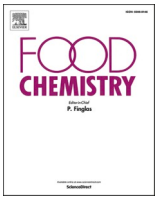
Food Chemistry 466 (2025) 142242

Contents lists available at ScienceDirect

Food Chemistry

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



The role of polyphenols in oxygen consumption and in the accumulation of acetaldehyde and Strecker aldehydes during wine oxidation

Ana Escudero [a,*], Elena Bueno-Aventín [a], Ignacio Ontañón [a], Purificación Fernández-Zurbano [b], Vicente Ferreira [a]

[a] Laboratorio de Análisis del Aroma y Enología (LAAE). Department of Analytical Chemistry, Universidad de Zaragoza, Instituto Agroalimentario de Aragón (IA2) (UNIZAR-CITA), Associate unit to Instituto de Ciencias de la Vid y del Vino (ICVV) (UR-CSIC-GR), C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain
[b] Instituto de Ciencias de la Vid y del Vino (ICVV) (UR-CSIC-GR), Finca La Grajera, 26007 Logroño, La Rioja, Spain

ARTICLE INFO

Chemical compounds:
Acetaldehyde (PubChem CID: 177)
Isobutanal (PubChem CID: 6561)
2-Methylbutanal (PubChem CID: 7284)
3-Methylbutanal (PubChem CID: 11552)
Methional (PubChem CID: 18635)
Phenylacetaldehyde (PubChem CID: 998)
Catechin (PubChem CID: 73160)
Delphinidin 3-glucoside (PubChem CID: 443650)
Coumaric acid (PubChem CID: 637542)
Malvidin 3-glucoside (PubChem CID: 11249520).

Keywords:
Wine aroma
Strecker aldehydes
Polyphenols
Acetaldehyde
Oxygen consumption
Antioxidant

ABSTRACT

This study explores the role of polyphenols in preventing oxidative deterioration of wine aroma. Wine models containing polyphenols extracted from grapes were fortified with delphinidin-3G (DELF) or catechin (CAT), and oxidized. DELF increased oxygen consumption rates (OCRs) and reduced the Strecker aldehydes (SAs) formation, while CAT decreased OCRs and increased SAs. Further oxidation of models with individual polyphenols: coumaric acid (COU), caffeic acid (CAF), CAT, epigallocatechin (EPIG), malvidin-3G (MV), DELF, quercetin (QUER), and myricetin (MYR) revealed that most polyphenols, except anthocyanins, slowed initial OCRs. Anthocyanins and trihydroxylated polyphenols consumed all oxygen. DELF arises as the ideal sacrificial antioxidant, consuming O_2 quickly and quantitatively, avoiding Fenton reaction and SAs accumulation. MV was similar but caused high SAs levels. EPIG and MYR prevented Fenton reaction but induced moderate SAs accumulation. COU hardly consumed O_2, but prevented Fenton reaction and did not induce SAs. These findings could help enhance wine quality and stability.

1. Introduction

Polyphenols are responsible for relevant sensory attributes of wine, including astringency, bitterness, and tactile perception (Ferrer-Gallego, Hernandez-Hierro, Rivas-Gonzalo, & Escribano-Bailon, 2014; Sun, Spranger, Roque-do-Vale, Leandro, & Belchior, 2001), all of them closely related to wine quality (Saenz-Navajas, Echavarri, Ferreira, & Fernandez-Zurbano, 2011). In addition, polyphenols are the most abundant natural wine antioxidants (Delgado, Zamora, & Hidalgo, 2015). Their antioxidant properties are primarily related to the oxidability of the hydroxyls present in the B-ring of the flavan nucleus, which, in turn, depends on the hydroxyls' number and relative position, as well as on the electroactivity of the different substituents present in the aromatic rings. More specifically, the polyphenols' electron-donor ability is determined by the B-ring's electronic chemistry, which also determines the polyphenols' ability to complex metal cations, while defining the chemical stability of the quinone and of hydroquinone radicals they produce (Hibi & Yanase, 2019; Rahman, Ichiyanagi, Komiyama, Hatano, & Konishi, 2006; Thavasi, Leong, & Bettens, 2006). Although the general antioxidant character of polyphenols has been well documented, few reports deal specifically with their ability to affect aromatic problems related to oxidation. One study, however, has addressed the ability of polyphenols to avoid the off-odors associated with lipid oxidation (Plaza et al., 2014).

The oxidative deterioration of wine aroma is mainly related to the accumulation of aldehydes, in particular to the accumulation of

* Corresponding author.
E-mail address: escudero@unizar.es (A. Escudero).

https://doi.org/10.1016/j.foodchem.2024.142242
Received 9 August 2024; Received in revised form 14 November 2024; Accepted 23 November 2024
Available online 26 November 2024

acetaldehyde and SAs, isobutanal, 2-methylbutanal (2 MB), 3-methylbutanal (3 MB), methional, and phenylacetaldehyde (Cullere, Cacho, & Ferreira, 2007; Escudero, Hernandez-Orte, Cacho, & Ferreira, 2000).

Acetaldehyde is the product of the oxidation of ethanol, which occurs through a Fenton process (J. C. Danilewicz, 2003; Waterhouse & Laurie, 2006). Such oxidation takes place when the H_2O_2 formed after the first reduction of O_2 cannot be rapidly oxidized to water by free SO_2 (Elias & Waterhouse, 2010). H_2O_2 is then catalytically decomposed by metal cations, thereby yielding the OH* radical (Elias, Andersen, Skibsted, & Waterhouse, 2009), which is so reactive that it indiscriminately oxidizes any alcohol present. As ethanol is by far the most abundant alcohol in wine, the radical 1-hydroxyethyl (1-HER) is the main product of this process. If such a radical is not quenched, it will further react with oxygen to produce a hydroxyethylperoxide radical, which then will eliminate a hydroperoxyl radical to form acetaldehyde (John C. Danilewicz, 2011; Elias & Waterhouse, 2010).

The ability of cinnamic acids to inhibit the oxidation of ethanol to acetaldehyde by quenching the 1-HER radical has already been demonstrated (Gislason, Currie, & Waterhouse, 2011; Kreitman, Laurie, & Elias, 2014). This ability contrasts with the pro-oxidant effects observed in the case of 4-methylcatechol, which promotes the oxidation of ethanol rather than preventing it (Elias & Waterhouse, 2010). Such contrasting oxidative patterns suggest that a wine's polyphenolic profile should substantially affect the fraction of ethanol oxidized to acetaldehyde. However, such an effect has never been clearly demonstrated. In fact, the ability to quench the 1-HER radical, measured 30 min after the onset of oxidation, is not clearly related to the system's ability to accumulate acetaldehyde (Marchante et al., 2020). Furthermore, in a recent study, wine models with different polyphenolic profiles accumulated thoroughly homogeneous levels of acetaldehyde, without any apparent correlation with their polyphenolic composition (Bueno-Aventin, Escudero, Fernandez-Zurbano, & Ferreira, 2021).

