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Article

VOLATILE PROFILE OF TWO MONOVARIETAL WHITE WINES UNDER DIFFERENT ANTIOXIDANT ENVIRONMENTS DURING STORAGE IN BOTTLE

PERFIL VOLÁTIL DE DOIS VINHOS BRANCOS MONOVARIETAIS SUJEITOS A DIFERENTES AMBIENTES ANTIOXIDANTES DURANTE A CONSERVAÇÃO EM GARRAFA

Cátia V. Almeida Santos[1], Marco Gomes da Silva[1,*], Maria João Cabrita[2,*]

[1]LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal.

[2]MED - Mediterranean Institute for Agriculture, Environment and Development & CHANGE – Global Change and Sustainability Institute, Departamento de Fitotecnia, Escola de Ciências e Tecnologia, Universidade de Évora, Pólo da Mitra, Ap. 94, 7006-554 Évora, Portugal.

***** Corresponding author: Tel.: + 351 212948350 Ext 10911F; e-mail: mdr@fct.unl.pt and Tel.: + 351266 760869; e-mail: mjbc@uevora.pt

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SUMMARY

The volatile organic compounds (VOCs) formed during winemaking can be modulated by several additives, namely by the use of sulphur dioxide (SO_2) which has been well-accepted on winemaking as a preservative agent. However, some drawbacks associated with SO_2 wine application led to the need to reduce or replace its use. In this work, VOCs profile after storage in bottle under different antioxidant conditions of two Portuguese monovarietal wines (‘Arinto’ and ‘Síria’) was studied. Wines were obtained by different winemaking environments (0, 50, 100 mg/L of SO_2 and 100 mg/L ascorbic acid for ‘Síria’ and 15, 30, 45 mg/L of SO_2 and 100 mg/L of ascorbic acid for ‘Arinto’ both with and without bentonite). After alcoholic fermentation, a second SO_2 treatment was applied: 0 and 60 mg/L of SO_2 to ‘Arinto’ wines and 30 and 60 mg/L of SO_2 to ‘Síria’ wines. Wines were kept over lees for three months, bottled and analysed after three months in bottle. The VOCs present were analysed by HS-SPME-GC/MS six months after fermentation. The maturation conditions did not influence the evolution of free and total SO_2. Regarding the VOCs profile evolution, the ANOVA analysis showed that esters are the most important group, presenting significant differences among samples. Through the PCA analysis, using wines after fermentation as reference, 74.13 % and 54.92 % of the variation were explained by the first two principal components for ‘Arinto’ and ‘Síria’, respectively. VOCs profile evolution of wines seems to be mainly influenced by the fermentation conditions.

RESUMO

Os compostos orgânicos voláteis (VOCs) originados no processo de produção do vinho podem ser modulados por vários aditivos, nomeadamente através da aplicação de dióxido de enxofre (SO_2) que tem sido bem aceite na indústria como um agente preservante. Contudo, algumas desvantagens associadas à sua aplicação têm levado à necessidade de reduzir ou substituir este aditivo. Neste trabalho foram estudados os perfis de VOCs após a maturação de dois vinhos brancos monovarietais (‘‘Arinto’’ e ‘‘Síria’’). Os vinhos foram elaborados sem diferentes condições antioxidantes (0, 50, 100 mg/L de SO_2 e 100 mg/L de ácido ascórbico para os vinhos ‘Síria’ e 15, 30, 45 mg/L de SO_2 e100 mg/L de ácido ascórbico para os vinhos ‘Arinto’, e na presença ou ausência de bentonite. Após a fermentação alcoólica foi efetuada uma segunda adição de SO_2, 0 e 60 mg/L de SO_2 aos vinhos ‘Arinto’ de 30 e 60 mg/L de SO_2 aos vinhos ‘Síria’. Os vinhos foram mantidos sobre as borras por 3 meses, foram engarrafados e permaneceram também 3 meses em garrafa antes de serem analisados. Os VOCs foram analisados por HS-SPME-GC/MS 6 meses após a fermentação. Após a fermentação, as condições aplicadas não influenciaram a evolução do SO_2 livre e total presentes nas amostras. Relativamente ao perfil de VOCs, a ANOVA revelou que os esteres foram o grupo mais importante, apresentando diferenças significativas entre amostras. Através de PCA, usando os vinhos após a fermentação como referência, as duas primeiras componentes principais explicam 74,13 % e 54,92 % da variabilidade entre as amostras para ‘Arinto’ e ‘Síria’, respetivamente. O perfil de VOCs evoluiu principalmente pela influência das condições antioxidantes na fermentação.

Keywords: White Wine, bentonite, ascorbic acid, sulphur dioxide, volatile organic compound, maturation on lees.
Palavras-chave: Vinho branco, bentonite, ácido ascórbico, dióxido de enxofre, compostos orgânicos voláteis, maturação sobre borras.

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INTRODUCTION

Wine is a complex chemical mixture whose aroma is mostly originated by volatile organic compounds (VOCs), which depend on grape quality, winemaking and ageing processes. The matrix composition continues to change even during storage. This evolution can affect wine aroma properties presenting a significant impact on consumer acceptance of the product (Bindon *et al.*, 2014; González-Barreiro *et al.*, 2015; Belda *et al.*, 2017; Piras *et al*., 2020; Echave *et al.*, 2021). Oxidative reactions play an important role in aroma evolution during storage, in particular on white wines, which are more prone to the non-enzymatic oxidative phenomenon (Pati *et al.*, 2014). In this process, a deterioration of white wines overall quality can occur by a controlled short-term oxidation promoting the development of a characteristic bottle bouquet (Cheynier *et al.*, 1989; Kallithraka *et al*, 2009).

The oxygen present on the headspace of the bottle and dissolved in wine is reduced to hydrogen peroxide (H_2O_2) among other reactive oxygen species by metal redox mediation by iron and copper. The H_2O_2 formed reduce ketones, aldehydes and polyphenols to quinones, which results in loss of characteristic aroma (Waterhouse and Laurie, 2006; Oliveira *et al.*, 2011). To prevent this aroma loss, several methods are used like the addition of antioxidant agents or in combination with a controlled maturation on lees. Sulphur dioxide (SO_2) is a well-accepted preventing agent in the wine industry. It is used at different stages of the process due to its different functions, namely, the ability to act as an antioxidant and antiseptic. When added to musts or wine an acid-based equilibrium occurs between three forms, molecular SO_2, sulphite ion (SO_3^{2-}) and bisulphite ion (HSO_3^-), known as the "free SO_2". It can also react with unsaturated compounds producing the commonly known as "bound SO_2". The HSO_3^- reacts with H_2O_2 produced by oxygen metal reduction promoting the reduction of phenolic compounds. Also, SO_2 reacts with quinones, reducing them back to the previous phenolic forms preventing wine aroma loss as already described (Roberts and McWeeny, 1972; Manzocco *et al.*, 1998). However, an excessive exposer of the population to this preservative agent has led to an increase of reported allergic episodes (Vally *et al.*, 2009; Zhang *et al.*, 2014). As a response to the health concern, European Union established a requirement of a warning in the label indicating the presence of sulphites when present above 10 mg/kg or 10 mg/L (EU-28, 2016). The drawbacks associated to SO_2 wine application either by the legal limits, health concerns, off-flavours that can be generated and formation of sulphuric acid, lead to the need to reduce or even replace the use of SO_2 (Guerrero and Cantos-Villar, 2015; Echave *et al.*, 2021). Maturation on lees has been used to increase the antioxidant protection of wine. Lees are a mixture of yeast cells, lactic acid bacteria and organic and inorganic precipitates. The contact of wine with this mass prior to bottling may promote the release of additional substances like polyphenols, mannoproteins or glutathione which, in a controlled manner, may help to prevent oxidation. Moreover, a controlled exposure has been indicated to generally improve wine sensory characteristics described as having more body (mouthfeel) and flavour (Fornairon-Bonnefond and Salmon, 2003; Comuzzo *et al.*, 2015).

Previously, the impact on VOCs profile of different antioxidant conditions (different application doses of SO_2 and its replacement by ascorbic acid) on monovarietal white wine fermentation was analysed (Almeida Santos *et al.*, 2020). The influence of the presence or absence of bentonite was also studied. The same monovarietal musts under the conditions applied on the study lead to different wine VOCs profiles with a varietal dependency. The modification of these parameters on the fermentation step should hence be taken into consideration by winemakers. The varieties evaluated in the study were 'Arinto' and 'Síria', two Portuguese autochthonous white grape varieties. Both varieties integrate the list of mandatory varieties to produce wine products entitled as protected designation of origin (PDO) "Alentejo" (Portugal). 'Arinto' variety is typical from the north of Portugal but gaining importance in other wine-producing regions like Alentejo, south of Portugal. 'Síria' is a variety very common on Alentejo that as gathering increasingly interest by winemakers (Fernão-Pires, 2018; Almeida Santos *et al.*, 2020).

This work is in line with the previous one (Almeida Santos *et al.*, 2020). The present work is focused on the effect of different antioxidant conditions on VOCs, which was assessed by headspace-solid phase microextraction-gas chromatography/mass spectrometry (HS-SPME-GC/MS), comparing wine VOCs after three months on lees and three months in bottle under different antioxidant environments.

MATERIALS AND METHODS

Wine samples

Wines studied in this work were obtained from 'Arinto' and Siria grapes harvested in September 2018 in Évora University vineyard. Grapes were destemmed, crushed, pressed and racked after a 24 h cold static sedimentation. The clarified must was divided into 10 L and 5 L vessels, and inoculated with a mixture of commercial *Saccharomyces cerevisiae* (mixture 1:1 of LEVULINE FB from Oenofrance and IOC 18–2007 from Lallemand OEnology). SO_2, 0, 50 and 100 mg/L of SO_2 ('Arinto' variety) and 0, 15, 30 and 45 mg/L of SO_2 ('Síria' variety) using a commercial 6 % aqueous solution of sodium bisulfite (SAI, SOLFOX 6 Nº CE: 231-870-1) and ascorbic acid (100 mg/L) (MERCK CAS:50-81-7) were added. Bentonite (0.1 g/L) (aqueous solution of 10 % (w/v), MICROCOL ALPHA, LAFFORT), was added only to half of the samples. Samples were fermented at 16 °C in duplicates. The lower doses of SO_2 used in 'Síria' musts are related to the presumably higher resistance to oxidation of this variety, according to local viticulture, but not yet studied in deep. After alcoholic fermentation, each wine was split into two sample series, and a second dose of 0 and 60 mg/L of SO_2 for 'Arinto' wines and 30 e 60 mg/L of SO_2 for 'Síria' wines was immediately added using the same commercial solution. Wines were kept in contact with lees for three months at 16 ºC, on amber 2.5 L glass carboys. After this period, wines were separated from lees, bottled and stored vertically for three months at 16 ºC on amber bottles of 75 mL. In total, 40 'Síria' wines and 30 'Arinto' wines were analysed. Figure 1 shows a summary of the experimental design. Wines were analyzed after alcoholic fermentation and after six months (three months sur lees and three months in bottle)

Oenological parameters as total acidity (potentiometric titration, Method OIV-MA-AS313-01) and volatile acidity (distillation and titration, Method OIV-MA-AS313-02), alcoholic strength (distillation, Method OIV-MA-AS312-01B), pH (potentiometry, Method OIV-MA-AS313-15), reducing sugars (Method OIV-MAAS311-01A) and sulphur dioxide (iodometric titration, Method OIV-MA-AS323-04B) were measured according to OIV methods (OIV, 2018; Almeida-Santos *et al*., 2020).

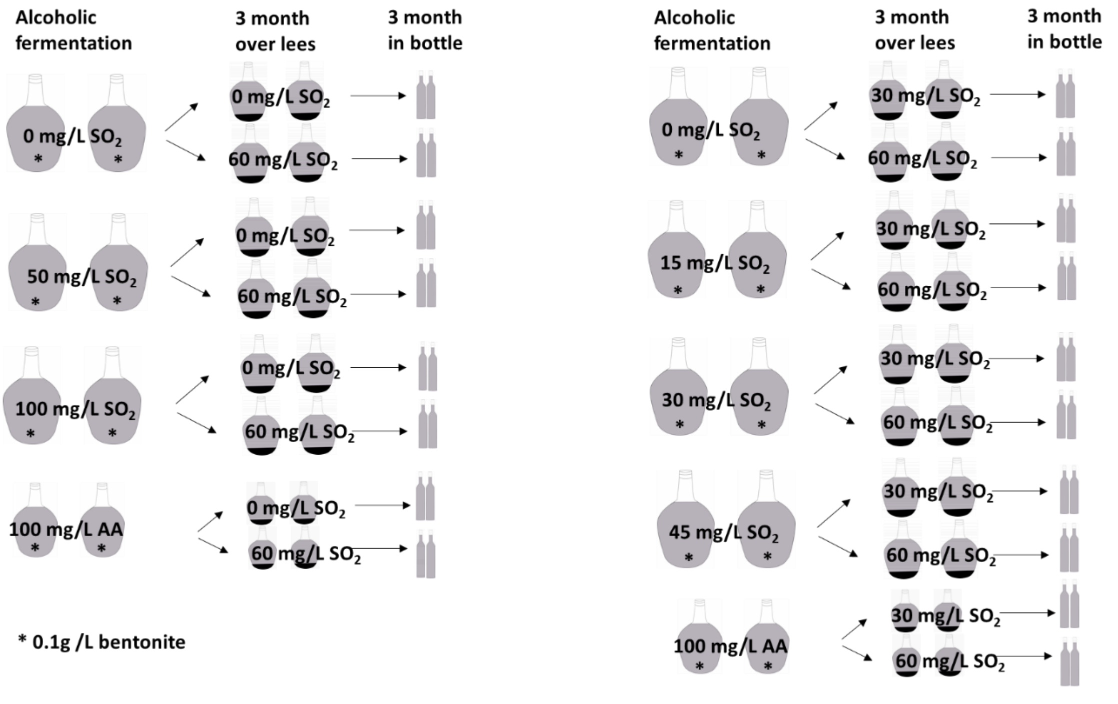

Figure 1. Experimental design of vinification protocol illustrating SO2 and AA (ascorbic acid) additions. Left scheme for 'Arinto' and right scheme for 'Síria'. Same protocol was used without bentonite addition (5 L vessels were used for AA due to insufficient must for 10 L vessels).

HS-SPME sampling of wine volatiles

The HS-SPME sampling experiments were carried out as reported by Almeida Santos *et al.* (2020). Briefly, to 5.0 mL of sample in a 22 mL vial, 2 g of sodium chloride were added. The vial was sealed with a Teflon-lined rubber septum/magnetic screw cap and was equilibrated for 5 min at 30 °C, and then the sample headspace was extracted for 30 min at the same temperature with SPME fiber. The extraction occurred by exposing 1 cm of a DVB/Carb/PDMS fiber, 50/30 μm film thickness (d_f), supplied from Supelco, (Bellefonte, PA, USA). Prior to use, the fiber was conditioned following the manufacturer's recommendations. Fiber blanks were run periodically to ensure the absence of contaminants and/or carryover. Thermal desorption of the analytes was carried out by exposing the fiber in the GC injection port at 260 °C for 3 min in splitless mode, for the same time period. All samples were analysed in duplicate.

GC/MS analysis

The analyses were performed on a GC/MS system consisting of a Bruker GC 456 with a Bruker mass selective detector Scion TQ. An automatic sampler injector was used: CTC Analysis autosampler CombiPAL. Chromatographic separation was achieved on a SupelcoWaxTM 10 PLUS capillary column (60 m × 0.25 mm i.d., 1.0 μm, d_f), supplied by Supelco Analytical (Supelco, Bellefonte, PA). The oven temperature program began at 40 °C hold for 5 min, raised to 240 °C at 4 °C/min, holding for 5 min. Helium was used as carrier gas at constant flow of 1.7 mL/min at the electronic flow control (EFC 21). The MS transfer line and source temperatures were set at 260 °C. Data were acquired with MSWS 8.2 Bruker and analyzed with Bruker MS Data Review 8.0. Spectra were matched with NIST MS Search Program Version 2.3. The recording of retention times and characteristic mass fragments was obtained at an electron ionization (EI) of 70 eV. The mass spectra of the analytes were recorded at full scan, from 40 to 450 Da. The analyses of a commercial hydrocarbon mixture (C8 - C20) under the same chromatographic conditions was used to calculate the linear retention indices (LRIs) for each compound. The relative amounts of individual components are expressed as percent peak areas relative to the total peak area of the chromatogram (Relative Peak Area - RPA).

Statistical analysis

Principal components analysis (PCA) was performed using XLSTAT Version 2020.5.1 by Addinsoft, to reduce the number of variables and to detect a pattern in the relationship between the variables (% of peak area of each compound) and the wine samples.

One-way analysis of variance (ANOVA) using Tukey´s multiple comparisons test was performed to compare the means at the level of significance of $p < 0.05$, for total and free SO_2 content in the wine samples. Two-way analysis of variance (ANOVA) using Tukey´s multiple comparisons test was performed to compare the means at the level of significance of $p < 0.05$, for VOCs, comparing wines immediately after fermentation and after 6 months (3 months on lees and 3 months on bottle). For ANOVA analysis three factors were considered, SO_2 doses on fermentation (0, 50, 100 mg/L for 'Arinto' wines and 0, 15, 30, 45 mg/L for 'Síria' wines), SO_2 doses after fermentation (0, 60 mg/L for 'Arinto' wines and 30 and 60 mg/L for 'Síria' wines) and the presence or absence of bentonite, using GraphPad Prism version 9.0.0 by GraphPad Software.

