

**Volatile and Glycosidically Bound Composition of
*Loureiro and Alvarinho Wines***

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ABSTRACT

Composition of *Loureiro* and *Alvarinho* wines from the *Vinhos Verdes* region, respecting free volatile compounds as well as glycosidically bound aroma precursors, was exhaustively determined by GC-MS after adsorption on XAD-2 resin. On the whole, were identified and quantified 120 volatile compounds in the free fraction and 77 glycosidically bound compounds, belonging to C₆-compounds, alcohols, fatty acids ethyl esters, esters of organic acids, acetates, monoterpenic alcohols, monoterpenic oxides and diols, C₁₃-norisoprenoids, volatile phenols, volatile fatty acids and carbonyl compounds. Globally, the wines of the two cultivars present similar composition on volatiles. However, respecting varietal compounds, *Loureiro* wines are richer than *Alvarinho* ones with regard to C₆-compounds and monoterpenic compounds, occurring the opposite for volatile phenols. It was also demonstrate that wines of both varieties may benefit the aroma reserve, present as glycoconjugates, as it is susceptible of being technologically explored. Linalool, Ho-trienol, α -terpineol, contributing with fruity and floral notes, and β -damascenone mostly for *Alvarinho*, conferring tropical fruit notes, are the varietal compounds which may particularly influence the aroma of these wines. Respecting fermentative compounds, *Alvarinho* is also particularly rich in fatty acids ethyl esters related to lipid metabolism and acetates of fusel alcohols, which can provide it a fruity character; *Loureiro* contains higher levels of esters of organic acids and 2-phenylethanol, conferring fruity and floral notes. Sensory analysis agree with chemical analyses showing a pronounced tree and tropical fruit character for *Alvarinho* wines while *Loureiro* wines present more intense citrus fruit notes.

Keywords: wine, aroma, volatiles, precursors, *Loureiro*, *Alvarinho*, *Vinhos Verdes*

INTRODUCTION

Wines with Appellation of Origin *Vinhos Verdes* are produced in a wide region in Northwestern Portugal, composed by 9 sub-regions (Amarante, Ave, Baião, Basto, Cávado, Lima, Monção, Paiva and Sousa). There are seven recommended white grape varieties (*Alvarinho, Arinto, Avesso, Azal, Batoca, Loureiro* and *Trajadura*) and eight red grape varieties (*Amaral, Borraçal, Brancelho, Espadeiro, Padeiro de Basto, Pedral, Rabo de Ovelha* and *Vinhão*) to produce these wines. Among the white cultivars, *Alvarinho* and *Loureiro* are employed to produce high quality monovarietal wines, which are characterized by freshness and floral and fruity flavors. In order to preserve these appreciated characteristics, traditional winemaking techniques are developed to encourage these notes and to avoid malolactic fermentation. The legislation stipulates ethanol concentrations of between 8.0 % and 11.5 %, but for *Alvarinho* wines it must be comprised between 11.5 % and 13.0 %; fix acidity, expressed as tartaric acid, must be at least 6 g/L (4.5 g/L for *Alvarinho*).

Depending on the origin, and considering the biotechnological sequence of winemaking, wine flavor can be classified into four different groups (Drawert, 1974; Cordonnier and Bayonove, 1978; Bayonove et al., 1998): varietal aroma, typical of grape variety, which depends essentially on soil, climate, phytotechny, sanitary conditions and degree of ripeness; pre-fermentative aroma, originated during grape processing and subsequent operations, namely transport, pressing, maceration, and clarification; fermentative aroma, produced by yeasts during alcoholic fermentation and lactic acid bacteria during malolactic fermentation, which depends mainly on fermentation temperature and microorganism species; post-fermentative aroma, which results from transformations occurred during conservation and ageing of wine. Because *Vinhos Verdes* are usually consumed young, the first three groups are the most important for the present work.

The wine constituents linked to grape variety are the monoterpenols, abundant in Muscat varieties, the methoxypyrazines, which characterize the *Cabernet* family, the C₁₃-norisoprenoids, numerous in *Chardonnay*, volatile thiols in *Sauvignon*, volatile phenols in "*Traminer aromatico*" and dimethyl sulfide in *Syrah*, but these compounds could also contribute significantly to the aroma of several other varieties (Versini, 1985; Allen et al., 1991; Sefton et al., 1993; Tominaga et al., 2000; Segurel et al., 2004 and 2005). Except for the methoxypyrazines, these constituents occur in grapes in the form of non-volatile precursors like fatty acids, glycosides, carotenoids, cysteine S-conjugates and phenolic compounds, which can originate flavour compounds during or after the technological sequence of winemaking (Bayonove et al., 1998). However, monoterpenols are also abundant as free odorants in some grape varieties, like *Muscat*

or *Gewürztraminer*. Pre-fermentative compounds are essentially C₆-alcohols and C₆-aldehydes formed from grape lipids, by a sequence of enzymes (Crouzet et al., 1998). Fermentative compounds are alcohols, esters, fatty acids, carbonyl compounds and some phenols (Bayonove et al., 1998); they contribute to the vinous character of wine.

Glycosidic precursors are of greater importance as they can be hydrolyzed to a certain extent during winemaking, wine conservation and ageing, chemically or by microorganisms or endogenous enzymes, and also by the addition of exogenous enzymes. It makes possible the production of aromatic wines, with varietal characteristics, from non-aromatic varieties (Günata et al., 1990 and 1993; D'Incecco et al., 2004).

Since *Vinhos Verdes*, namely *Loureiro* and *Alvarinho*, are quite important for the economy of this demarcated region and because they are over all appreciated by their aromatic characteristics, it is very important to study the volatile composition as well as the aroma precursors of these wines. Former studies indicate that *Loureiro* can be classified among monoterpene dependent aromatic varieties, and that *Loureiro* and *Alvarinho* varieties have an important reserve of volatile compounds that can be exploited technologically (Oliveira et al., 2000); furthermore, terpenol profile of both fractions, free and glycosidically bound, are largely different (Oliveira et al., 2004). Except for the Galician congeners *Loureira* and *Albariño* wines (Versini et al., 1994), were not found any published data referring to free volatile compounds or glycoconjugates of *Loureiro* and *Alvarinho* wines, neither exhaustively nor concomitantly.

The aim of this work was to study the global composition of *Loureiro* and *Alvarinho* young wines, in terms of free volatile compounds and also of glycosidically bound precursors. To reach these purposes, 3 *Alvarinho* and 2 *Loureiro* wines were elaborated from grapes harvested at different *terroirs* inside the *Vinhos Verdes* Region. Chemical and sensory analyses were conducted.

MATERIALS AND METHODS

The evaluation of the volatile composition of wines was made after 8 months of conservation in bottle, the recommendable time for the wine to be drunk, in expert's opinion. General analyses of wines was done at *Comissão de Viticultura da Região dos Vinhos Verdes*.

Grape Samples

Grapes from *Loureiro* and *Alvarinho* varieties were manually harvested in 1998 in two different vineyards; both soils are from granitic origin. The most recommended sub-regions (Lima and Monção) for the monovarietal wine production and an alternative sub-region (Cávado and Lima) inside the *Vinhos Verdes* Region were selected. For the *Alvarinho* variety, an additional vineyard cultivated in a pebble soil was chosen. The codes attributed to the samples were the following: **L_{CT}** – *Loureiro, Casa da Tapada*, sub-region of *Cavado*; **L_{AV}** – *Loureiro, Estação Vitivinícola Amândio Galhano (Arcos de Valdevez)*, sub-region of *Lima*; **A_{AV}** – *Alvarinho, Estação Vitivinícola Amândio Galhano (Arcos de Valdevez)*, sub-region of *Lima*; **A_{SS}** – *Alvarinho, Solar de Serrade*, sub-region of *Monção*; **A_{CR}** – *Alvarinho, Lagoa Verde (Calhau Rolado – pebble)*, sub-region of *Monção*.

