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# Air Depleted and Solvent Impregnated Cork Powder as a New Natural and Sustainable Wine Fining Agent

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## Abstract

We recently proposed a simple methodology to improve cork powder waste adsorption properties through vacuum degassing and solvent impregnation, to use this abundant and cheap material as a new wine fining agent. Its applicability was first shown for red wine 4-ethylphenol (4-EP) and 4-ethylguaiaicol (4-EG) reduction. Nowadays, the presence of 4-EP and 4-EG is a serious problem in the wine industry, known as “Brett character”, by the negative aroma imparted by these volatile phenols (VPs) to red wine. There are only some curative treatments to remove these compounds without impacting negatively on wine quality. Optimised cork powder was used successfully as a new treatment for the reduction of these negative VPs (41–75% for 4-EP and 40–69% for 4-EG) increasing at the same time wine sensory performance. Wine treated with cork powder reduced 6.9% phenolic acids and catechin and 2.3% monomeric anthocyanins without any significant change in colour intensity. In this chapter, the cork complex structure is discussed, besides the impact of its use in wine containing VPs on physicochemical composition and quality. This new application of this natural, abundant and cheap material has the potential of being a new wine fining agent with low environmental impact.

**Keywords:** cork composition, adsorption properties, red wine, volatile phenols, aroma, phenolic compounds, sensory attributes

## 1. Introduction

Cork, the outside part of the oak (*Quercus suber* L.), is a natural, renewable, sustainable raw material, which is periodically harvested from the tree, usually every 9–12 years, depending on the cultivation region [1]. *Quercus suber* L. is a tree that grows slowly in some regions of the western Mediterranean (Portugal, Spain, Southern France, part of Italy and North Africa) and China [2–4]. Portugal is the main cork producer, transforming about 75% of all the cork [3, 4]. Industrial transformation of cork generates up to 25 wt.% of cork dusts as by-product [5, 6].

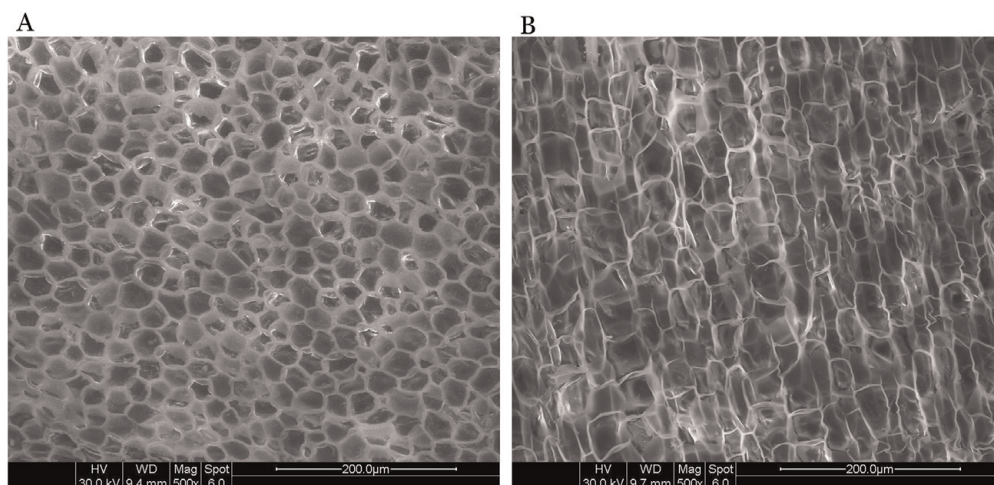
Cork wastes and cork powders have been used as bioadsorbents for removing pesticides and other pollutants from wastewaters with promising results [7].

Biosorption is an emergent technology expected to show strong growth soon because it offers high cost effectiveness, although further improvements in its performance are needed [1]. Environmental protection legislation is becoming progressively important and effective solutions will be at premium [8].

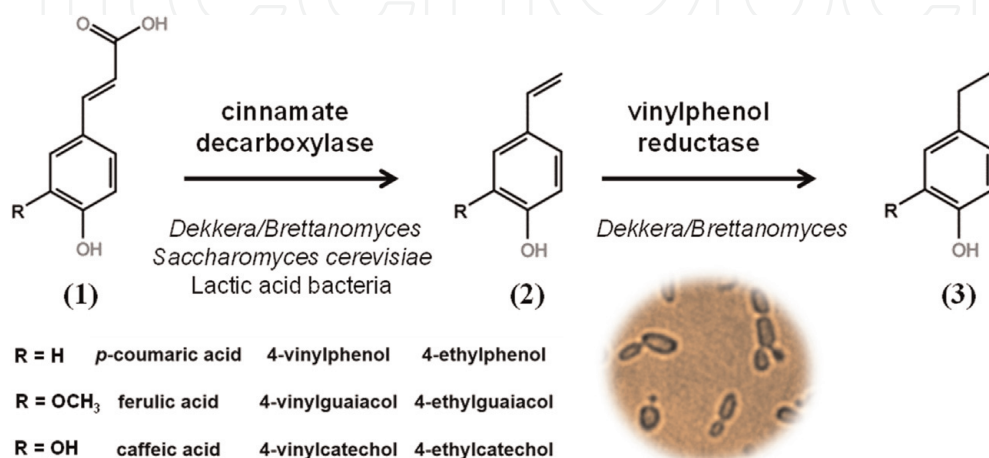
The cork material is compact, devoid of intercellular spaces and with a regular honeycomb organisation (**Figure 1**). This material is composed by dead parenchymatous cells with voids, prismatic, air-filled interiors, hexagonal on average and are arranged base-to-base in an alignment oriented in the tree's radial direction [9].

The cells are small and have sizes under those of synthetic foams. The area of the prism base is  $4-6 \times 10^{-6} \text{ cm}^2$  with a mean prism edge of 13–15  $\mu\text{m}$ ; prim height is usually in the range of 30–40  $\mu\text{m}$ . The mean cell volume is approximately  $2 \times 10^{-8} \text{ cm}^3$  and the number of cells per unit is  $4-7 \times 10^7 \text{ cm}^{-3}$ . The cell walls are thin with a thickness of 1–1.5  $\mu\text{m}$ . The solid mass volume fraction of the cork is only about 10%.

Cork powder maintains the cork cellular structure intact [10], and its adsorption properties can be improved by removing the air and simultaneous impregnation with ethanol rendering the cell wall components more accessible to the adsorbates [10]. This simple treatment was shown to increase cork powder adsorption capacity of 4-EP and 4-EG by at least 4 times in a real wine matrix, with the cork powder



**Figure 1.** Structure of cork as observed by SEM in the two main sections: (A) tangential section, perpendicular to the tree's radial direction; (B) transverse section, perpendicular to the tree's axial direction.



**Figure 2.** Formation of volatile phenols from hydroxycinnamate precursors or their degradation products (vinylphenols) in wines by *Dekkera/Brettanomyces*.

adsorption capacity increasing with the increase in concentration of these wine contaminants [10].

In red winemaking, especially those aged in wood barrels, the contamination and growth of *Dekkera/Brettanomyces* yeasts result in the formation of 4-EP and 4-EG by decarboxylation of *p*-coumaric and ferulic acids present in wine and subsequent reduction of the correspondent vinylphenols (**Figure 2**) [11, 12].

These VPs are responsible for negative aromatic notes like horsy sweat, smoky, barnyard and medicinal [11, 13]. This important sensory defect has been reported in several wine styles around the world, especially, premium wines [14, 15], considered negative by professionals, consumers and wine industry [16, 17], and thus, VPs are a generalised problem in red winemaking.

For these reasons, several treatments to avoid or to reduce compounds have been tested. Preventive action includes, for example, the maintenance of adequate levels of sulphur dioxide throughout the winemaking process, reduction/elimination of oxygen levels in wine, use of dimethyl dicarbonate (DMDC) before bottling and the addition of fungal chitosan, which are some of the measures that have found some degree of success [18, 19]. Several remediation treatments have also been developed to eliminate the already formed VPs from wine or to decrease the headspace content by decreasing their partition coefficients to the gas phase without changing the total wine VP content. Of these methods, those tested in wines presenting good removal efficiency at practical application doses are activated carbons [20, 21], potassium caseinate [22], egg albumin [22] and esterified cellulose [23]. Nevertheless, although they are efficient in reducing the total amount of VPs in wines, the use of potassium caseinate and egg albumin presented the risk of the potential allergenicity of these fining agents and therefore it is mandatory to label the wine bottle if the residual concentration is higher than 0.25 mg/L (EU Regulation 579/2012). For the decrease of headspace abundance of VPs chitosans has been shown to be effective [24].

