reach a balance in the medium with SO$_2$ (h)
acetaldehyde	0.0024×10^{-3}	5	70
pyruvic acid	0.3×10^{-3}	20	48
2-oxoglutaric acid	0.5×10^{-3}	60	2

to be removed (**Scheme 2**). These three compounds, present in large concentrations in sweet white wines (acetaldehyde, 0.005−0.5 g/L; pyruvic acid, 0.01−0.5 g/L; and 2-oxoglutaric acid, 0.02−0.35 g/L) (*25, 26*), are derived from the yeast metabolism (*27*). These compounds are largely responsible for the SO$_2$ binding power of wines, and concentrations were easily monitored by enzymatic detection.

Selection of a Suitable Scavenging Molecule. The scavenger had to be capable of reacting with carbonyl functions (*28, 29*) under the following specific conditions, to preserve the orga-noleptic properties of the wine: (i) active in dilute alcohol media at room temperature; (ii) no catalyst required and no new compounds released into the media, except water; and (iii) finally, the scavenging molecule had to be easily grafted on an insoluble polymer support. After careful examination of the literature and some preliminary experiments (not reported), the scavenging function selected was phenylsulfonylhydrazine **1** (*30–32*). The chemical equilibrium described in **Scheme 3** releases water into the medium at levels unlikely to affect wine composition. The efficiency of phenylsulfonylhydrazine in removing carbonyl compounds was already reported in the literature but under different experimental conditions using organic solvents (*33*).

Evaluating the Efficiency of Phenylsulfonylhydrazine. Compound **2** produced by the reaction of phenylsulfonylhydra-
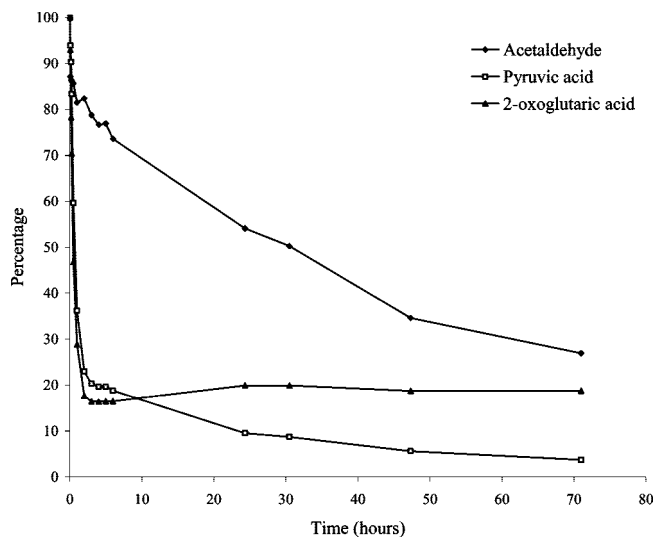
zine with carbonyl compounds is an imine. The aim was to maximize the conversion of carbonyls into imines, under the specific conditions of this study. The only variable was the relative concentration of the reactants. First, the ability of **1** to displace the reaction equilibrium efficiently toward the formation of compound **2** was evaluated, i.e., the efficiency of the homogeneous combination of the selected carbonyl compounds with phenylsulfonylhydrazine under the experimental conditions specified above. The formation of compound **2** correlated with the release of water into the media, which upset the equilibrium in the dilute alcohol medium; therefore, the efficiency of the method had to be verified. Selected carbonyl compounds, i.e., acetaldehyde, pyruvic acid, and 2-oxoglutaric acid, reacted with 3 equiv of the phenylsulfonylhydrazine, to evaluate its efficiency. After 15 min of the reaction, 96% of the acetaldehyde, 91% of the pyruvic acid, and 91% of the 2-oxoglutaric acid had reacted with the phenylsulfonylhydrazine. No further change in the concentration was observed after 1 h, except in the case of 2-oxoglutaric acid, where the reaction had continued to completion.