On the other hand, several studies have shown that the amount of acetaldehyde accumulated during wine oxidation in the absence of SO_2 is much lower than the amount that would be expected if all H_2O_2 formed was primarily transformed into 1-HER and later into acetaldehyde (Bueno et al., 2018; Bueno-Aventin et al., 2021; Marrufo-Curtido, Ferreira, & Escudero, 2022b). Given that PLS models relating acetaldehyde accumulation rates to chemical composition have suggested that such low accumulation rates are associated with the presence of anthocyanins, and since these molecules' ability to react to acetaldehyde is well documented (Francia-Aricha, Guerra, Rivas-Gonzalo, & Santos-Buelga, 1997; Rivas-Gonzalo, Bravo-Haro, & Santos-Buelga, 1995; Timberlake & Bridle, 1976), it was initially assumed that acetaldehyde was the primary product of oxidation but that a significant fraction of the molecule was rapidly removed by reaction with anthocyanins and other wine polyphenols. However, recent studies have shown that the kinetics of the reaction between acetaldehyde and wine polyphenols at room temperature are too slow to be compatible with such assumptions (Marrufo-Curtido et al., 2022b; Marrufo-Curtido, Ferreira, & Escudero, 2022a). Thus, the currently favored hypothesis is that anthocyanins might exert a more direct impact on the fate of H_2O_2 formed during wine oxidation in the absence of SO_2.

Regarding the accumulation of SAs, the role of polyphenols in the Strecker degradation of the precursor amino acids has been well known since the 1970s (Mathew & Parpia, 1971; Saijo & Takeo, 1970). Rizzi (Rizzi, 2006) established that polyphenols (catechin, epicatechin, caffeic and chlorogenic acids) are able to degrade methionine and phenylalanine to form the respective aldehydes (methional and phenylacetaldehyde) via phenolic oxidation to o-quinone in the presence of metal ions (phosphate buffer, pH 7.17, stored at 22 °C). More recently, Monforte et al. demonstrated that Strecker degradation effectively takes place in wine conditions at >40 °C (Monforte, Martins, & Ferreira, 2018, 2020). Regarding the specific role of the different polyphenols, Delgado et al. (Delgado et al., 2015) studied the influence of the structural characteristics of polyphenols on their ability to produce phenylacetaldehyde from phenylalanine at 180 °C. They concluded that all polyphenols containing two hydroxyls in *para* or in *ortho* positions produce the Strecker degradation, except if two further hydroxyls are in the *meta* position on an additional aromatic ring. Moreover, PLS models suggested that the accumulation of SAs, except for phenylacetaldehyde, during wine oxidation was negatively related to the presence of anthocyanins (Bueno et al., 2018). On the other hand, a recent study demonstrated that wine models differing in terms of polyphenol composition have quite different abilities to form SAs during oxidation (Bueno-Aventin et al., 2021). PLS modeling of results further suggested that delphinidin 3-glucoside (plus cyanidin 3-glucoside and petunidin 3-glucoside) and prodelphinidins inhibit the accumulation of SAs, while flavanols, catechin, and phenolic acids promote it. The strongest observed effects were apparently linked to delphinidin 3-glucoside and catechin. Interestingly, the same study also revealed that the samples which consumed O_2 more rapidly tended to accumulate lower amounts of SAs. This, in turn, could be related to their higher level of delphinidin 3-glucoside and their lower level of catechin.

Strong evidence thus indicates that polyphenolic profiles modulate or determine OCRs and the accumulation of SAs during aging; however, the effects of polyphenolic profiles on the oxidation of ethanol and the accumulation of acetaldehyde remain obscure. In any case, the role of individual polyphenols in all these oxidation outcomes remains unclear. In view of this current state of research, the present paper features, in a first step, the experimental verification of previous PLS models, suggesting that delphinidin 3-glucoside and catechin are key determinants of OCRs and of SAs accumulation rates during wine oxidation. The second section of this paper contains a more detailed study of the effects of individual polyphenols on OCRs and on the accumulation rates of both SAs and acetaldehyde during wine oxidation.

2. Materials and methods

2.1. Reagents, solvents, and standards

Hydrochloric acid (37 %), sodium hydrogencarbonate, and sodium metabisulfite (97 %) were acquired from Panreac (Barcelona, Spain). L (+)-tartaric acid (99 %), glycerol (99,5 %), iron (II) chloride tetrahydrate (>99 %), manganese (II) chloride tetrahydrate (>99 %), copper (I) chloride (99,9 %), acetaldehyde (>99,5 %), L-leucine (Leu) (>98 %), L-isoleucine (Ile) (>98 %), D-valine (Val) (>98 %), *L*-phenylalanine (Phe) (>98 %), D-methionine (Met) (>98 %), L-cysteine hydrochloride anhydrous (>98 %), L-glutathione reduced (>98 %), quercetin (QUER) (95 %), and hydrogen sulfide (≥ 99.5 %) were procured from Sigma-Aldrich (Madrid, Spain). Highest purity (> 98 %) grade caffeic acid (CAF), coumaric acid (COU) and ovalbumin (≥ 90 %), (−)-epicatechin (purity ≥90 %), phloroglucinol, sodium citrate trihydrate, methanol of LC-MS LiChrosolv grade, LC-MS grade formic acid used as the mobile phase additive, and all the solvents for the phloroglucinolysis reactions, extraction, isolation, and analysis were purchased from FLUKA Sigma-Aldrich (St. Louis, USA). LiChrolut EN sorbent, 1 mL cartridge and PTFE frits, dichloromethane, and ethanol were purchased from Merck (Darmstadt, Germany). The resins Sep Pak—C18, format 10 g, came from Waters (Ireland). Sodium hydroxide (99 %), HPLC-grade acetonitrile (ACN), and o-phosphoric acid were purchased from Scharlab (Sentmenat, Spain). Isobutyraldehyde (99 %), 2-methylbutanal (95 %), 3-methylbutanal (95 %), phenylacetaldehyde (95 %) and methional (98 %), 2-methylpentanal (98 %), 3-methylpentanal (97 %), and O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, 98 %) were supplied by Merck (USA). Phenylacetaldehyde-d2 (95 %) and methional-d2 were purchased from Eptes (Vevey, Switzerland). Water was purified in a Milli-Q system from Millipore (Bedford, Germany). Highest purity (> 98 %) grade (+)-catechin (CAT), (−)-epicatechin, (−)-gallocatechin, (−)-epigallocatechin (EPIG), (−)-epicatechin gallate, procyanidin B1, and procyanidin B2 were obtained from TransMIT PlantMetaChem (Giessen, Germany). Highest

purity (> 95 %) grade, malvidin 3-glucoside chloride (MV), malvidin chloride, delphinidin chloride and delphinidin 3-glucoside chloride (DELF) were supplied by Extrasynthese (Genay, France). Myricetin (MYR) (98 %) was supplied by Activate Scientific (Ely, UK). The phloroglucinolated derivatives epicatechin 4-phloroglucinol, epicatechin-gallate 4-phloroglucinol, and epigallocatechin 4-phloroglucinol were prepared according to Arapitsas et al. (Arapitsas, Perenzoni, Guella, & Mattivi, 2021).

2.2. Polyphenolic and aroma fractions (PAFs)

The two PAFs were extracted from 2 lots of grapes from La Rioja, a Spanish winemaking region, and from two different grape varieties (Tempranillo and Garnacha) as described in Alegre et al. (Alegre, Arias-Perez, Hernandez-Orte, & Ferreira, 2020). The obtaining procedure was explained in Supplementary material.

2.3. Preparation of wine models

This operation was carefully carried out inside a glovebox (Jacomex) containing less than 1 mg L^{-1} O_2.