The success of cork powder in adsorption of VPs from such a complex matrix as wine without affecting the wine quality significantly in terms of phenolic composition is certainly due to the structure and chemical composition of its main components namely suberin, lignin and cell wall polysaccharides.

## 2. Cork chemical composition

The chemical composition of cork has been widely examined [25–33] and presented some variability that depends on factors such as geographic origin, soil

Principal components (%)	Range	Average
Suberin	40–53	45.8
Lignin	21–29	24.4
Polysaccharides	10–16	12.5
Extractives	6–19	12.6
Tannins	6–7	6.5
Ash	0.85–2.1	1.4

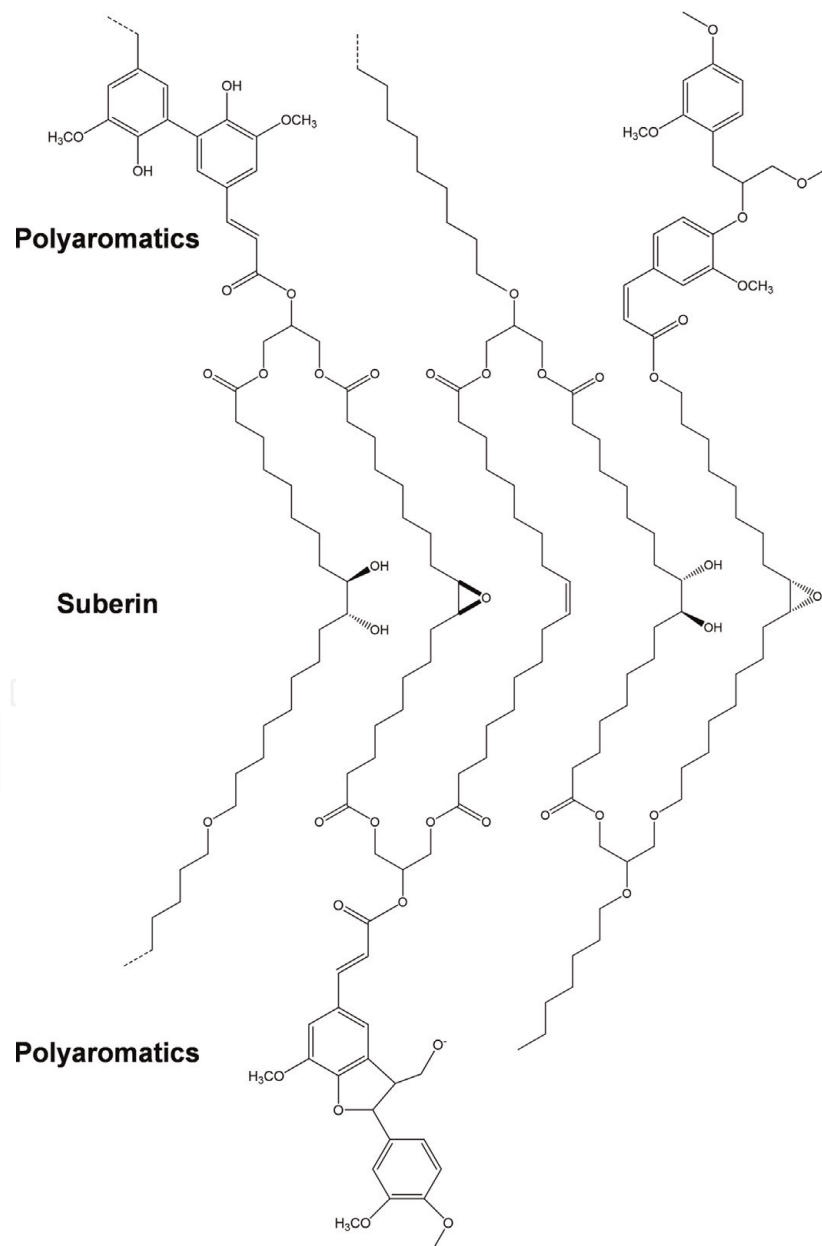
*Adapted from [1, 25, 34–36].*

**Table 1.**  
*Chemical composition of cork.*

and climate conditions, genetic origin, tree dimensions, age and growth conditions (**Table 1**). Cork from *Quercus suber L.* has specific properties such as low permeability and great elasticity; this is the result, at least partially, from its specific chemical composition (and more especially from that of suberin) [26, 29, 31–33]. The cork cell wall structure consists in a thin internal primary cork cell wall rich in lignin and a thick secondary wall rich in suberin, alternating with a wax lamella and a thin tertiary wall of polysaccharides.

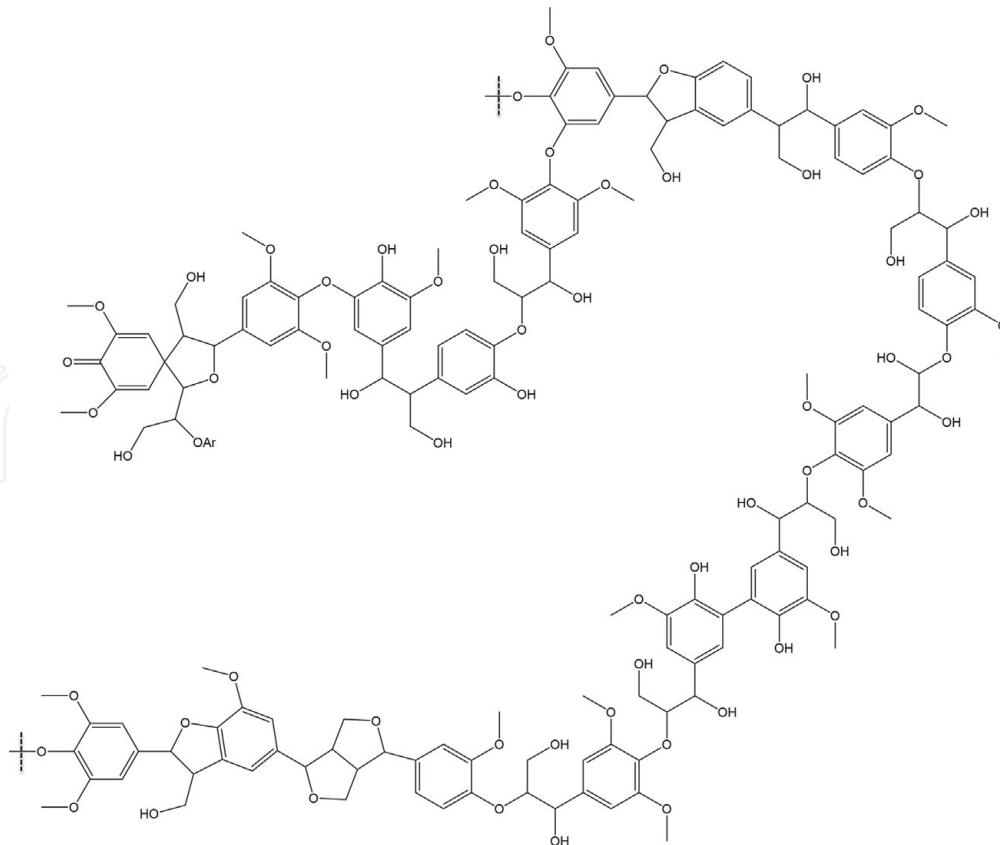
## 2.1 Suberin

Suberin, a natural aliphatic-aromatic crosslinked polyester, is the major component of cork, accounting for 30–50% of its weight. It is a very important structural component of the cell wall and its removal destroys cell integrity. Suberin polymeric structure is mainly composed by two types of monomers, glycerol and long-chain fatty acids and alcohols, which are linked by ester bonds, **Figure 3** [9].