Vinifications

The wines which correspond to samples referred above were made according to the traditional technology applied in *Vinhos Verdes* Region. The must, obtained by crushing, pressing and static sedimentation, was inoculated with the yeast *Saccharomyces cerevisiae bayanus* QA23. Fermentations took place at 18 °C, in 10 L vessels, and were done in duplicate for precaution. The produced wines were combined and the blend was treated with 0.4 g/L of sodium bentonite – *Volclay KWK Food Grade, 20–70 mesh, 10 %* in aqueous solution. Next, the SO₂ content was corrected to 35 mg/L, and finally submitted to cold stabilization (between 0 °C and 3 °C) before bottling. The conservation of the wines occurred at cellar temperature and in the dark. These wines do not perform malolactic fermentation.

Solvents

All solvents were analytical grade and further purified. Diethyl ether (*Merck*) was distilled on iron (II) sulphate (*Merck*). Dichloromethane (*Merck*) was washed with de-ionised water, and then distilled. Pentane (*Carlo Erba*) was washed with H₂SO₄ (*Merck*), KMnO₄ (*Carlo Erba*) and de-ionised water, and next it was distilled on potassium hydroxide (*Merck*). Azeotrope pentane-dichloromethane was distilled after combination of pentane and dichloromethane (2:1, v/v) and it was redistilled whenever necessary.

Extraction of Volatiles and Glycoconjugates from Wines

To 100 mL of wine, previously centrifuged (25 min, *RCF* = 12 225, 4 °C) and diluted with de-ionised water to reduce ethanol content to less than 5 %, were added 14.5 µg

of 4-nonanol (*Merck*). The solution was passed through an Amberlite XAD-2 resin (20–60 mesh, *Supelco*) column according to the method of Günata et al. (1985). Free and glycosidically bound fractions were eluted successively with 50 mL of azeotrope pentane-dichloromethane and 50 mL of ethyl acetate. Pentane-dichloromethane eluate was dried over anhydrous sodium sulphate and concentrated to about 2 mL by solvent evaporation at 34 °C through a Vigreux column, prior no analysis. The ethyl acetate eluate was concentrated to dryness in vacuum (40 °C) and dissolved in 100 µL of citrate-phosphate buffer (pH=5). Residual free compounds were extracted five times with azeotropic mixture and discarded. 14 mg of enzyme AR2000 (*Gist-Brocades*) was added to the glycosidic extract and the mixture was incubated at 40 °C for 12 h. Released aglycons were extracted with pentane-dichloromethane; 7.25 µg of 4-nonanol, as internal standard, was added to the organic phase and it was concentrated to 200 µL, through a Dufton column. Analyses were made in triplicate.

Gas-chromatography-Mass Spectrometry (GC-MS)

Gas chromatographic analysis of volatile compounds was performed using a GC-MS composed by a Varian 3400 Chromatograph and an *ion-trap* mass spectrometer Varian Saturn II. Each 1 µL injection was made separately in two capillary columns, coated with CP-Wax 52 CB or CP-Wax 57 CB (both with 50 m x 0.25 mm i.d., 0.2 µm film thickness, *Chrompack*), respectively. The temperature of the injector (SPI – septum-equipped programmable temperature) was programmed from 20 °C to 250 °C, at 180 °C/min. The temperature of the oven was held at 60 °C, for 5 min, then programmed from 60 °C to 250 °C (60 °C to 220 °C for the second column), at 3 °C/min, then held 20 min at 250 °C (30 min at 220 °C) and finally programmed from 250 °C to 255 °C at 1 °C/min (220 °C to 225 °C at 2 °C/min). The carrier gas was helium N60 (*Air Liquide*), at 103 kPa. The detector was set to electronic impact mode (70 eV), with an acquisition range (*m/z*) from 29 to 360, and an acquisition frequency of 610 ms.

Identification and Quantification of Volatile Compounds

Identification was performed using the software Saturn, version 5.2 (*Varian*), by comparing mass spectra and retention times with those of pure standard compounds. In some cases, the identification was achieved by comparing retention index and mass spectra with those of published data. The quantification was performed using the data obtained in CP-Wax 52 CB column, mainly. The second column, CP-Wax 57 CB, served

essentially to confirm spectra of the co-eluted compounds and, in general, it was useful for the alcohols. All the compounds were quantified as 4-nonanol equivalents.

Sensory Analyses

Wines were submitted to sensory evaluation, by 7 tasters, at *Comissão de Viticultura da Região dos Vinhos Verdes* (CVRVV). Judges were chosen amongst wine experts and they had a full knowledge about the products. *Loureiro* and *Alvarinho* wines, in duplicate, were coded randomly and tasted independently using the distribution prepared according to aleatory tables. Normalized glasses were used (ISO 3591) and the room was kept at 21 °C and 65 % of relative humidity. The wine score card was that used by the Tasting Room of CVRVV, evaluating several attributes (scale 0 to 5) relating to visual, olfactory and gustative observations. Tasters also classified global appreciation (scale 0 to 20).

Statistical Analyses

Statistical differences between wines, respecting chemical analysis, were checked by Analysis of Variance (ANOVA). Homogeneity of variances was checked with the Levene test and normality of the variables was checked by the Kolmogorov-Smirnov test with Lilliefors correction, both at a significance level of 5 %. Whenever one of these two conditions fails, the non-parametric Kruskal-Wallis test was applied. Also, global classification obtained in sensory analysis was studied by means of Analysis of Variance in order to evaluate hypothetical differences between wines of the same variety.

Similarities between wines, respecting specific compounds, were analysed by Principal Component Analysis, being component extraction achieved by correlation matrix and their number fixed according to Kaiser criterion, *i. e.*, all the components with eigenvalues over 1.

The software used was SPSS 14.0 for Windows.

RESULTS AND DISCUSSION

General Analyses

General characteristics of wines are summarized in Table 1. *Loureiro* wine fulfils the criteria to obtain the Appellation of Origin *Vinho Verde* label. However, A_{SS} and A_{CR} *Alvarinho* wines had an alcoholic content above the permitted limit of 13.0 %.

Volatile Composition of *Loureiro* and *Alvarinho* Wines

The volatile extracts were obtained by solid phase extraction of diluted wines (lowering the alcoholic content below 5 %) using XAD-2 resin as report previously (Voirin et al., 1992; Aubert et al., 1997). GC-MS analysis of these extracts allowed the identification and quantification of 120 volatiles belonging to C₆-compounds (5), alcohols (24), fatty acid ethyl esters related to lipid metabolism (6) and to nitrogen metabolism (3), esters of organic acids (10), acetates (7), monoterpenic alcohols (8), monoterpenic oxides and diols (14), C₁₃-norisoprenoids (13), volatile phenols (13), volatile fatty acids related to lipid metabolism (8) and to nitrogen metabolism (3), carbonyl compounds (4) and also pantolactone and N-(2-phenylethyl)-acetamide. This classification takes into account the chemical structure of the volatile compounds, the pathways leading to their formation and the olfactory perception threshold.

Table 2 shows the mean level obtained for each compound in the five samples analysed. These levels were determined as 4-nonanol equivalents.