2.3.1. Fortification experiment with reconstituted PAFs

The 100 mL ethanolic extracts were reconstituted with water containing 5 g L^{-1} of tartaric acid, adjusted to 3.5 pH, and spiked with glycerol (5 g L^{-1}), 5 mg Fe L^{-1}, 0.2 mg Mn L^{-1} and 0.2 mg Cu L^{-1} to form 750 mL samples of model wines 13.3 % (*v*/v) in ethanol. The models were spiked with 200 μg L^{-1} of H_2S and left to stand for a week in the anoxic chamber. After this, the models were spiked with 10 mg L^{-1} of Leu, Ile, Val, Phe, Met, cysteine, and reduced glutathione (GSH). Each PAF was then separated into two aliquots, one of them doped with a polyphenol and the other not, the latter remaining as a control sample. 300 mg L^{-1} of delphinidin 3-glucoside was added to the PAF from the Garnacha variety, and 30 mg L^{-1} of catechin was added to the Tempranillo PAF.

2.3.2. Experiment with synthetic wine (SW) doped with a polyphenol

MilliQ water containing 13.3 % (v/v) ethanol, 5 g L^{-1} of tartaric acid, pH adjusted to 3.5 and spiked with glycerol (5 g L^{-1}), 5 mg Fe L^{-1}, 0.2 mg Mn L^{-1}, and 0.2 mg Cu L^{-1} were spiked with 200 μg L^{-1} of H_2S and left to stand for a week within the anoxic chamber. After this, the synthetic wine was spiked with 10 mg L^{-1} of cysteine and GSH, as well as with 88 uM of Leu, Ile, Val, Phe, and Met. It was then separated into nine aliquots, eight of which were doped with 820 uM of a polyphenol, whereas the ninth was not, remaining as a control sample. The selected polyphenols were: catechin and epigallocatechin (dihydroxylated and trihydroxylated flavanols), malvidin 3-glucoside and delphinidin 3-glucoside (monohydroxylated and trihydroxylated anthocyanins), caffeic and coumaric acids (dihydroxylated and monohydroxylated phenol, respectively) and quercetin and myricetin (dihydroxylated and trihidroxylated flavonols). The same experiment was made with malvidin (aglyconic form) and delphinidin (aglyconic form) but only OCRs results were shown.

2.4. Forced oxidation procedure

Each wine model was removed from the glove box, saturated with air by vigorous shaking, and then distributed into two 13 mL glass tubes of perfectly known internal volume containing Pst3 Nomasense oxygen sensors. Each tube contained the volumes of liquid and headspace required to deliver an O_2 concentration as described by Marrufo-Curtido et al. (Marrufo-Curtido, Carrascon, Bueno, Ferreira, & Escudero, 2018). Reconstituted PAFs started with 50 mg O_2 L^{-1}, and synthetic wine tubes began with 20 mg O_2 L^{-1}. Reconstituted PAF tubes were incubated in an agitated thermostatic bath (Grant instruments OLS Aqua Pro) at 35 °C for 32 days, and synthetic wine tubes for 38 days. The dissolved oxygen level was controlled. OCRs were calculated as consumed O_2 (mg L^{-1}) per day in the first period of oxidation (4 days).

2.5. Chemical characterization of the PAFs

In the experiment on reconstituted PAFs, both polyphenolic fractions diluted in water at 13.3 % *v*/v were chemically characterized prior to the aging treatment. Anthocyanins were analyzed by ultra-HPLC−MS/MS as described by Arapitsas et al. (Arapitsas, Perenzoni, Nicolini, & Mattivi, 2012). Flavanols, flavonols, and hydroxycinnamic acids were analyzed as described by Vrhovsek et al. (Vrhovsek et al., 2012) by UHPLC−MS/MS. The mean degree of polymerization (mDP) was determined by UPLC−MS/MS analysis of the phloroglucinol reaction as described by Arapitsas et al. (Arapitsas et al., 2021).

2.6. Chemical characterization of oxidized wine models

In both experiments, we determined the accumulation of Strecker aldehydes at the end of oxidative aging. We also assessed the amount of remaining polyphenols in the samples of synthetic wine doped with the different polyphenols, and we quantified the accumulated amount of acetaldehyde after oxidation.

Total Strecker aldehydes were subjected to GC–MS analysis after derivatization with PFBHA as described by Castejón-Musulén et al. (Castejón-Musulén et al., 2022).

Total acetaldehyde was determined by HPLC with ultraviolet (UV) detection after previous derivatization with DNPH as described by Han et al. (Han, Wang, Webb, & Waterhouse, 2015).

The remaining polyphenols were determined by UPLC-QTOF MS using the procedure described by Arapitsas and Mattivi (Arapitsas & Mattivi, 2018), and they were quantified by response factor, using the signal obtained in the initial doped synthetic wines preserved in anoxia at 4 °C until the end of oxidative aging.

2.7. Data analysis

Samples from both experiments were prepared and treated in duplicate. Basic statistical analyses were carried out with Excel 2020 (Microsoft, Seattle, WA, USA). *t*-test and analysis of variance (ANOVA) was carried out with XLSTAT (Addinsoft, 2015 version).

3. Results and discussion

3.1. Confirming the role of delphinidin 3-glucoside and catechin in wine oxidation

The first objective was to verify the prominent role attributed to delphinidin 3-glucoside and catechin in oxygen consumption and accumulation of Strecker aldehydes by PLS models in previous work (Bueno-Aventin et al., 2021). To achieve this, each component was separately added to two reconstituted monovarietal polyphenolic extracts, whose polyphenolic compositions are given in Table S1 (Supplementary Material). Delphinidin 3-glucoside was added to the Garnacha extract, and catechin to the Tempranillo extract. Models were then subjected to a controlled oxidation process in which the oxygen consumption rates and the accumulation of Strecker aldehydes were studied.

The results of O_2 consumption are given in Fig. 1 and entirely confirm what the models had suggested: the model containing polyphenols extracted from Tempranillo was a quick O_2 consumer, and oxygen consumption rates significantly decreased when catechin was added. Conversely, the model containing polyphenols extracted from Garnacha was a slow O_2 consumer and the addition of delphinidin 3-glucoside had a dramatic impact on OCRs, so that the model became the fastest O_2 consumer.

Results regarding the accumulation of Strecker aldehyde, shown in

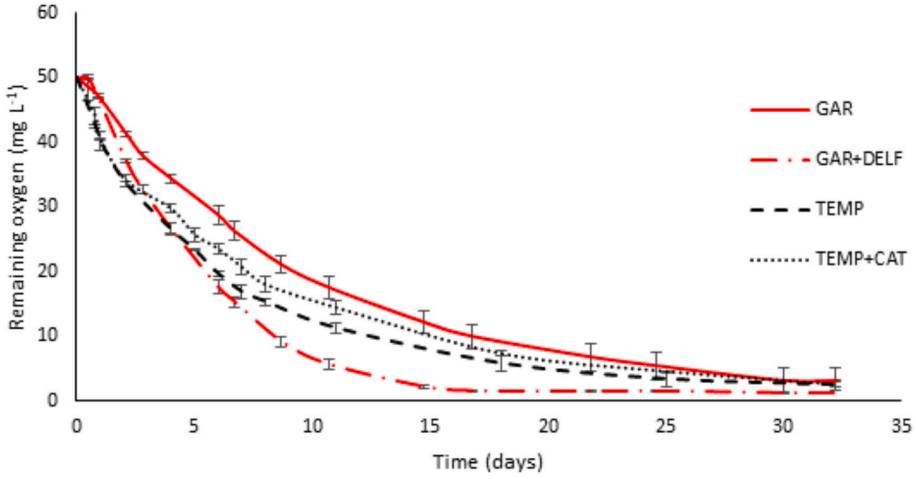


Fig. 1. Oxygen consumption during the oxidative aging of four wine models containing polyphenols extracted from tempranillo or garnacha and their corresponding fortified samples with catechin or delphinidin 3-glucoside, respectively. Initial O_2 level was 50 mgL^{-1}. Error bars are standard deviations ($n = 2$). GAR: garnacha. TEMP: tempranillo. DELF: delphinidin 3-glucoside. CAT: catechin.