**Figure 3.** Schematic representation of suberin structure (adapted from Graça [37]).





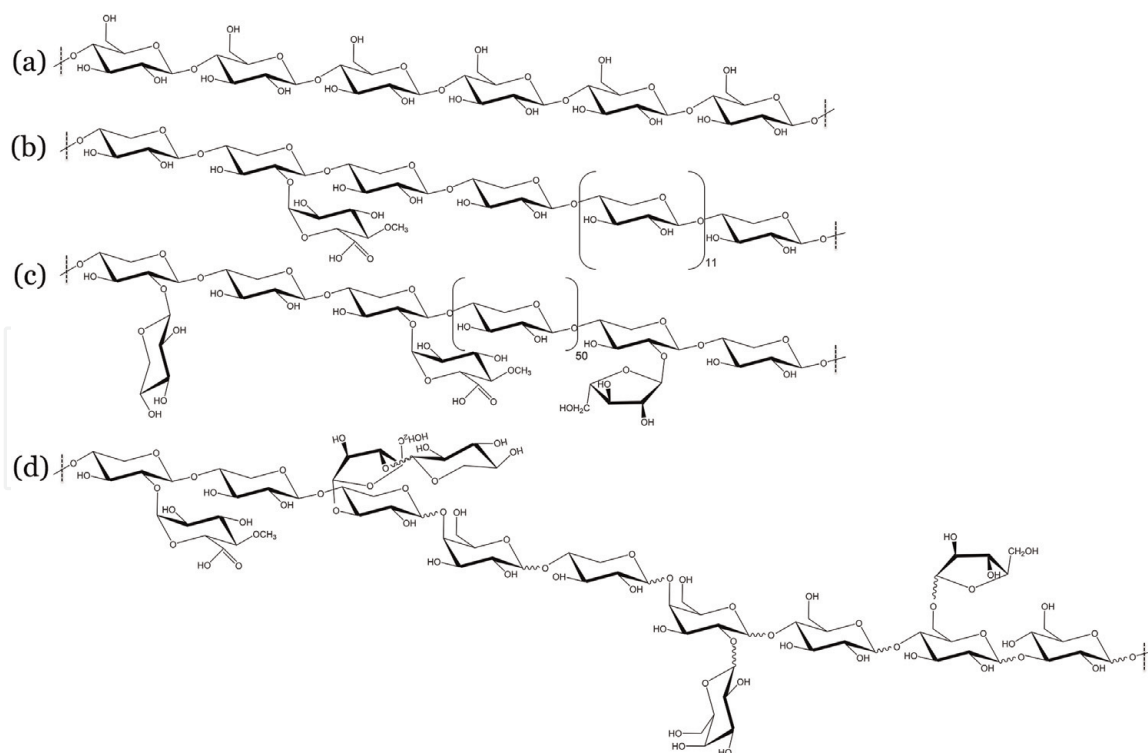
**Figure 4.**  
Schematic representation of lignin structure (adapted from Achyuthan et al. [39]).

## 2.2 Lignin

Lignin is the second most important component in cork cell walls accounting for 15–30% of its weight [9]. It is a crosslinked polymer of aromatic nature. Due to the importance of lignin, many studies were done in wood pulping and more recently, for biomass deconstruction [38]. Lignin is a polymer made up by three monomer types of phenyl propane (*p*-coumaryl, coniferyl and sinapyl alcohols) linked through a free-radical reaction started via enzymatic phenoxy radical formation (Figure 4). The inter-unit linkages in the polymer can be of several kinds:  $\beta$ -O-4',  $\alpha$ -O-4',  $\beta$ - $\beta'$ ,  $\beta$ -5', 5-5', 4-O-5' or  $\beta$ -1'. The specific relation of the monomers and intermonomeric linkages depend on the material [9]. In cork, lignin also contributes to the mechanical support and rigidity of the cell walls. If lignin is selectively removed from cell walls, a total collapse of the cells is observed.

## 2.3 Polysaccharides

In cork, the cell wall polysaccharides, cellulose and hemicelluloses, represent approximately 20% of its weight. Cellulose is in the primary and tertiary cell walls of cork, accounting for nearly 10% [40]. There is less information concerning the molecular weight, crystallinity and chain orientation of cork cellulose. Cellulose is water insoluble due to an extensive intermolecular hydrogen bonding between adjacent polymers, and interaction with water often only occurs in the amorphous regions. The hemicelluloses are another water insoluble group of polysaccharides present in cork cell walls. The main known hemicellulose polysaccharides comprise three different groups of polysaccharides (Figure 5), the 4-O-methylglucuronoxylan, arabino-4-O-methylglucuronoxylan and 4-O-methylglucuron-arabinogalactoglucoxytan [41–44]. Xylans in the cell walls are amorphous and the



**Figure 5.** Schematic structures of main cork cell wall polysaccharides: (a) cellulose, (b) 4-O-methylglucuronoxylan, (c) arabino-4-O-methylglucuronoxylan and (d) 4-O-methylglucurono-arabinogalactoxyln.

irregular occurrence of branching of the main chain does not permit strong intermolecular association by hydrogen bonding; nevertheless, they are extracted using strong alkaline solutions (4–10% w/v NaOH). Pectins also exist in low quantities in cork, approximately 1.5%, placed in the middle lamella [45].

## 2.4 Extractable components

Cork contains 8–20% of low molecular weight compounds including fatty acids, terpenes, long-chain aliphatic compounds and saccharides, collectively known as extractives [34, 46]. Cork contains also about 6% of tannins [36]. The most important of these components are waxes and tannins [31]. Waxes are extracted by low polarity solvents, such as benzene, chloroform, ethyl acetate [47], hexane [36] and ether [26]. The waxes are responsible for the cork impermeability. The waxes extracted were found to consist of two fractions: neutral and acidic. The neutral fraction is mostly composed of fatty alcohols ( $C_{18}$ – $C_{26}$ ) with some unsaturated groups and triterpenes.

The acid fraction is essentially composed of fatty acids ( $C_{14}$ – $C_{24}$ ) with unsaturated  $\omega$ -hydroxyacids, 18-hydroxy-9,12-octadienoic and 18-hydroxy-9-octadecenoic acids. More or less 50% of the waxes are triterpenes from friedelin and lupine families including friedelin, 3- $\alpha$ -hydroxyfriedelan-2-one, botulin, betulinic acid,  $\beta$ -sitosterol and sitost-4-en-3-one [48]. Cork extractable phenolic compounds include ellagic acid and some quantities of gallic acid, protocatechuic acid/aldehyde, aesculetin, vanillic acid, caffeic acid, vanillin, scopoletin, ferulic acid, coniferyl aldehyde and sinapaldehyde [49, 50]. The extraction of tannins can be done by polar solvents such as water [51] and ethanol [52]. Cork tannins include roburins A and E, grandini, vescalagin and castalagin. The yields of these two components change in function of the nature of the cork (virgin or reproduction) where significant variation is found in the bibliography [1].

### 3. Optimised cork powder (CKP) as a wine fining agent to remove negative volatile phenols in contaminated red wine

The air removal of the cork powder cell structure and simultaneous impregnation with ethanol with or without previous removal of cork extractives increased significantly the 4-ethylphenol and 4-ethylguaiacol adsorption performance (Table 2).

Although a significant removal of wine VPs was observed, the overall quality of the treated wine cannot be accessed only by the decrease in these negative aroma compounds, as the impact on the other wine positive aroma components is important to define the final overall sensory olfactory quality [15, 20, 21, 22, 24]. The red wine colour characteristics are important for consumer acceptance of the treated wine, because there is straight relation between the colour and the wine's phenolic composition, namely anthocyanins, whose concentration can be changed by the fining procedure.

In order to have a deeper insight on the impact of optimised cork powder in the wine chemical composition besides the removal efficiency of the VPs, the change in the headspace aroma abundance of wine, phenolic composition and chromatic characteristics were studied and the overall impact on the wine sensory characteristics was evaluated by an expert panel.

#### 3.1 Impact of optimised cork powder on the wine aroma headspace abundance

Air removal and ethanol impregnation of cork samples with and without extractive removal decreased the total headspace aroma abundance (CKNI 32% and CKFI 37%) significantly. The decrease in the particle size of the CKF did not differ significantly on the removal of headspace aroma compounds, although there was an average decrease of 3.7% in relation to CKF (Table 3). The duplication in application dose of CKFI75 resulted in a significant decrease of the total abundance of headspace aroma by more 29% (Table 3). There was a significant correlation ( $r = 0.731$ ,  $n = 14$ ,  $p < 0.003$ ) between the headspace aroma abundance and the octanol-water partition coefficient ( $\log P$ ) of the aroma compounds, strongly

Factors		Wine spiked levels			
		Medium		High	
A	B	4-EP	4-EG	4-EP	4-EG
No impregnation	CKN	85.3 ± 2.7 <sup>a</sup>	9.2 ± 0.2 <sup>a</sup>	109.6 ± 5.1 <sup>a</sup>	10.5 ± 0.6 <sup>a</sup>
	CKF	168.8 ± 4.2 <sup>b</sup>	19.2 ± 2.7 <sup>b</sup>	738 ± 36.9 <sup>b</sup>	71.5 ± 5.4 <sup>b</sup>
Vacuum impregnation	CKNI	270.9 ± 11.8 <sup>c</sup>	43.4 ± 2.1 <sup>c</sup>	888.0 ± 16.3 <sup>c</sup>	133.8 ± 2.0 <sup>c</sup>
	CKFI	306.0 ± 2.3 <sup>d</sup>	60.5 ± 1.6 <sup>d</sup>	1036.5 ± 18.1 <sup>d</sup>	149.1 ± 3.3 <sup>d</sup>
A		0.0000001	0.000011	0.0000001	0.0000001
B		0.0000001	0.0000001	0.0000001	0.0000001
A × B		0.0029	0.083033	0.0000001	0.000018

<sup>a</sup>Values are presented as mean ± standard deviation; medium spiking levels: 750 µg/L 4-EP and 150 µg/L 4-EG; high 1500 µg/L 4-EP and 300 µg/L 4-EG. Means within a column followed by the same letter are not significantly different ANOVA and Tukey post-hoc test ( $p < 0.05$ ).