Varietal Compounds

They are, mainly, monoterpenic compounds (alcohols, oxides and diols), C₁₃-norisoprenoids and some volatile phenols. Unsaturated C₆-alcohols are related to varietal origin because they can be formed, via C₆-aldehydes, through enzymatic reactions from linolenic and linoleic acids present in grapes (Crouzet et al., 1998). Therefore, they will be considered as constituents of potential varietal aroma (Nicolini et al., 1996). However, because of their mainly fermentative origin, 1-hexanol, 4-ethylphenol, 4-vinylguaiaicol and 4-vinylphenol were excluded from the varietal group (Joslin and Ough 1978; Chatonnet et al., 1992 and 1993).

Regarding the 5 samples studied, although the profiles of varietal compounds are similar, ANOVA shows that *Loureiro* presents globally higher contents of varietal C₆-compounds and monoterpenic compounds (alcohols, oxides and diols), mainly for L_{AV}, but the difference between the levels of monoterpenols in A_{SS} and L_{CT} was not statistically significant ($p > 0.05$). Contrarily, *Alvarinho* wines have higher levels of varietal volatile phenols. Alternative sub-regions (L_{CT} and A_{AV}) are systematically poor than recommended sub-regions (L_{AV} and A_{SS}) respecting monoterpenic compounds (including alcohols, oxides and diols) and C₁₃-norisoprenoids ($p < 0.05$).

All the C₆-compounds follow the group tendency except (*Z*)-3-hexen-1-ol which is more abundant in *Alvarinho* wines; moreover, the relative abundance of (*E*) and (*Z*) isomers varies according to the cultivar, being (*E*) isomer always greater than (*Z*) isomer for *Loureiro*, occurring the opposite for *Alvarinho*. The (*E*)/(*Z*) isomer ratio is

almost constant for the wines of each variety, with mean values of 6.81 ± 0.76 ($n=6$) and 0.64 ± 0.06 ($n=9$) for *Loureiro* and *Alvarinho*, respectively (95 % confidence level). As already mentioned, these results seem to indicate the possibility to discriminate wines from these two varieties (Oliveira et al., 2006).

Wines made with grapes from the recommended sub-regions (L_{AV} and A_{SS}/A_{CR}) present levels of monoterpenic alcohols higher than those from the selected alternative sub-regions (L_{CT} and A_{AV}) ($p < 0.05$). These compounds are always globally more abundant in *Loureiro* wines, except A_{SS} which presents similar levels to L_{CT} , and myrcenol has only been detected in *Loureiro*'s. Linalool contributes certainly to the fruity and floral aroma of these wines, as its olfactory perception threshold is $25 \mu\text{g/L}$ (Escudero et al., 2004; Ribéreau-Gayon et al., 2000). Also Ho-trienol and α -terpineol, with perception thresholds of $110 \mu\text{g/L}$ and $330 \mu\text{g/L}$, respectively, may also influence contribute with similar notes (Meilgaard, 1975; Simpson, 1979; Ribéreau-Gayon et al., 2000; Escudero et al., 2004). It must be noted that linalool is present in *Loureiro* wines at lower concentrations than in grapes, probably due to inefficient extraction during winemaking procedures. On the contrary, its level in *Alvarinho* wines is much higher than in grapes, very poor in this compound (Oliveira et al., 2000) which could be attributed to the hydrolysis of precursors. In addition, the levels of Ho-trienol and α -terpineol in wines of both varieties were much higher than in the corresponding grapes. That could be explained by the chemical modifications of some monoterpene compounds occurring at acidic pH (Williams et al., 1980 and 1982) since the corresponding glycoconjugates hardly occurred in grapes. Finally, the quantitative determination of geraniol in most samples was not possible due to its co-elution with hexanoic acid.

Concerning monoterpenic oxides and diols, *Loureiro* is richer than *Alvarinho* for the majority of compounds, particularly pyran linalool oxides and 3,7-dimethylocta-1,7-dien-3,6-diol; on the contrary, (*Z*)-8-hydroxylinalool is more abundant for *Alvarinho* wines, although A_{AV} , L_{CT} and L_{AV} showed no significant differences ($p > 0.05$). Two other compounds, *exo*-2-hydroxy-1,8-cineole and *p*-1-menthen-7,8-diol, have only been detected in *Loureiro* wines, but at trace levels. It must be emphasized that this group of compounds is much more abundant in wines than in the free fraction of grapes, showing their origin from glycosylated precursors or chemical modification of some monoterpenols (Williams et al., 1980 and 1982). 3,7-dimethylocta-1,5-dien-3,7-diol for the samples of both varieties, 3,7-dimethylocta-1,7-dien-3,6-diol and linalool oxides for *Loureiro* and trans-pyran linalool oxide for *Alvarinho* are the compounds which show higher increase from grapes to wines. As observed for monoterpenic alcohols, wines made with grapes from the recommended sub-regions (L_{AV} and

A_{SS}/A_{CR}) present levels of monoterpenic oxides and diols higher than those from the selected alternative sub-regions (L_{CT} and A_{AV}) ($p < 0.05$).

Regarding C_{13} -norisoprenoids, only few micrograms per liter of some compounds were quantified, being 3-oxo- α -ionol, megastigm-7-ene-3,9-diol and β -damascenone the most abundant. Total levels are similar for the wines of both varieties, but those from the chosen alternative sub-regions (L_{CT} and A_{AV}) present the lowest levels ($p < 0.05$). Total levels found in wines are much higher than those found in the corresponding grapes, probably due to precursor hydrolysis. Additionally, β -damascenone with perception threshold of 45 ng/L may influence certainly the aroma of these wines, particularly *Alvarinho* ones, contributing with floral and tropical fruit notes (Ribéreau-Gayon et al., 2000). Vitispiranes, 1,1,6-trimethyl-1,2-dihydronaphtalene (TDN), β -damascenone and, partly, 3-hydroxy- β -damascone appear in wines due to the chemical transformation at wine pH of some C_{13} -norisoprenoid aglycons, some of them quantified and presented in Table 3. It is known that TDN may derive from 3-hydroxy- β -ionone, 3,4-dihydroxy- β -ionol, 3,4-dihydroxy-7,8-dihydro- β -ionol, 3,9-dihydroxytheaspirane and 3,4-dihydroxy-7,8-dihydro- α -ionone and vitispirane from 3,4-dihydroxy-7,8-dihydro- β -ionol, megastigm-4-ene-3,6,9-triol and 3,4-dihydroxy-6,9-epoxymegastigmane (Winterhalter 1993; Winterhalter and Schreier 1994; Winterhalter and Skouroumounis 1997; Winterhalter et al., 1998); β -damascenone and 3-hydroxy- β -damascone have also different precursors, 3-hydroxy-7,8-dehydro- β -ionol and 3,6,9-trihydroxymegastigma-6,7-diene (Winterhalter and Schreier 1994; Puglisi et al., 2005).

Volatile phenols arising from glycoconjugates hydrolysis are present also at low levels, but 4-vinylguaiacol and 4-vinylphenol (having also a fermentative origin) are more abundant.

Wines of the two varieties can be discriminated by means of Principal Component Analysis, applied to the varietal compounds (Figure 1). The two first components represent 91.8 % of the initial variance. Component 1 (55.2 %) permits to discriminate between *Alvarinho* and *Loureiro* wines based mainly on the higher levels of monoterpene compounds for the last variety. Component 2 (36.6 %) distinguishes, for both varieties, recommend sub-region from alternative sub-region; as described above, wines from recommended sub-regions are richer in norisoprenoids and monoterpenic compounds. It must be emphasised that if fermentative compounds were considered, this discrimination was not possible.

