Food Chemistry 141 (2013) 612–615

Contents lists available at SciVerse ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Short communication

Reducing the sulfur-dioxide binding power of sweet white wines by solid-phase extraction

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ARTICLE INFO

Article history:
Received 5 July 2012
Received in revised form 30 January 2013
Accepted 11 March 2013
Available online 20 March 2013

Keywords:
Carbonyl compound
Sulfur dioxide
Sweet wines
Selective liquid–solid extraction

ABSTRACT

The high sulfur-dioxide binding power of sweet white wines may be reduced by extracting the naturally present carbonyl compounds from wine that are responsible for carbonyl bisulphites formation. The carbonyl compounds mainly responsible for trapping SO_2 are acetaldehyde, pyruvic acid, and 2-oxoglutaric acid. The method employed was selective solid phase extraction, using phenylsulfonylhydrazine as a scavenging agent. The scavenging function was grafted onto a support prepared from raw materials derived from lignin. This approach is more acceptable to winemakers than the polymer media previously reported, as it reduces the possible contamination of wine to molecules already present in the wine making process.

1. Introduction

Sulfur dioxide, the most widely used additive in winemaking (Ribéreau-Gayon, Peynaud, Ribéreau-Gayon, & Sudraud, 1977), is essential for wine conservation, thanks to its combined antioxidant and antibacterial properties. Sulfur dioxide, in both its free and bound forms, presents toxicity, which has led health authorities to regulate acceptable levels in wine. Nowadays, sweet white wines made from botrytized grapes are among those with the highest SO_2 levels. We recently developed a new methodology, using model media and based on selective liquid–solid extraction, to reduce the binding power of wines (Blasi, Barbe, Dubourdieu, & Deleuze, 2008; Blasi, Barbe, Maillard, Dubourdieu, & Deleuze, 2007). Some of the carbonyl compounds responsible for SO_2 binding power (Barbe, de Revel, Joyeux, Lonvaud-Funel, & Bertrand, 2000) were removed using phenylsulfonylhydrazine grafted on an insoluble medium, via a heterogeneous reaction. This removal did not cause any noticeable changes in the other major volatiles, suggesting that this operation would not alter the organoleptic properties of wine (Scheme 1) (Flynn et al., 1997; Kaldor, Siegel, Fritz, Dressman, & Hahn, 1996; Ley et al., 2000; Thurman & Mills, 1998). Good results were obtained by removing acetaldehyde, pyruvic acid, and 2-oxoglutaric acid, under operating conditions similar to those applied in winemaking (Scheme 2) (Blasi et al., 2008).

However, the insoluble media used in these studies consisted of modified, commercially-available sulfonic resin. Contaminant analysis indicated the presence of traces of undesirable compounds in the wine after treatment. We, therefore, decided to adapt the medium by synthesising it from lignin extracted from various sources.

This paper presents the decrease in SO_2-binding power of several sweet white wines, using these new types of media.

2. Materials and methods

2.1. Reagents

Tartaric acid, diethyl ether, hexane, tetrahydrofuran, dichloromethane, dimethylformamide, and kits for the enzymatic determination of pyruvic acid were obtained from Sigma–Aldrich (Saint-Quentin Fallavier, France). Boerhinger Mannheim kits for enzymatic determination of acetaldehyde, as well as glutamate dehydrogenase, and NADH, were purchased from R-Biopharm (Saint-Didier au Mont d'Or, France). Solvents were used without further purification.

2.2. Supports preparation

Two types of supports were used in this study. One support was obtained from industrial Kraft lignin (support 1) and one was based on lignin extracted from cooperage oak wood (support 2). Their synthesis and functionalisation have been reported

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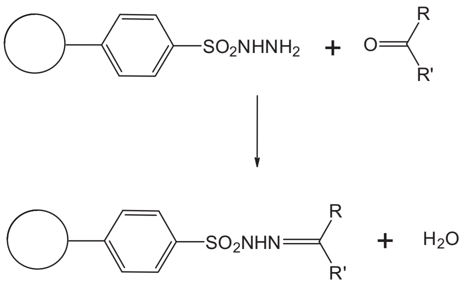
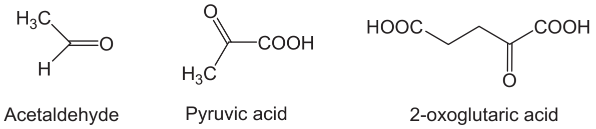
http://dx.doi.org/10.1016/j.foodchem.2013.03.031



Scheme 1. Extraction reaction.



Scheme 2. Selected carbonyl compounds.

elsewhere (Saidane, Barbe, Birot, & Deleuze, 2010, 2012). The SO_2-$NHNH_2$ loading was 0.5 mmol g^{-1} and 0.7 mmol g^{-1} for support 1 and support 2, respectively.