**Table 2.**

Amount of 4-EP and 4-EG (µg/L) removed from wines at two spiked levels<sup>a</sup> of natural cork powder (CKN) and dichloromethane and ethanol extractive free cork powder (CKF) before and after air removal and impregnation with ethanol (CKNI and CKFI) [10].



Compounds	ID	RI calculated	RI	Odour descriptor	ODT (mg/L)	T0	TF	CKNI	CKFI	CKFI75250	CKFI75500
Ethyl acetate	—	725	715	Fruity	7.5	23.97 ± 1.67 <sup>a</sup>	23.29 ± 2.97 <sup>a</sup>	14.32 ± 0.88 <sup>b</sup>	14.13 ± 0.42 <sup>b</sup>	14.70 ± 1.84 <sup>b</sup>	8.53 ± 1.49 <sup>c</sup>
3-Methylbutan-1-ol-acetate	std	1121	1126	Banana	0.03	65.09 ± 15.64 <sup>a</sup>	67.59 ± 19.86 <sup>a</sup>	44.36 ± 3.22 <sup>a</sup>	39.81 ± 4.81 <sup>ab</sup>	35.30 ± 3.50 <sup>ab</sup>	16.93 ± 3.95 <sup>b</sup>
2-Methyl-1-butanol	std	1229	1223	Malty	0.48	112.02 ± 8.60 <sup>a</sup>	109.52 ± 8.6 <sup>a</sup>	77.47 ± 2.20 <sup>c</sup>	71.24 ± 3.46 <sup>c</sup>	76.13 ± 5.49 <sup>c</sup>	50.10 ± 8.03 <sup>d</sup>
Ethyl hexanoate	std	1229	1262	Green apple	0.014	27.62 ± 16.17 <sup>a</sup>	27.87 ± 15.68 <sup>a</sup>	25.65 ± 0.67 <sup>ab</sup>	22.45 ± 1.30 <sup>ab</sup>	20.69 ± 4.13 <sup>b</sup>	12.92 ± 2.43 <sup>b</sup>
Ethyl octanoate	std	1441	1429	Fruity	0.005	164.67 ± 19.71 <sup>a</sup>	167.17 ± 10.85 <sup>a</sup>	104.94 ± 6.78 <sup>b</sup>	90.56 ± 12.53 <sup>b</sup>	75.94 ± 27.94 <sup>b</sup>	43.14 ± 1.49 <sup>c</sup>
Ethyl decanoate	std	1648	1646	Fruity	1.5	78.55 ± 3.63 <sup>a</sup>	78.95 ± 5.89 <sup>a</sup>	67.12 ± 6.21 <sup>ab</sup>	53.94 ± 7.51 <sup>b</sup>	36.93 ± 23.29 <sup>c</sup>	19.61 ± 2.20 <sup>c</sup>
Diethyl succinate	std	1683	1698	Light fruity	7.5	66.90 ± 1.14 <sup>a</sup>	64.40 ± 3.94 <sup>a</sup>	41.95 ± 1.74 <sup>cd</sup>	41.22 ± 1.81 <sup>d</sup>	39.72 ± 3.78 <sup>d</sup>	23.56 ± 5.20 <sup>e</sup>
Phenylethyl acetate	std	1809	1833	Flowery	0.25	31.16 ± 4.66 <sup>a</sup>	30.16 ± 3.51 <sup>a</sup>	22.82 ± 0.89 <sup>b</sup>	20.54 ± 1.13 <sup>b</sup>	14.80 ± 6.94 <sup>c</sup>	8.49 ± 2.96 <sup>c</sup>
2-Phenylethanol	std	2000	1911	Roses	14.0	365.23 ± 19.85 <sup>a</sup>	362.73 ± 31.57 <sup>a</sup>	247.32 ± 7.78 <sup>b</sup>	240.73 ± 15.31 <sup>a</sup>	216.92 ± 39.38 <sup>b</sup>	136.16 ± 60.27 <sup>c</sup>
4-Ethylguaiacol	std	2012	1989	Smoke	0.15	n.d.	16.62 ± 0.89 <sup>a</sup>	9.21 ± 0.41 <sup>c</sup>	9.05 ± 0.68 <sup>c</sup>	8.00 ± 2.25 <sup>c</sup>	3.70 ± 1.07 <sup>d</sup>
<b>Reduction SPME (%)</b>								<b>44.6</b>	<b>45.6</b>	<b>50.6</b>	<b>77.8</b>
Octanoic acid	std	2036	2030	Rancid	0.5	17.87 ± 0.57 <sup>a</sup>	17.62 ± 0.73 <sup>a</sup>	6.00 ± 3.79 <sup>cd</sup>	8.98 ± 0.97 <sup>bc</sup>	7.19 ± 1.32 <sup>cd</sup>	2.30 ± 1.20 <sup>d</sup>
4-Ethylphenol	std	2084	2142	Phenolic	0.4	n.d.	18.25 ± 1.23 <sup>a</sup>	10.37 ± 0.31 <sup>c</sup>	9.83 ± 0.89 <sup>c</sup>	7.94 ± 2.19 <sup>c</sup>	3.37 ± 1.35 <sup>d</sup>
<b>Reduction SPME (%)</b>								<b>43.1</b>	<b>46.1</b>	<b>56.5</b>	<b>81.5</b>
Decanoic	std	2129	2196	Rancid	1.0	4.14 ± 0.45 <sup>a</sup>	4.19 ± 0.43 <sup>a</sup>	1.49 ± 0.17 <sup>ab</sup>	2.53 ± 2.76 <sup>ab</sup>	1.24 ± 0.62 <sup>ab</sup>	n.d
Dodecanoic	std	2136	2156	Waxy	6.1	5.48 ± 0.36 <sup>a</sup>	5.23 ± 0.59 <sup>a</sup>	0.93 ± 0.15 <sup>c</sup>	0.90 ± 0.41 <sup>c</sup>	0.90 ± 0.13 <sup>c</sup>	n.d
<b>Total area-VPs</b>						<b>962.7 ± 28.0<sup>a</sup></b>	<b>958.7 ± 46.7<sup>a</sup></b>	<b>652.9 ± 10.1<sup>cd</sup></b>	<b>607.0 ± 32.1<sup>d</sup></b>	<b>571.1 ± 68.3<sup>d</sup></b>	<b>296.7 ± 71.1<sup>e</sup></b>
<b>Reduction (%)</b>						—	—	<b>31.9</b>	<b>36.7</b>	<b>40.4</b>	<b>69.1</b>

Results are expressed in absolute area ( $\times 10^5$ ). Data are presented as  $\bar{X} \pm s$ ; ID, identification; std, standard; and RI, retention index [60–62], MW, molecular weight; LOD, limit of olfactory detection). Odour descriptor [63–65]. Values within a line followed by the same letter are not significantly different ANOVA and Tukey post-hoc test ( $p < 0.05$ ). n.d., not detected; uncontaminated (T0) spiked red wine (TF) and wines treated with corks.  
 $p < 0.05$ .

**Table 3.**

Headspace aroma profile of red wines before (VP-free T0 and VP-spiked with 750  $\mu\text{g/L}$  of 4-EP and 150  $\mu\text{g/L}$  of 4-EG, TF) and after treatment with natural cork and dichloromethane and ethanol extractive free cork after air removal and ethanol impregnation (CKNI and CKFI) and cork powders with a particle size below 75  $\mu\text{m}$  at two application doses (250 and 500 g/hL) (CKF75250 and CKFI75500).

suggesting that the interaction of the volatile compounds including the VPs with the cork powder is of hydrophobic nature as observed for the interaction of other molecules with cork [7, 53, 54]. When compared to activated carbons applied at 100 g/hL, CKFI75250 (250 g/hL) showed a lower impact on the headspace aroma abundance (40 vs. 75%) and even CKFI75500 (500 g/hL) resulted in a lower reduction of 69%. Therefore, cork powder decreased the wine headspace aroma compounds lesser than the activated carbons [21].