According to Meilgaard (1975), who has classified the volatile compounds of beer according to their odour activity values (*OAV*), defined as the ratio between

concentration and olfactory perception threshold (*OPT*), any constituent having *OAV* above 0.1 units would influence the overall flavour. If this rule may be applicable to wines, apart from the forementioned varietal compounds, also (*Z*)-3-hexen-1-ol (*OPT* = 400 µg/L; grass and green leaves descriptors) for *Alvarinho* and citronellol (18 µg/L; citronella), neroloxide (100 µg/L; fragrant, green) and guaiacol (11 µg/L; phenolic, chemical) may contribute, although marginally, to the overall flavour of these wines (Meilgaard, 1975; Simpson, 1979; Ribéreau-Gayon et al., 2000; Escudero et al., 2004); their *OAVs* are near or slightly above 0.1 units. Geraniol, with *OPT* of 36 µg/L, may also confer floral notes to the wines (Ribéreau-Gayon et al., 2000); nevertheless, its level determination was not possible except for L_{CT} .

Fermentative Compounds

This group comprises alcohols, fatty acid ethyl esters, esters of organic acids, acetates, volatile fatty acids and carbonyl compounds. Other compounds like volatile phenols (4-vinylguaicol, 4-vinylphenol and 4-ethylphenol), pantolactone and N-(2-phenylethyl)-acetamide are also included.

It is well known that concentration of individual fermentative compounds depends overall on the adopted winemaking procedures; additionally, most of the technological parameters, *e. g.* clarification practices, fermentation temperature, yeast strain, fining procedures, etc, can be controlled by the winemaker (Henschke and Jiranek 1993; Lubbers et al., 1993; Bayonove et al., 1998). In this way, although the 5 samples studied in this work were made exactly using the same procedures, comparison of monovarietal wines respecting groups of fermentative compounds does not assume an important role, as it happen with varietal compounds.

However, these compounds make up the background of the aroma of all these varietal wines. Fusel alcohols seem to have a positive influence on the fermentative aroma as their levels do not exceed 300 mg/L (Rapp and Mandery, 1986). Analysing the other groups of fermentative compounds, it can be observed that *Alvarinho* wines show significantly higher levels than *Loureiro* ones ($p < 0.05$) for fatty acid ethyl esters related to lipid metabolism (only A_{SS} and A_{CR}), acetates of fusel alcohols and volatile phenols having fermentative origin, particularly 4-vinylphenol and 4-vinylguaicol. Contrarily, esters of organic acids and 2-phenylethanol are slightly more abundant for L_{AV} , L_{CT} and A_{AV} wines than for A_{SS} and A_{CR} ones ($p < 0.05$).

Individually and considering the Odour Activity Values, it is interesting to observe that ethyl octanoate, having an olfactory perception threshold (*OPT*) of 5 µg/L (Escudero et al., 2004) with apple and fruity descriptors (Meilgaard, 1975), is the most powerful

flavour compound, with values of about 100 for *Loureiro* wines as well as for A_{AV} , and considerably above 100 for A_{SS} and A_{CR} ones. Also ethyl hexanoate ($OPT = 14 \mu\text{g/L}$), 3-methylbutyl acetate ($30 \mu\text{g/L}$) –except for L_{CT-} , ethyl butyrate ($20 \mu\text{g/L}$) – A_{SS} and A_{CR} , only–, and the sum 2-methyl-1-butanol + 3-methyl-1-butanol ($7000 \mu\text{g/L}$), present values above 10 (Escudero et al., 2004). The sum 2-methylbutyric acid + 3-methylbutyric acid ($34 \mu\text{g/L}$) also present OAV near 10, except for L_{AV} . Additionally, there were found 2 volatile fatty acids, hexanoic ($420 \mu\text{g/L}$) and octanoic ($500 \mu\text{g/L}$) having OAV between 5 and 10. It is well recognized that esters may contribute to the overall flavour of wines with fruity notes (*e. g.* papaya, banana and apple) while volatile fatty acids may give essentially unpleasant fatty acid, cheese and vegetable oil notes (Meilgaard, 1975; Escudero et al., 2004). Additionally, there were found 4 compounds having OAV values between 1 and 5: ethyl decanoate ($200 \mu\text{g/L}$; fruity, apple, fatty acid), 2-phenylethanol ($7500 \mu\text{g/L}$; roses), ethyl 3-methylbutyrate ($3 \mu\text{g/L}$; fruity, apple) and decanoic acid ($1000 \mu\text{g/L}$; waxy, rancid, soapy) (Salo, 1970; Meilgaard, 1975; Escudero et al., 2004).

As referred for varietal compounds, and considering those fermentative compounds with OAV between 0.1 and 1 units, 1-hexanol ($OPT = 8000 \mu\text{g/L}$; coconut, green leaves descriptors), ethyl 2-methylbutyrate ($18 \mu\text{g/L}$; fruity), 4-vinylguaiacol ($130 \mu\text{g/L}$; phenolic, clove, smoky) and 4-vinylphenol ($180 \mu\text{g/L}$; stramonium, almond shell) may contribute to the overall flavour of these wines (Meilgaard, 1975; Boidron et al., 1988; Escudero et al., 2004)

Glycosidically Bound Composition of *Loureiro* and *Alvarinho* Wines

Glycosidically bound compounds were eluted after the volatiles from the XAD-2 column, and the aglycons released from these extracts with adequate glycosidase activities were analyzed by GC-MS, as reported previously (Voirin et al 1992; Aubert et al., 1997). That allowed the identification and quantification of 77 compounds belonging to C_6 -compounds (6), alcohols (15), monoterpenic alcohols (7), monoterpenic oxides and diols (14), C_{13} -norisoprenoids (15), volatile phenols (14), volatile fatty acids (5) and carbonyl compounds (1).

Table 3 shows the mean level obtained for each compound in the five samples analyzed. These levels were semi-quantitative data only, determined as 4-nonanol equivalents.

It can be observed that C_6 -compounds present negligible levels and there were not relevant differences between samples of the two varieties, except between L_{AV} and A_{SS} ($p < 0.05$). Respecting alcohols, it can be observed higher levels for L_{AV} wine, only.

Linalool (except for A_{AV}) and mainly geraniol present higher concentration for *Alvarinho* wines which is in agreement with that found in grapes (Oliveira et al., 2000). Total levels of monoterpenic alcohols in wines of both varieties are lower than in the corresponding grapes, indicating precursor hydrolysis and/or partial extraction of glycosidic compounds from grape to must. However, they are statistically ($p < 0.05$) more abundant for L_{AV} , A_{SS} and A_{CR} , which correspond to the recommended sub-regions for *Loureiro* and *Alvarinho* wines production, respectively.

Monoterpenic oxides and diols are more abundant in L_{AV} , A_{SS} and A_{CR} , as found for monoterpenic alcohols ($p < 0.05$). Isomer *trans* of furan linalool oxide is more abundant in L_{AV} wine, whereas *Alvarinho* wines are richer in isomer *cis*; also *p*-1-menthen-7,8-diol is characteristic of *Loureiro* wines, presenting L_{AV} the higher levels. The levels of (*Z*)-8-hydroxylinalool are significantly higher in A_{SS} and A_{CR} wines ($p < 0.05$), as found in grapes (12.0 $\mu\text{g/L}$ - L_{CT} , 13.8 $\mu\text{g/L}$ - L_{AV} , 82.2 $\mu\text{g/L}$ - A_{AV} , 183.3 $\mu\text{g/L}$ - A_{SS} , 162.0 $\mu\text{g/L}$ - A_{CR}); moreover, the ratio (*Z*)/(*E*) of 8-hydroxylinalool is significantly different for the two varieties ($p < 0.05$), with mean values of 0.82 ± 0.26 for *Loureiro* ($n=6$) and 4.88 ± 0.87 for *Alvarinho* ($n=9$), as found in grapes of the same samples (Oliveira et al., 2000). This ratio could be used to differentiate *Loureiro* from *Alvarinho* wines, in addition to the ratio (*E*)/(*Z*) of free 3-hexen-1-ol isomers.