RESULTS AND DISCUSSION

SO_2 in wine samples

After alcoholic fermentation of 'Arinto' and 'Síria' wines, total and free SO_2 content was analysed. A second addition of SO_2 with two different doses was applied (0 and 60 mg/L of SO_2 to 'Arinto' wines, 30 and 60 mg/L of SO_2 to 'Síria' wines) and total and free SO_2 content was analyzed again, using the same iodometric titration method, after six months (three months on lees and three months on bottle). On 'Síria' wines, 30 mg/L of SO_2 instead of 0 mg/L of SO_2 was applied since these wines were fermented with lower antioxidant doses and presented lower levels of total SO_2.

Table I for 'Arinto' wines and Table II for 'Síria' wines summarized the SO_2 content for both wines with and without bentonite. The results show that both SO_2 forms (total and free) decreased with time in both wine samples, considering the sum of the initial concentration of SO_2 present on initial wines and the second addition of SO_2. The decline of total SO_2 may indicate its effectiveness as an antioxidant during the time, as already reported (Carrascón *et al.*, 2018).

When performing ANOVA on the averages data for total and free SO_2 on each wine, the observed differences do not have a response trend in relation to the applied conditions according to the three factors in the study (initial and second antioxidant conditions and presence or absence of bentonite on fermentation). Both total and free SO_2 behaved as described before (Gambuti *et al.*, 2020), showing a decreasing content over time, regardless of the added SO_2 applied (Sacks *et al.*, 2020; Stockley *et al.*, 2021).

Volatile organic compounds identification

The HS-SPME-GC/MS method was applied to wine samples to characterize the VOCs profile. Each sample was analysed in duplicate (antioxidant dose combinations and presence or absence of bentonite on fermentation). Duplicates are indeed enough, since according to recently published works with comparable matrices (Almeida Santos *et al.*, 2020; Ferreira *et al.*, 2021; Saracino *et al.*, 2021; Pereira *et al.*, 2021; Ferreira *et al.*, 2022) results showed that duplicates instead of triplicates do not jeopardize the associated error of the measurement and the resulted error for both cases was very similar. This fact allows to perform more analysis by time unit promoting the throughput of samples, an important issue in routine analysis, when needed.

Table I

Free and total SO_2 content of initial 'Arinto' wines, with and without bentonite addition and six months after the alcoholic fermentation (AF) and the second SO_2 addition

Initial antioxidant condition	Fermented with bentonite SO_2 addition (mg/L) after AF	Free SO_2 (mg/L)	Total SO_2 (mg/L)
0 mg/L of SO_2	-	8.5(±0.7)	34.0(±2.8)
50 mg/L of SO_2	-	9.5(±0.7)	74.0(±0.0)
100 mg/L of SO_2	-	11.0(±1.4)	108.5(±0.7)
100 mg/L of ascorbic acid	-	9.0(±2.8)	45.5(±2.1)
0 mg/L of SO_2	0	4.0(±0.0)	22.0(±2.8)^{Aa}
	60	5.0(±0.0)	72.5(±2.1)^{Ab}
50 mg/L of SO_2	0	5.5(±0.7)	55.0(±5.7)^{Aba}
	60	8.5(±0.7)	101.5(±3.5)^{ABb}
100 mg/L of SO_2	0	7.0(±2.8)	86.0(±4.2)^{Ba}
	60	9.5(±2.1)	123.5(±2.1)^{Bb}
100 mg/L of ascorbic acid	0	6.0(±0.0)	22.0(±0.0)^{Aa}
	60	4.0(±0.0)	68.0(±0.0)^{Aa}
Initial antioxidant condition	**Fermented without bentonite SO_2 addition (mg/L) after AF**	**Free SO_2 (mg/L)**	**Total SO_2 (mg/L)**
0 mg/L of SO_2	-	7.0(±0.0)	42.0(±1.4)
50 mg/L of SO_2	-	12.0(±0.0)	80.0(±1.4)
100 mg/L of SO_2	-	11.5(±0.7)	110.5(±3.5)
100 mg/L of ascorbic acid	-	11.0(±1.4)	49.0(±1.4)
0 mg/L of SO_2	0	5.0(±0.0)	27.5(±3.5)^{Aa}
	60	8.5(±0.7)	79.0(±1.4)^{Ab}
50 mg/L of SO_2	0	7.5(±0.7)	52.0(±2.8)^{ABa}
	60	8.0(±2.8)	79.5(±36.1)^{Aa}
100 mg/L of SO_2	0	8.0(±1.4)	83.5(±2.1)^{Ba}
	60	8.5(±0.7)	128.5(±2.1)^{Bb}
100 mg/L of ascorbic acid	0	7.0(±0.0)	26.0(±0.0)^{Aa}
	60	7.0(±0.0)	76.0(±0.0)^{Aa}

Different capital letters means that each calculated value differ significantly ($p < 0.05$) according to the initial antioxidant condition factor; different lowercase letters means that each calculated value differ significantly ($p<0.05$) according to second antioxidant addition factor.

Table II

Free and total SO_2 content of initial 'Síria' wines with and without bentonite addition, and 6 months after alcoholic fermentation (AF) and the second SO_2 addition

Initial antioxidant condition	Fermented with bentonite SO_2 addition (mg/L) after fermentation	Free SO_2 (mg/L)	Total SO_2 (mg/L)
0 mg/L of SO_2	-	8.0(±2.8)	35.5(±0.7)
15 mg/L of SO_2	-	6.0(±1.4)	43.0(±1.4)
30mg/L of SO_2	-	7.0(±0.0)	58.5(±0.7)
45mg/L of SO_2	-	9.0(±1.4)	54.0(±0.0)
100 mg/L of ascorbic acid	-	7.0(±2.8)	40.0(±1.4)
0 mg/L of SO_2	30	7.0(±2.8)	35.5(±3.5)^{Aa1}
	60	6.5(±0.7)	33.0(±24.0)^{Aa1}
15 mg/L of SO_2	30	8.0(±2.8)	45.5(±2.1)^{Aa1}
	60	6.5(±0.7)	63.5(±2.1)^{Ba1}
30 mg/L of SO_2	30	9.0(±2.8)	56.0(±4.2)^{Aa1}
	60	9.0(±0.0)	72.0(±1.4)^{Ba1}
45 mg/L of SO_2	30	5.5(±0.7)	47.0(±9.9)^{Aa1}
	60	7.5(±3.5)	63.5(±3.5)^{Ba1}
100 mg/L of ascorbic acid	30	7.5(±3.5)	41.5(±2.1)^{Aa1}
	60	6.5(±2.1)	58.0(±5.7)^{Ba1}
Initial antioxidant condition	**Fermented without bentonite SO_2 addition (mg/L) after fermentation**	**Free SO_2 (mg/L)**	**Total SO_2 (mg/L)**
0 mg/L of SO_2	-	4.0(±0.0)	41.0(±2.8)
15 mg/L of SO_2	-	6.0(±2.8)	56.0(±5.7)
30mg/L of SO_2	-	6.5(±0.7)	55.5(±6.4)
45mg/L of SO_2	-	8.5(±2.1)	57.5(±3.536)
100 mg/L of ascorbic acid	-	3.5(±0.7)	48.5(±0.7)
0 mg/L of SO_2	30	7.5(±2.1)	44.5(±2.1)^{Aa2}
	60	5.5(±0.7)	67.0(±2.8)^{Ab2}
15 mg/L of SO_2	30	8.0(±1.4)	51.5(±5.0)^{ABa1}
	60	5.5(±0.7)	74.0(±1.4)^{Ab1}
30 mg/L of SO_2	30	9.0(±1.4)	60.5(±2.1)^{ABab1}
	60	8.5(±0.7)	82.5(±2.1)^{Ab1}
45 mg/L of SO_2	30	6.5(±2.1)	52.5(±5.0)^{Ba1}
	60	7.5(±0.7)	76.0(±5.7)^{Ab1}
100 mg/L of ascorbic acid	30	6.5(±0.7)	46.5(±2.1)^{ABa1}
	60	6.5(±0.7)	64.5(±0.7)^{Ab1}

Different capital letters means that each calculated value differ significantly ($p<0.05$) according to initial antioxidant condition factor; different lowercase letters means that each calculated value differ significantly ($p<0.05$) according to second antioxidant addition factor; different number means that each calculated value differ significantly ($p < 0.05$) according to presence or absence of bentonite

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VOCs were tentatively identified by matching mass spectra with spectra of reference compounds in NIST library. Linear retention indices (LRI) were also calculated using a commercial hydrocarbon mixture (C8 - C20) and compared with LRIs described in the literature (Bianchi *et al.*, 2007; Oliveira *et al.*, 2008; Mateus *et al.*, 2010; Di Mattia *et al.*, 2015; Almeida Santos *et al.*, 2020; Pereira *et al.*, 2021). Table III presents the information regarding VOCs tentatively identified by compound number.

Volatile organic compounds in wines

Only compounds that present a relative area above 0.0001% of the total chromatogram area were considered for statistical purposes. For both wines, the relative amount of each compound was calculated as the percentage ratio of the respective peak area in relation to the total peak area analyzed (RPA) of the chromatogram (Table IV for 'Arinto' wines and Table V for 'Síria' wines). 93 VOCs, which were present at least in one replicate sample, were tentatively identified. Additionally, 54 more compounds were also detected, but their identification was not possible to assign since the library match was below 850. This limit was established for identification assignments. comparing with literature data of the correspondent LRI data. The analyses of the VOCs profile for both wines ('Arinto' and 'Síria') allowed to observe that esters (44 compounds), alcohols (19 compounds), carboxylic acids (7 compounds), ethers (4 compounds), ketones (3 compounds) and aldehydes (4 compounds) were the most frequent chemical groups, together with 12 miscellaneous compounds, also confirmed by the literature (Cabrita *et al.*, 2006; Almeida Santos *et al.*, 2020; Petronilho *et al.*, 2020). Regarding total chromatographic area, it was higher for wines fermented with bentonite analyzed after six months. For these wines it was possible to tentatively identify compounds accounting for 99 % of the total chromatographic area for both 'Arinto' and 'Síria' wines. Same result was obtained for wines fermented without bentonite analyzed after six months. The total area by chemical classes for each oxidant condition after six months (Table IV and Table V) was compared with the total area of wines after alcoholic fermentation, reported on a previous work (Almeida Santos *et al.,* 2020). Esters and alcohols presented the highest variations in both wines. Figure 2 (a and b for 'Arinto' wines; c and d for 'Síria' wines, with and without bentonite respectively) illustrate the variations of VOCs in wines with six months using wines after alcoholic fermentation as reference.

Clearly, the effect of adding or not adding bentonite during fermentation, impacts the evolution of volatiles over time (Figure 2). The evolution over six months led to an increasing of esters and a decrease of alcohols. The increase of esters amounts during ageing at temperatures above 5 ºC has been also reported by Garde-Cerdán *et al.* (2008). However, the total concentration of alcohols decreased, contrary of results reported for wines bottled above 5 ºC (Garde-Cerdán *et al.*, 2008).

For VOCs, a two-way ANOVA using Tukey´s multiple comparisons test at the level of significance of $p<0.05$, was performed considering: initial and second antioxidant conditions and the presence or absence of bentonite on fermentation (Tables IV, V, VI and VII). A total of 11 compounds for 'Arinto' and 'Síria' wines presented at least one statistical difference: ethyl acetate (**1**), isoamyl acetate (**9**), isoamyl propionate (**11**), ethyl hexanoate (**14**), ethyl octanoate (**23**), ethyl decanoate (**33**) and 2-propanol (**52**) for both wine varieties. In general, compounds **1**, **9**, **11**, **14** and **23** increased after wine maturation. Changes were even clearer between different antioxidant conditions on wines fermented with bentonite. Ethyl esters were already reported by other authors as being affected by bentonite (Vincenzi *et al.*, 2015), indicating a decrease in their amount. 'Arinto' wines were more sensitive to the conditions applied. A decrease on ethyl esters of branched-chain fatty acids during maturation on lees was observed. This suggests an increase of long-chain alcohols and volatile fatty acids. The presence of lees and the autolysis on yeast cells also seems to contribute to the release of fatty acids that will produce VOCs such as esters, aldehydes, and ketones (Styger *et al.*, 2011). Ethyl decanoate (**33**) and 2-propanol (**52**) on 'Arinto' wines fermented without bentonite increased, while in all the other wines decreased. Propyl acetate (**3**), 1-hexanol (**58**) and phenethyl alcohol (**68**) for 'Arinto' wines and ethyl 9-decanoate isomer (**37**) and heptanoic acid (**78**) for 'Síria' wines in general increased with time. This increase was less noticeable for the higher dose of SO_2 applied. On the other hand, acetaldehyde ethyl amyl acetal (**47**) decrease over time on 'Síria' wines fermented without bentonite

Table III

VOCs tentatively identified in all analysed samples of ‘Arinto’ and ‘Síria’ wines

Compound no.	LRI cal [LRI lit][a]	Possible compound [Common name]	Most abundant ions (m/z)
		Esters	
1	901 [863-893]	Ethyl Acetate	43/61/70
2	962 [955-977]	Ethyl 2-methylpropanoate [Ethyl isobutanoate]	45/57/71
3	973 [924-985]	Propyl acetate	43/61/71
4	1014 [963-1018]	2-Methylpropyl acetate [Isobutyl acetate]	43/56/71
5	1034 [978-1045]	Ethyl butyrate	71/43/88/73/41
6	1059 [978-1071]	Ethyl 2-methylbutanoate	57/102/41/74
7	1061 [1013-1071]	Butyl acetate	43/56/61
8	1063 [1009-1066]	Ethyl 3-methylbutyrate [Ethyl isovalerate]	57/41/70/88
9	1118 [1071-1131]	3-Methylbutyl acetate [Isoamyl acetate]	43/55/70
10	1136 [1122-1142]	Ethyl pentanoate	57/88/43/70/101
11	1194 [1177]	3-Methylbutyl propanoate [Isoamyl propionate]	57/70/55/43
12	1202 [1125-1176]	Pentyl acetate [Amyl acetate][c]	43/55/70
13	1208[b]	3-Methylbutyl butyrate [Isoamyl butyrate][c]	71/43/105/55
14	1234 [1198-1244]	Ethyl hexanoate	88/99/43/70/60
15	1258 [1267]	Ethyl 5-hexenoate isomer	43/56/69/88
16	1274 [1251-1287]	Hexyl acetate	43/56/69/61
17	1318 [1304-1325]	Propyl hexanoate	43/99/67/117/41/82
18	1327 [1292-1307]	Acetate 3-hexenoate isomer[c]	67/43/82
19	1328 [1304-1322]	Ethyl heptanoate [Grape oil]	88/43/70/113/101/60
20	1337 [1327-1353]	Ethyl 2-hexenoate isomer	55/99/73/41
21	1367 [1304-1322]	Heptyl acetate	43/70/56
22	1390 [1351-1391]	Methyl octanoate	74/87/43/55
23	1438 [1402-1454]	Ethyl octanoate	88/57/43/127
24	1450 [1455-1472]	3-Methylbutyl hexanoate [Isoamyl caproate]	70/43/99/55
25	1460 [1429-1489]	Octyl acetate	43/56/70/83
26	1489[b]	Ethyl 7-octenoate isomer[c]	55/96/88/70
27	1518 [1508-1538]	Propyl octanoate	61/145/127/41
28	1533 [1525-1576]	2-Methylpropyl octanoate [Isobutyl octanoate][c]	56/41/127/145
29	1535 [1511-1561]	Ethyl nonanoate [Wine ether]	88/101/70/41/55
30	1561[b]	Ethyl 2-octenoate isomer	73/105/55/41/86
31	1587 [1570-1625]	Methyl decanoate	74/87/43/55
32	1618[b]	Methyl 8-methyl-nonanoate isomer[c]	74/45/57/87
33	1641 [1636-1680]	Ethyl decanoate	88/101/70/55/41
34	1644 [1660-1693]	3,7-Dimethyl-6-octen-1-yl acetate [Citronellol acetate]	41/69/81/55/95
35	1658 [1642-1695]	3-Methylbutyl octanoate [Isoamyl caprylate]	43/70/127
36	1673 [1622-1680]	Diethyl succinate	101/129/55
37	1690 [1663-1727]	Ethyl 9-decenoate isomer	55/88/135
38	1695 [1676-1689]	Ethyl 4-decenoate isomer	55/69/84/41/101/152
39	1837 [1837-1881]	Ethyl dodecanoate [Ethyl laurate]	88/70/41
40	1845 [1863-1897]	3-methylbutyl decanoate [Isoamyl decanoate]	70/43/55
41	1848 [1737-1852]	2-Phenylethyl acetate	104/91/43
42	1914 [1841]	Ethyl 3-methylbutyl succinate [Ethyl isopentyl succinate]	101/129/55
43	ND [2233-2241]	Ethyl hexadecanoate [Ethyl palmitate][c]	88/41/157
44	ND [2241-2274]	Ethyl tetradecanoate [Ethyl myristate]	41/88/70/157
		Ethers	
45	ND[b]	Ethoxyethene [Ethyl vinyl ether]	43/72/59
46	982 [924-985]	2,4,5-trimethyl-1,3-dioxolane	43/101/73/55
47	1097 [1088]	1-(1-Ethoxyethoxy)pentane [Acetaldehyde ethyl amyl acetal]	73/45
48	1757[b]	Octyl ether[d]	57/71/41/83
		Ketones	
49	1401 [1386-1387]	2-Nonanone	58/43
50	1606 [1543-1627]	2-Undecanone	58/43/71
51	1737[b]	2-Dodecanone[c]	43/58/72
		Alcohols	
52	945 [927-968]	2-Propanol	45/44/43
53	1087 [1047-1111]	2-Methylpropyl alcohol [Isobutanol]	41/55/73
54	1147 [1102-1175]	1-Butanol	43/56/70
55	1191 [1173-1211]	3-Methylbutan-1-ol [Isoamyl alcohol]	55/41/70
56	1316 [1302-1328]	4-Methylpentan-1-ol [Isohexyl alcohol]	56/69/55/41
57	1348 [1334-1357]	3-Methylpentan-1-ol[c]	56/96/41
58	1350 [1292-1348]	1-Hexanol	56/41/69
59	1385 [1358-1379]	3-Hexen-1-ol[c]	41/67/95/82/55
60	1453 [1449-1455]	1-Heptanol	70/55/41/88
61	1467 [1445-1482]	1-Octen-3-ol [Vinyl pentyl carbinol][c]	57/72/55
62	1506 [1508-1541]	2-Nonanol[c]	45/69/41
63	1556 [1519-1605]	1-Octanol	56/55/41/69/83
64	1566 [1558-1620]	2,3-Butanediol[c]	45/57
65	1716 [1669-1712]	2-Undecanol[d]	45/83/57/69/97
66	1736 [1720-1794]	1-Decanol[d]	41/55/69/83
67	1757 [1760-1799]	3,7-Dimethyloct-6-en-1-ol [Citronellol]	41/67/55/81/95
68	1926 [1873-1947]	Phenethyl alcohol	91/65/122
69	1990 [1963-1988]	1-Dodecanol[c]	41/55/69/83/97
70	ND [2042-2057]	Nerolidol isomer[c]	41/69/93/107
		Aldehydes	
71	ND [700-744]	Acetaldehyde [Ethanal]	44/43
72	1247 [1218-1228]	2-Hexenal isomer[c]	41/55/69/83
73	1401 [1388-1415]	Nonanal	41/57/70/82
74	1504 [1470-1495]	Decanal[d]	45/69/41