### 3.2 Impact of optimised cork powder on wine chromatic characteristics and phenolic compounds

Application of optimised cork powder results in a decrease of the colour intensity, although being only significantly different from the control for the CKFI and CKFI75500. For the  $L^*$  and  $a^*$ , the same was observed (**Table 4**). These variations for the colour intensity are not due to a decrease in the concentration of monomeric anthocyanins that generally did not change by the use of all cork powders (**Table 5**). For the individual phenolic acids overall, their levels did not change significantly, or their decrease was significant but small, and these decreases occurred mainly for the CKFI75 at the two application doses (decreased for *trans*-caftaric acid—5.6%; coumaric acid—5.9%; caffeic acid—20%; ferulic acid—12% and coumaric acid ethyl ester—19%) (**Table 5**). For catechin, there was no change in its levels for all cork powders applied. These results show that optimised cork powders, either with or without extractive removal, have a low impact on wine phenolic composition; nevertheless, the ethanol impregnated extractive free corks had a significant impact on wine colour intensity, suggesting that these corks influence wine polymeric pigments as no significant changes on monomeric anthocyanins were observed. The impact for cork powders on wine phenolic composition and colour intensity of wines was lower than that generally observed for activated carbons used at 100 g/hL [20].

### 3.3 Impact of optimised cork powder on wine sensory attributes

To validate the impact of natural and extractive free ethanol impregnated cork powder samples on the headspace VP decrease and its effect on the sensory perception and quality of wines, CKNI, CKFI and CKFI75—treated wines at the two application doses (250 and 500 g/hL, CKFI75250 and CKFI75500, respectively) were subjected to sensory analysis by an expert panel. As expected, the presence of these VPs affect the aroma profile of spiked wine (TF) significantly and negatively (**Table 6**), by the increase of the phenolic attribute, decreasing the wine fruity and floral attributes significantly [20, 24, 55]. The panel consensus on each wine attribute was accessed through the percentage of variance explained by the first PCA [56] applied to the panel scores for each attribute. The variance explained by PC1 ranged from 45 to 87%, yielding the *C*-indexes presented in **Table 6**. Similar values have been reported for trained panels assessing different attributes and different products [20, 24, 62]. Colour intensity, floral, fruity, phenolic, acidity, balance and persistence wine attributes resulted in a consensus among judges (**Table 6**). For the colour hue, limpidity, oxidised (visual), vegetable, oxidised (aroma) and body, the judges attributed identical scores. There is no consensus on the other sensory wine attributes that could be due to the low difference of the attributes among samples or changes in motivation, sensitivity and psychological answer behaviour [57].

In accordance with the instrumental colour intensity, sensory colour intensity of the wines treated with ethanol impregnated extractive free cork powders was significantly lower than T0 and TF, with the increase in the application dose

Samples	L*	a*	b*	C*	h°	ΔE	Colour intensity (A.U.)	Hue
T	10.84 ± 0.49 <sup>a</sup>	40.55 ± 0.68 <sup>a</sup>	35.62 ± 0.31 <sup>ab</sup>	53.97 ± 0.72 <sup>ab</sup>	0.72 ± 0.00 <sup>a</sup>	—	10.04 ± 1.04 <sup>a</sup>	0.66 ± 0.00 <sup>a</sup>
CKNI	13.17 ± 0.18 <sup>b</sup>	43.32 ± 0.23 <sup>b</sup>	35.47 ± 0.00 <sup>ab</sup>	55.99 ± 0.18 <sup>b</sup>	0.69 ± 0.00 <sup>c</sup>	3.54 ± 0.29 <sup>ab</sup>	9.09 ± 0.07 <sup>ab</sup>	0.72 ± 0.00 <sup>b</sup>
CKFI	13.87 ± 0.08 <sup>c</sup>	44.37 ± 0.01 <sup>b</sup>	36.22 ± 0.29 <sup>b</sup>	57.28 ± 0.19 <sup>b</sup>	0.68 ± 0.00 <sup>c</sup>	4.88 ± 0.01 <sup>b</sup>	8.97 ± 0.17 <sup>b</sup>	0.71 ± 0.01 <sup>b</sup>
CKFI75250	10.85 ± 0.72 <sup>a</sup>	40.72 ± 1.14 <sup>a</sup>	34.08 ± 0.99 <sup>ab</sup>	53.10 ± 1.51 <sup>ab</sup>	0.70 ± 0.00 <sup>b</sup>	1.99 ± 0.48 <sup>a</sup>	9.40 ± 0.07 <sup>ab</sup>	0.74 ± 0.00 <sup>c</sup>
CKFI75500	14.84 ± 0.20 <sup>c</sup>	45.32 ± 0.34 <sup>b</sup>	36.17 ± 0.27 <sup>b</sup>	57.98 ± 0.44 <sup>b</sup>	0.67 ± 0.00 <sup>c</sup>	6.35 ± 0.41 <sup>b</sup>	8.34 ± 0.01 <sup>b</sup>	0.76 ± 0.01 <sup>c</sup>

Data are presented as  $\bar{X} \pm s$ ; data within a column followed by the same letter are not significantly different (Tukey,  $p < 0.05$ ). L\*, lightness; a\*, redness; b\*, yellowness; ΔE\*, colour difference. The values corresponding to ΔE\* were obtained taking as a reference the untreated wine (T) and wines treated with corks (CKNI, CKFI, CKFI75250 and CKFI75500). A.U., absorbance units.  $p < 0.05$ .

**Table 4.**

Chromatic characteristics of red wines before (TF) and after treatment with natural cork and dichloromethane and ethanol extractive free cork after air removal and ethanol impregnation (CKNI and CKFI) and cork powders with a particle size below 75 μm at two application doses (250 and 500 g/hL).

Samples	Del-3-Glc	Cya-3-Glc	Pet-3-Glc	Peo-3-Glc	Mal-3-Glc	Del-3-AcGlc	Cya-3-AcGlc	Mal-3-AcGlc	Del-3-CoGlc	Cya-3-CoGlc	Mal-3-CoGlc
T	1.18 ± 0.00	8.24 ± 0.17 <sup>a</sup>	13.58 ± 0.30 <sup>a</sup>	4.77 ± 0.07 <sup>a</sup>	155.84 ± 0.69 <sup>a</sup>	1.58 ± 0.02 <sup>a</sup>	0.98 ± 0.00 <sup>a</sup>	26.04 ± 0.46 <sup>a</sup>	1.37 ± 0.02 <sup>a</sup>	1.49 ± 0.15 <sup>a</sup>	13.70 ± 0.78 <sup>a</sup>
CKNI	1.12 ± 0.02	7.66 ± 0.12 <sup>b</sup>	13.10 ± 0.06 <sup>a</sup>	4.55 ± 0.04 <sup>b</sup>	150.37 ± 1.21 <sup>b</sup>	1.24 ± 0.01 <sup>d</sup>	0.79 ± 0.03 <sup>b</sup>	25.66 ± 0.30 <sup>a</sup>	1.24 ± 0.02 <sup>a</sup>	1.43 ± 0.04 <sup>a</sup>	12.09 ± 0.53 <sup>ab</sup>
CKFI	1.14 ± 0.03	8.00 ± 0.05 <sup>ab</sup>	13.59 ± 0.03	4.78 ± 0.03 <sup>a</sup>	156.65 ± 1.05 <sup>a</sup>	1.50 ± 0.00 <sup>b</sup>	0.87 ± 0.01 <sup>ab</sup>	26.69 ± 0.35 <sup>a</sup>	1.31 ± 0.02 <sup>b</sup>	1.23 ± 0.04 <sup>a</sup>	12.61 ± 0.14 <sup>ab</sup>
CKFI75250	1.15 ± 0.02	7.71 ± 0.19 <sup>ab</sup>	13.66 ± 1.15	4.53 ± 0.01 <sup>b</sup>	154.04 ± 0.36 <sup>ab</sup>	1.42 ± 0.04 <sup>c</sup>	0.83 ± 0.04 <sup>ab</sup>	25.89 ± 0.91 <sup>a</sup>	1.29 ± 0.05 <sup>a</sup>	1.08 ± 0.28 <sup>a</sup>	11.89 ± 0.48 <sup>b</sup>
CKFI75500	1.12 ± 0.01	7.93 ± 0.06 <sup>ab</sup>	13.42 ± 0.23	4.67 ± 0.08 <sup>ab</sup>	154.08 ± 2.30 <sup>ab</sup>	1.34 ± 0.02 <sup>c</sup>	0.84 ± 0.05 <sup>ab</sup>	26.68 ± 0.56 <sup>a</sup>	1.30 ± 0.04 <sup>a</sup>	1.18 ± 0.01 <sup>a</sup>	12.04 ± 0.32 <sup>ab</sup>