As observed for monoterpenic compounds, C_{13} -norisoprenoids are more abundant in L_{AV} than in L_{CT} and in A_{CR} and A_{SS} than in A_{AV} ($p < 0.05$).

The levels of bound volatile phenols were low and generally lower than the corresponding free ones. This difference was much more important regarding the volatile fatty acids. These compounds found in the glycoside fractions could be analytical artefacts, as no such glycoside was ever identified in grape. Finally, the trace levels of benzaldehyde could be explained by the occurrence of mandelonitrile glycosides, but these compounds were also never reported in grapes.

Sensory Analysis of *Loureiro* and *Alvarinho* Wines

Loureiro wines were clear, both revealing a pale citrus colour. They were classified of medium quality respecting overall sensations, including olfactory and gustative ones ($L_{AV}=L_{CT}=3$; scale 0–5); L_{CT} and L_{AV} wines reveal similar characteristics. Statistically, reporting on global classification (mean values: $L_{CT}=13.8$ and $L_{AV}=13.5$; scale 0–20), there was no difference between the two wines ($F=0.292$, $p > 0.05$).

Alvarinho wines were clear and show a medium quality color, characterized as open straw. Respecting overall sensations, A_{AV} reveals a difference with A_{CR} and A_{SS} ; A_{SS} is slightly better, respecting gustative examination. Analysis of Variance on final

classification shows significant differences between wines ($F=6.513$, $p<0.01$); A_{AV} shows lower classification being different from the other two ($A_{AV}=13.6$; $A_{CR}=15.4$; $A_{SS}=15.6$). Final classification reflects the mentioned characteristics for the individual examinations, particularly the olfactive ($A_{AV}=3$; $A_{CR}=A_{SS}=4$) and the gustative ones ($A_{AV}=A_{CR}=3$; $A_{SS}=4$). It must be remarked that A_{AV} is made from grapes harvested outside the Monção sub-region, the only one recommend for *Alvarinho* wines production; A_{AV} also reveals a poor concentration, respecting free and bound aroma compounds (Table 2 and Table 3).

As can be observed in Figure 2, which represents the olfactory descriptors, wines from *Alvarinho* variety are characterized by a more intense tropical fruit, dried fruit and tree fruit characters, while *Loureiro* wines have a more pronounced citrus fruit aroma. These descriptors agree with results from chemical composition, namely those compounds presenting *OAV* near or above the unity.

In summary, the presented work showed that *Loureiro* wines are globally richer than *Alvarinho* ones respecting monoterpenic compounds in both free and glycosidically bound forms. Moreover, wines produced with grapes harvested at recommended sub-regions contain higher levels of the generality of volatiles and glycoconjugates. Pebble soil originated wines with lesser concentration compared to granitic soil.

Apart from compounds having fermentative origin, *e. g.* esters, alcohols, acids and some phenols, the varietal compounds which could influence particularly the aroma of these wines seem to be only linalool, Ho-trienol, α -terpineol and β -damascenone. Terpenols seem to be more important to *Loureiro* wines and the C_{13} -norisoprenoids for *Alvarinho* ones. Fermentation compounds seem to contribute in a larger extent to the aroma of *Alvarinho* wines.

The presented results also seem to indicate the possibility of discriminating *Loureiro* from *Alvarinho* wines by the ratio between (*E*) and (*Z*) isomers of 3-hexen-1-ol, in free form, and of 8-hydroxylinalool, in the glycosidically bound form. Nevertheless, additional studies, with a larger number of grape samples and various degrees of ripness may be conducted in order to confirm these evidences.

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Table 1. General analysis of *Loureiro* and *Alvarinho* wines

	<i>Loureiro</i>		<i>Alvarinho</i>		
	L _{CT}	L _{AV}	A _{AV}	A _{SS}	A _{CR}
Ethanol/(% vol.)	11.3	10.2	12.6	13.5	13.9
Reducing sugars/(g/L)	2.3	1.1	1.5	3.4	2.9
Total acidity*/(g/L)	9.3	10.6	11.1	7.6	6.9
Volatile acidity**/(g/L)	0.39	0.33	0.37	0.40	0.40
pH	2.87	2.81	3.02	3.03	3.06

nomenclature for L_{CT}, L_{AV}, A_{AV}, A_{SS} and A_{CR} was referred in Materials and Methods section

*, as tartaric acid

**, as acetic acid

Table 2. Mean levels* (C) with 95 % confidence limits for the volatile compounds found in *Loureiro* and *Alvarinho* wines