[a] Retention indices calculated from C8 to C20 n-linear alkanes; [b] Identification by NIST comparation; [c] Just observed on ‘Síria’ wines, [d] Just observed on ‘Arinto’ wines, LRI lit - retention indices reported in the literature for wax capillary column (Janzantti and Monteiro, 2017; Wang *et al.*, 2017; Kong *et al.*, 2019; de-la-Fuente-Blanco *et al.*, 2020; Almeida Santos *et al.*, 2020; Pereira *et al.*, 2021)

Table III (continuation)

VOCs tentatively identified in all analysed samples of 'Arinto' and 'Síria' wines

Compound no.	LRI cal [LRI lit][a]	Possible compound [Common name]	Most abundant ions (m/z)
		Carboxylic acids	
75	1477 [1453-1496]	Acetic acidc	43/60
76	1669 [1627-1689]	Butanoic acid[c]	60/73
77	1710 [1666-1703]	3-Methylbutanoic acid [Isovaleric acid][c]	60/41
78	1924 [1935-1965]	Heptoic acid	60/73/41
79	ND [2051-2091]	Octanoic acid	60/70/41/101
80	ND [2154-2169]	Nonanoic acid[c]	41/60/73/115/129
81	ND [2269-2276]	Decanoic acid[c]	41/60/73/129
		Miscellaneous	
82	ND[b]	Carbon disulfided	76/44
83	1176 [1129-1147]	1,4-Dimethyl benzene [p-Xylene][c]	91/106/43
84	1270[b]	Styrene[d]	104/78
85	1346 [1309-1363]	Ethyl 2-hydroxypropanoate [Ethyl lactate]	45/75
86	1380 [1369-1409]	3-Ethoxypropan-1-ol	58/45/71
87	1509[b]	1-(2-Methoxypropoxy)-propan-2-ol[d]	75/59
88	1540 [1510-1552]	2-Methylthiolan-3-one	60/116
89	1550 [1611-1530]	Ethyl 3-hydroxybutyrate[c]	43/71/117
91	1636 [1618-1625]	Ethyl 2-furylcarboxylate[d]	95/112
90	1729 [1698-1755]	3-(Methylsulfanyl)-1-propanol [Methionol]	106/57/45/73
92	1875 [1816-1833]	β-Damascenone[c]	69/121/41
93	ND [2165-2192]	Vinylguaiacol[c]	135/150/107/77/45
		Unknowns	
94	944	Unknown 1[d]	43/101/73
95	978	Unknown 2	45/43
96	1048	Unknown 3[c]	44/45/43/55/73/91
97	1057	Unknown 4[c]	44/59/69
98	1102	Unknown 5[c]	91/42/59
99	1137	Unknown 6[d]	101/73/55
100	1143	Unknown 7	101/43/73
101	1174	Unknown 8[c]	43/55/71
102	1216	Unknown 9[d]	43/56/41/69/61
103	1249	Unknown 10[c]	105/77
104	1250	Unknown 11[d]	105/77/75/71
105	1258	Unknown 12[c]	77/105/70/43
106	1306	Unknown 13[d]	43/67/56
107	1320	Unknown 14[d]	41/69/56/99/117
108	1327	Unknown 15[c]	43/67/82
109	1359	Unknown 16[c]	43/70/56
110	1360	Unknown 17	43/133/58/151/179
111	1433	Unknown 18[d]	70/55/41/88
112	1440	Unknown 19[c]	81/67/53
113	1533	Unknown 20[c]	56/41/73/127/83
114	1542	Unknown 21	55/73/99/68/59/125
115	1565	Unknown 22	41/57/77/105/127/145
116	1572	Unknown 23[c]	96/55/41/81/67
117	1573	Unknown 24[d]	89/55/73/41/138
118	1610	Unknown 25[c]	45
119	1612	Unknown 26[c]	41/55/67/81/96/138
120	1623	Unknown 27[d]	101/73
121	1633	Unknown 28[c]	88/70/55/101/41
122	1653	Unknown 29[c]	42/91
123	1654	Unknown 30[c]	88/91
124	1657	Unknown 31[d]	101/91/129
125	1662	Unknown 32	43/69/55/83/61/97
126	1689	Unknown 33[c]	42
127	1705	Unknown 34	55/69/41/61/84/70/101
128	1725	Unknown 35	43/61/88
129	1732	Unknown 36[d]	45/173/70
130	1734	Unknown 37[c]	43/55/69/83/97
131	1748	Unknown 38[c]	133/151
132	1749	Unknown 39[d]	45/88/133
133	1772	Unknown 40[c]	43
134	1780	Unknown 41[c]	87/88/73/102
135	1782	Unknown 42	87/45/74/60
136	1792	Unknown 43	59
137	1801	Unknown 44[d]	91/45
138	1819	Unknown 45	87/43/74/102
139	1900	Unknown 46[c]	43/61/71
140	1918	Unknown 49[c]	55/88/41/69/70
141	1922	Unknown 47	41/55/79/108
142	1939	Unknown 48	41/55/69/83/96
143	1989	Unknown 50	59
144	ND	Unknown 51[c]	43/60/71
145	ND	Unknown 52[c]	41/69/93/107
146	ND	Unknown 53	117/71/43
147	ND	Unknown 54[c]	41/55/69

[a] Retention indices calculated from C8 to C20 n-linear alkanes; [b] Identification by NIST comparation; [c] Just observed on 'Síria' wines, [d] Just observed on 'Arinto' wines, LRI lit - retention indices reported in the literature for wax capillary column (Janzantti and Monteiro, 2017; Wang *et al.*, 2017; Kong *et al.*, 2019; de-la-Fuente-Blanco *et al.*, 2020; Almeida Santos *et al.*, 2020; Pereira *et al.*, 2021)

Table IV

Relative amount of each compound calculated as the percentage ratio of the respective peak area in relation to the total peak area analysed (RPA) of the chromatogram for ‘Arinto’ wines fermented without bentonite

	Fermentation							
	0 mg/L SO_2		50 mg/L SO_2		100 mg/L SO_2		100 mg/L AA	
Compound no.	After fermentation 0 mg/L SO_2	After fermentation 60 mg/L SO_2	After fermentation 0 mg/L SO_2	After fermentation 60 mg/L SO_2	After fermentation 0 mg/L SO_2	After fermentation 60 mg/L SO_2	After fermentation 0 mg/L SO_2	After fermentation 60 mg/L SO_2
1	5.474^{Aa1} ± 0.000	5.182^{Aa1} ± 0.002	5.283^{Aa1} ± 0.002	5.428^{Aa1} ± 0.007	9.126^{Ba1} ± 0.061	4.936^{Ab1} ± 0.002	7.757^{Ca1} ± 0.000	6.959^{Ab1} ± 0.000
2	0.031 ± 0.000	0.036 ± 0.000	0.046 ± 0.000	0.041 ± 0.000	0.032 ± 0.000	0.036 ± 0.000	0.071 ± 0.000	0.058 ± 0.000
3	7.174^{Aa1} ± 0.101	0.035^{Ab1} ± 0.000	0.036^{Ba1} ± 0.000	0.038^{Aa1} ± 0.000	0.0296^{Ba1} ± 0.000	0.031^{Aa1} ± 0.000	0.056^{Ba1} ± 0.000	0.052^{Aa1} ± 0.000
4	0.060 ± 0.000	0.060 ± 0.000	0.059 ± 0.000	0.064 ± 0.000	0.057 ± 0.000	0.062 ± 0.000	0.074 ± 0.000	0.062 ± 0.000
5	0.603 ± 0.000	0.625 ± 0.000	0.668 ± 0.000	0.693 ± 0.001	0.623 ± 0.000	0.608 ± 0.000	0.895 ± 0.000	0.829 ± 0.000
6	0.017 ± 0.000	0.019 ± 0.000	0.015 ± 0.000	0.017 ± 0.000	0.012 ± 0.000	0.013 ± 0.000	0.023 ± 0.000	0.022 ± 0.000
7	0.015 ± 0.000	0.010 ± 0.000	0.007 ± 0.000	0.017 ± 0.000	0.011 ± 0.000	0.016 ± 0.000	0.023 ± 0.000	0.022 ± 0.000
9	8.302^{Aa1} ± 0.001	9.427^{Aa1} ± 0.007	8.712^{Aa1} ± 0.004	8.960^{Ab1} ± 0.001	9.455^{Aa1} ± 0.024	10.909^{Aa1} ± 0.001	0.448^{Ba1} ± 0.000	0.420^{Ba1} ± 0.000
12	0.013^{Aa1} ± 0.000	0.026^{Aa1} ± 0.000	0.029^{Aa1} ± 0.000	0.025^{Aa1} ± 0.000	0.016^{Aa1} ± 0.000	0.009^{Aa1} ± 0.000	7.283^{Aa1} ± 0.000	8.175^{Bb1} ± 0.000
14	8.356^{Aa1} ± 0.002	8.479^{Aa1} ± 0.003	7.545^{Aa1} ± 0.012	8.146^{Aa1} ± 0.001	8.346^{Aa1} ± 0.025	9.490^{Ab1} ± 0.005	15.834^{Ba1} ± 0.000	14.293^{Bb1} ± 0.000
16	1.376 ± 0.005	2.206 ± 0.001	1.689 ± 0.003	2.163 ± 0.007	2.162 ± 0.002	2.338 ± 0.000	1.232 ± 0.000	1.687 ± 0.000
18	0.019 ± 0.000	0.017 ± 0.000	0.017 ± 0.000	0.015 ± 0.000	0.021 ± 0.000	0.027 ± 0.000	0.026 ± 0.000	0.026 ± 0.000
19	0.011 ± 0.000	0.015 ± 0.000	0.014 ± 0.000	0.014 ± 0.000	0.012 ± 0.000	0.015 ± 0.000	0.040 ± 0.000	0.023 ± 0.000
22	0.008 ± 0.000	0.012 ± 0.000	0.010 ± 0.000	0.013 ± 0.000	0.014 ± 0.000	0.020 ± 0.000	0.008 ± 0.000	0.010 ± 0.000
23	16.457^{Aa1} ± 0.012	19.188^{Aa1} ± 0.012	16.463^{Aa1} ± 0.038	20.782^{Aa1} ± 0.021	22.290^{Aa1} ± 0.059	27.728^{Bb1} ± 0.000	15.455^{Ba1} ± 0.000	19.265^{Ab1} ± 0.000
24	0.028 ± 0.000	0.035 ± 0.000	0.025 ± 0.000	0.038 ± 0.000	0.037 ± 0.000	0.054 ± 0.000	0.024 ± 0.000	0.037 ± 0.000
28	0.017 ± 0.000	0.019 ± 0.000	0.014 ± 0.000	0.020 ± 0.000	0.019 ± 0.000	0.021 ± 0.000	0.016 ± 0.000	0.019 ± 0.000
29	0.053 ± 0.000	0.068 ± 0.000	0.052 ± 0.000	0.047 ± 0.000	0.037 ± 0.000	0.044 ± 0.000	0.115 ± 0.000	0.093 ± 0.000
30	0.034 ± 0.000	0.014 ± 0.000	0.019 ± 0.000	0.007 ± 0.000	0.010 ± 0.000	0.006 ± 0.000	0.039 ± 0.000	0.028 ± 0.000
31	0.007 ± 0.000	0.012 ± 0.000	0.010 ± 0.000	0.008 ± 0.000	0.009 ± 0.000	0.008 ± 0.000	0.008 ± 0.000	0.007 ± 0.000
33	7.401^{Aa1} ± 0.018	7.968^{ABa1} ± 0.013	7.004^{Aa1} ± 0.018	7.803^{Aa1} ± 0.009	7.769^{Aa1} ± 0.013	5.997^{Ba1} ± 0.003	4.924^{Ba1} ± 0.000	5.597^{Ab1} ± 0.000
35	0.071 ± 0.000	0.084 ± 0.000	0.075 ± 0.000	0.093 ± 0.000	0.088 ± 0.000	0.093 ± 0.000	0.077 ± 0.000	0.084 ± 0.000
36	0.149 ± 0.000	0.183 ± 0.000	0.219 ± 0.001	0.212 ± 0.001	0.185 ± 0.001	0.198 ± 0.000	0.242 ± 0.000	0.272 ± 0.000
37	0.839 ± 0.001	0.934 ± 0.000	1.017 ± 0.003	1.261 ± 0.000	1.822 ± 0.002	1.674 ± 0.000	1.141 ± 0.000	1.370 ± 0.000
39	0.392 ± 0.000	0.537 ± 0.000	0.710 ± 0.001	0.844 ± 0.001	0.765 ± 0.003	0.786 ± 0.000	0.600 ± 0.000	0.745 ± 0.000
40	0.476 ± 0.001	0.482 ± 0.001	0.463 ± 0.000	0.361 ± 0.000	0.448 ± 0.001	0.482 ± 0.001	0.426 ± 0.000	0.692 ± 0.000
41	0.036 ± 0.000	0.035 ± 0.000	0.032 ± 0.000	0.026 ± 0.000	0.029 ± 0.000	0.019 ± 0.000	0.029 ± 0.000	0.035 ± 0.000
42	0.011 ± 0.000	0.010 ± 0.000	0.013 ± 0.000	0.014 ± 0.000	0.010 ± 0.000	0.011 ± 0.000	0.011 ± 0.000	0.015 ± 0.000
44	0.036 ± 0.000	0.055 ± 0.000	0.068 ± 0.000	0.041 ± 0.000	0.040 ± 0.000	0.034 ± 0.000	0.050 ± 0.000	0.051 ± 0.000
46	0.014 ± 0.000	0.000 ± 0.000	0.014 ± 0.000	0.011 ± 0.000	0.012 ± 0.000	0.006 ± 0.000	0.040 ± 0.000	0.009 ± 0.000
48	0.014 ± 0.000	0.013 ± 0.000	0.013 ± 0.000	0.003 ± 0.000	0.003 ± 0.000	0.002 ± 0.000	0.010 ± 0.000	0.003 ± 0.000
49	0.036 ± 0.000	0.030 ± 0.000	0.028 ± 0.000	0.031 ± 0.000	0.022 ± 0.000	0.025 ± 0.000	0.038 ± 0.000	0.035 ± 0.000
50	0.006 ± 0.000	2.259 ± 0.032	0.011 ± 0.000	0.004 ± 0.000	0.002 ± 0.000	0.004 ± 0.000	0.011 ± 0.000	0.003 ± 0.000
52	25.508^{Aa1} ± 0.048	26.644^{Ab1} ± 0.010	30.012^{Ba1} ± 0.037	24.884^{Bb1} ± 0.003	21.091^{Ca1} ± 0.022	20.589^{Ca1} ± 0.002	33.132^{Da1} ± 0.000	30.737^{Db1} ± 0.000
53	0.262 ± 0.000	0.310 ± 0.000	0.359 ± 0.000	0.378 ± 0.000	0.260 ± 0.001	0.195 ± 0.000	0.044 ± 0.000	0.027 ± 0.000
55	10.644^{Aa1} ± 0.010	9.823^{ABCa1} ± 0.000	11.695^{Aa1} ± 0.021	10.615^{Ab1} ± 0.012	9.164^{Ba1} ± 0.019	8.600^{Ba1} ± 0.002	0.011^{Ca1} ± 0.000	0.015^{Ca1} ± 0.000
58	0.662^{Aa1} ± 0.001	0.402^{Aa1} ± 0.002	0.598^{Aa1} ± 0.002	0.379^{Aa1} ± 0.002	0.415^{Aa1} ± 0.000	0.403^{Aa1} ± 0.000	0.997^{Aa1} ± 0.000	0.878^{Aa1} ± 0.000
61	0.010 ± 0.000	0.005 ± 0.000	0.018 ± 0.000	0.010 ± 0.000	0.030 ± 0.000	0.024 ± 0.000	0.026 ± 0.000	0.014 ± 0.000
64	0.028 ± 0.000	0.023 ± 0.000	0.030 ± 0.000	0.027 ± 0.000	0.022 ± 0.000	0.021 ± 0.000	0.039 ± 0.000	0.027 ± 0.000
67	0.034 ± 0.000	0.031 ± 0.000	0.032 ± 0.000	0.032 ± 0.000	0.026 ± 0.000	0.023 ± 0.000	0.041 ± 0.000	0.039 ± 0.000
68	3.587^{ABa1} ± 0.007	3.304^{ABa1} ± 0.001	4.665^{Aa1} ± 0.018	4.863^{Aa1} ± 0.005	4.036^{ABa1} ± 0.016	3.342^{Ba1} ± 0.001	6.382^{Ba1} ± 0.000	5.712^{Ab1} ± 0.000
73	0.007 ± 0.000	0.016 ± 0.000	0.008 ± 0.000	0.021 ± 0.000	0.007 ± 0.000	0.008 ± 0.000	0.019 ± 0.000	0.027 ± 0.000