	Gallic acid	Catechin	<i>t</i> -Caftaric acid	Coutaric acid	Caffeic acid	<i>p</i> -Coumaric acid	Ferulic acid	Caffeic acid ethyl ester	Coumaric acid ethyl ester
T	24.11 ± 1.55 <sup>a</sup>	9.28 ± 1.53 <sup>a</sup>	30.02 ± 0.25 <sup>a</sup>	11.23 ± 0.18 <sup>ab</sup>	0.84 ± 0.00 <sup>a</sup>	0.72 ± 0.01 <sup>a</sup>	0.57 ± 0.00 <sup>a</sup>	0.39 ± 0.00 <sup>a</sup>	3.89 ± 0.04 <sup>a</sup>
CKNI	21.92 ± 1.79 <sup>a</sup>	8.55 ± 1.16 <sup>a</sup>	29.61 ± 0.28 <sup>a</sup>	11.02 ± 0.20 <sup>ab</sup>	0.80 ± 0.08 <sup>a</sup>	0.57 ± 0.03 <sup>b</sup>	0.54 ± 0.00 <sup>b</sup>	0.33 ± 0.04 <sup>ab</sup>	3.37 ± 0.18 <sup>b</sup>
CKFI	22.50 ± 0.30 <sup>a</sup>	8.48 ± 1.10 <sup>a</sup>	29.23 ± 0.02 <sup>ab</sup>	10.81 ± 0.01 <sup>ab</sup>	0.69 ± 0.01 <sup>b</sup>	0.55 ± 0.00 <sup>b</sup>	0.52 ± 0.01 <sup>c</sup>	0.33 ± 0.00 <sup>ab</sup>	3.28 ± 0.03 <sup>b</sup>
CKFI75250	22.77 ± 0.07 <sup>a</sup>	8.27 ± 0.26 <sup>a</sup>	28.57 ± 0.44 <sup>b</sup>	10.56 ± 0.29 <sup>b</sup>	0.67 ± 0.03 <sup>b</sup>	0.68 ± 0.02 <sup>a</sup>	0.50 ± 0.01 <sup>c</sup>	0.31 ± 0.02 <sup>ab</sup>	3.15 ± 0.15 <sup>b</sup>
CKFI75500	25.02 ± 0.09 <sup>a</sup>	7.74 ± 0.61 <sup>a</sup>	28.09 ± 0.56 <sup>b</sup>	10.57 ± 0.18 <sup>b</sup>	0.66 ± 0.00 <sup>b</sup>	0.67 ± 0.01 <sup>a</sup>	0.50 ± 0.01 <sup>c</sup>	0.31 ± 0.01 <sup>b</sup>	3.12 ± 0.02 <sup>b</sup>

Values are presented as  $\bar{X} \pm s$ ; means within a column followed by the same letter are not significantly different (Tukey,  $p < 0.05$ ). Del-3-Glc, delphinidin-3-glucoside, Cya-3-Glc, cyanidin-3-glucoside, Pet-3-Glc, petunidin-3-glucoside, Peo-3-Glc, peonidin-3-glucoside, Mal-3-Glc, malvidin-3-glucoside, Del-3-AcGlc, delphinidin-3-acetylglucoside, Cya-3-AcGlc, cyanidin-3-acetylglucoside, Pet-3-AcGlc, petunidin-3-acetylglucoside, Peo-3-AcGlc, peonidin-3-acetylglucoside, Mal-3-AcGlc, malvidin-3-acetylglucoside, Del-3-CoGlc, delphinidin-3-coumaroylglucoside, Cya-3-CoGlc, cyanidin-3-coumaroylglucoside, Pet-3-CoGlc, petunidin-3-coumaroylglucoside, Peo-3-CoGlc, peonidin-3-coumaroylglucoside and Mal-3-CoGlc, malvidin-3-coumaroylglucoside. Data within a column followed by the same letter are not significantly different ANOVA and Tukey post-hoc test ( $p < 0.05$ ).

**Table 5.**

Monomeric anthocyanin and phenolic acid composition of spiked red wines (TF) and after treatment with natural cork and dichloromethane and ethanol extractive free cork after air removal and ethanol impregnation (CKNI and CKFI) and cork powders with a particle size below 75  $\mu\text{m}$  at two application doses (250 and 500 g/hL) (CKFI75250 and CKFI75500).

	T0	TF	CKNI	CKFI	CKFI75250	CKFI75500	<i>p</i>	C-index <sup>1</sup>
Intensity	3.70 ± 0.48 <sup>a</sup>	3.70 ± 0.48 <sup>a</sup>	3.60 ± 0.52 <sup>ab</sup>	3.40 ± 0.52 <sup>b</sup>	3.40 ± 0.52 <sup>b</sup>	2.70 ± 0.48 <sup>c</sup>	<i>p</i> < 0.000001	3.3
Hue	3.40 ± 0.52 <sup>a</sup>	3.40 ± 0.52 <sup>a</sup>	3.40 ± 0.52 <sup>a</sup>	3.30 ± 0.48 <sup>a</sup>	3.40 ± 0.52 <sup>a</sup>	3.00 ± 0.67 <sup>b</sup>	<i>p</i> < 0.000001	—
Limpidity	3.40 ± 0.84	3.40 ± 0.84	3.40 ± 0.84	3.40 ± 0.84	3.40 ± 0.84	3.40 ± 0.84	<i>p</i> = 1.0	—
Oxidised (visual)	1.80 ± 0.42	1.80 ± 0.42	1.80 ± 0.42	1.80 ± 0.42	1.80 ± 0.42	2.00 ± 0.00	<i>p</i> < 0.811	—
Fruity	3.60 ± 0.52 <sup>a</sup>	1.70 ± 0.48 <sup>b</sup>	2.20 ± 1.14 <sup>c</sup>	2.20 ± 0.79 <sup>c</sup>	2.60 ± 1.07 <sup>d</sup>	2.20 ± 1.23 <sup>c</sup>	<i>p</i> < 0.000001	1.6
Floral	2.50 ± 0.53 <sup>a</sup>	1.30 ± 0.65 <sup>b</sup>	1.40 ± 0.52 <sup>b</sup>	1.60 ± 0.84 <sup>c</sup>	1.80 ± 1.03 <sup>d</sup>	1.40 ± 0.52 <sup>b</sup>	<i>p</i> < 0.000001	2.5
Vegetable	1.40 ± 0.52 <sup>a</sup>	1.80 ± 0.42 <sup>b</sup>	1.80 ± 0.42 <sup>b</sup>	1.70 ± 0.48 <sup>b</sup>	1.70 ± 0.48 <sup>b</sup>	1.80 ± 0.42 <sup>b</sup>	<i>p</i> < 0.00016	—
Phenolic	1.10 ± 0.32 <sup>a</sup>	3.80 ± 0.63 <sup>b</sup>	2.70 ± 0.48 <sup>c</sup>	2.70 ± 0.48 <sup>c</sup>	2.80 ± 0.42 <sup>c</sup>	2.80 ± 0.42 <sup>c</sup>	<i>p</i> < 0.000001	6.3
Oxidised (aroma)	2.00 ± 0.67 <sup>a</sup>	2.60 ± 0.52 <sup>b</sup>	2.40 ± 0.84 <sup>ab</sup>	2.80 ± 0.42 <sup>b</sup>	2.40 ± 0.84 <sup>ab</sup>	2.80 ± 0.42 <sup>b</sup>	<i>p</i> < 0.066	—
Bitterness	1.70 ± 0.67 <sup>a</sup>	2.30 ± 0.48 <sup>b</sup>	2.20 ± 0.42 <sup>b</sup>	2.20 ± 0.42 <sup>b</sup>	2.20 ± 0.42 <sup>b</sup>	2.00 ± 0.67 <sup>a</sup>	<i>p</i> < 0.0307	0.9
Acidity	2.20 ± 0.79	2.70 ± 0.48	2.60 ± 0.52	2.60 ± 0.52	2.60 ± 0.52	2.30 ± 0.48	<i>p</i> < 0.0605	1.1
Astringency	2.00 ± 0.67 <sup>a</sup>	2.60 ± 0.52 <sup>b</sup>	2.80 ± 0.42 <sup>c</sup>	2.40 ± 0.52 <sup>d</sup>	2.40 ± 0.52 <sup>d</sup>	2.50 ± 0.85 <sup>bd</sup>	<i>p</i> < 0.000001	0.8
Body	2.70 ± 0.48	2.50 ± 0.53	2.40 ± 0.52	2.50 ± 0.53	2.40 ± 0.84	2.50 ± 0.53	<i>p</i> < 0.333	—
Balance	3.00 ± 0.67 <sup>a</sup>	2.20 ± 0.42 <sup>b</sup>	2.0 ± 0.67 <sup>b</sup>	2.40 ± 0.52 <sup>b</sup>	2.40 ± 0.52 <sup>b</sup>	2.20 ± 0.42 <sup>b</sup>	<i>p</i> < 0.0037	1.1
Persistence	3.00 ± 0.67 <sup>a</sup>	2.00 ± 0.67 <sup>b</sup>	2.20 ± 0.42 <sup>c</sup>	2.40 ± 0.52 <sup>d</sup>	2.40 ± 0.52 <sup>d</sup>	2.40 ± 0.52 <sup>d</sup>	<i>p</i> < 0.000001	3.1

<sup>1</sup>Consonance analysis results—no variance observed for most panellists. Data are presented as the  $\bar{X} \pm s$  ( $n = 12$ ); data within a line followed by the same letter are not significantly different (Duncan  $p < 0.05$ ).