2.3. Wine samples

The wines studied were two different bottled (i.e., sulfited) sweet white from Sauternes (Bordeaux area, France) from the 2008 vintage. The initial free, bound, and total SO_2 concentrations were 8 mg l^{-1}, 140 mg l^{-1} and 148 mg l^{-1}, in the wine used for extractions with support 1 (Blank 1), and 5 mg l^{-1}, 155 mg l^{-1}, and 160 mg l^{-1} in the wine used for extractions with support 2 (Blank 2).

2.4. Carbonyl compound removal from wine

Reactions took place at room temperature without any agitation. Experiments using different amounts of supports were performed with an 80 ml wine sample and contact times from 1 to 4 weeks.

2.5. Carbonyl compound analysis

Acetaldehyde and pyruvic acid concentrations in wine were determined using commercial enzymatic kits. The enzymatic method described by Blouin (1965) was used for 2-oxoglutaric acid. Optical densities for enzymatic determination were measured at $\lambda = 340$ nm on a Spectronic 20 Genesys spectrophotometer. Values are given in mmol $l^{-1} \pm 3\%$.

2.6. SO_2 measurements

Free and total SO_2 concentrations were determined by iodometry, as previously described (Ribéreau-Gayon, Peynaud, Sudraud, & Ribéreau-Gayon, 1982).

3. Results and discussion

3.1. Selecting the carbonyl compounds to be removed

Acetaldehyde, pyruvic acid, and 2-oxoglutaric acid were selected as the carbonyl compounds to be removed from sweet wines, with the aim of significantly reducing their binding power, on the basis of previous research (Blasi et al., 2007). Their HSO_3^- binding efficiency is quantified by the dissociation constant (K_d) of the bisulfite combination (Margalit, 2004, chap. 7). K_d values are 2.4×10^{-6} mol l^{-1} for acetaldehyde, 0.3×10^{-3} mol l^{-1} for pyruvic acid, and 0.5×10^{-3} mol l^{-1} for 2-oxoglutaric acid (Burroughs & Sparks, 1973).

3.2. Removing carbonyl compounds from wine

The same extraction protocol was applied for both supports. The effect of different molar ratios, between the amount of extracting agent and the estimated initial total amounts of free acetaldehyde, pyruvic acid, and 2-oxoglutaric acid present in the wine (1/1, 2/1, and 3/1) were investigated. Contact time between the scavenging support and the wine varied from 1 to 4 weeks at room temperature, without stirring.

The efficiency of carbonyl removal from wine, using supports 1 and 2, according to the amount of extracting agent used and contact time, are shown in Tables 1 and 2.

The first observation was that carbonyl compounds were effectively removed from wine using both supports. In the best cases, up to 75% of the estimated total amount of free carbonyl compounds was actually extracted. Extraction efficiency varied according to the type of carbonyl compound, contact time and amount of support used.

Acetaldehyde and pyruvic acid presented similar behaviours: a clear improvement in removal efficiency was observed as the amount of scavenging agent increased. For these compounds, an increase in contact time had much less impact. Extraction of 2-oxoglutaric acid appeared to be more efficient: most of it was already removed after 1 week of contact with wine, irrespective of the amount of extraction agent used.

As a general rule, the supports tested exhibited similar behaviours. However, support 1, prepared from Kraft lignin, was the most efficient at lower molar ratios, and apparently reached equilibrium after just 1 week. In contrast, support 2, prepared from modified oak wood lignin, was less efficient at lower molar ratios and took about 3 weeks to reach equilibrium. This suggested that support 1 probably had better functionalised site accessibility. However, the finding that support 2 had a higher efficiency of about 10% at the highest molar ratio is difficult to explain.

A comprehensive set of extraction data was collected, including the bound and free SO_2 concentrations measured after carbonyl compound removal with both supports after a contact time of 4 weeks. These data are presented in Table 3.

The data presented in Table 3 (column 4) indicate that significant amounts of the total initial free carbonyl compounds present in the sample were extracted from the wine by the process, irrespective of the support used. Extraction efficiency increased significantly with the amount of extracting agent used (column 5). This extraction efficiency appears to be slightly more important for support 2 than for support 1, mainly when high levels of extracting agent are used. However, the extraction is never total, irrespective of the amount of extracting agent used, due to equilibrium of the species present in the solution.

The total and free SO_2 concentrations measured, before and after processing, revealed that carbonyl compound removal was accompanied by a decrease in total SO_2, associated with a gradual increase in free SO_2. This confirmed that this technique actually reduced the bound SO_2 concentration, as expected. This suggests that, when free carbonyl compounds react with grafted phenylsulfonylhydrazine and are extracted from the wine, some of the corresponding carbonyl bisulfites dissociate to form free carbonyl compounds and HSO_3^-, in agreement with the mass action law.

An increase in the amount of scavenging agent used in the process had a rather limited impact on the free SO_2 concentration (Table 3, column 7). This may be explained by a limited use of the