	roi	RI	L _{CT}		L _{AV}		A _{AV}		A _{SS}		A _{CR}	
			C/(µg/L)	±	C/(µg/L)	±	C/(µg/L)	±	C/(µg/L)	±	C/(µg/L)	±
C₆-compounds (5)												
1-hexanol	<i>a</i>	1348	722.0	38.8	976.8	109.4	806.2	77.1	739.5	152.0	686.9	221.3
(<i>E</i>)-3-hexen-1-ol	<i>a</i>	1358	166.0	12.5	182.7	11.6	54.3	5.3	46.6	4.9	44.8	16.9
(<i>Z</i>)-3-hexen-1-ol	<i>a</i>	1379	22.3	3.1	29.6	3.9	96.9	9.5	71.3	4.8	62.6	29.5
(<i>E</i>)-2-hexen-1-ol	<i>a</i>	1400	tr		0.2	0.7	tr		tr		—	
(<i>Z</i>)-2-hexen-1-ol	<i>a</i>	1410	1.9	0.3	2.0	0.5	1.2	0.4	0.8	0.1	0.7	0.3
total			912.2		1191.3		958.6		858.2		795.0	
Alcohols (24)												
2-methyl-3-buten-2-ol	<i>a</i>	1068	5.2	3.2	6.7	2.8	?		3.7	0.9	?	
2-methyl-1-propanol	<i>a</i>	1082	991.3	509.8	775.1	100.2	1733.5	183.3	1067.2	344.2	1342.8	788.2
1-butanol	<i>a</i>	1140	23.2	13.5	18.3	1.8	48.4	4.8	50.0	15.0	85.3	55.5
1-penten-3-ol	<i>a</i>	1162	tr		tr		tr		tr		tr	
4-methyl-2-pentanol	<i>a</i>	1164	49.5	16.2	41.6	10.6	56.7	8.0	52.4	11.7	50.0	20.4
2-methyl-1-butanol + 3-methyl-1-butanol	<i>a</i>	1204	61467.3	22370.4	54741.1	12317.2	78960.6	37919.4	71637.3	29248.7	67852.1	30478.6
3-methyl-3-buten-1-ol	<i>a</i>	1243	4.1	1.7	3.6	0.9	6.1	0.4	4.1	1.6	5.7	1.6
1-pentanol	<i>a</i>	1244	5.2	1.2	6.5	2.9	14.4	1.1	10.0	4.5	15.2	9.1
2-methyl-1-pentanol	<i>b,c</i>	1298	0.3	0.5	0.6	0.1	—		—		—	
4-methyl-1-pentanol	<i>a</i>	1309	22.6	4.9	24.3	3.7	19.0	4.2	32.5	4.9	20.9	8.3
(<i>Z</i>)-2-penten-1-ol	<i>a</i>	1313	0.7	0.2	0.3	0.1	1.0	0.4	0.4	0.3	0.7	0.8
3-methyl-2-buten-1-ol + 2-heptanol	<i>a</i>	1316	2.3	0.5	2.8	0.7	1.9	0.4	1.3	0.3	1.8	1.0
3-methyl-1-pentanol	<i>a</i>	1322	76.8	7.3	54.5	29.1	53.7	3.5	113.7	8.7	74.2	34.8
3-ethoxy-1-propanol	<i>a</i>	1369	44.8	1.5	58.2	7.4	108.1	10.6	54.2	11.5	127.9	79.7
1-octen-3-ol	<i>a</i>	1445	0.9	0.5	1.0	0.4	1.2	0.2	0.6	0.3	0.5	0.1
1-heptanol	<i>a</i>	1449	17.9	2.3	14.7	0.9	41.1	1.4	12.3	2.8	7.5	1.4
2-nonanol	<i>a</i>	1541	0.8	0.3	1.0	0.3	1.8	0.5	2.7	5.1	2.2	1.6
1-octanol	<i>a</i>	1552	7.4	1.5	13.5	3.1	8.7	0.8	8.3	0.6	7.8	1.0
3-(methylthio)-1-propanol	<i>a</i>	1709	145.2	6.8	79.8	11.8	80.8	7.6	98.5	20.6	54.1	36.0
benzyl alcohol	<i>a</i>	1869	15.5	1.7	18.2	8.3	10.8	3.6	13.7	1.8	9.5	2.5
2-phenylethanol	<i>a</i>	1908	37117.9	14846.1	23561.6	3908.8	21167.5	4985.5	15894.8	6174.5	16610.0	5182.0
tyrosol	<i>a</i>	3008	138.9	51.4	152.1	30.8	68.4	30.5	123.0	30.0	98.3	44.3
total			100137.8		79575.5		102383.7		89180.7		86366.5	
total**			1552.6		1272.8		2255.6		1648.6		1904.4	
Fatty acid ethyl esters – lipid metabolism (6)												
ethyl butyrate	<i>a</i>	1032	99.6	8.1	141.7	4.7	124.4	15.7	211.2	28.6	246.6	12.4
ethyl hexanoate	<i>a</i>	1234	312.7	12.1	422.8	51.1	324.9	26.9	488.5	46.4	621.9	75.8
ethyl octanoate	<i>a</i>	1434	468.9	22.8	545.5	48.3	510.4	25.0	672.7	170.3	861.9	247.3
ethyl decanoate	<i>a</i>	1636	124.2	5.7	107.1	16.8	155.6	11.5	240.1	104.9	256.7	98.1
ethyl 9-decenoate	<i>b,c</i>	1688	65.5	0.7	52.7	8.5	93.7	6.6	67.5	28.2	55.4	18.3
ethyl dodecanoate	<i>a</i>	1855	2.5	1.7	3.8	1.8	6.1	0.6	6.3	4.6	8.3	5.1
total			1073.4		1273.6		1215.1		1686.3		2050.8	
Fatty acid ethyl esters - nitrogen metabolism (3)												
ethyl 2-methylbutyrate	<i>a</i>	1049	5.6	1.9	3.2	1.4	1.8	0.7	5.1	2.5	2.8	1.5
ethyl 3-methylbutyrate	<i>a</i>	1066	12.4	5.1	8.5	2.2	7.8	1.1	11.3	0.8	9.3	1.7
ethyl benzeneacetate	<i>a</i>	1782	5.3	1.4	2.0	0.6	1.7	0.4	2.8	0.8	1.2	0.4
total			23.3		13.7		11.3		19.2		13.3	
Esters of organic acids (10)												
ethyl pyruvate	<i>a</i>	1267	8.9	3.0	7.1	1.6	9.1	4.3	9.6	0.0	6.0	4.4
ethyl lactate	<i>a</i>	1338	456.8	51.0	472.3	103.5	635.6	31.8	437.7	72.9	573.2	132.5