**Table 6.**

Mean scores of each attribute after sensory analysis of volatile phenol-free (T0) and volatile phenol-spiked (TF) red wine after treatment with natural cork and dichloromethane and ethanol extractive free cork after air removal and ethanol impregnation (CKNI and CKFI) and cork powders with a particle size below 75  $\mu\text{m}$  at two application doses (250 and 500 g/hL) (CKFI75250 and CKFI75500).



(CKFI75500) presenting a significantly lower score than CKFI75250 and CKFI. This decrease in colour intensity in the CKFI75500 is also followed by a decrease in the sensory hue, being in accordance with the significant change in  $h^\circ$  and  $L^*$  for this sample. Neither natural nor extractive free cork powders changed significantly the limpidity and oxidised visual sensory attributes.

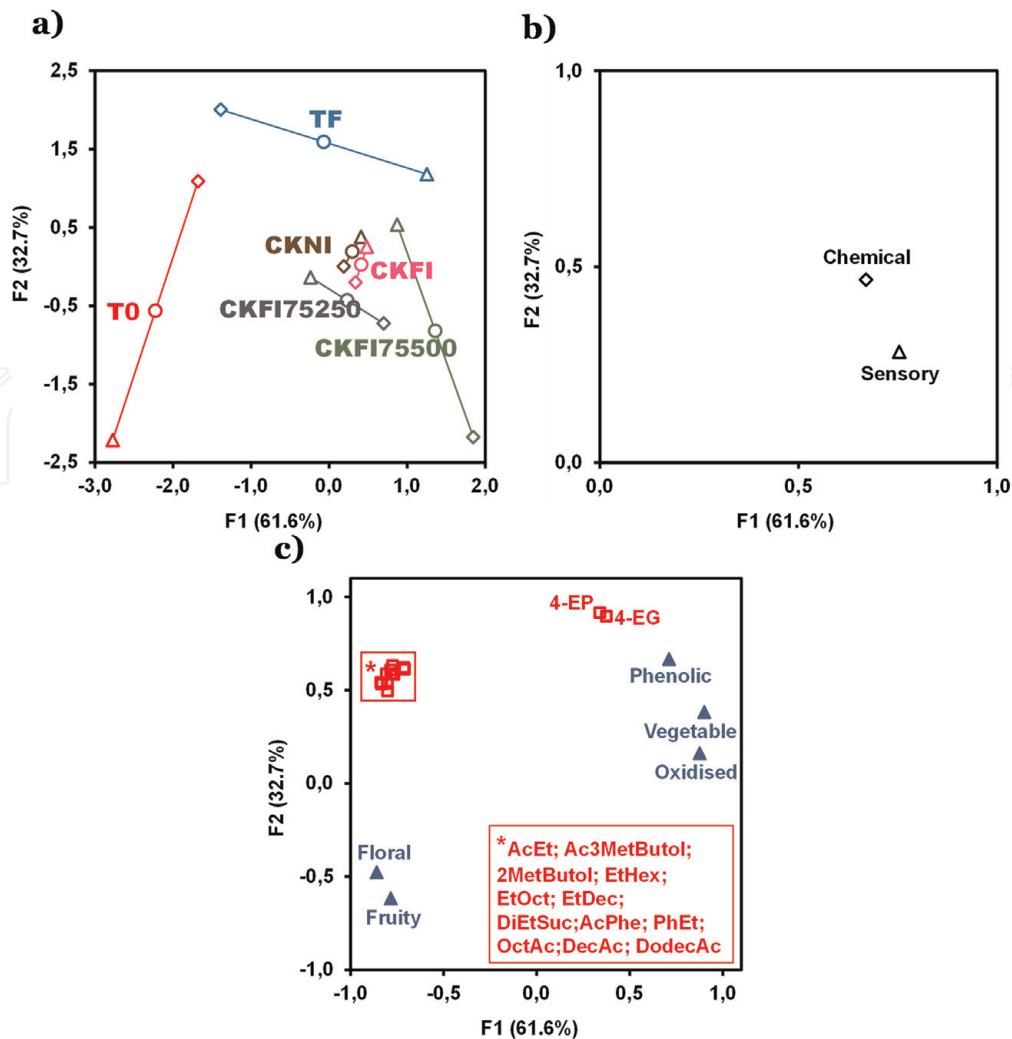
For VP-spiked wine, the application of all cork powders in two application doses (250 and 500 g/hL) of CKFI75 decreased the negative phenolic attribute significantly compared to the spiked wine (TF); however, the scores obtained were also significantly higher than those observed for the initial unspiked wine (T0). For the fruity aroma attribute, the application of all cork powder allowed recovering significantly the fruity aroma attribute in relation to the VP-spiked wine (TF); nevertheless, the scores were also significantly lower than that observed for the original unspiked wine (T0). The fruity aroma attribute was significantly higher for the CKFI75250 than for all other cork powder samples even higher than CKFI75500. This could be due to the higher decrease in headspace aroma abundance responsible for the fruity notes for this application dose as discussed previously.

For the floral attribute, only CKFI and CKFI75250 allowed increasing significantly this sensory attribute in relation to the TF, and again the scores obtained for the cork-treated wines were significantly lower than that obtained for T0. As observed for the fruity attribute, also for the floral attribute the increase in application dose of CKFI75 decreased the floral attribute of the wine (**Table 6**). The TF wine presented an increased vegetable attribute that did not decrease with the application of cork powder samples, nevertheless, the scores observed were very low (**Table 6**). No significant differences were observed for the oxidised aroma attribute in all samples (T0, TF and cork powder treated wines).

The application of cork powder did not change the acidity and body of the wine samples significantly; however, significant differences were obtained for bitterness, astringency, balance and persistence (**Table 6**). The spiking wine resulted in a significant increase in the bitterness attribute in relation to the T0. Except for CKFI75500, the other cork powders did not decrease bitterness to the levels observed for T0. For astringency, spiking of wine with VPs increase this sensory attribute, and no cork-powder sample decreased the astringency to the initial levels (T0), nevertheless CKFI and CKFI75250 were able to decrease significantly the astringency in relation to TF. For CKNI, a significant increase of astringency in relation to TF was observed, and this can be explained probably by a migration of phenolic compounds from this cork-powder [58, 59]. For balance, TF significantly decreased this sensory attribute, and the application of all cork powders did not lead to scores significantly different from the TF. For persistence, the application of cork powders to TF significantly increased the persistence of wine; however, the scores obtained were significantly lower than the persistence of T0 (**Table 6**).

### **3.4 Impact of wine chemical composition on sensory profile of red wine treated with extractive free and ethanol impregnated cork powder and application doses**

The sensory scores provided by the expert panel for aroma (**Figure 6**), taste and tactile/textural descriptors (**Figure 7**) and the chemical composition of wines, concerning the abundance of headspace aroma compounds and phenolic compounds, respectively, were subjected to multiple factor analysis. From the variable map, it can be concluded that for the first and second factors, both groups of variables contribute almost equally (53 and 46%, and 36 and 64% for the sensory and chemical data for the first and second factors, respectively) (**Figure 6b**).