RPA – percentage ratio of the respective peak area relative to the total peak area; n = 2 with SO_2 and n = 1 with ascorbic acid. Different capital letters means that each value differ significantly ($p<0.05$) according to initial antioxidant condition factor; different lowercase letters means that each value differ significantly ($p <0.05$) according to second antioxidant addition factor; different number means that each value differ significantly ($p <0.05$) according to presence or absence on fermentation of bentonite.

Table IV (continuation)

Relative amount of each compound calculated as the percentage ratio of the respective peak area in relation to the total peak area analysed (RPA) of the chromatogram for ‘Arinto’ wines fermented without bentonite

	Fermentation							
	0 mg/L SO_2		50 mg/L SO_2		100 mg/L SO_2		100 mg/L AA	
Compound no.	After fermentation 0 mg/L SO_2	After fermentation 60 mg/L SO_2	After fermentation 0 mg/L SO_2	After fermentation 60 mg/L SO_2	After fermentation 0 mg/L SO_2	After fermentation 60 mg/L SO_2	After fermentation 0 mg/L SO_2	After fermentation 60 mg/L SO_2
74	0.005 ± 0.000	0.003 ± 0.000	0.002 ± 0.000	0.002 ± 0.000	0.002 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
79	0.674 ± 0.001	0.481 ± 0.001	0.743 ± 0.003	0.804 ± 0.002	0.923 ± 0.003	0.706 ± 0.000	0.643 ± 0.000	0.770 ± 0.000
82	0.022 ± 0.000	0.029 ± 0.000	0.032 ± 0.000	0.031 ± 0.000	0.023 ± 0.000	0.026 ± 0.000	0.033 ± 0.000	0.041 ± 0.000
84	0.116 ± 0.002	0.450 ± 0.001	0.596 ± 0.008	0.099 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.008 ± 0.000	0.006 ± 0.000
85	0.028 ± 0.000	0.037 ± 0.000	0.026 ± 0.000	0.033 ± 0.000	0.023 ± 0.000	0.011 ± 0.000	0.111 ± 0.000	0.121 ± 0.000
86	0.023 ± 0.000	0.025 ± 0.000	0.030 ± 0.000	0.038 ± 0.000	0.025 ± 0.000	0.016 ± 0.000	0.035 ± 0.000	0.043 ± 0.000
90	0.008 ± 0.000	0.007 ± 0.000	0.013 ± 0.000	0.012 ± 0.000	0.011 ± 0.000	0.008 ± 0.000	0.021 ± 0.000	0.011 ± 0.000
91	0.000 ± 0.000	0.000 ± 0.000	0.007 ± 0.000	0.006 ± 0.000	0.005 ± 0.000	0.003 ± 0.000	0.023 ± 0.000	0.012 ± 0.000
94	0.559 ± 0.000	0.128 ± 0.000	0.439 ± 0.002	0.335 ± 0.003	0.240 ± 0.001	0.170 ± 0.000	1.069 ± 0.000	0.255 ± 0.000
95	0.024 ± 0.000	0.040 ± 0.000	0.051 ± 0.000	0.041 ± 0.000	0.035 ± 0.000	0.020 ± 0.000	0.035 ± 0.000	0.042 ± 0.000
105	0.008 ± 0.0000	0.006 ± 0.0000	0.006 ± 0.0000	0.007 ± 0.0000	0.006 ± 0.0000	0.005 ± 0.0000	0.050 ± 0.000	0.052 ± 0.000
106	0.008 ± 0.0000	0.009 ± 0.0000	0.015 ± 0.0000	0.012 ± 0.0000	0.013 ± 0.0001	0.017 ± 0.0000	0.009 ± 0.000	0.012 ± 0.000
107	0.018 ± 0.0000	0.016 ± 0.0000	0.018 ± 0.0001	0.015 ± 0.0000	0.014 ± 0.0001	0.021 ± 0.0000	0.019 ± 0.000	0.021 ± 0.000
110	0.031 ± 0.0001	0.032 ± 0.0000	0.033 ± 0.0000	0.022 ± 0.0000	0.025 ± 0.0000	0.019 ± 0.0000	0.033 ± 0.000	0.030 ± 0.000
115	0.004 ± 0.0000	0.004 ± 0.0000	0.003 ± 0.0000	0.004 ± 0.0000	0.004 ± 0.0000	0.004 ± 0.0000	0.003 ± 0.000	0.005 ± 0.000
120	0.000 ± 0.0000	0.000 ± 0.0000	0.001 ± 0.0000	0.004 ± 0.0000	0.001 ± 0.0000	0.000 ± 0.0000	0.000 ± 0.000	0.006 ± 0.000
128	0.027 ± 0.0002	0.009 ± 0.0000	0.017 ± 0.0001	0.012 ± 0.0000	0.015 ± 0.0000	0.013 ± 0.0001	0.013 ± 0.000	0.010 ± 0.000
129	0.010 ± 0.0000	0.013 ± 0.0000	0.018 ± 0.0001	0.006 ± 0.0000	0.006 ± 0.0000	0.005 ± 0.0000	0.011 ± 0.000	0.006 ± 0.000
134	0.009 ± 0.0000	0.009 ± 0.0000	0.010 ± 0.0000	0.008 ± 0.0000	0.008 ± 0.0000	0.010 ± 0.0000	0.016 ± 0.000	0.012 ± 0.000
138	0.047 ± 0.0002	0.026 ± 0.0000	0.039 ± 0.0002	0.028 ± 0.0000	0.034 ± 0.0000	0.032 ± 0.0001	0.076 ± 0.000	0.033 ± 0.000
139	0.008 ± 0.0000	0.008 ± 0.0000	0.013 ± 0.0001	0.005 ± 0.0000	0.007 ± 0.0000	0.005 ± 0.0000	0.017 ± 0.000	0.010 ± 0.000
141	0.013 ± 0.0000	0.010 ± 0.0000	0.008 ± 0.0000	0.005 ± 0.0000	0.004 ± 0.0000	0.007 ± 0.0000	0.015 ± 0.000	0.007 ± 0.000
143	0.007 ± 0.0000	0.007 ± 0.0000	0.009 ± 0.0000	0.006 ± 0.0000	0.006 ± 0.0000	0.006 ± 0.0000	0.011 ± 0.000	0.009 ± 0.000
146	0.012 ± 0.0000	0.013 ± 0.0000	0.018 ± 0.0000	0.015 ± 0.0000	0.011 ± 0.0000	0.012 ± 0.0000	0.025 ± 0.000	0.022 ± 0.000

RPA – percentage ratio of the respective peak area relative to the total peak area; n = 2 with SO_2 and n = 1 with ascorbic acid. Different capital letters means that each value differ significantly ($p<0.05$) according to initial antioxidant condition factor; different lowercase letters means that each value differ significantly ($p<0.05$) according to second antioxidant addition factor; different number means that each value differ significantly ($p<0.05$) according to presence or absence on fermentation of bentonite

Table V

Relative amount of each compound calculated as the percentage ratio of the respective peak area in relation to the total peak area analysed (RPA) of the chromatogram for 'Arinto' wines fermented with bentonite.

	Fermentation							
	0 mg/L SO_2		50 mg/L SO_2		100 mg/L SO_2		100 mg/L ascorbic acid	
	After fermentation							
Compound no.	0 mg/L SO_2	60 mg/L SO_2	0 mg/L SO_2	60 mg/L SO_2	0 mg/L SO_2	60 mg/L SO_2	0 mg/L SO_2	60 mg/L SO_2
1	6.835^{Aa2} ± 0.001	6.260^{Aa2} ± 0.002	6.020^{Aa2} ± 0.008	5.270^{Aa2} ± 0.004	3.362^{Aa2} ± 0.019	4.345^{Aa2} ± 0.001	6.403^{Aa2} ± 0.000	5.806^{Aa2} ± 0.000
2	0.057 ± 0.000	0.051 ± 0.000	0.044 ± 0.000	0.040 ± 0.000	0.020 ± 0.000	0.032 ± 0.000	0.049 ± 0.000	0.052 ± 0.000
3	0.048^{Aa2} ± 0.000	0.051^{Aa1} ± 0.000	0.046^{Aa1} ± 0.000	0.044^{Aa1} ± 0.000	0.022^{Aa1} ± 0.000	0.032^{Aa1} ± 0.000	0.037^{Aa1} ± 0.000	0.035^{Aa1} ± 0.000
4	0.071 ± 0.000	0.064 ± 0.000	0.073 ± 0.000	0.059 ± 0.000	0.038 ± 0.000	0.050 ± 0.000	0.063 ± 0.000	0.051 ± 0.000
5	0.810 ± 0.000	0.792 ± 0.001	0.718 ± 0.001	0.641 ± 0.000	0.457 ± 0.003	0.637 ± 0.000	0.823 ± 0.000	0.785 ± 0.000
6	0.018 ± 0.000	0.017 ± 0.000	0.018 ± 0.000	0.015 ± 0.000	0.007 ± 0.000	0.010 ± 0.000	0.018 ± 0.000	0.014 ± 0.000
9	8.239^{Aa2} ± 0.002	8.862^{Aa2} ± 0.003	11.128^{Aa2} ± 0.002	9.941^{Aa2} ± 0.001	6.990^{Aa2} ± 0.043	9.547^{Aa2} ± 0.001	7.224^{Aa1} ± 0.000	6.695^{Aa1} ± 0.000
12	0.006^{Aa1} ± 0.000	0.009^{Aa1} ± 0.000	0.009^{Aa1} ± 0.000	0.008^{Aa1} ± 0.000	0.011^{Aa1} ± 0.000	0.010^{Aa1} ± 0.000	0.017Aa1 ± 0.000	0.018^{Bb2} ± 0.000
14	8.058^{Aa2} ± 0.007	8.053^{Aa2} ± 0.004	8.871^{Aa2} ± 0.013	8.788^{Aa2} ± 0.004	6.653^{Aa2} ± 0.040	9.561^{Aa2} ± 0.002	8.230^{Aa1} ± 0.000	6.637^{Aa2} ± 0.000
15	0.039 ± 0.000	0.034 ± 0.000	0.056 ± 0.000	0.041 ± 0.000	0.021 ± 0.000	0.031 ± 0.000	0.035 ± 0.000	0.025 ± 0.000
16	1.516 ± 0.001	1.943 ± 0.000	1.971 ± 0.002	2.065 ± 0.001	1.442 ± 0.010	2.138 ± 0.001	1.214 ± 0.000	1.350 ± 0.000
19	0.009 ± 0.000	0.011 ± 0.000	0.008 ± 0.000	0.013 ± 0.000	0.008 ± 0.000	0.016 ± 0.000	0.019 ± 0.000	0.017 ± 0.000
22	0.007 ± 0.000	0.009 ± 0.000	0.008 ± 0.000	0.013 ± 0.000	0.011 ± 0.000	0.023 ± 0.000	0.008 ± 0.000	0.006 ± 0.000
23	16.199^{Aa2} ± 0.017	17.068^{ABa2} ± 0.032	18.441^{Aa2} ± 0.025	23.272^{Aa2} ± 0.002	17.533^{Aa2} ± 0.100	27.958^{Ab2} ± 0.000	16.292^{Aa1} ± 0.000	12.497^{Ba2} ± 0.000
24	0.025 ± 0.000	0.029 ± 0.000	0.026 ± 0.000	0.034 ± 0.000	0.026 ± 0.000	0.053 ± 0.000	0.026 ± 0.000	0.019 ± 0.000
28	0.014 ± 0.000	0.017 ± 0.000	0.015 ± 0.000	0.018 ± 0.000	0.013 ± 0.000	0.022 ± 0.000	0.018 ± 0.000	0.012 ± 0.000
29	0.037 ± 0.000	0.039 ± 0.000	0.025 ± 0.000	0.045 ± 0.000	0.023 ± 0.000	0.046 ± 0.000	0.071 ± 0.000	0.050 ± 0.000
30	0.023 ± 0.000	0.019 ± 0.000	0.015 ± 0.000	0.005 ± 0.000	0.001 ± 0.000	0.003 ± 0.000	0.020 ± 0.000	0.025 ± 0.000
31	0.006 ± 0.000	0.006 ± 0.000	0.009 ± 0.000	0.008 ± 0.000	0.006 ± 0.000	0.008 ± 0.000	0.008 ± 0.000	0.007 ± 0.000
33	6.733^{Aa2} ± 0.008	6.681^{Aa2} ± 0.019	7.877^{Aa2} ± 0.012	7.540^{Aa2} ± 0.037	6.140^{Aa2} ± 0.042	6.419^{Aa2} ± 0.011	5.735^{Aa1} ± 0.000	4.052^{Aa2} ± 0.000
35	0.074 ± 0.000	0.076 ± 0.000	0.083 ± 0.000	0.093 ± 0.000	0.082 ± 0.001	0.106 ± 0.000	0.084 ± 0.000	0.056 ± 0.000
36	0.226 ± 0.000	0.243 ± 0.000	0.306 ± 0.003	0.196 ± 0.001	0.111 ± 0.000	0.209 ± 0.000	0.221 ± 0.000	0.309 ± 0.000
37	1.040 ± 0.001	1.052 ± 0.002	1.130 ± 0.001	1.244 ± 0.003	1.786 ± 0.011	2.274 ± 0.003	1.176 ± 0.000	0.946 ± 0.000
39	0.630 ± 0.000	0.810 ± 0.001	0.548 ± 0.001	0.702 ± 0.000	0.584 ± 0.003	0.967 ± 0.001	0.615 ± 0.000	0.900 ± 0.000
40	0.427 ± 0.001	0.332 ± 0.001	0.449 ± 0.000	0.366 ± 0.001	0.499 ± 0.003	0.555 ± 0.002	0.426 ± 0.000	0.410 ± 0.000
41	0.028 ± 0.000	0.025 ± 0.000	0.030 ± 0.000	0.021 ± 0.000	0.023 ± 0.000	0.027 ± 0.000	0.029 ± 0.000	0.029 ± 0.000
42	0.012 ± 0.000	0.011 ± 0.000	0.009 ± 0.000	0.009 ± 0.000	0.007 ± 0.000	0.009 ± 0.000	0.009 ± 0.000	0.013 ± 0.000
44	0.039 ± 0.000	0.035 ± 0.000	0.036 ± 0.000	0.032 ± 0.000	0.039 ± 0.000	0.058 ± 0.000	0.054 ± 0.000	0.068 ± 0.000
46	0.018 ± 0.000	0.007 ± 0.000	0.014 ± 0.000	0.007 ± 0.000	0.008 ± 0.000	0.003 ± 0.000	0.029 ± 0.000	0.026 ± 0.000
47	0.007 ± 0.000	0.004 ± 0.000	0.004 ± 0.000	0.003 ± 0.000	0.003 ± 0.000	0.002 ± 0.000	0.009 ± 0.000	0.006 ± 0.000
48	0.001 ± 0.000	0.001 ± 0.000	0.016 ± 0.000	0.003 ± 0.000	0.002 ± 0.000	0.007 ± 0.000	0.003 ± 0.000	0.004 ± 0.000
49	0.038 ± 0.000	0.034 ± 0.000	0.029 ± 0.000	0.023 ± 0.000	0.014 ± 0.000	0.019 ± 0.000	0.033 ± 0.000	0.029 ± 0.000
50	0.005 ± 0.000	0.005 ± 0.000	0.010 ± 0.000	0.003 ± 0.000	0.002 ± 0.000	0.003 ± 0.000	0.004 ± 0.000	0.008 ± 0.000
52	27.510^{Aa2} ± 0.016	26.645^{Aa2} ± 0.023	25.975^{Aa2} ± 0.021	24.529^{ABa2} ± 0.020	15.159^{Ba2} ± 0.076	20.3706^{Aa2} ± 0.011	28.337^{Aa1} ± 0.000	31.138^{Ba2} ± 0.000
53	0.451 ± 0.001	0.447 ± 0.001	0.249 ± 0.000	0.262 ± 0.000	0.140 ± 0.001	0.218 ± 0.000	0.480 ± 0.000	0.573 ± 0.000
55	12.559^{ACa1} ± 0.004	12.125^{Aa1} ± 0.010	10.035^{ABa1} ± 0.012	9.319^{Aa1} ± 0.006	5.853^{Ba1} ± 0.032	8.177^{Aa1} ± 0.007	13.625^{ACa1} ± 0.000	15.273^{Aa1} ± 0.000
58	0.692^{Aa1} ± 0.001	0.580^{Aa1} ± 0.001	0.631^{Aa1} ± 0.002	0.419^{Aa1} ± 0.000	28.896^{Ba2} ± 0.404	0.310^{Ab1} ± 0.000	0.703^{Aa1} ± 0.000	0.781^{Aa1} ± 0.000
61	0.009 ± 0.000	0.006 ± 0.000	0.017 ± 0.000	0.012 ± 0.000	0.028 ± 0.000	0.027 ± 0.000	0.020 ± 0.000	0.020 ± 0.000
64	0.038 ± 0.000	0.044 ± 0.000	0.027 ± 0.000	0.024 ± 0.000	0.016 ± 0.000	0.022 ± 0.000	0.035 ± 0.000	0.043 ± 0.000
65	0.006 ± 0.000	0.005 ± 0.000	0.003 ± 0.000	0.003 ± 0.000	0.001 ± 0.000	n.d.	0.004 ± 0.000	n.d.