Table 1
Accumulations (μg L^{-1}) and accumulation rates (μg L^{-1}/consumed O_2 (mg L^{-1})) of Strecker aldehydes in models containing polyphenols extracted from tempranillo or garnacha and their corresponding fortified samples with catechin or delphinidin 3-glucoside, respectively. *P* value of one tailed *t*-test.

	Isobutanal			2-methybutanal			3-mehyilbutanal			Methional			Phenylacetaldehyde			Total Strecker aldehydes		
Accumulation (μg L^{-1})																		
TEMP	11.64	±	0.58	15.69	±	2.13	14.88	±	0.61	31.01	±	2.65	44.60	±	3.73	117.82	±	2.35
TEMP+CAT	15.56	±	3.00	17.93	±	3.40	16.14	±	1.24	34.34	±	1.02	47.68	±	3.69	131.65	±	6.48
p (t-test)	0.106			0.256			0.163			0.120			0.247			0.042		
GAR	56.14	±	4.33	71.05	±	4.28	93.04	±	4.64	189.28	±	7.99	187.56	±	3.39	597.08	±	5.18
GAR +DELF	21.11	±	0.83	28.82	±	0.95	38.20	±	1.98	70.05	±	4.46	73.82	±	4.55	231.99	±	3.04
p (t-test)	0.004			0.003			0.002			0.001			0.001			0.001		
Accumulation rates (μg L^{-1}/consumed O_2 (mg L^{-1}))																		
TEMP	0.24	±	0.01	0.33	±	0.04	0.31	±	0.02	0.65	±	0.07	0.94	±	0.09	2.48	±	0.09
TEMP+CAT	0.33	±	0.07	0.38	±	0.07	0.34	±	0.03	0.72	±	0.02	1.00	±	0.07	2.77	±	0.16
p (t-test)	0.108			0.250			0.183			0.136			0.250			0.058		
GAR	1.20	±	0.14	1.52	±	0.16	1.99	±	0.18	4.04	±	0.34	4.00	±	0.24	12.75	±	0.22
GAR +DELF	0.43	±	0.02	0,59	±	0.02	0.78	±	0.04	1.44	±	0.09	1.51	±	0.09	4.75	±	0.06
p (t-test)	0.009			0.007			0.006			0.004			0.003			0.005		

Table 1, also confirm previous observations (Bueno-Aventin et al., 2021). The reconstituted Tempranillo extract produced quantities significantly and remarkably lower than the Garnacha extract in both absolute and O_2-normalized terms. The addition of catechin to the model from Tempranillo slightly increased the accumulation of Strecker aldehydes, although significance was only reached in the total accumulated absolute value. The addition of delphinidin 3-glucoside to the model from Garnacha had a more evident and significant impact, strongly bringing down levels of accumulated and O_2-normalized SA accumulation rates.

Given the significance of these effects, a more detailed study about the impact of individual polyphenols on wine oxidation, controlling OCRs, and the accumulation of SAs and acetaldehyde, has been carried out.

3.2. Effects of individual polyphenols on oxygen consumption rates

The effects of polyphenols on OCRs are shown in Fig. 2, while Table 2 shows data about levels of polyphenols remaining after the oxidation and the total O_2 consumed during the experiment. It should be mentioned that myricetin and quercetin were not perfectly solubilized in the initial models, which suggests that recorded OCRs for these two compounds may correspond to molar concentrations smaller than those of the other polyphenols. Regarding OCRs, three clearly different patterns are observed:

1. Avid O_2 consumers. The two anthocyanins, particularly delphinidin-3G, consume O_2 very fast (average OCRs 4.02 ± 0.02 and 2.41 ± 0.76 mg L^{-1} per day for delphinidin and malvidin glucosides, respectively). Consumption takes place since the beginning of the experiment, without any lag phase.
2. Delayed fast O_2 consumers. Epigallocatechin, and myricetin (B-ring three hydroxylated) are efficient O_2 consumers (average OCRs 2.32 ± 0.65 and 0.92 ± 0.03 mg L^{-1} per day, respectively), but consumption only takes place after a 1 to 2 days lag phase. Remarkably, such lag phase is not observed in the synthetic wine not containing polyphenols (only reduced metal cations and major wine sulfhydryls) which indicates that it is induced specifically by the addition of the polyphenol.
3. Delayed slow O_2 consumers. The rest of the polyphenols were not able to consume O_2 efficiently and, in fact, all of them retarded O_2 consumption several days with respect to the control and consumed less than half of the oxygen present in the system in the 38 days of the experiment. Two subgroups emerge here:
   a. Coumaric acid (monohydroxylated phenol) suffered a very short lag phase (2 days), and O_2 recordings did not increase in the first days.