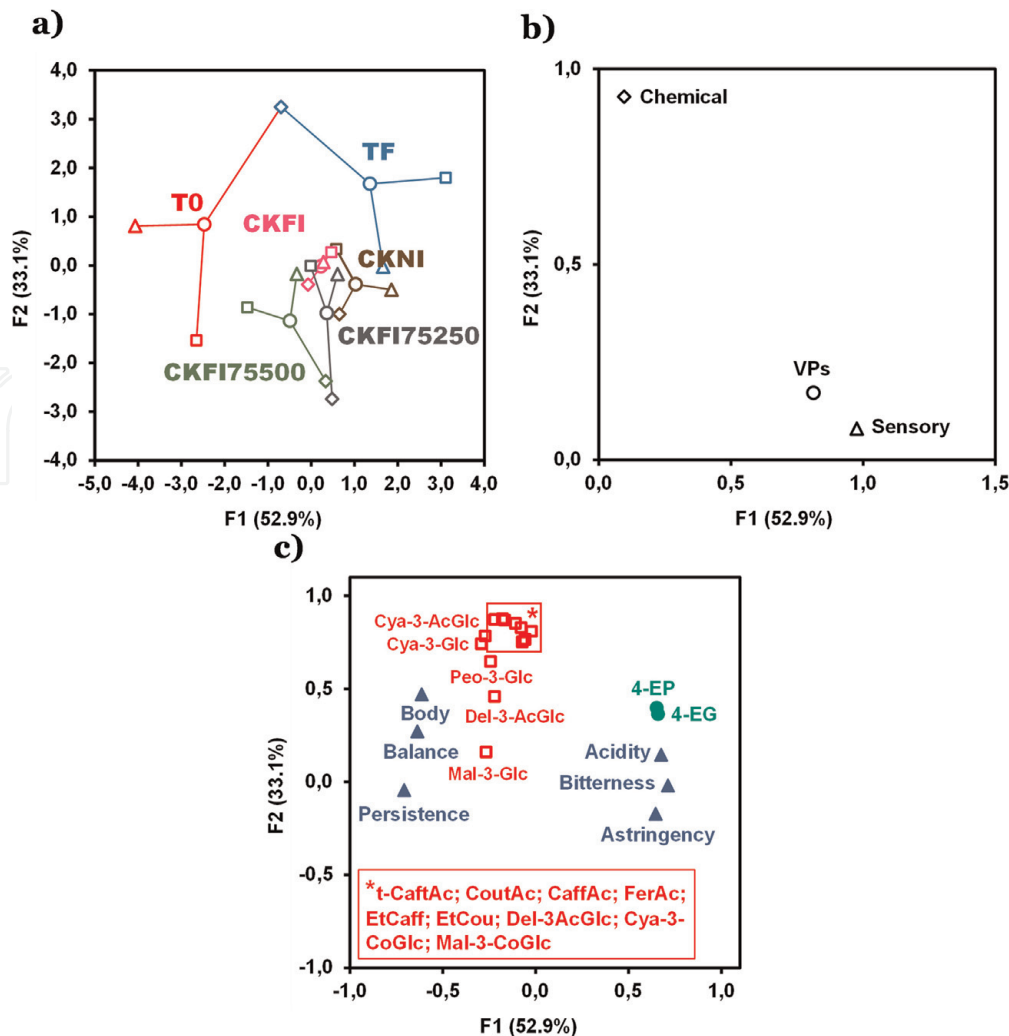


**Figure 6.**

Multiple factorial analysis of aroma sensory and chemical data: (a) representation of wine samples and clouds; (b) representation of groups (tables) of variables and (c) distribution of variables. VP-free (To) and VP-spiked (TF) red wines and after treatment with natural cork and dichloromethane and ethanol extractive free cork after air removal and ethanol impregnation (CKNI and CKFI) and cork powders with a particle size below 75  $\mu\text{m}$  at two application doses (250 and 500 g/hL, CKFI75250 and CKFI75500, respectively). Centroid (O); sensory data ( $\Delta$ ); chemical data ( $\diamond$ ). AcEt, ethylacetate; Ac3 MetBut, 3-methylbutan-1-ol acetate; 3-MetButol, 3-methylbutan-1-ol; EtOct, ethyl octanoate; EtDec, ethyl decanoate; DiEtSuc, diethyl succinate; PhEt, 2-phenylethanol; 4-EG, 4-ethylguaiaicol; 4-EP, 4-ethylphenol; OctAc, octanoic acid; DecAc, decanoic acid; DodAc, dodecanoic acid.

The phenolic negative attribute and the 4-EP and 4-EG headspace abundance were positively correlated with F1, showing that the reduction of the headspace abundance of 4-EP and 4-EG caused by CKNI, CKFI, CKFI75250 and CKFI75500 was important for the decrease of this wine defect. The fruity and floral positive attributes were negatively correlated with F1, showing that the decrease of the headspace abundance of these VPs was important for their perception. However, the abundance of the other headspace aroma compounds was also important for their perception, as they also present negative F1 score. These results are in accordance with previous works that verified that the absence of wine aroma defects, including VPs, was more important for the final wine aroma profile, where that negative off-odorants exert a strong aroma suppression impact on fruity aroma [20, 21, 24, 61, 66].

The phenolic composition of wines although changed significantly, especially after application of the CKFI75 at the two levels, the decrease was not high; nevertheless, significant differences were observed for bitterness, astringency, balance and persistence by sensory analysis, parameters usually linked to the phenolic



**Figure 7.** Multiple factorial analysis of taste and tactile/textural sensory data, phenolic compound chemical data and volatile phenol headspace abundance: (a) representation of wine samples and clouds; (b) representation of groups (tables) of variables and (c) distribution of variables. VP-free (To) and VP-spiked (TF) red wines and after treatment with natural cork, dichloromethane and ethanol extractive free after air removal and ethanol impregnation (CKNI and CKFI) and cork powders with a particle size below 75  $\mu\text{m}$  at two application doses (250 and 500 g/hL, CKFI75250 and CKFI75500, respectively). Centroid (O); sensory data ( $\Delta$ ); chemical data ( $\diamond$ ); VP headspace abundance ( $\bullet$ ). TotPhe, total phenols; FlavPhe, flavonoid phenols; t-CaftAc, trans-caftaric acid; CoutAc, coumaric acid; Del-3-Glc, delphinidin-3-O-glucoside, Cya-3-Glc, cyanidin-3-O-glucoside, Peo-3-AcGlc, peonidin-3-O-(6-O-acetyl)-glucoside; VPs, volatile phenols; 4-EP, 4-ethylphenol; 4-EG, 4-ethylguaiacol.

composition of wines [67]. By the phenolic composition of treated wines, the headspace abundance of 4-EP and 4-EG was also used for MFA, because it is actually known that the aroma can interact with the perceived bitterness and astringency of foods, where wines are included [24, 67]. The first factor was important to describe the sensory and VP headspace abundance variables (Figure 7b). In the case of the chemical variables, only the second factor was important for its description. The correlation maps of observations and variables (Figure 7c) show that the persistence, body and balance attributes were correlated with F1 in the negative direction. However, acidity, bitterness and astringency attributes were correlated with F1 in the positive direction, and there was also a positive correlation between VP headspace abundance with this factor. The correlation of bitterness and astringency, unpleasant wine sensory attributes, with the headspace abundance of VPs, responsible for the negative phenolic aroma, can be explained by the relationship between several aroma compounds with the bitterness and astringency of foods, shown also for wine [24, 68]. The significant decrease observed in some phenolic compounds

after application of ethanol impregnated cork-powders does not seem to be responsible for the change in the taste/tactile descriptors observed after wine treatment.

The results obtained from MFA supported the results from sensory analysis of the wines obtained after treatment with the different ethanol impregnated cork powders at the applied doses, highlighting the efficiency of extractive free cork-powders, especially cork powder with a lower particle size at 250 g/hL application dose (CKFI75250), for decreasing the levels of 4-EP and 4-EG in wines and for recovery of fruity and floral aroma attributes. A decrease in phenolic, bitterness and astringency attributes was also observed. The results obtained for visual (colour), aroma, taste and tactile/textural descriptors determined by the expert panel, validated by the wine chemical composition after treatment with ethanol impregnated cork powders show that the wine treated with CKFI75250 resulted in a significant increase in the sensory quality compared to TF, although not identical to T0 wine. This is explained by the efficient removal of VPs and no negative impact on the wine phenolic composition and a lower impact on the headspace aroma compounds when compared to CKFI75500.

#### **4. Conclusions**

Optimised cork powder can be a new, cheap, sustainable and efficient fining agent for removal of VPs from wines presenting the unpleasant “Brett character”. Its efficiency is shown by the capacity to adsorb significant amounts of 4-EP and 4-EG from a real red wine matrix, presenting a lower impact on the headspace positive aroma compounds when compared to other oenological solutions, already tested. The low impact on the phenolic composition of wines, especially on the monomeric anthocyanins, makes its impact on wine colour limited. Contaminated wines treated with optimised cork powder (extractive free and solvent impregnation) show a significant decrease of the negative phenolic attribute and a significant increase in the positive sensory fruity and floral attributes. This natural product can, in the near future, represent a new oenological fining solution with low environmental impact, contributing to a more sustainable wine industry.

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#### **Conflict of interest**

No conflict of interest.

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