RPA – percentage ratio of the respective peak area relative to the total peak area; n = 2 with SO_2 and n = 1 with ascorbic acid. Different capital letters means that each value differ significantly ($p<0.05$) according to initial antioxidant condition factor; different lowercase letters means that each value differ significantly ($p <0.05$) according to second antioxidant addition factor; different number means that each value differ significantly ($p <0.05$) according to presence or absence on fermentation of bentonite.

Table V (continuation)

Relative amount of each compound calculated as the percentage ratio of the respective peak area in relation to the total peak area analysed (RPA) of the chromatogram for 'Arinto' wines fermented with bentonite

	Fermentation							
	0 mg/L SO_2		50 mg/L SO_2		100 mg/L SO_2		100 mg/L ascorbic acid	
	After fermentation							
Compound no.	0 mg/L SO_2	60 mg/L SO_2	0 mg/L SO_2	60 mg/L SO_2	0 mg/L SO_2	60 mg/L SO_2	0 mg/L SO_2	60 mg/L SO_2
67	0.046 ± 0.000	0.043 ± 0.000	0.023 ± 0.000	0.025 ± 0.000	0.014 ± 0.000	0.015 ± 0.000	0.034 ± 0.000	0.036 ± 0.000
68	5.403^{Aa2} ± 0.013	5.786^{Aa1} ± 0.016	3.408^{Aa2} ± 0.000	3.555^{Aa2} ± 0.002	2.635^{Aa2} ± 0.011	4.063^{Aa1} ± 0.000	5.673^{Aa1} ± 0.000	8.768^{Aa2} ± 0.000
73	0.011 ± 0.000	0.045 ± 0.000	0.020 ± 0.000	0.057 ± 0.000	0.023 ± 0.000	0.018 ± 0.000	0.093 ± 0.000	0.013 ± 0.000
79	1.076 ± 0.001	1.059 ± 0.001	0.719 ± 0.001	0.715 ± 0.001	0.837 ± 0.006	1.258 ± 0.000	0.832 ± 0.000	1.424 ± 0.000
82	0.033 ± 0.000	0.032 ± 0.000	0.033 ± 0.000	0.029 ± 0.000	0.019 ± 0.000	0.028 ± 0.000	0.041 ± 0.000	0.018 ± 0.000
85	0.037 ± 0.000	0.038 ± 0.000	0.011 ± 0.000	0.018 ± 0.000	0.012 ± 0.000	0.022 ± 0.000	0.108 ± 0.000	0.144 ± 0.000
86	0.045 ± 0.000	0.051 ± 0.000	0.016 ± 0.000	0.019 ± 0.000	0.012 ± 0.000	0.022 ± 0.000	0.036 ± 0.000	0.080 ± 0.000
90	0.011 ± 0.000	0.014 ± 0.000	0.012 ± 0.000	0.010 ± 0.000	0.007 ± 0.000	0.012 ± 0.000	0.012 ± 0.000	0.024 ± 0.000
91	0.011 ± 0.000	0.008 ± 0.000	0.008 ± 0.000	0.003 ± 0.000	0.004 ± 0.000	0.004 ± 0.000	0.026 ± 0.000	0.030 ± 0.000
94	0.561 ± 0.001	0.195 ± 0.000	0.531 ± 0.001	0.258 ± 0.002	0.261 ± 0.001	0.051 ± 0.000	0.702 ± 0.000	0.379 ± 0.000
95	0.039 ± 0.000	0.041 ± 0.000	0.030 ± 0.000	0.036 ± 0.000	0.024 ± 0.000	0.033 ± 0.000	0.049 ± 0.000	0.057 ± 0.000
99	0.010 ± 0.000	0.007 ± 0.000	0.005 ± 0.000	0.006 ± 0.000	0.006 ± 0.000	0.007 ± 0.000	0.011 ± 0.000	0.012 ± 0.000
100	0.009 ± 0.000	0.010 ± 0.000	0.009 ± 0.000	0.007 ± 0.000	0.004 ± 0.000	0.003 ± 0.000	0.011 ± 0.000	0.008 ± 0.000
106	0.008 ± 0.000	0.009 ± 0.000	0.015 ± 0.000	0.012 ± 0.000	0.013 ± 0.000	0.017 ± 0.000	0.009 ± 0.000	0.012 ± 0.000
107	0.018 ± 0.000	0.016 ± 0.000	0.018 ± 0.000	0.015 ± 0.000	0.014 ± 0.000	0.021 ± 0.000	0.019 ± 0.000	0.021 ± 0.000
110	0.019 ± 0.000	0.021 ± 0.000	0.025 ± 0.000	0.025 ± 0.000	0.016 ± 0.000	0.023 ± 0.000	0.022 ± 0.000	0.025 ± 0.000
128	0.014 ± 0.000	0.022 ± 0.000	0.026 ± 0.000	0.009 ± 0.000	0.006 ± 0.000	0.011 ± 0.000	0.016 ± 0.000	0.038 ± 0.000
132	0.005 ± 0.000	0.006 ± 0.000	0.003 ± 0.000	0.004 ± 0.000	0.003 ± 0.000	0.005 ± 0.000	0.008 ± 0.000	0.006 ± 0.000
134	0.011 ± 0.000	0.009 ± 0.000	0.011 ± 0.000	0.010 ± 0.000	0.007 ± 0.000	0.008 ± 0.000	0.009 ± 0.000	0.012 ± 0.000
137	0.016 ± 0.000	0.034 ± 0.000	0.049 ± 0.000	0.016 ± 0.000	0.012 ± 0.000	0.026 ± 0.000	0.027 ± 0.000	0.049 ± 0.000
143	0.011 ± 0.000	0.009 ± 0.000	0.011 ± 0.000	0.010 ± 0.000	0.007 ± 0.000	0.008 ± 0.000	0.009 ± 0.000	0.012 ± 0.000
146	0.019 ± 0.000	0.017 ± 0.000	0.015 ± 0.000	0.011 ± 0.000	0.009 ± 0.000	0.014 ± 0.000	0.020 ± 0.000	0.028 ± 0.000

n.d. – not detected. RPA – percentage ratio of the respective peak area relative to the total peak area; n = 2 with SO2 and n = 1 with ascorbic acid. Different. Different capital letters means that each value differ significantly ($p < 0.05$) according to initial antioxidant condition factor, different lowercase letters means that each value differ significantly ($p < 0.05$) according to second antioxidant addition factor; different number means that each value differ significantly ($p < 0.05$) according to presence or absence on fermentation of bentonite.

Table VI

Relative amount of each compound calculated as the percentage ratio of the respective peak area in relation to the total peak area analysed (RPA) of the chromatogram for 'Síria' wines fermented without bentonite

Com-pound	Fermentation																			
	0 mg/L SO_2				15 mg/L SO_2				30 mg/L SO_2				45 mg/L SO_2				100 mg/L ascorbic acid			
	After fermentation$_2$																			
	30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2	
1	6.171^{Aa1}	±0.0038	4.670^{Aa1}	±0.0184	4.314^{Ba1}	±0.0207	5.906^{Aa1}	±0.0018	5.370^{ABa1}	±0.0048	4.992^{Aa1}	±0.0011	5.755^{ABa1}	±0.0022	4.953^{ABa1}	±0.0017	5.460^{ABa1}	±0.0022	5.570^{Aa1}	±0.0007
2	0.030	±0.0000	0.030	±0.0001	0.029	±0.0001	0.027	±0.0000	0.022	±0.0000	0.019	±0.0000	0.026	±0.0001	0.018	±0.0000	0.024	±0.0000	0.026	±0.0000
3	0.070	±0.0001	0.050	±0.0000	0.066	±0.0001	0.049	±0.0000	0.071	±0.0000	0.046	±0.0000	0.053	±0.0000	0.046	±0.0000	0.069	±0.0001	0.053	±0.0000
4	0.065	±0.0000	0.074	±0.0000	1.062	±0.0141	0.076	±0.0001	0.072	±0.0001	0.069	±0.0000	0.073	±0.0000	0.070	±0.0000	0.070	±0.0000	0.074	±0.0000
5	0.423	±0.0001	0.407	±0.0000	0.427	±0.0000	0.452	±0.0003	0.388	±0.0004	0.360	±0.0001	0.415	±0.0000	0.380	±0.0000	0.387	±0.0001	0.401	±0.0001
7	0.009	±0.0000	0.010	±0.0000	0.007	±0.0000	0.008	±0.0000	0.006	±0.0000	0.006	±0.0000	0.005	±0.0000	0.006	±0.0000	0.006	±0.0000	0.006	±0.0000
8	0.008	±0.0000	0.009	±0.0000	0.007	±0.0000	0.008	±0.0000	0.006	±0.0000	0.007	±0.0000	0.007	±0.0000	0.007	±0.0000	0.008	±0.0000	0.006	±0.0000
9	5.585^{Aa1}	±0.0034	8.301^{Ab1}	±0.0136	7.501^{Ba1}	±0.0053	8.923^{Aa1}	±0.0116	7.847^{Ba1}	±0.0087	0.003^{Bb1}	±0.0000	7.614^{Ba1}	±0.0036	9.516^{Ab1}	±0.0011	6.712^{Aa1}	±0.0001	8.434^{Aa1}	±0.0014
10	0.005	±0.0000	0.004	±0.0000	0.004	±0.0000	0.004	±0.0000	0.004	±0.0000	0.015	±0.0000	0.004	±0.0000	0.004	±0.0000	0.004	±0.0000	0.003	±0.0000
11	0.002	±0.0000	0.002	±0.0000	0.002	±0.0000	0.003	±0.0000	0.002	±0.0000	0.026	±0.0000	0.002	±0.0000	0.003	±0.0000	0.002	±0.0000	0.002	±0.0000
12	0.014^{Aa1}	±0.0000	0.013^{Aa1}	±0.0000	0.013^{Aa1}	±0.0000	0.015^{Aa1}	±0.0000	0.012^{Aa1}	±0.0000	6.706^{Bb1}	±0.0062	0.013^{Aa1}	±0.0000	0.012^{Aa1}	±0.0000	0.013^{Aa1}	±0.0000	0.012^{Aa1}	±0.0000
13	8.572^{Aa1}	±0.0061	7.432^{Aa1}	±0.0077	7.365^{Aa1}	±0.0033	7.853^{Aa1}	±0.0020	6.378^{Aa1}	±0.0046	6.364^{Aa1}	±0.0013	7.773^{Aa1}	±0.0037	6.082^{Aa1}	±0.0023	7.041Aa1	±0.0008	7.655^{Aa1}	±0.0056
14	7.694^{Aa1}	±0.0034	7.938^{Aa1}	±0.0005	7.942^{Aa1}	±0.0023	8.565^{Aa1}	±0.0093	8.236^{Aa1}	±0.0068	7.622^{Aa1}	±0.0017	8.102^{Aa1}	±0.0062	8.432^{Aa1}	±0.0001	8.098^{Aa1}	±0.0019	8.269^{Ab1}	±0.0005
16	0.350	±0.0005	0.676	±0.0025	0.665	±0.0006	0.983	±0.0013	0.667	±0.0008	0.959	±0.0003	0.717	±0.0001	1.123	±0.0005	0.528	±0.0004	0.830	±0.0004
17	0.004	±0.0000	0.006	±0.0000	0.007	±0.0000	0.008	±0.0000	0.007	±0.0000	0.009	±0.0000	0.008	±0.0000	0.010	±0.0000	0.006	±0.0000	0.007	±0.0000
18	0.018	±0.0000	0.019	±0.0000	0.019	±0.0000	0.022	±0.0000	0.017	±0.0000	0.019	±0.0000	0.017	±0.0000	0.019	±0.0000	0.018	±0.0000	0.021	±0.0000
19	0.050	±0.0002	0.045	±0.0001	0.023	±0.0001	0.027	±0.0000	0.021	±0.0001	0.022	±0.0000	0.023	±0.0001	0.023	±0.0000	0.023	±0.0001	0.023	±0.0000
21	0.005	±0.0000	0.008	±0.0000	0.006	±0.0000	0.010	±0.0000	0.004	±0.0000	0.008	±0.0000	0.006	±0.0000	0.010	±0.0000	0.003	±0.0000	0.004	±0.0000
22	0.021	±0.0000	0.015	±0.0000	0.130	±0.0015	0.022	±0.0000	0.022	±0.0000	0.023	±0.0000	0.024	±0.0000	0.022	±0.0000	0.020	±0.0000	0.019	±0.0000
23	25.187^{Aa1}	±0.0135	26.728^{Aa1}	±0.0092	25.818^{ABa1}	±0.0073	25.482^{Aa1}	±0.0188	27.458^{Ba1}	±0.0066	24.700^{Ab1}	±0.0128	25.508^{Aa1}	±0.0197	26.958^{Aa1}	±0.0055	25.695^{ABa1}	±0.0120	25.265^{Ba1}	±0.0030
26	0.017	±0.0001	0.020	±0.0000	0.117	±0.0015	0.012	±0.0000	0.008	±0.0000	0.008	±0.0000	0.009	±0.0000	0.007	±0.0000	0.006	±0.0000	0.008	±0.0000
28	0.057	±0.0000	0.043	±0.0001	0.048	±0.0000	0.048	±0.0000	0.040	±0.0001	0.048	±0.0000	0.050	±0.0000	0.041	±0.0000	0.048	±0.0000	0.045	±0.0000
29	0.053	±0.0001	0.027	±0.0001	0.024	±0.0000	0.024	±0.0000	0.023	±0.0001	0.029	±0.0000	0.035	±0.0000	0.033	±0.0001	0.030	±0.0000	0.024	±0.0000
32	0.013	±0.0000	0.012	±0.0000	0.017	±0.0000	0.011	±0.0000	0.011	±0.0000	0.015	±0.0000	0.018	±0.0000	0.015	±0.0000	0.015	±0.0001	0.011	±0.0000
33	12.670^{Aa1}	±0.0148	12.128^{Aa1}	±0.0068	12.230^{Aa1}	±0.0088	10.390^{Aa1}	±0.0226	11.722^{Aa1}	±0.0095	11.098^{Aa1}	±0.0158	11.0107^{Aa1}	±0.0233	11.570^{Aa1}	±0.0274	12.778^{Aa1}	±0.0071	10.699A^{a1}	±0.0145
35	0.201	±0.0001	0.133	±0.0001	0.163	±0.0001	0.143	±0.0001	0.127	±0.0001	0.142	±0.0001	0.151	±0.0000	0.134	±0.0002	0.140	±0.0001	0.118	±0.0001
36	0.418	±0.0026	0.115	±0.0005	0.105	±0.0002	0.087	±0.0001	0.049	±0.0001	0.058	±0.0001	0.117	±0.0003	0.058	±0.0001	0.296	±0.0004	0.234	±0.0001
37	5.413^{Aa1}	±0.0090	4.423^{Aa1}	±0.0036	4.577A^{a1}	±0.0037	4.423^{Aa1}	±0.0052	4.112^{Aa1}	±0.0002	4.248^{Aa1}	±0.0081	5.014^{Aa1}	±0.0023	4.410^{Aa1}	±0.0027	4.586^{Aa1}	±0.0011	4.554^{Aa1}	±0.0060
38	0.026	±0.0000	0.018	±0.0000	0.020	±0.0000	0.017	±0.0000	0.013	±0.0000	0.016	±0.0000	0.015	±0.0000	0.016	±0.0000	0.016	±0.0000	0.014	±0.0000
39	0.029	±0.0000	0.019	±0.0000	0.015	±0.0000	0.025	±0.0001	0.015	±0.0000	0.038	±0.0000	0.043	±0.0002	0.039	±0.0002	0.015	±0.0000	0.036	±0.0002
40	0.258	±0.0001	0.242	±0.0003	0.410	±0.0013	0.349	±0.0015	0.232	±0.0001	0.225	±0.0007	0.298	±0.0009	0.241	±0.0011	0.451	±0.0010	0.387	±0.0010
42	0.030	±0.0002	0.009	±0.0000	0.008	±0.0000	0.008	±0.0000	0.005	±0.0000	0.006	±0.0000	0.009	±0.0000	0.005	±0.0000	0.012	±0.0000	0.012	±0.0000
43	0.273	±0.0007	0.199	±0.0002	0.201	±0.0002	0.262	±0.0001	0.172	±0.0002	0.193	±0.0002	0.264	±0.0005	0.209	±0.0001	0.192	±0.0001	0.215	±0.0002
44	0.055	±0.0002	0.032	±0.0001	0.049	±0.0001	0.045	±0.0000	0.032	±0.0001	0.034	±0.0000	0.048	±0.0001	0.032	±0.0000	0.038	±0.0000	0.040	±0.0000
46	0.006	±0.0000	0.005	±0.0000	0.004	±0.0000	0.004	±0.0000	0.004	±0.0000	0.004	±0.0000	0.002	±0.0000	0.004	±0.0000	0.002	±0.0000	0.003	±0.0000
47	0.009^{Aa1}	±0.0001	0.002^{Aa1}	±0.0000	0.002^{Aa1}	±0.0000	0.002^{Aa1}	±0.0000	n.d.		8.132^{Bb1}	±0.0032	0.001^{Aa1}	±0.0000	n.d.		0.003^{Aa1}	±0.0000	n.d.	
49	0.022	±0.0001	0.015	±0.0000	0.011	±0.0000	0.027	±0.0001	0.010	±0.0001	0.020	±0.0001	0.022	±0.0000	0.019	±0.0000	0.036	±0.0001	0.025	±0.0000
50	0.005	±0.0000	0.003	±0.0000	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		0.009	±0.0000	0.003	±0.0000
51	0.008	±0.0000	0.010	±0.0000	0.005	±0.0000	0.003	±0.0000	0.003	±0.0000	0.002	±0.0000	0.005	±0.0000	0.005	±0.0000	0.003	±0.0000	n.d.	
52	19.249^{Aa1}	±0.0132	20.581^{ABa1}	±0.0306	21.188^{Aa1}	±0.0133	19.970^{ABa1}	±0.0108	20.219^{Aa1}	±0.0016	18.774^{Ba1}	±0.0164	18.961^{Aa1}	±0.0144	20.277^{ABa1}	±0.0195	21.044^{Aa1}	±0.0164	21.294^{Aa1}	±0.0087
53	0.375	±0.0004	0.267	±0.0005	0.282	±0.0001	0.297	±0.0000	0.204	±0.0002	0.232	±0.0001	0.294	±0.0000	0.188	±0.0002	0.263	±0.0000	0.289	±0.0003
54	0.019	±0.0000	0.014	±0.0000	0.016	±0.0000	0.017	±0.0000	0.015	±0.0000	0.002	±0.0000	0.019	±0.0000	0.013	±0.0000	0.017	±0.0000	0.019	±0.0000
56	0.003	±0.0000	0.003	±0.0000	0.002	±0.0000	0.003	±0.0000	0.002	±0.0000	0.002	±0.0000	0.004	±0.0000	0.002	±0.0000	0.002	±0.0000	0.002	±0.0000