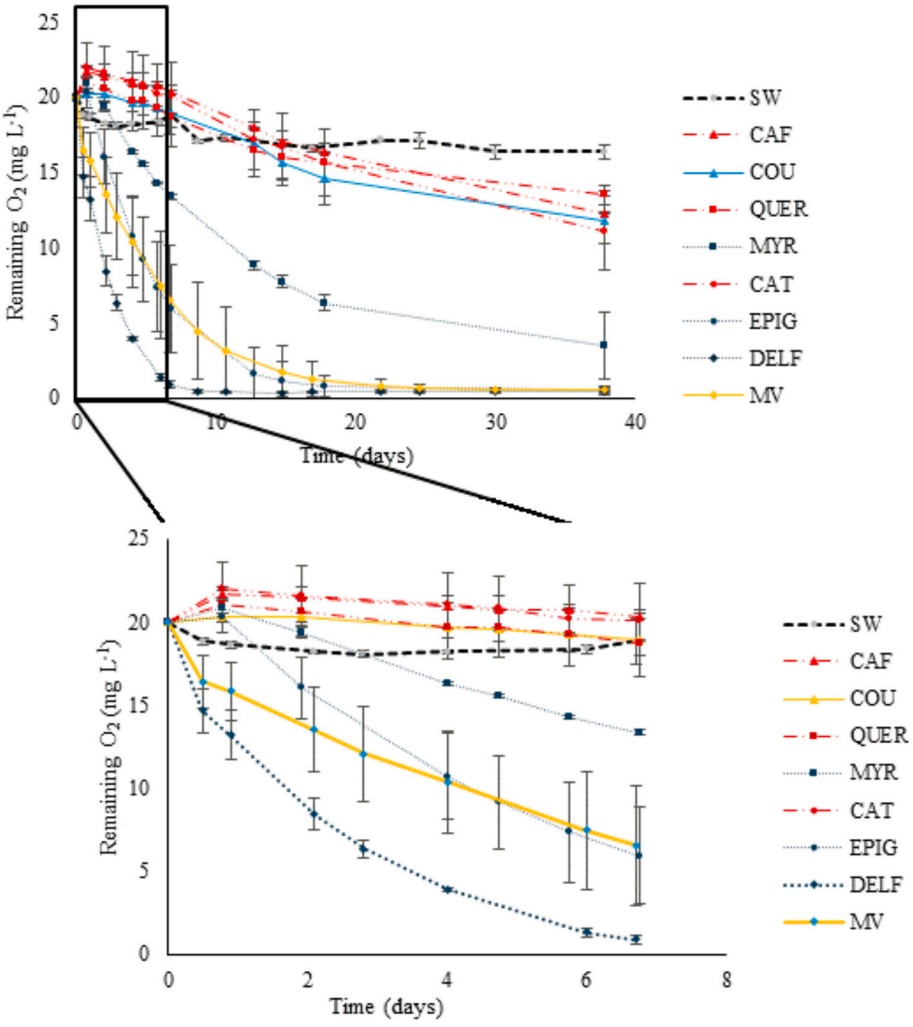


Fig. 2. Oxygen consumption during the oxidative aging of synthetic wines containing metal cations and wine mercaptans (H_2S, cysteine and glutathione) and one selected phenol (plus the control). Initial O_2 level was 20 mgL^{-1}. Error bars are standard deviations (n = 2). Yellow dots and lines correspond to monohydroxylated phenols, red to dihydroxylated and blue to trihydroxylated. Phenolic acids (▲), flavonols (■), anthocyanins (◆) and flavanols (●). SW: synthetic wine. CAF: caffeic acid. COU: coumaric acid. QUER: quercetin. MYR: myricetin. CAT: catechin. EPIG: epigallocatechin. DELF: delphinidin 3-glucoside. MV: malvidin 3-glucoside. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Major effects of oxidation on wine models containing metal cations, wine mercaptans and one specific polyphenol (plus the control). Amount of remaining polyphenol, consumed O_2, accumulated acetaldehyde and ratio of accumulated acetaldehyde to expected acetaldehyde -in the assumption that 1.76 mg L^{-1} of O_2 was devoted to oxidize cations and mercaptans and 91 % of the H_2O_2 formed ends oxidizing ethanol- (expressed as %).

	Polyphenol (uM)	Consumed O_2 (mg L^{-1})	Consumed O_2 (uM)	Accumulated acetaldehyde (mg L^{-1})	Accumulated acetaldehyde (uM)	Accumulated/ expected(%)
Coumaric	820 ± 32.21	8.16 ± 1.62 ^{CD}	255 ± 51 ^{CD}	3.46 ± 0.01^{D}	78.6 ± 0.2^{D}	43 ± 8.6^{CD}
Caffeic	720.35 ± 55.75	7.71 ± 0.05 ^{CD}	241 ± 1.6 ^{CD}	5.22 ± 0.54^{BC}	119 ± 12^{BC}	70 ± 7.3^{ABC}
Catechin	19.97 ± 0.21	8.87 ± 2.64 ^{C}	277 ± 83 ^{C}	8.56 ± 1.18^{A}	195 ± 27^{A}	97 ± 21^{A}
Epigallocatechin	27.37 ± 0.38	19.48 ± 0.27 ^{AB}	609 ± 8.4 ^{AB}	5.18 ± 0.07^{BC}	118 ± 1.6^{BC}	23 ± 0.5^{D}
Malvidin 3-glucoside	316.36 ± 29.80	19.50 ± 0.14 ^{AB}	609 ± 4.4 ^{AB}	4.07 ± 0.64^{CD}	92.5 ± 15^{CD}	18 ± 2.9^{D}
Delphinidin 3-glucoside	354.42 ± 58.75	19.60 ± 0.14 ^{A}	613 ± 4.4 ^{A}	5.73 ± 0.18^{B}	130 ± 4.1^{B}	25 ± 0.8^{D}
Quercetin	3.45 ± 1.70*	6.48 ± 0.64 ^{CD}	203 ± 20 ^{CD}	5.07 ± 0.55^{BC}	115 ± 13^{BC}	85 ± 12^{AB}
Myricetin	45.08 ± 5.15*	16.54 ± 2.27 ^{B}	517 ± 71 ^{B}	9.64 ± 0.15^{A}	219 ± 3.4^{A}	52 ± 7.2^{BCD}
Synthetic wine		4.28 ± 0.89 ^{D}	134 ± 28 ^{D}	3.14 ± 0.52^{D}	71.4 ± 12^{D}	99 ± 26^{A}

Different letters in columns indicate significant differences between samples according to sample factor ANOVA (Fischer posthoc test. $p < 0.05$). Monohydroxylated polyphenols are underlined, dihydroxylated in italics and trihydroxylated in bold letters.
* Remaining levels of quercetin and myricetin were determined by epigallocatechin response factor, due to lack of solubility of flavonols in initial models.

b. Caffeic acid, quercetin and catechin (dihydroxylated phenols), suffered a longer lag phase (4–9 days), and O_2 recordings increased in the first days.

It is generally accepted that the ability of polyphenols to consume oxygen is related to the level of hydroxylation of the B-ring (Thavasi et al., 2006) (Lindberg Madsen, Andersen, Jorgensen, & Skibsted, 2000) (Jakubek et al., 2023), and in fact, such effect is clearly observed in the

two last groups. However, this rule hardly applies to the case of anthocyanins, which follow a quite unique pattern of O_2 consumption characterized by a nearly immediate and very fast O_2 consumption, in spite of having clearly different structures in their B-rings (trihydroxylated in delphinidin-3G and monohydroxylated with two metoxy groups in malvidin-3G). Instead, as have been recently proposed (Cruz, Basilio, Mateus, de Freitas, & Pina, 2022) their oxidation could occur via the formation of a radical in their opened C-ring after de-glucosidation. Attending to such mechanism, the rate-determining step is the hydrolysis of the glycoside. In fact, non-glucosidated malvidin and delfinidin (very unstable and insignificant in grapes and wines) oxidized significantly faster (from 2.41 to 3.84 in the case of malvidin, and from 4.02 to 4.93 mg L^{-1} of O_2 per day in the case of delfinidin).

Moreover, the differences between mono and di-hydroxylated polyphenols may give some clue about the surprising ability of non-anthocyanic polyphenols to induce a lag phase, in fact preventing the oxidation of major wine sulfhydryls, which, to the best of our knowledge, it is here reported for the first time. As di-hydroxylated polyphenols induce a longer lag phase, it can be hypothesized that it is their ability to complex to both Fe(II) and, particularly, Fe(III), which difficult the uptake of oxygen by the mercaptans, which will be majorly complexed to Cu(I). Catechin and quercetin can form strong complexes to Fe (III) (Elhabiri, Carrer, Marmolle, & Traboulsi, 2007; Escandar & Sala, 1991), avoiding the oxidation of mercaptans by this cation, mediated or not by the oxidation of Cu(I) to Cu(II), as suggested by Kreitman et al. (Kreitman, Danilewicz, Jeffery, & Elias, 2016). This also helps explaining why delphinidin-3G increases OCRs in a complex medium and why catechin decreases it, as it was demonstrated in section 3.1.