Impact of the Presence of Sugars on Reaction Efficiency. The results of the reactions between acetaldehyde, pyruvic acid, and 2-oxoglutaric acid (model medium B) and 3 equiv of phenylsulfonylhydrazine in the presence of glucose and fructose are presented in **Figure 1**. The reactivity of acetaldehyde and 2-oxoglutaric acid was not affected by the presence of glucose or fructose. The open forms of the sugars (about 1% under these conditions) contained a carbonyl function (*34*), and there was, thus, a possible competition between this carbohydrate form and the carbonyl compounds to be removed. This effect was not observed in the case of acetaldehyde and 2-oxoglutaric acid. However, competition between the carbonyl function of pyruvic

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Table 3. Results of Grafting the Phenylsulfonylhydrazine Removal Function on Supports

	initial support	particle size[a] (μm)	cross-linking level[a] (%)	phenylsulfonylhydrazine loading[b] (10^{-3} mol/g)	solvent swelling[c] (mL/g)
support P1	Dowex 50Wx2	150–300	2	0.71	3.9
support P2	Dowex 50Wx4	150–300	4	1.91	1.7
support P3	Dowex 50Wx8	150–300	8	1.89	0.7

[a] Supplier data. [b] Determined from N elemental analysis. [c] See the Materials and Methods.

Table 4. Percentage of Heterogeneous Removal in the Model Solution at Equilibrium

	acetaldehyde medium[a]	pyruvic acid medium[a]	2-oxoglutaric acid medium[a]	acetaldehyde medium[b]	pyruvic acid medium[b]	2-oxoglutaric acid medium[b]
support P1	85	20	100	70	0	100
support P2	95	70	50	20	65	60
support P3	95	35	100	40	25	100

[a] Reaction results after 120 h without SO_2. [b] Reaction results after 480 h with SO_2.

acid and that of the open form of glucose or fructose lengthened the removal time. This may be due to the affinity of sulfonylhydrazine for glucose, as reported in the literature (*33, 35*). When phenylsulfonylhydrazine was added to the sugar solution 48 h before the addition of pyruvic acid, its homogeneous removal was slower than previously observed (**Figure 2**). When the carbonyl compound, sugar, and phenylsulfonylhydrazine were combined at the same time, 90% of the pyruvic acid reacted within 90 min, while only 80% was removed after 2 weeks when phenylsulfonylhydrazine was added to the sugar solution in advance. There was competition between pyruvic acid and sugars, but phenylsulfonylhydrazine has a greater affinity for pyruvic acid than for sugars.

Removal of Carbonyl Compounds in Homogeneous Media. The results for acetaldehyde, pyruvic acid, and 2-oxoglutaric acid removal in the presence of 3 equiv of phenylsulfonylhydrazine are shown in **Figure 3**. After 1 h, at least 90% of all three carbonyl compounds had been removed. Acetaldehyde was removed in 5 min; pyruvic acid was removed in 20 min; and 2-oxoglutaric acid was removed in 60 min. The process was slightly less efficient than in mixed removals (90−95 versus 91−100%).

Figure 4 shows the results for the same experiment in the presence of sulfur dioxide. Acetaldehyde removal was less efficient when sulfur dioxide was added. The time to reach equilibrium increased (70 h for acetaldehyde, 45 h for pyruvic acid, and 2 h for 2-oxoglutaric acid). Furthermore, an inversion in the kinetics was observed: 2-oxoglutaric acid was removed faster than pyruvic acid, and acetaldehyde was slowest.

The affinity of a carbonyl compound for sulfur dioxide is quantified by measuring its dissociation constant (K_d), i.e., its capacity to form a carbonyl bisulfite derivative (*36–38*). **Table 2** shows that, in the absence of sulfur dioxide, the time required to reach equilibrium increased with K_d, suggesting that the relative carbonyl affinities for phenylsulfonylhydrazine were analogous to those of sulfur dioxide. In the presence of sulfur dioxide, carbonyl bisulfites are formed preferentially and the time to reach equilibrium was inversely correlated with the affinity of carbonyl compounds for sulfur dioxide. The higher the affinity of the carbonyl for sulfur dioxide, the more difficult it was to break the bond between the compound and sulfur dioxide to produce a new reaction with phenylsulfonylhydrazine. The balance was always in favor of the hydrazide compound; i.e., hydrazide derivatives are more stable (less energetic) than carbonyl bisulfites. Therefore, homogeneous removal of the carbonyl compounds responsible for the binding power of wine using phenylsulfonylhydrazine was possible under these experimental conditions.