n.d. -Not detected; RPA – percentage ratio of the respective peak area relative to the total peak area; (n = 2). Different capital letters means that each value differ significantly ($p<0.05$) according to initial antioxidant condition factor; different lowercase letters means that each value differ significantly ($p<0.05$) according to second antioxidant addition factor; different number means that each value differ significantly ($p<0.05$) according to presence or absence on fermentation of bentonite

Table VI (continuation)

Relative amount of each compound calculated as the percentage ratio of the respective peak area in relation to the total peak area analysed (RPA) of the chromatogram for 'Síria' wines fermented without bentonite.

Com-pound	Fermentation																			
	0 mg/L SO_2				15 mg/L SO_2				30 mg/L SO_2				45 mg/L SO_2				100 mg/L ascorbic acid			
	After fermentation$_2$																			
	30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2	
57	0.013	±0.0000	0.009	±0.0000	0.010	±0.0000	0.011	±0.0000	0.007	±0.0000	0.007	±0.0000	0.012	±0.0000	0.008	±0.0000	0.008	±0.0000	0.010	±0.0000
58	0.272	±0.0004	0.233	±0.0000	0.210	±0.0000	0.250	±0.0001	0.186	±0.0003	0.179	±0.0001	0.228	±0.0005	0.185	±0.0001	0.190	±0.0000	0.199	±0.0001
59	0.003	±0.0000	0.003	±0.0000	0.003	±0.0000	0.003	±0.0000	0.003	±0.0000	0.003	±0.0000	0.003	±0.0000	0.003	±0.0000	0.003	±0.0000	0.002	±0.0000
60	0.004	±0.0000	0.008	±0.0000	0.004	±0.0000	0.003	±0.0000	0.003	±0.0000	0.004	±0.0000	0.003	±0.0000	0.002	±0.0000	0.002	±0.0000	0.002	±0.0000
61	0.011	±0.0000	0.008	±0.0000	0.015	±0.0000	0.018	±0.0001	0.011	±0.0001	0.005	±0.0000	0.052	±0.0003	0.017	±0.0000	0.004	±0.0001	0.005	±0.0000
62	0.017	±0.0000	0.011	±0.0000	0.018	±0.0001	0.013	±0.0000	0.013	±0.0000	0.011	±0.0000	0.013	±0.0000	0.008	±0.0000	0.010	±0.0000	0.011	±0.0000
63	0.179	±0.0002	0.188	±0.0005	0.212	±0.0008	0.146	±0.0002	0.166	±0.0009	0.182	±0.0002	0.366	±0.0002	0.192	±0.0008	0.219	±0.0013	0.172	±0.0001
64	0.040	±0.0000	0.025	±0.0000	0.031	±0.0000	0.029	±0.0000	0.023	±0.0000	0.027	±0.0000	0.032	±0.0000	0.025	±0.0000	0.032	±0.0001	0.027	±0.0000
67	0.010	±0.0000	0.001	±0.0000	0.006	±0.0000	0.004	±0.0000	0.003	±0.0000	0.002	±0.0000	0.004	±0.0000	0.004	±0.0000	0.005	±0.0000	0.003	±0.0000
68	2.119	±0.0026	1.574	±0.0030	1.325	±0.0007	1.606	±0.0002	1.276	±0.0007	1.225	±0.0007	2.317	±0.0008	1.285	±0.0011	1.346	±0.0002	1.417	±0.0011
73	0.015	±0.0001	0.072	±0.0004	0.019	±0.0002	0.021	±0.0002	0.017	±0.0002	0.026	±0.0003	0.022	±0.0002	0.010	±0.0001	0.013	±0.0001	0.018	±0.0001
75	0.841	±0.0012	0.484	±0.0022	0.667	±0.0016	0.600	±0.0006	0.659	±0.0016	0.599	±0.0003	0.061	±0.0000	0.657	±0.0011	0.966	±0.0022	0.683	±0.0007
76	0.023	±0.0000	0.011	±0.0000	0.014	±0.0000	0.017	±0.0000	0.010	±0.0000	0.013	±0.0000	0.019	±0.0000	0.011	±0.0000	0.016	±0.0000	0.015	±0.0000
77	0.010	±0.0000	0.003	±0.0000	0.002	±0.0000	0.003	±0.0000	0.002	±0.0000	0.002	±0.0000	0.005	±0.0000	n.d.		n.d.		n.d.	
78	0.613^{Aa1}	±0.0000	0.349^{Aa1}	±0.0003	0.414^{Aa1}	±0.0000	0.512^{Aa1}	±0.0001	0.373^{Aa1}	±0.0001	0.434^{Aa1}	±0.0006	0.742^{Aa1}	±0.0001	0.408^{Aa1}	±0.0000	0.485^{Aa1}	±0.0003	0.488^{Aa1}	±0.0001
79	1.016	±0.0060	0.925	±0.0009	1.017	±0.0002	1.166	±0.0002	1.097	±0.0007	1.036	±0.0017	2.100	±0.0007	1.147	±0.0007	1.253	±0.0015	1.128	±0.0001
80	n.d.		0.088	±0.0009	n.d.		n.d.		0.000	±0.0000	n.d.		0.046	±0.0000	n.d.		n.d.		0.000	±0.0000
81	0.346	±0.0003	0.370	±0.0004	0.250	±0.0008	0.303	±0.0006	0.330	±0.0002	0.305	±0.0005	0.559	±0.0007	0.397	±0.0012	0.467	±0.0005	0.331	±0.0007
83	n.d.		0.010	±0.0001	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.	
85	0.196	±0.0000	0.116	±0.0006	0.112	±0.0004	0.019	±0.0000	0.088	±0.0003	0.009	±0.0000	0.037	±0.0002	0.007	±0.0000	0.129	±0.0005	0.084	±0.0002
86	0.026	±0.0000	0.016	±0.0001	0.018	±0.0000	0.020	±0.0000	0.016	±0.0000	0.018	±0.0000	0.033	±0.0002	0.016	±0.0000	0.024	±0.0001	0.023	±0.0001
90	0.017	±0.0001	0.030	±0.0000	0.023	±0.0001	0.021	±0.0000	0.015	±0.0001	0.018	±0.0001	0.017	±0.0000	0.008	±0.0000	0.008	±0.0000	0.014	±0.0001
92	0.021	±0.0000	0.009	±0.0000	0.013	±0.0000	0.014	±0.0000	0.010	±0.0000	0.011	±0.0000	0.019	±0.0000	0.012	±0.0000	0.012	±0.0000	0.013	±0.0000
93	0.022	±0.0000	0.023	±0.0000	0.023	±0.0000	0.025	±0.0000	0.021	±0.0000	0.019	±0.0000	n.d.		0.031	±0.0000	0.022	±0.0000	0.020	±0.0000
95	0.052	±0.0000	0.068	±0.0003	0.081	±0.0002	0.053	±0.0000	0.054	±0.0000	0.050	±0.0001	0.065	±0.0001	0.057	±0.0001	0.058	±0.0001	0.061	±0.0001
97	0.138	±0.0001	0.093	±0.0003	0.132	±0.0001	0.127	±0.0001	0.098	±0.0000	0.114	±0.0000	0.135	±0.0003	0.092	±0.0001	0.135	±0.0002	0.150	±0.0001
98	0.002	±0.0000	0.024	±0.0003	0.004	±0.0000	0.003	±0.0000	0.002	±0.0000	0.002	±0.0000	0.003	±0.0000	0.003	±0.0000	0.004	±0.0000	0.001	±0.0000
101	0.003	±0.0000	0.005	±0.0000	0.003	±0.0000	0.015	±0.0000	0.010	±0.0000	0.004	±0.0000	0.006	±0.0000	0.005	±0.0001	0.001	±0.0000	0.008	±0.0000
110	0.015	±0.0000	0.024	±0.0000	0.017	±0.0000	0.017	±0.0000	0.017	±0.0001	0.016	±0.0000	0.013	±0.0000	0.019	±0.0000	0.012	±0.0000	0.011	±0.0000
115	0.042	±0.0001	0.025	±0.0000	0.024	±0.0000	0.021	±0.0000	0.019	±0.0001	0.020	±0.0000	0.023	±0.0000	0.019	±0.0000	0.027	±0.0001	0.028	±0.0000
118	0.051	±0.0001	0.053	±0.0001	0.070	±0.0002	0.038	±0.0001	0.048	±0.0003	0.054	±0.0000	0.095	±0.0002	0.056	±0.0002	0.058	±0.0003	0.048	±0.0000
119	0.026	±0.0000	0.012	±0.0000	0.018	±0.0000	0.019	±0.0000	0.013	±0.0000	0.016	±0.0000	0.019	±0.0001	0.015	±0.0000	0.015	±0.0000	0.015	±0.0000
131	0.033	±0.0000	0.036	±0.0001	0.048	±0.0001	0.030	±0.0001	0.037	±0.0000	0.037	±0.0000	0.027	±0.0000	0.047	±0.0000	0.033	±0.0000	0.033	±0.0000
133	0.012	±0.0000	0.011	±0.0000	0.010	±0.0000	0.009	±0.0000	0.007	±0.0000	0.009	±0.0000	0.022	±0.0001	0.010	±0.0000	0.009	±0.0000	0.011	±0.0000
136	0.009	±0.0000	0.005	±0.0000	0.007	±0.0000	0.006	±0.0000	1.517	±0.0214	0.006	±0.0000	0.010	±0.0000	0.004	±0.0000	0.006	±0.0000	0.006	±0.0000
138	0.033	±0.0000	0.051	±0.0001	0.043	±0.0002	0.028	±0.0000	0.032	±0.0002	0.046	±0.0002	0.067	±0.0003	0.030	±0.0000	0.030	±0.0001	0.038	±0.0000
140	0.094	±0.0004	0.071	±0.0002	0.052	±0.0002	0.048	±0.0002	0.030	±0.0000	0.034	±0.0001	0.034	±0.0001	0.030	±0.0001	0.044	±0.0000	0.039	±0.0000
142	0.008	±0.0000	0.028	±0.0000	0.013	±0.0000	0.010	±0.0000	0.012	±0.0001	0.014	±0.0001	0.012	±0.0000	0.013	±0.0000	0.009	±0.0000	0.010	±0.0000
144	0.007	±0.0000	0.010	±0.0000	0.015	±0.0000	0.013	±0.0000	0.017	±0.0000	0.018	±0.0000	0.028	±0.0000	0.034	±0.0001	0.021	±0.0001	0.016	±0.0000
145	0.012	±0.0000	0.010	±0.0000	0.009	±0.0000	0.008	±0.0000	0.008	±0.0000	0.008	±0.0000	0.010	±0.0000	0.006	±0.0000	0.006	±0.0000	0.006	±0.0000
146	0.014	±0.0000	0.012	±0.0000	0.012	±0.0000	0.013	±0.0000	0.013	±0.0000	0.010	±0.0000	0.024	±0.0001	0.013	±0.0000	0.011	±0.0000	0.012	±0.0000
147	0.040	±0.0001	0.028	±0.0000	0.024	±0.0000	0.028	±0.0000	0.017	±0.0000	0.017	±0.0000	0.074	±0.0001	0.025	±0.0001	0.041	±0.0001	0.032	±0.0000

n.d. -Not detected; RPA – percentage ratio of the respective peak area relative to the total peak area; (n = 2). . Different capital letters means that each value differ significantly ($p<0.05$) according to initial antioxidant condition factor; different lowercase letters means that each value differ significantly ($p<0.05$) according to second antioxidant addition factor; different number means that each value differ significantly ($p<0.05$) according to presence or absence on fermentation of bentonite.

Table VII

Relative amount of each compound calculated as the percentage ratio of the respective peak area in relation to the total peak area analysed (RPA) of the chromatogram for ‘Síria’ wines fermented with bentonite.