Regarding levels of polyphenol remaining after the oxidation, the effects of the family of polyphenol, and hence, of the C-ring, become dominant. Data in Table 2 reveals that the two phenolic acids were poorly consumed by oxygen, that the decrease of the two anthocyanins corresponds to the oxygen consumption (1:1 stoichiometry), while the two flavanols and the two flavonols were nearly completely depleted during the oxidation, so that only residual levels of these compounds remained. This implies that catechin and quercetin oxidation takes place with an apparent 3:1 stoichiometry, while that of epigallocatechin and myricetin with a 1.4:1. The higher decrease of catechin during oxidation has been previously observed (Vlahou, Christofi, Roussis, & Kallithraka, 2022) and can be explained by the tendency of flavanols to form dimers, trimers or higher oligomers mainly by intermolecular bonds (Mouls & Fulcrand, 2012). Although the structures formed are known to be more easily oxidizable (Hibi & Yanase, 2019(Chung, Kurisawa, Kim, Uyama, & Kobayashi, 2004) their presence did not imply a higher consumption of oxygen, but of the monomer. Likewise, oxidation decreases quercetin generating various products (Sadžak, Eraković, & Šegota, 2023).

Fig. 2 also shows that the model wine rapidly consumed 1.8 mg L^{-1} of the oxygen on the first two days; in the course of the following 36 days, it consumed 2.5 mg L^{-1} (78 uM). The initial consumption rate can be ascribed to the oxidation of the metal cations Fe(II) and Cu(I), which were added in reduced forms, as well as to the oxidation of the sulfhydryl compounds present in the SW. Specifically, the oxidation of 5 mg L^{-1} of Fe yielded 89 uM of electrons; the oxidation of 0.2 mg L^{-1} of Cu yielded 3.0 uM; that of 10 mg L^{-1} of Cys yielded 83 uM, that of 10 mg L^{-1} of GSH yielded 33 uM, and the oxidation of 0.2 mg L^{-1} of H_2S yielded 12 uM. That makes up a total of 220 uM of substances capable of donating an electron, which explains the reduction to water of 55 uM of O_2, equivalent to approx. 1.76 mg L^{-1}. It is thus plausible that in the 4.28 mg L^{-1} of O_2 consumed by the model wine, somewhat more than 2.5 mg L^{-1} served to oxidize matrix compounds such as alcohol, glycerin, and tartaric acid.

3.3. *Effects of individual polyphenols on the accumulation of acetaldehyde*

Results of acetaldehyde accumulation during oxidation of the model wines are shown in Table 2. Accumulated levels ranged from 3.14 mg L^{-1}, measured in the control, to 9.64 mg L^{-1}, measured in the model wine with myricetin.

Acetaldehyde is, attending to the generally accepted wine oxidation mechanisms, the main product of wine oxidation in the absence of SO_2. It is generally accepted that O_2 first oxidizes an ortho-diphenol to form a quinone, become itself reduced to H_2O_2. If this peroxide is not quenched by SO_2, it will be catalytically decomposed (Fenton reaction) yielding the OH* radical, which is so reactive that it will react indiscriminately to any organic matter present, abstracting an H* from an alcohol, preferably (John C. Danilewicz, 2013; Laurie & Waterhouse, 2006). As ethanol makes up 91 % of the organic matter present in the wine model, it can be assumed that 91 % of the O_2 consumed will form a molarly equivalent amount of the 1-hydroxyethyl radical (1-HER). If this radical is not quenched, it will be transformed in acetaldehyde. Under these hypotheses, and further considering that 1.76 mg L^{-1} of O_2 was devoted to oxidize cations and mercaptans, it is possible to estimate, for a given amount of O_2 consumed above 1.76 mg L^{-1}, the expected amount of acetaldehyde: 0.91 uMol per uMol of O_2 consumed by polyphenols (the one given in Table 2 minus 1.76 mg L^{-1}). The comparison between the acetaldehyde measured in the models to that expected is given as ratio in the last column of the Table 2. The smaller the percentage, the higher the unfulfillment of the hypotheses.

As can be seen in the table, the highest value of such a ratio is found for synthetic wine, for which accumulated acetaldehyde is 99 % of that expected. Note that this model did not contained polyphenols and, as it was assumed that cation metals and sulfhydryls oxidize O_2 to H_2O, this implies that the 2.5 mg L^{-1} of O_2 in excess were essentially devoted to oxidize ethanol (and glycerol and tartaric acid) following a Fenton scheme. A very similar ratio is found for catechin: 97 %. I.e., catechin oxidizes mostly in accordance with the previous hypotheses: it oxidizes to its quinone, forming an equimolar amount of H_2O_2. However, the quinone of catechin hardly interacts with H_2O_2 or with the 1-HER radical, so that all H_2O_2 formed ends oxidizing ethanol (and any other alcohol present in the corresponding proportion). As discussed in the previous section, the quinone reacts to unreacted catechin to form dimers or higher order oligomers which also do not interact with H_2O_2 or 1-HER radical. Quercetin and caffeic acid had lower ratios, but not significantly different to those of the synthetic wine or to the one containing catechin, implying that for the three dihydroxylated polyphenols assayed in this study, the radical mediated oxidation is the dominant outcome.

Things are completely different, however, for malvidin-3G, epigallocatechin and delphinidin-3G, for which the accumulated acetaldehyde was only 18 % to 25 % of what was expected, implying that for these compounds the Fenton oxidation is a minor outcome. This suggests that these compounds oxidize initially to a highly reactive compound (not a quinone, in the case of malvidin-3G) which further interacts with H_2O_2 or with the 1-HER radical, avoiding the oxidation of ethanol. Coumaric acid, whose ability to quench the 1-HER radical has been specifically demonstrated (Gislason et al., 2011; Kreitman et al., 2014) and myricetin, only form 43 % and 52 % of the expected acetaldehyde, respectively, significantly below the control. I.e., the mono- and trihydroxylated polyphenols considered in this study partly avoid Fenton oxidation in wine.

It could be argued that the low accumulation of acetaldehyde is the consequence not of a lack of formation, but of the fact that it is known that flavanols and anthocyanins are reactive to acetaldehyde (Bakker & Timberlake, 1997; Marquez, Duenas, Serratosa, & Merida, 2012; Nave, Teixeira, Mateus, & de Freitas, 2010). This, in fact, was our main hypothesis when we first observed that acetaldehyde accumulation was negatively related to the presence of anthocyanins (Bueno et al., 2018), introducing the concept of “aldehyde reactive polyphenols” or ARPs (Carrascón et al., 2018). However, this hypothesis was later rejected since aldehyde consumption kinetics in wine are a) extremely low, and b) poorly related to wine polyphenolic composition (Marrufo-Curtido

et al., 2022a, 2022b). Results for Strecker aldehydes, whose accumulation are maxima for malvidine-3G, as will be shown in the next section, also do not support the ARPs hypothesis.