Removal of Carbonyl Compounds in Heterogeneous Media. The supports selected were commercially available macroporous sulfonic acid resins with different cross-linking levels. Dowex 50Wx2 is a gel-type support characterized by a low cross-linking level (2%) that induces no apparent porosity in the dry state and a large swelling capacity in solvents, compatible with its chemical nature (*39*). Dowex 50Wx4 and Dowex 50Wx8 are macroporous supports characterized by a permanent porosity and a measurable specific surface area; they differs by they cross-linking level (4 and 8%, respectively). This high cross-linking level is responsible for a lower swelling capacity than gel-type supports, at least in hydroalcoholic media (*40*). These starting supports were derivatized in a two-step procedure (**Figure 1**) to produce phenylsulfonylhydrazine-grafted supports P1, P2, and P3. Characteristics of starting resins and final grafted supports are described in **Table 3**. The efficiency of carbonyl removal in model solution, using these supports, with and without sulfur dioxide, is shown in **Table 4**. Heterogeneous reaction kinetics were significantly slower than those under homogeneous conditions (hours versus minutes). This phenomenon, common in solid-phase chemistry, may be related to limitations on liquid diffusion into the pore network of the support (*39*). In the absence of sulfur dioxide, equilibrium was reached after 120 h in every case. The removal of acetaldehyde was almost complete with all supports tested. In the case of pyruvic acid, removal efficiency was low with supports P1 and P3, whereas support P2 had an efficiency of 70%. In the case of 2-oxoglutaric acid, the compound was completely removed with supports P1 and P3 but only half removed with support P2. Equilibrium was reached after 480 h in the presence of sulfur dioxide in every case, but efficiency was lower for acetaldehyde and pyruvic acid than in the absence of sulfur dioxide. Considering the removal of 2-oxoglutaric acid, supports had more or less the same efficiency with and without SO_2. Heterogeneous removal of the selected carbonyl compounds was possible using phenylsulfonylhydrazine grafted on an insoluble polymer support under experimental conditions *a priori*, compatible with winemaking. The fact that the presence of sulfur dioxide in the medium had little impact on the removal efficiency indicates that this technique could be used at any time in the winemaking process, even on unfermented must. Although the supports were selected with different cross-linking values to evaluate the impact of this parameter upon removal (*39*), there was no consistent correlation with removal efficiency. Each support was efficient with only one or two compounds, which varied from one support to another. Under homogeneous conditions, the efficiency of carbonyl reactions with phenyl-

sulfonylhydrazine correlated with their affinity to sulfur dioxide, which was not the case under heterogeneous conditions. Kinetics was considerably modified when phenylsulfonylhydrazine and the imine product were grafted onto an insoluble support, because the protagonists were in different phases. Parameters, such as swelling in solvents, functionality loading, and cross-linking levels differed from one support to another, affecting the accessibility of carbonyl compounds to the removal function (*40*). These differences may explain the difficulty of correlating removal results with equilibrium constants and variations in the behavior of the supports tested. The large number of parameters involved in heterogeneous systems make it difficult to select the best support among the three tested. These results show that heterogeneous selective liquid–solid removal of acetaldehyde, pyruvic acid, and 2-oxoglutaric acid is possible under experimental conditions *a priori*, compatible with winemaking. Phenylsulfonylhydrazine grafted onto porous polymer supports is an efficient scavenger under these conditions. The minimal impact of sulfur dioxide in the medium indicates that this application is usable at any stage in the winemaking process. Applications of this process on sweet white wines will be reported in a forthcoming paper.

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