Com-pound	Fermentation																			
	0 mg/L SO_2				15 mg/L SO_2				30 mg/L SO_2				45 mg/L SO_2				100 mg/L ascorbic acid			
	After fermentation																			
	30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2	
1	4.666^{Aa1}	±0.001	5.085^{Aa1}	±0.002	5.045^{Aa1}	±0.001	5.176^{Aa1}	±0.003	5.270^{Aa1}	±0.001	5.370^{Aa1}	±0.000	5.367A^{a1}	±0.005	5.244^{Aa1}	±0.004	5.786^{Aa1}	±0.004	3.547^{Ab2}	±0.029
2	0.023	±0.000	0.023	±0.000	0.033	±0.000	0.027	±0.000	0.025	±0.000	0.027	±0.000	0.030	±0.000	0.026	±0.000	0.029	±0.000	0.028	±0.000
3	0.067	±0.000	0.045	±0.000	0.067	±0.000	0.068	±0.000	0.063	±0.000	0.049	±0.000	0.043	±0.000	0.042	±0.000	0.066	±0.000	0.029	±0.000
4	0.063	±0.000	0.070	±0.000	0.063	±0.000	0.064	±0.000	0.073	±0.000	0.074	±0.000	0.070	±0.000	0.069	±0.000	0.075	±0.000	0.044	±0.000
5	0.354	±0.000	0.368	±0.000	0.393	±0.000	0.401	±0.000	0.441	±0.000	0.435	±0.000	0.425	±0.000	0.407	±0.000	0.438	±0.000	0.248	±0.002
7	0.004	±0.000	0.004	±0.000	0.005	±0.000	0.005	±0.000	0.004	±0.000	0.005	±0.000	0.005	±0.000	0.005	±0.000	0.005	±0.000	0.004	±0.000
8	0.007	±0.000	0.007	±0.000	0.007	±0.000	0.009	±0.000	0.008	±0.000	0.010	±0.000	0.009	±0.000	0.007	±0.000	0.012	±0.000	0.005	±0.000
9	7.410^{Aa1}	±0.004	8.653^{Aa1}	±0.001	7.116^{Aa1}	±0.005	5.366^{Ba2}	±0.020	8.733^{Aa1}	±0.004	9.326^{Aa2}	±0.009	8.165^{Aa1}	±0.003	8.668^{Aa1}	±0.001	8.237^{Aa1}	±0.005	5.217^{Bb2}	±0.041
10	0.004	±0.000	0.004	±0.000	0.005	±0.000	0.008	±0.000	0.004	±0.000	0.004	±0.000	0.005	±0.000	0.004	±0.000	0.004	±0.000	0.002	±0.000
11	0.001	±0.000	0.002	±0.000	0.002	±0.000	n.d.		0.002	±0.000	0.003	±0.000	0.002	±0.000	0.002	±0.000	0.003	±0.000	0.002	±0.000
12	6.254^{Aa2}	±0.008	6.611^{ABa2}	±0.008	7.922^{Aa2}	±0.001	8.082^{Aa2}	±0.001	6.970^{Aa2}	±0.008	7.299^{Aa1}	±0.001	7.820^{Aa2}	±0.009	7.688^{Aa2}	±0.006	7.843^{Aa2}	±0.010	4.994^{Bb2}	±0.043
14	6.732^{Aa1}	±0.001	6.834^{Aa1}	±0.001	6.624^{Aa1}	±0.001	6.755^{Aa2}	±0.003	7.929^{Aa1}	±0.001	7.487^{Aa1}	±0.005	7.116^{Aa1}	±0.002	6.970^{Aa1}	±0.003	7.868^{Aa1}	±0.001	4.466B^{a2}	±0.034
16	0.584	±0.000	0.841	±0.000	0.628	±0.001	0.641	±0.001	0.770	±0.000	1.059	±0.001	0.771	±0.001	0.951	±0.001	0.673	±0.001	0.507	±0.004
18	0.012	±0.000	0.013	±0.000	0.011	±0.000	0.012	±0.000	0.010	±0.000	0.012	±0.000	0.011	±0.000	0.011	±0.000	0.013	±0.000	0.008	±0.000
19	0.019	±0.000	0.045	±0.000	0.028	±0.000	0.029	±0.000	0.023	±0.000	0.020	±0.000	0.028	±0.000	0.032	±0.000	0.032	±0.000	0.024	±0.000
21	0.005	±0.000	0.008	±0.000	0.009	±0.000	0.009	±0.000	0.009	±0.000	0.015	±0.000	0.012	±0.000	0.019	±0.000	0.006	±0.000	0.007	±0.000
22	0.017	±0.000	0.018	±0.000	0.017	±0.000	0.018	±0.000	0.016	±0.000	0.016	±0.000	0.020	±0.000	0.019	±0.000	0.023	±0.000	0.012	±0.000
23	23.924^{Aa1}	±0.007	23.516^{Aa2}	±0.018	21.7423^{ABa2}	±0.005	22.155^{ABa2}	±0.002	23.779^{Ba2}	±0.007	22.181^{Ba2}	±0.008	22.794^{Aa2}	±0.006	22.313^{Aa2}	±0.015	24.737^{ABa1}	±0.014	14.492^{ABb2}	±0.109
26	0.012	±0.000	0.011	±0.000	0.018	±0.000	0.019	±0.000	0.018	±0.000	0.012	±0.000	0.024	±0.000	0.020	±0.000	0.018	±0.000	0.011	±0.000
28	0.033	±0.000	0.035	±0.000	0.029	±0.000	0.029	±0.000	0.079	±0.000	0.045	±0.000	0.039	±0.000	0.032	±0.000	0.037	±0.000	0.021	±0.000
29	0.052	±0.000	0.049	±0.000	0.037	±0.000	0.037	±0.000	0.026	±0.000	0.028	±0.000	0.044	±0.000	0.066	±0.000	0.050	±0.000	0.037	±0.000
30	0.026	±0.000	0.022	±0.000	0.029	±0.000	0.030	±0.000	0.026	±0.000	0.025	±0.000	0.032	±0.000	0.026	±0.000	0.034	±0.000	0.018	±0.000
33	14.566^{Aa1}	±0.022	13.279^{Aa1}	±0.015	10.832^{BCDa1}	±0.008	11.049^{ABa1}	±0.011	13.021^{Ba1}	±0.022	11.807^{ABa1}	±0.010	10.471^{Ca2}	±0.026	10.685^{Ba1}	±0.021	9.806^{Da2}	±0.013	6.130^{Cb2}	±0.043
35	0.315	±0.000	0.284	±0.000	0.242	±0.000	0.248	±0.000	0.190	±0.000	0.193	±0.000	0.227	±0.000	0.184	±0.001	0.197	±0.000	0.115	±0.001
36	0.131	±0.000	0.103	±0.000	0.133	±0.000	0.137	±0.000	0.078	±0.000	0.065	±0.000	0.097	±0.000	0.074	±0.000	0.224	±0.000	0.107	±0.001
37	4.953^{Aa1}	±0.007	5.018^{ABa1}	±0.007	5.515^{Aa1}	±0.000	5.623^{ABa1}	±0.002	5.638^{Aa1}	±0.007	5.745^{ABa1}	±0.000	6.099^{Aa1}	±0.001	6.301^{Aa1}	±0.002	5.329^{Aa1}	±0.001	3.412^{Ba1}	±0.027
38	0.124	±0.000	0.100	±0.000	0.072	±0.000	0.073	±0.000	0.026	±0.000	0.025	±0.000	0.027	±0.000	0.023	±0.000	0.025	±0.000	0.016	±0.000
40	1.127	±0.004	1.035	±0.001	0.930	±0.001	0.949	±0.001	0.971	±0.004	1.171	±0.000	1.387	±0.002	1.359	±0.002	0.957	±0.000	0.640	±0.005
42	1.127	±0.004	1.035	±0.001	0.930	±0.001	0.949	±0.001	0.971	±0.004	1.171	±0.000	1.387	±0.002	1.359	±0.002	0.957	±0.000	0.640	±0.005
43	0.058	±0.000	0.118	±0.000	0.160	±0.000	0.162	±0.000	0.109	±0.000	0.112	±0.000	0.169	±0.000	0.220	±0.001	0.168	±0.000	0.071	±0.000
44	0.022	±0.000	0.028	±0.000	0.031	±0.000	0.035	±0.000	0.022	±0.000	0.025	±0.000	0.049	±0.000	0.043	±0.000	0.035	±0.000	0.018	±0.000
49	0.005	±0.000	0.018	±0.000	0.036	±0.000	0.041	±0.000	0.013	±0.000	0.031	±0.000	0.030	±0.000	0.030	±0.000	0.029	±0.000	0.026	±0.000
51	0.006	±0.000	0.003	±0.000	0.008	±0.000	0.007	±0.000	0.010	±0.000	0.005	±0.000	0.005	±0.000	0.004	±0.000	0.009	±0.000	1.889	±0.027
52	22.094^{ABa2}	±0.013	22.196^{Aa1}	±0.014	24.220^{Aa2}	±0.009	24.680^{Ba2}	±0.003	19.902^{Ba1}	±0.013	21.442^{Aa2}	±0.029	22.329^{Aa2}	±0.006	21.911^{Aa1}	±0.000	20.556^{ABa1}	±0.020	13.560^{Cb2}	±0.115
53	0.223	±0.000	0.257	±0.000	0.331	±0.000	0.337	±0.000	0.213	±0.000	0.259	±0.000	0.328	±0.001	0.345	±0.000	0.281	±0.000	0.205	±0.002
54	0.013	±0.000	0.015	±0.000	0.016	±0.000	0.019	±0.000	0.012	±0.000	0.015	±0.000	0.017	±0.000	0.016	±0.000	0.017	±0.000	0.011	±0.000
56	0.002	±0.000	0.003	±0.000	0.002	±0.000	0.002	±0.000	0.004	±0.000	0.003	±0.000	0.004	±0.000	0.004	±0.000	0.004	±0.000	0.003	±0.000
57	0.011	±0.000	0.010	±0.000	0.016	±0.000	0.016	±0.000	0.012	±0.000	0.012	±0.000	0.019	±0.000	0.015	±0.000	0.020	±0.000	0.012	±0.000
58	0.178	±0.000	0.172	±0.000	0.213	±0.000	0.217	±0.000	0.204	±0.000	0.207	±0.000	0.201	±0.000	0.175	±0.000	0.250	±0.000	0.139	±0.001
59	0.003	±0.000	0.003	±0.000	0.003	±0.000	0.003	±0.000	0.003	±0.000	0.003	±0.000	0.003	±0.000	0.003	±0.000	0.003	±0.000	0.002	±0.000
61	0.007	±0.000	0.013	±0.000	n.d.		n.d.		0.033	±0.000	0.029	±0.000	0.041	±0.000	0.024	±0.000	0.032	±0.000	0.018	±0.000
62	0.013	±0.000	0.008	±0.000	0.022	±0.000	0.023	±0.000	0.015	±0.000	0.010	±0.000	0.012	±0.000	0.010	±0.000	0.019	±0.000	0.008	±0.000
63	0.392	±0.002	0.235	±0.000	0.442	±0.001	0.450	±0.001	0.182	±0.002	0.209	±0.002	0.184	±0.000	0.229	±0.001	0.131	±0.000	0.088	±0.001

n.d. -Not detected; RPA – percentage ratio of the respective peak area relative to the total peak area; (n = 2). Different capital letters means that each value differ significantly ($p<0.05$) according to initial antioxidant condition factor; different lowercase letters means that each value differ significantly ($p<0.05$) according to second antioxidant addition factor; different number means that each value differ significantly ($p<0.05$) according to presence or absence on fermentation of bentonite.

Table VII (continuation)

Relative amount of each compound calculated as the percentage ratio of the respective peak area in relation to the total peak area analysed (RPA) of the chromatogram for 'Síria' wines fermented with bentonite.

Com-pound	Fermentation																			
	0 mg/L SO_2				15 mg/L SO_2				30 mg/L SO_2				45 mg/L SO_2				100 mg/L ascorbic acid			
	After fermentation																			
	30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2		30 mg/L SO_2		60 mg/L SO_2	
68	1.398	±0.002	1.427	±0.002	2.009	±0.000	2.051	±0.000	1.595	±0.001	1.535	±0.001	1.713	±0.002	1.850	±0.001	1.954	±0.001	1.106	±0.009
69	0.016	±0.000	0.013	±0.000	0.013	±0.000	0.013	±0.000	0.021	±0.000	0.007	±0.000	0.005	±0.000	0.006	±0.000	0.008	±0.000	0.003	±0.000
70	n.d.		n.d.		n.d.		n.d.		0.081	±0.000	0.044	±0.000	0.040	±0.000	0.025	±0.000	0.033	±0.000	0.015	±0.000
72	0.005	±0.000	0.004	±0.000	0.002	±0.000	0.002	±0.000	0.003	±0.000	0.004	±0.000	0.003	±0.000	0.003	±0.000	0.003	±0.000	0.002	±0.000
73	0.005	±0.000	0.014	±0.000	0.003	±0.000	0.002	±0.000	0.053	±0.001	0.011	±0.000	0.026	±0.000	0.005	±0.000	0.008	±0.000	0.002	±0.000
75	0.875	±0.000	0.702	±0.000	1.516	±0.003	1.395	±0.004	0.460	±0.001	0.584	±0.002	0.688	±0.000	0.637	±0.001	0.755	±0.001	0.442	±0.004
76	n.d.		n.d.		n.d.		n.d.		0.012	±0.000	0.016	±0.000	0.023	±0.000	0.022	±0.000	0.023	±0.000	0.015	±0.000
77	0.008	±0.000	0.009	±0.000	0.014	±0.000	0.014	±0.000	0.007	±0.000	0.006	±0.000	0.007	±0.000	0.007	±0.000	0.005	±0.000	0.003	±0.000
78	0.439^{Aa1}	±0.000	0.455^{Aa1}	±0.000	0.522^{Aa1}	±0.000	0.536^{Aa1}	±0.000	0.386^{Aa1}	±0.001	0.470^{Aa1}	±0.000	0.555^{Aa1}	±0.000	0.534^{Aa1}	±0.001	0.517^{Aa1}	±0.000	36.741^{Bb2}	±0.513
79	1.024	±0.000	1.006	±0.000	1.248	±0.000	1.284	±0.001	1.150	±0.001	1.292	±0.002	1.277	±0.001	1.417	±0.001	1.333	±0.001	0.745	±0.006
81	0.502	±0.000	0.334	±0.000	0.378	±0.001	0.393	±0.001	0.471	±0.001	0.432	±0.000	0.326	±0.001	0.412	±0.001	0.337	±0.000	0.203	±0.001
85	0.189	±0.000	0.073	±0.000	0.231	±0.000	0.235	±0.000	0.072	±0.001	0.018	±0.000	0.044	±0.000	0.031	±0.000	0.187	±0.001	0.059	±0.001
86	0.017	±0.000	0.015	±0.000	0.029	±0.000	0.030	±0.000	0.011	±0.000	0.015	±0.000	0.016	±0.000	0.018	±0.000	0.017	±0.000	0.011	±0.000
89	0.086	±0.001	0.004	±0.000	0.006	±0.000	0.007	±0.000	0.004	±0.000	0.003	±0.000	0.003	±0.000	0.004	±0.000	0.004	±0.000	0.002	±0.000
90	0.013	±0.000	0.014	±0.000	0.023	±0.000	0.024	±0.000	0.029	±0.000	0.010	±0.000	0.015	±0.000	0.018	±0.000	0.020	±0.000	0.010	±0.000
92	0.007	±0.000	0.007	±0.000	0.011	±0.000	0.012	±0.000	0.008	±0.000	0.010	±0.000	0.014	±0.000	0.013	±0.000	0.013	±0.000	0.008	±0.000
93	0.013	±0.000	0.019	±0.000	0.021	±0.000	0.021	±0.000	0.018	±0.000	0.021	±0.000	0.019	±0.000	0.021	±0.000	0.025	±0.000	0.013	±0.000
95	0.058	±0.000	0.074	±0.000	0.093	±0.000	0.120	±0.000	0.058	±0.000	0.075	±0.000	0.099	±0.000	0.100	±0.000	0.072	±0.000	0.056	±0.001
97	0.098	±0.000	0.113	±0.000	0.156	±0.000	0.158	±0.000	0.075	±0.000	0.112	±0.000	0.128	±0.000	0.146	±0.000	0.099	±0.000	0.079	±0.001
98	n.d.		n.d.		n.d.		n.d.		0.007	±0.000	0.002	±0.000	n.d.		n.d.		0.007	±0.000	0.001	±0.000
101	0.012	±0.000	0.013	±0.000	0.012	±0.000	0.012	±0.000	0.012	±0.000	0.016	±0.000	0.018	±0.000	0.014	±0.000	0.017	±0.000	0.011	±0.000
108	0.006	±0.000	0.009	±0.000	0.006	±0.000	0.006	±0.000	0.007	±0.000	0.009	±0.000	0.008	±0.000	0.008	±0.000	0.008	±0.000	0.005	±0.000
110	0.017	±0.000	0.014	±0.000	0.012	±0.000	0.012	±0.000	0.024	±0.000	0.017	±0.000	0.014	±0.000	0.010	±0.000	0.022	±0.000	0.011	±0.000
112	0.004	±0.000	0.004	±0.000	0.005	±0.000	n.d.		0.005	±0.000	n.d.		n.d.		n.d.		n.d.		n.d.	
115	0.025	±0.000	0.027	±0.000	0.022	±0.000	0.023	±0.000	0.019	±0.000	0.018	±0.000	0.026	±0.000	0.019	±0.000	0.029	±0.000	0.019	±0.000
118	0.027	±0.000	0.018	±0.000	0.019	±0.000	0.020	±0.000	0.015	±0.000	0.013	±0.000	0.013	±0.000	0.012	±0.000	0.011	±0.000	0.007	±0.000
126	0.013	±0.000	0.010	±0.000	0.014	±0.000	0.014	±0.000	0.012	±0.000	0.005	±0.000	0.007	±0.000	0.008	±0.000	0.008	±0.000	0.004	±0.000
131	0.169	±0.000	0.119	±0.000	0.099	±0.000	0.105	±0.000	0.062	±0.000	0.066	±0.000	0.066	±0.000	0.058	±0.000	0.066	±0.000	0.043	±0.000
133	0.018	±0.000	0.012	±0.000	0.015	±0.000	0.016	±0.000	0.014	±0.000	0.008	±0.000	0.008	±0.000	0.010	±0.000	0.010	±0.000	0.005	±0.000
136	0.007	±0.000	0.006	±0.000	0.007	±0.000	0.007	±0.000	0.006	±0.000	0.004	±0.000	0.005	±0.000	0.004	±0.000	0.008	±0.000	0.003	±0.000
138	0.062	±0.000	0.033	±0.000	0.048	±0.000	0.047	±0.000	0.053	±0.000	0.020	±0.000	0.022	±0.000	0.030	±0.000	0.027	±0.000	0.013	±0.000
139	0.003	±0.000	0.002	±0.000	n.d.		0.002	±0.000	0.003	±0.000	n.d.		n.d.		n.d.		n.d.		n.d.	
141	0.006	±0.000	0.005	±0.000	0.004	±0.000	0.005	±0.000	0.004	±0.000	0.007	±0.000	0.007	±0.000	0.005	±0.000	0.005	±0.000	0.002	±0.000
142	0.072	±0.000	0.053	±0.000	0.085	±0.000	0.087	±0.000	0.060	±0.000	0.070	±0.000	0.065	±0.000	0.052	±0.000	0.057	±0.000	0.036	±0.000
143	0.011	±0.000	0.010	±0.000	0.012	±0.000	0.013	±0.000	0.009	±0.000	0.007	±0.000	0.006	±0.000	0.005	±0.000	0.009	±0.000	0.003	±0.000
146	0.016	±0.000	0.011	±0.000	0.015	±0.000	0.018	±0.000	0.014	±0.000	0.013	±0.000	0.013	±0.000	0.014	±0.000	0.016	±0.000	0.008	±0.000
147	0.053	±0.000	0.030	±0.000	0.046	±0.000	0.051	±0.000	0.057	±0.000	0.050	±0.000	0.040	±0.000	0.057	±0.000	0.039	±0.000	0.020	±0.000

n.d. -Not detected; RPA – percentage ratio of the respective peak area relative to the total peak area, (n=2). Different capital letters means that each value differ significantly ($p<0.05$) according to initial antioxidant condition factor; different lowercase letters means that each value differ significantly ($p<0.05$) according to second antioxidant addition factor; different number means that each value differ significantly ($p<0.05$) according to presence or absence on fermentation of bentonite