3.4. Effects of individual polyphenols on the accumulation of Strecker aldehydes

The total quantity of Strecker aldehydes assessed in the model wines after oxidation can be seen in Table 3, which shows that the accumulated quantities of aldehydes differed significantly and remarkably from one another, in function of the individual polyphenol present in the different models. As expected, minimal amounts were found in synthetic wine not containing polyphenols, while maxima levels were found in the model containing malvidin-3-glucoside followed by those of epigallocatechin and myricetin. Among polyphenols, minimal amounts were registered in the models with coumaric acid and delphinidin 3-glucoside.

The presence of residual amounts of Strecker aldehydes in the model not containing polyphenols is not surprising. Little amounts could be formed directly by radicals, as described for beer or synthetic wines (Monforte et al., 2020; Wietstock & Methner, 2013), but in addition, our model wine contains tartaric acid and glycerol, which, attending to the reactive characteristics of the radical OH* will have been oxidized. Both of them, can easily form α-dicarbonyls potentially able to trigger the Strecker degradation of amino acids to form aldehydes. In particular, tartaric acid can produce a series of α-dicarbonyls, including dioxosuccinic acid, oxalic acid, glyoxylic acid, and even glyoxal (Elias & Waterhouse, 2010; Es-Safi, Le Guerneve, Fulcrand, Cheynier, & Moutounet, 1999; Fenton, 1905).

Given the considerable differences between the various models in terms of consumed quantities of oxygen (Table 2), the production of SA was normalized by the O_2 consumed (excluding the 1.76 mg L^{-1} consumed by cations and sulfhydryls). Those results are shown in Fig. 3 and clearly show that models can be broadly classified into three categories attending to their ability to induce the Strecker degradation of amino acids when consuming oxygen:

1. Low: minimum SA production was observed in the models containing delphinidin 3-glucoside, for which only 0.1 % of the oxygen consumed ended producing SAs (3.5 μg L^{-1} per mg L^{-1} of oxygen consumed), followed by coumaric acid and the SW which used 0.2 % (less than 7 μg L^{-1} of per mg L^{-1} of oxygen consumed).
2. Medium: catechin, epigallocatechin and myricetin used around 0.4 % of O_2 to form SAs (between 11 and 14 μg L^{-1} of aldehyde by mg L^{-1} of oxygen consumed).
3. High: caffeic acid, malvidin-3G and quercetin, used 0.54 to 0.63 % of the O_2 consumed to form SAs (between 17 and 21 μg L^{-1} of aldehyde per mg L^{-1} of oxygen consumed).

Interestingly, in this case, chemical class or the degree of hydroxylation in the B-ring do not seem to have much influence. Rather, the ability to induce the Strecker degradation of amino acids should be linked to the relative stabilities of the a-dicarbonyls formed by the oxidation of the polyphenol and driving the Strecker degradation. In the case of delfinidin-3-glucoside, such dicarbonyl, namely the quinone in the B-ring, is just a transitory state which quickly reduces by taking electrons from the cleavage of the C ring (Dangles & Fenger, 2018; Es-Safi et al., 2008; Fenger, Robbins, Collins, & Dangles, 2020; Kamiya, Yanase, & Nakatsuka, 2014; Zhang, Li, Fan, & Duan, 2020) and will be, therefore, not available for reaction with the amino acids. On the contrary, malvidin-3-glucoside cannot form a quinone, but oxidizes forming a quite stable intermediary radical with α-dicarbonyl structure, as recently reported (Cruz et al., 2022). Such radical, even if formed for delphinidin-3G, would be far more unstable due to the higher degree of hydroxylation in B. Similar conclusions would be reached attending to the relative stabilities of the chalcone radicals, reportedly more unstable for delphinidin (Chorfa, Savard, & Belkacemi, 2018; Serifi et al., 2012). The low production of SA by coumaric acid should be attributed to the fact that this phenol cannot form a quinone with the capacity of triggering the Strecker degradation. In addition to malvidin-3G, also quercetin and caffeic acid, have a significantly higher ability to induce the Strecker degradation. Both of them are o-dihydroxypolyphenols able to form relatively stable o-quinones. On the contrary, epigallocatechin and myricetin, whose quinones are more reactive, form significantly smaller levels of SAs. The relatively low tendency of catechin, particularly in comparison to quercetin, to form SAs has not an obvious explanation.

In any case, and considering the quantitative prominence in red wines of anthocyanins, these results further explain the fact that Garnacha wines accumulate higher levels of SAs during their oxidation than wines from Tempranillo (Bueno-Aventin et al., 2021), since Garnacha have a higher malvidine 3-glucoside/delphinidin-3-glucoside ratio than Tempranillo (Arozarena et al., 2002).

Table 3
Accumulation of Strecker aldehydes (μg L^{-1}) in the oxidation of wine models containing containing metal cations, wine mercaptans, amino acids and one specific polyphenol (plus the control).

	Isobutanal			2-methybutanal			3-mehyilbutanal			Methional			Phenylacetaldehyde			Total Strecker aldehydes		
Coumaric	1.87	±	0.36 ^{E}	4.85	±	0.50 ^{DE}	5.33	±	0.38 ^{DE}	17.37	±	0.56 ^{E}	13.02	±	0.21 ^{F}	42.44	±	0.87 ^{F}
Caffeic	5.86	±	0.50 ^{C}	8.43	±	0.47 ^{DE}	16.20	±	2.41 ^{C}	40.40	±	4.12 ^{D}	31.09	±	3.30 ^{E}	101.98	±	10.80 ^{D}
Catechin	4.27	±	0.28 ^{D}	9.43	±	3.58 ^{CD}	10.64	±	0.56 ^{CDE}	34.19	±	0.36 ^{D}	32.06	±	0.31 ^{DE}	90.58	±	5.09 ^{D}
Epigallocatechin	16.09	±	1.80 ^{A}	22.34	±	2.34 ^{B}	33.61	±	2.28 ^{B}	81.06	±	5.71 ^{B}	66.50	±	3.42 ^{B}	219.6	±	15.55 ^{B}
Malvidin 3-glucoside	17.6	±	0.34 ^{A}	26.09	±	7.19 ^{A}	52.33	±	8.75 ^{A}	108.4	±	12.38 ^{A}	110.89	±	2.53 ^{A}	317.1	±	0.68 ^{A}
Delphinidin 3-glucoside	3.89	±	0.53 ^{D}	9.63	±	0.99 ^{CD}	9.18	±	1.25 ^{CDE}	22.19	±	3.65 ^{E}	17.05	±	3.24 ^{F}	61.94	±	9.66 ^{E}
Quercetin	3.79	±	0.35 ^{D}	9.32	±	2.29 ^{CD}	10.90	±	0.34 ^{CD}	34.57	±	2.47 ^{D}	37.96	±	2.59 ^{D}	96.54	±	2.78 ^{D}
Myricetin	9.16	±	0.58 ^{B}	15.48	±	1.05 ^{C}	28.26	±	0.72 ^{B}	65.73	±	1.70 ^{C}	55.77	±	5.08 ^{C}	174.41	±	9.13 ^{C}
Synthetic wine	0.86	±	0.11 ^{E}	2.17	±	0.30 ^{E}	3.69	±	0.28 ^{E}	5.41	±	0.49 ^{F}	2.93	±	0.72 ^{G}	15.06	±	1.89 ^{G}

Different letters in columns indicate significant differences between samples (Malvidin 3-glucoside excluded) according to sample factor ANOVA (Fischer posthoc test. $p < 0.05$). Monohydroxylated polyphenols are underlined, dihydroxylated in italics and trihydroxylated in bold letters.