ethyl 3-hydroxybutyrate	<i>a</i>	1512	29.4	2.6	36.2	4.2	71.2	8.6	58.4	7.9	98.7	61.1
diethyl malonate	<i>a</i>	1574	1.7	0.1	1.7	0.2	4.2	0.2	3.1	0.2	3.3	0.9
ethyl 2-furoate	<i>a</i>	1618	2.0	0.6	2.2	0.5	3.1	0.6	4.4	1.3	4.8	0.9
diethyl succinate	<i>a</i>	1672	1192.6	27.5	896.4	7.1	977.2	77.9	966.3	101.5	758.7	68.2
diethyl glutarate	<i>a</i>	1774	6.4	0.7	6.2	0.2	11.2	0.5	8.2	1.1	12.2	2.7
diethyl malate	<i>a</i>	2037	2351.7	275.4	2477.7	292.6	3609.2	243.6	1248.8	108.7	1152.1	91.7
diethyl tartrate	<i>a</i>	2351	32.2	10.8	43.2	10.4	4.0	1.6	10.6	5.2	8.0	4.1
monoethyl succinate	<i>a</i>	2377	3941.4	712.0	3473.8	525.2	2215.1	947.8	3305.1	604.4	2544.1	125.0
total			8023.1		7416.8		7539.9		6052.2		5161.1	
Acetates (7)												
2-methylpropyl acetate	<i>a</i>	1009	6.2	4.7	11.3	6.6	19.8	6.9	16.9	12.0	40.3	19.3
butyl acetate	<i>a</i>	1071	2.6	1.5	tr		6.7	1.0	1.5	1.0	4.4	2.5
3-methylbutyl acetate	<i>a</i>	1125	209.0	24.6	331.3	16.4	701.4	120.1	823.5	36.8	1584.6	344.8
hexyl acetate	<i>a</i>	1272	23.2	0.8	47.1	1.4	56.9	1.8	64.5	8.8	108.4	19.2
(<i>Z</i>)-3-hexenyl acetate	<i>a</i>	1307	1.8	0.8	2.7	0.7	1.2	0.2	1.3	0.2	2.9	0.3
2-phenylethyl acetate	<i>a</i>	1810	145.0	12.0	93.2	8.5	152.4	4.5	189.4	10.1	279.9	27.8
tryptophyl acetate	<i>b,c</i>	3369	25.0	3.9	6.1	1.4	—		3.9	1.7	5.2	1.1
total			412.8		491.7		938.4		1101.0		2025.7	
Monoterpenic alcohols (8)												
myrcenol	<i>b,c</i>	1533	4.7	2.3	8.0	5.6	—		—		—	
linalool	<i>a</i>	1541	58.1	2.5	68.6	5.3	27.3	1.4	78.4	5.5	49.6	8.1
4-terpineol	<i>a</i>	1597	1.3	0.3	1.0	0.1	0.6	0.3	0.8	0.4	0.4	0.5
Ho-trienol	<i>a</i>	1605	50.6	9.8	102.0	24.7	35.6	6.2	60.8	15.9	44.0	11.4
α -terpineol	<i>a</i>	1691	77.0	3.3	111.6	11.5	23.9	1.9	67.8	8.3	41.1	11.9
citronellol	<i>a</i>	1760	2.1	0.5	2.6	0.4	2.5	0.6	4.0	0.8	3.0	1.8
nerol	<i>a</i>	1793	3.3	3.6	3.1	1.3	3.0	1.3	5.7	2.1	3.1	1.7
geraniol	<i>a</i>	1847	11.1	21.1	?		?		?		?	
total			208.2		296.9		92.9		217.5		141.2	
Monoterpenic oxides and diols (14)												
<i>trans</i> -furan linalool oxide	<i>a</i>	1436	17.4	2.8	29.1	3.3	9.7	3.6	13.6	5.8	17.0	3.8
<i>cis</i> -furan linalool oxide	<i>a</i>	1464	5.9	0.4	11.5	0.1	2.4	0.3	3.6	0.9	3.0	1.3
neroloxide	<i>b,c</i>	1467	11.8	0.6	16.3	0.6	8.2	1.2	11.6	1.7	9.9	3.4
<i>trans</i> -pyran linalool oxide	<i>a</i>	1732	62.7	15.2	73.3	7.8	17.2	1.9	7.0	1.1	12.3	1.7
<i>cis</i> -pyran linalool oxide	<i>a</i>	1756	11.0	1.5	17.9	2.8	1.1	0.3	0.5	0.2	0.7	0.2
<i>exo</i> -2-hydroxy-1,8-cineole	<i>a</i>	1857	0.9	0.4	0.9	0.5	—		—		—	
3,7-dimethylocta-1,5-dien-3,7-diol	<i>a</i>	1935	186.4	30.2	297.7	32.4	70.6	15.4	217.1	17.3	209.4	19.5
linalool hydrate	<i>a</i>	1967	29.9	9.7	47.6	5.3	5.1	1.9	15.1	5.9	11.9	2.3
terpin hydrate	<i>a</i>	2087	4.4	0.2	11.0	3.5	tr		3.2	1.1	2.7	0.8
3,7-dimethylocta-1,7-dien-3,6-diol	<i>a</i>	2121	28.9	4.2	64.4	7.2	5.8	1.8	12.3	6.0	11.9	5.0
citronellol hydrate	<i>a</i>	2196	1.0	1.3	1.0	0.2	0.8	0.5	0.7	0.4	0.6	0.3
8-hydroxy-6,7-dihydro-linalool	<i>a</i>	2197	0.8	0.3	1.1	0.6	0.7	0.1	1.9	0.9	1.6	0.1
(<i>Z</i>)-8-hydroxy-linalool	<i>a</i>	2302	1.1	1.1	2.0	0.4	1.1	0.5	15.8	4.2	11.4	0.9
<i>p</i> -1-menthen-7,8-diol	<i>a</i>	2517	1.0	0.7	1.4	0.6	—		—		—	
total			363.2		575.2		122.7		302.4		292.4	
C₁₅-norisoprenoids (13)												
vitispirane I	<i>a</i>	1524	tr		1.4	0.7	1.0	0.4	2.1	0.5	1.8	0.5
vitispirane II	<i>a</i>	1527	tr		0.8	0.3	0.8	0.2	1.8	1.1	1.5	0.4
1,1,6-trimethyl-1,2-dihydronaphthalene	<i>b,c</i>	1741	—		tr		—		—		—	
β -damascenone	<i>a</i>	1816	1.1	0.3	1.3	0.3	2.1	0.2	3.4	0.2	2.3	0.7
3-hydroxy- β -damascenone	<i>a</i>	2529	tr		tr		0.4	2.4	0.7	0.2	tr	
3-hydroxy-7,8-dihydro- β -ionone	<i>a</i>	2553	—		tr		—		—		—	
megastigm-7-ene-3,9-diol	<i>d</i>	2568	1.9	0.7	4.4	0.9	1.1	1.6	4.8	0.5	3.9	3.1
3-oxo- α -ionol	<i>a</i>	2628	9.8	2.9	7.6	1.5	8.2	2.6	7.0	0.7	8.4	2.7
3-hydroxy-7,8-dihydro- β -ionol	<i>a</i>	2654	0.5	2.3	0.6	0.3	1.1	1.0	0.8	0.5	0.6	0.4

3-oxo-7,8-dihydro- α -ionol	<i>a</i>	2702	tr	0.5	0.0	0.6	0.1	0.9	0.3	tr	
3-hydroxy-5,6-epoxy- β -ionone	<i>a</i>	2721	—	—	—	—	—	tr	—	—	
3-hydroxy-7,8-dehydro- β -ionol	<i>a</i>	2742	—	tr	—	0.3	1.4	0.7	0.1	tr	
vomifoliol		3139	1.4	0.6	2.4	0.3	tr	tr	—	0.7	0.4
total			14.7		19.0			15.6		22.2	
Volatile phenols (13)											
methyl salicylate	<i>a</i>	1770	tr	tr	tr	tr	tr	tr	tr	tr	
guaiacol	<i>a</i>	1852	1.5	2.1	1.2	1.5	1.5	2.8	2.7	2.0	1.9
phenol	<i>a</i>	2006	2.1	1.1	1.6	0.5	2.4	1.6	1.1	0.2	1.6
4-ethylphenol	<i>a</i>	2172	0.9	0.6	0.5	0.3	1.3	0.3	1.2	0.5	2.1
4-vinylguaiacol	<i>a</i>	2192	21.2	6.7	24.5	1.3	44.8	7.5	62.9	12.9	85.3
4-vinylphenol	<i>a</i>	2409	tr	tr	tr	tr	17.7	5.2	20.9	5.9	18.0
vanillin	<i>a</i>	2560	0.9	2.6	—	—	tr	tr	tr	tr	4.4
methyl vanillate	<i>a</i>	2601	tr	tr	tr	tr	11.3	9.1	7.9	1.6	8.0
acetovanillone	<i>a</i>	2635	9.8	2.1	10.8	1.7	12.3	1.0	11.6	0.7	11.8
3,4-dimethoxyphenol	<i>a</i>	2759	—	—	—	—	0.3	0.4	0.7	0.1	0.5
2-(4'-guaiaicyl)-ethanol	<i>a</i>	2844	2.4	1.6	6.7	2.5	1.0	0.1	2.5	0.2	tr
3,4,5-trimethoxybenzyl alcohol	<i>a</i>	2879	3.9	1.2	5.1	1.8	5.0	0.1	8.0	0.8	8.3
3,4,5-trimethoxyphenol	<i>a</i>	3060	0.6	0.3	2.6	1.2	1.0	0.7	1.9	0.8	2.1
total			43.3		53.0			98.6		121.4	
Volatile fatty acids – lipid metabolism (8)											
acetic acid	<i>a</i>	1453	12.8	8.4	9.4	4.2	17.6	10.1	16.1	6.1	18.9
butanoic acid	<i>a</i>	1626	103.0	8.5	125.3	20.1	135.8	15.1	139.2	33.5	168.7
hexanoic acid	<i>a</i>	1841	2320.5	197.6	3045.0	497.4	2845.6	155.2	3643.4	326.3	4003.5
(<i>E</i>)-2-hexenoic acid	<i>a</i>	1964	16.8	1.9	23.0	5.9	18.6	3.9	16.9	3.4	18.4
octanoic acid	<i>a</i>	2057	2668.4	156.0	3565.4	264.1	2971.1	331.0	3419.2	218.5	4403.7
decanoic acid	<i>a</i>	2269	1288.8	35.6	1418.4	111.3	1193.6	82.2	1542.7	311.6	1579.7
dodecanoic acid	<i>a</i>	2481	9.5	0.3	12.6	3.9	12.2	3.0	13.7	4.9	17.3
hexadecanoic acid	<i>a</i>	2903	tr	tr	tr	tr	tr	tr	tr	tr	tr
total			6419.8		8199.1		7194.5		8791.2		10210.2
Volatile fatty acids – nitrogen metabolism (3)											
2-methylpropanoic acid	<i>a</i>	1567	58.6	6.3	52.1	7.6	75.5	8.0	56.7	10.8	63.5
3-methylbutyric acid + 2-methylbutyric acid	<i>a</i>	1667	359.7	30.6	206.9	16.7	318.9	21.7	311.7	50.4	238.3
total			418.3		259.0		394.4		368.4		301.8
Carbonyl compounds (4)											
2-nonanone	<i>a</i>	1386	—	0.2	1.5	0.1	2.1	0.3	2.7	0.5	1.8
2-furaldehyde	<i>a</i>	1460	0.5	0.0	0.3	0.3	1.6	0.4	0.6	0.1	0.8
benzaldehyde	<i>a</i>	1517	7.0	0.6	7.1	0.7	7.6	0.3	7.9	0.8	7.5
4-ethylbenzaldehyde	<i>a</i>	1703	26.2	3.4	25.7	8.7	26.9	1.1	27.2	5.1	26.0
total			33.7		34.6		38.2		38.4		36.1
Other (2)											
pantolactone	<i>a</i>	2026	3.4	2.6	6.9	2.0	6.6	0.6	4.8	1.2	4.7
N-(2-phenylethyl)-acetamide	<i>a</i>	2575	171.7	3.4	89.5	6.5	90.6	10.2	53.5	8.2	21.2
total			175.1		96.4		97.2		58.3		25.9
Total			120063.1		100956.1		123321.9		110295.5		109097.0
Total**			21477.9		22653.4		23193.8		22763.4		24634.9