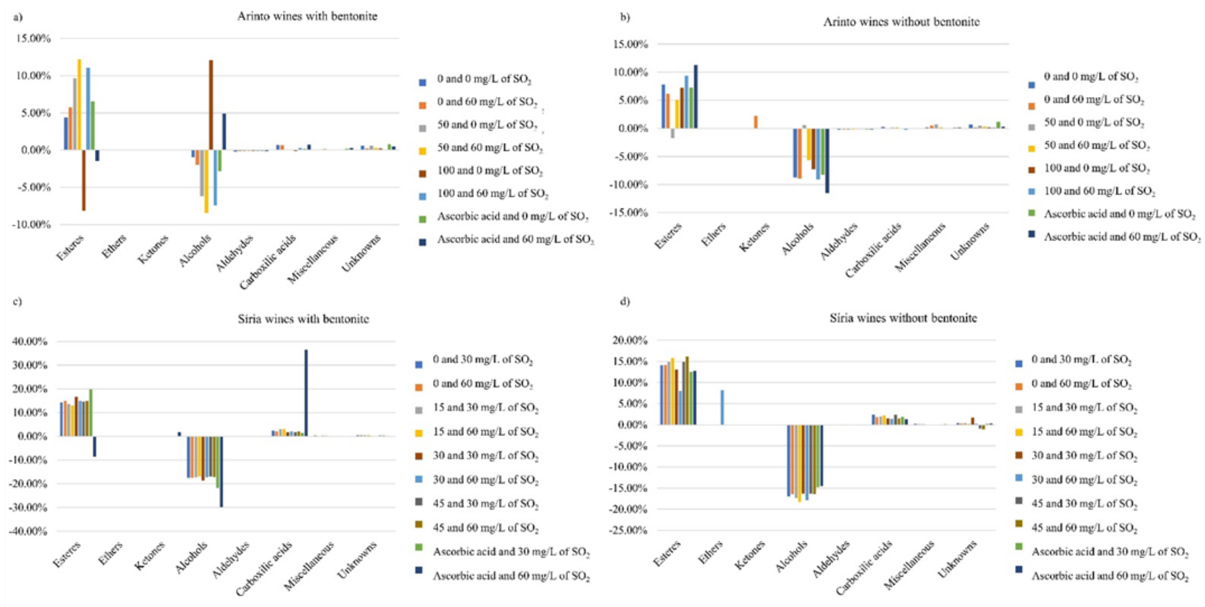


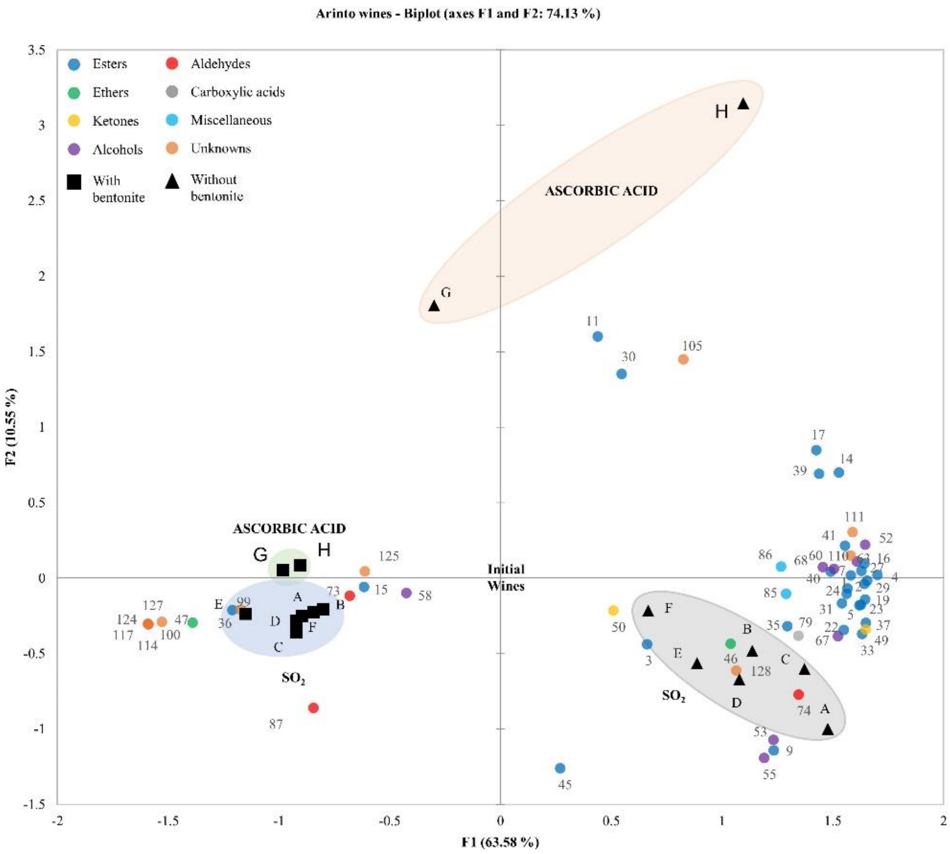
Figure 2. Graphical representation of the difference between total area of wines analyzed after 6 months and the initial wines by chemical class for each condition. a) 'Arinto' wines fermented with bentonite; b) 'Arinto' wines fermented without bentonite; c) 'Síria' wines fermented with bentonite; d) 'Síria' wines fermented without bentonite.

Principal component analysis of volatile organic compounds after storage in bottle

Principal Component Analysis (PCA) was conducted to study the evolution of wines subject to different oxidant conditions (from fermentation to bottle) and allow to observe how the presence of bentonite could impact on VOCs profile of the 'Arinto' and 'Síria' wines. This statistical procedure is very useful for chromatographic aroma analysis, also demonstrated elsewhere (Gomes Da Silva and Chaves Das Neves, 1997; Gomes Da Silva and Chaves Das Neves, 1999; Mateus *et al.*, 2010; Almeida Santos *et al.*, 2020; Pereira *et al.*, 2021) in order to understand underlying data structures. Indeed, PCA reduces the number of variables that explain the system variance allowing to detect a pattern in the relationship between the variables and the wines. For the PCAs illustrated in Figure 3 ('Arinto' wines) and Figure 4 ('Síria' wines), the relative area of the tentatively identified VOCs (Table III) were used. These relative areas were normalized against the initial wines (after alcoholic fermentation), fermented with or without bentonite under different antioxidant combinations ('Arinto' wines fermented with 0, 50 and 100 mg/L of SO_2 and 100 mg/L of ascorbic acid and 'Síria' with 0, 15, 30 and 45 mg/L of SO_2 and 100 mg/L ascorbic acid). As described before (Almeida Santos *et al.*, 2020), when data are normalized considering as reference the initial wines without treatments, there are more evident differences among samples. Hence, this methodology was applied. For maturation, 'Arinto' wines were kept with additional 0 and 60 mg/L of SO_2, and 'Síria' wine with 30 and 60 mg/L of SO_2. For 'Arinto' and 'Síria' wines, 74% and 55 % of the variance was explained by the first and second principal components (PC1 and PC2), respectively.

Figure 3 shows the PCA for 'Arinto' wines. PC1 explains 63.58% of the variance and clearly separates the samples regarding the presence of bentonite. The PC2 explains 10.55% of the variance and separates the samples by the combination of the antioxidant conditions. On the positive side of PC1 is possible to observe only wines fermented without bentonite (except for G sample), and in the negative side of PC1 the wines fermented in the presence of bentonite. Indeed, wine samples that fermented without bentonite and with ascorbic acid (G and H samples), are the ones that presented a more distinct VOCs profile evolution. Differentiation is due to the contribution of isoamyl propionate (**11**), ethyl 2-octenoate isomer (**30**) and unknown 12 (**105**). Regarding the other samples fermented without bentonite, a higher dispersion is observed, comparing with the wines fermented with bentonite. Propyl acetate (**3**), 2,4,5-trimethyl-1,3-dioxolane (**46**), 2-undecanone (**50**), decanal (**74**) and unknown 35 (**128**) seem to explain this behaviour.

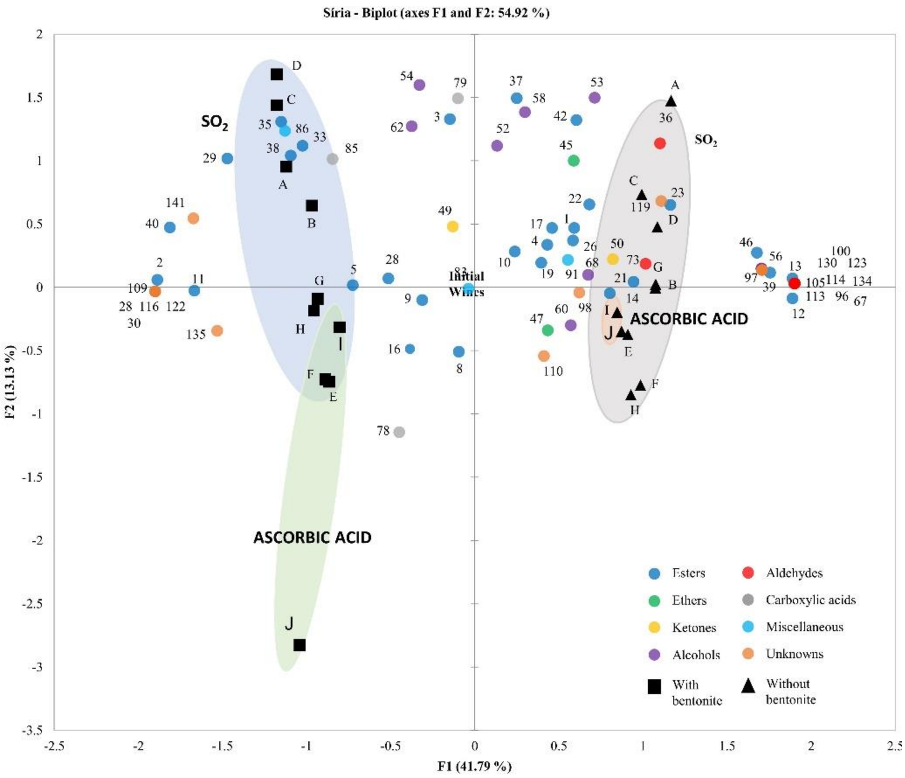
Besides the VOCs profile of the studied wines after fermentation presented good separation after PCA analysis, as described before (Almeida Santos *et al.*, 2020), an effect is now observed regarding the different conditions applied. Indeed, the evolution of wines fermented with bentonite lead to less differentiation consider the combination of the antioxidant conditions. Among this group of samples, the wines that fermented with 100 mg/L of SO_2 and without a second antioxidant addition presented a VOCs profile slightly different. Diethyl succinate (36), an ester associated with the ageing of wine (Comuzzo et al., 2020) and the unknown compound 6 (99) are responsible for that differentiation. Also, wines fermented with ascorbic acid with and without a second antioxidant addition are separated from the group by the unknown compound 32 (125).



On fermentation	[SO_2] after fermentation (mg/L)	Code
0 mg/L SO_2	0	A
	60	B
50 mg/L SO_2	0	C
	60	D
100 mg/L SO_2	0	E
	60	F
100 mg/L ascorbic acid	0	G
	60	H

Figure 3. Principal component biplot illustrating the simultaneous projection of the wine and volatile compounds on 'Arinto' wines. The initial wines, after fermentation were used as reference. Black squares – wines fermented with bentonite; Black triangle – wines fermented without bentonite; Dark blue dots – esters; Dark green dots – ethers; Yellow dots – ketones; Purple dots – alcohols; red dots – aldehydes; Grey dots – carboxylic acids; Light blue – miscellaneous; Orange – unknowns.

Figure 4 illustrates the PCA for 'Síria' wines, in which PC1 and PC2 explain 41.79% and 13.13% of the variance, respectively. PC1 clear separates wines by the presence or absence of bentonite. The 'Síria' wines fermented with bentonite were observed on the negative side of PC1. Regarding the combination of ascorbic acid and SO_2 on the fermentation and maturation, wines are clearly separated along PC2. Ethyl hexanoate (14), heptyl acetate (21), ethyl octanoate (23), diethyl succinate (36), 2-undecanone (50), nonanal (73) and unknown compound 26 (119) contribute to the distribution observed. On the other hand, wines fermented without bentonite are on the positive side of PC1. Ethyl decanoate (33), isoamyl caprylate (35), ethyl 4-decenoate isomer (38), ethyl lactate (85) and 3-ethoxypropan-1-ol (86) seem to



On fermentation	[SO_2] after fermentation (mg/L)	Code
0 mg/L SO_2	30	A
	60	B
15 mg/L SO_2	30	C
	60	D
30 mg/L SO_2	30	E
	60	F
45 mg/L SO_2	30	G
	60	H
100 mg/L ascorbic acid	30	I
	60	J

Figure 4. Principal component biplot illustrating the simultaneous projection of the wine and volatile compounds on 'Síria' wines. The initial wines, after fermentation were used as reference. Black squares – wines fermented with bentonite; Black triangle – wines fermented without bentonite; Dark blue dots – esters; Dark green dots – ethers; Yellow dots – ketones; Purple dots – alcohols; red dots – aldehydes; Grey dots – carboxylic acids; Light blue – miscellaneous; Orange – unknowns.

explain the discrimination of wines which fermented and maturate under lower antioxidant conditions. Ethyl butyrate (5), hexyl acetate (16) and butanoic acid (78) contribute to the distribution of wines under higher antioxidant conditions.

CONCLUSIONS

In this work, 'Arinto' and 'Síria' wines were produced under different antioxidant conditions, in the presence or absence of bentonite, and were maturated in different antioxidant conditions. The study of maturated wines allowed studying their impact on the respective VOCs profiles. Regarding free and total SO_2 it was possible to conclude that replacing SO_2 by ascorbic acid, does not change the SO_2 decrease observed. The same can be seen for samples treated with and without bentonite for both varieties. Regarding the VOCs profiles, 11 relevant compounds reflecting the conditions impact were identified by ANOVA analysis, such as the esters ethyl acetate (**1**), isoamyl acetate (**9**), isoamyl propionate (**11**), ethyl hexanoate (**14**), ethyl octanoate (**23**), ethyl decanoate (**33**) and alcohol 2-propanol (**52**) in both wines. Isoamyl butyrate (**13**), ethyl 9-decanoate isomer (**37**), heptanoic acid (**78**) and acetaldehyde ethyl amyl acetal (**47**) only affected 'Síria' wines, and propyl acetate (**3**), isoamyl alcohol (**55**), 1-hexanol (**58**) and phenethyl alcohol (**68**) only impacted on 'Arinto' wines. Through the PCA analysis, using wines after fermentation as reference, it was possible to observe that VOCs profile evolution of wines was mainly influenced by the fermentation conditions and less by the post-fermentation antioxidant conditions. Regarding the second antioxidant conditions, 'Síria' wines were more sensitive than 'Arinto' wines. 'Arinto' wines fermented without bentonite and ascorbic acid lead to completely different VOCs profiles.

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