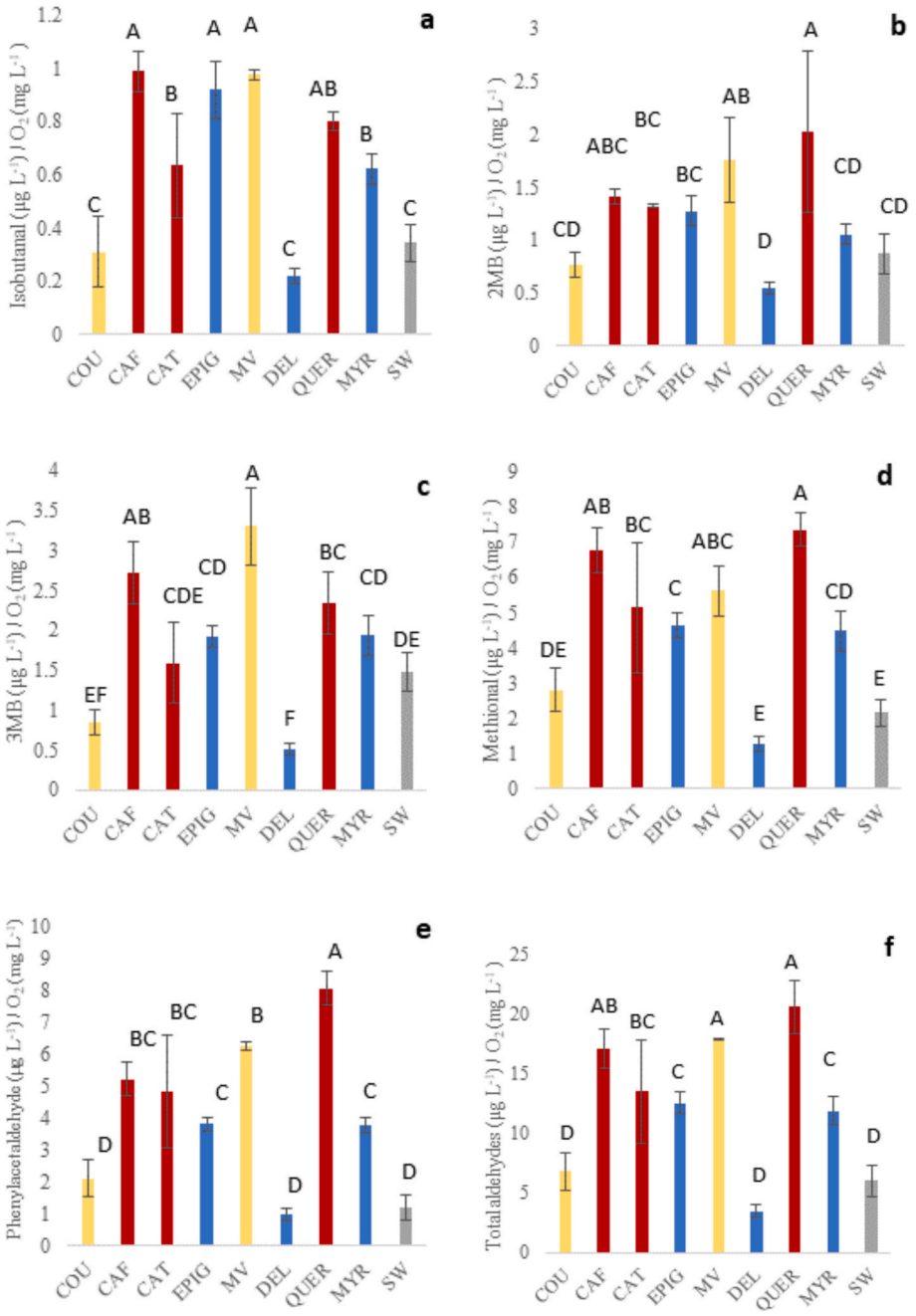


Fig. 3. Oxygen-normalized accumulation rates of Strecker aldehydes (µg L^{-1} of aldehyde per mg L^{-1} of consumed O_2 - excluding the 1.76 mg L^{-1} consumed by cations and sulfhydryls-) of wine models containing metal cations, wine mercaptans and one specific polyphenol (plus the control). a) Isobutanal, b) 2-methylbutanal, c) 3-methylbutanal, d) methional, e) phenylacetaldehyde and f) total Strecker aldehydes. Different letters indicate significant differences (fischer posthoc test. $p < 0.05$). SW: synthetic wine. CAF: caffeic acid. COU: coumaric acid. QUER: quercetin. MYR: myricetin. CAT: catechin. EPIG: epigallocatechin. DELF: delphinidin 3-glucoside. MV: malvidin 3-glucoside.

4. Conclusions

This study has confirmed the importance of the polyphenolic profile on the fate of wine during oxidation, and has revealed the existence of relevant differences between individual polyphenols regarding both, the rate at which wines consume oxygen and the different sensory and chemical consequences of such consumption.

Delphinidin-3-glucoside arises as the most effective antioxidant, representing the ideal "sacrificial" behavior. It consumes quickly quantitative amounts of oxygen (1:1 stoichiometry), prevents the oxidation of ethanol and avoids the formation of SAs. It is followed in effectivity by malvidin-3-glucoside, which however, forms high levels of SAs.

The two B-ring trihydroxylated polyphenols, the flavanol epigallocatechin and the flavonol myricetin, were less effective at O_2 consumption, were degraded during oxidation (>1.4:1 apparent stoichiometry), prevented effectively the oxidation of ethanol, particularly epigallocatechin, and showed a moderate tendency to form SAs.

Coumaric acid emerges as quite distinctive antioxidant, since it hardly consumed oxygen but it was able to moderately avoid the oxidation of ethanol and the accumulation of SAs.

Dihydroxylated polyphenols consume oxygen slowly, cannot prevent the oxidation of ethanol, and form moderate (catechin) to high (quercetin, caffeic acid) levels of SAs. In addition, both catechin and quercetin

are strongly degraded during oxidation (4:1 apparent stoichiometry).

This study focused on the potential of wine polyphenols to prevent oxidative deterioration of wine aroma could help improve the quality and stability of wines.

CRediT authorship contribution statement

Ana Escudero: Writing – review & editing, Supervision, Formal analysis, Data curation, Conceptualization. **Elena Bueno-Aventín:** Writing – original draft, Methodology, Formal analysis, Data curation. **Ignacio Ontañón:** Software, Methodology, Formal analysis, Conceptualization. **Purificación Fernádez-Zurbano:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **Vicente Ferreira:** Writing – review & editing, Visualization, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was funded by the Spanish Ministry of Economy and Competitiveness (MINECO) (projects AGL2017-87373-C3 and PID2021-126031OB-C21/C22) and was partly co-funded by the European Union (FEDER). EB has received funding from the Spanish Government grant no FPU2017/03410. LAAE acknowledges the continuous support of Diputación General de Aragón (T53) and the European Social Fund.

Authors would like to acknowledge the use of Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza and are grateful to Dr. Victor de Freitas for the scientific discussion on anthocyanins oxidation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2024.142242.

Data availability

No data was used for the research described in the article.

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