roi, reliability of identification

RI, linear retention index on column CP-Wax 52 CB

a, identified by comparing retention time and mass spectra with those of a pure standard

b, identified by comparing retention index with published data

c, identified by comparing mass spectra with published data

d, tentative identification: molecular weight = 212 g/mol; *m/z* (%) = 43 (100.0), 41 (42.8), 39 (30.9), 29 (25.2), 79 (20.4), 55 (18.2), 97 (18.0), 120 (16.6), 94 (15.4), 77 (14.4); other characteristic ions, *m/z* (%) = 212 (int, M⁺), 179 (int, M⁺-H₂O-CH₃), 161 (int, M⁺-2H₂O-CH₃)

*, levels were determined as 4-nonanol equivalents

** , without 2-methyl-1-butanol, 3-methyl-1-butanol and 2-phenylethanol

?, quantification not possible

—, not detected

tr, traces

Table 3. Mean levels* (C) with 95 % confidence limits for the volatile aglycons of glycosidically bound compounds found in *Loureiro* and *Alvarinho* wines

	roi	RI	L _{CT}		L _{AV}		A _{AV}		A _{SS}		A _{CR}	
			C/(µg/L)	±	C/(µg/L)	±	C/(µg/L)	±	C/(µg/L)	±	C/(µg/L)	±
C₆-compounds (6)												
hexanal	a	1089	0.2	0.2	tr		tr		0.1	0.0	0.3	0.2
1-hexanol	a	1348	8.1	3.9	10.0	2.1	8.4	3.1	6.0	0.5	8.7	6.3
(E)-3-hexen-1-ol	a	1358	tr		0.2	0.1	tr		tr		tr	
(Z)-3-hexen-1-ol	a	1379	0.8	0.5	1.2	0.3	1.5	0.5	0.8	0.1	0.9	0.5
(E)-2-hexen-1-ol	a	1400	2.9	1.4	1.9	0.5	1.2	0.2	0.5	0.0	0.8	0.2
(Z)-2-hexen-1-ol	a	1410	—		tr		—		—		—	
total			12.0		13.1		11.1		7.4		10.7	
Alcohols (15)												
2-methyl-1-propanol	a	1082	2.1	2.1	2.2	1.2	5.2	2.1	0.9	0.1	0.8	0.4
1-butanol	a	1140	0.7	0.6	0.9	0.4	2.3	1.2	1.3	0.5	2.5	1.4
2-methyl-1-butanol + 3-methyl-1-butanol	a	1204	57.2	19.7	33.7	17.6	77.4	15.9	17.1	1.5	22.8	12.3
3-methyl-3-buten-1-ol + 1-pentanol	a	1243	1.9	1.0	3.2	0.9	1.9	0.6	1.5	0.5	2.6	1.6
(Z)-2-penten-1-ol + 3-methyl-2-buten-1-ol + 2-heptanol	a	1316	1.1	1.0	1.8	0.5	1.0	0.4	1.2	0.5	1.6	1.1
1-octen-3-ol	a	1445	0.7	0.1	0.6	0.4	0.9	0.3	0.4	0.0	1.1	0.4
1-heptanol	a	1449	?		0.5	0.1	?		0.3	0.1	?	
1-octanol	a	1552	0.6	0.5	0.8	0.3	0.4	0.0	0.8	0.0	0.7	0.5
1-phenylethanol	a	1809	1.3	0.3	2.0	0.7	0.9	0.1	0.6	0.1	1.0	0.7
benzyl alcohol	a	1869	68.1	36.7	190.1	43.6	52.9	18.8	73.2	30.6	79.5	66.3
2-phenylethanol	a	1908	78.9	33.0	133.6	13.1	64.9	14.9	48.3	8.1	59.9	46.1
Total			212.6		369.4		207.8		145.6		172.5	
Monoterpenic alcohols (7)												
Linalool	a	1541	1.1	0.7	0.7	0.1	1.3	0.4	4.4	0.5	4.0	2.7
4-terpineol	a	1597	tr		tr		—		—		—	
Ho-trienol	a	1605	1.5	0.5	4.7	1.0	2.3	0.8	5.4	0.2	4.3	2.6
α-terpineol	a	1691	7.6	3.6	15.1	2.5	0.5	0.2	2.3	0.1	1.4	0.6
citronellol	a	1760	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.0	tr	
nerol	a	1793	1.4	0.3	3.9	0.5	1.0	0.4	3.0	0.1	2.0	1.4
geraniol	a	1847	4.7	0.5	4.1	0.4	11.2	3.2	19.1	1.3	18.5	5.3
total			16.5		28.6		16.4		34.3		30.2	
Monoterpenic oxides and diols (14)												
<i>trans</i> - furan linalool oxide	a	1436	34.8	16.6	56.7	8.9	15.2	4.9	18.6	0.5	30.1	19.2
<i>cis</i> - furan linalool oxide	a	1464	6.6	3.1	7.7	1.3	11.0	2.8	14.6	0.0	17.1	9.7
<i>trans</i> - pyran linalool oxide	a	1732	7.3	3.6	14.5	2.1	6.1	2.4	15.6	4.3	17.0	14.0
<i>cis</i> - pyran linalool oxide	a	1756	1.6	0.2	2.4	0.6	2.8	0.8	3.5	0.6	4.5	4.0
<i>exo</i> -2-hydroxy-1,8-cineole	a	1857	1.5	0.8	3.6	0.9	0.4	0.1	tr		0.6	0.4
3,7-dimethylocta-1,5-dien-3,7-diol	a	1935	13.9	5.7	11.4	1.9	16.5	16.8	16.3	1.2	30.1	13.5
linalool hydrate	a	1967	5.2	1.9	8.1	0.9	1.9	1.5	1.8	0.1	2.5	1.0
3,7-dimethylocta-1,7-dien-3,6-diol	a	2121	4.4	2.9	22.3	1.9	0.8	0.3	5.4	0.2	2.8	2.0
citronellol hydrate + 8-hydroxy-6,7-dihydro-linalool	a	2196	1.5	0.7	6.6	1.2	1.6	1.0	6.1	1.2	4.4	2.1
(E)-8-hydroxylinalool	a	2265	8.0	3.7	28.7	1.7	6.5	2.6	27.9	6.1	17.7	15.4
(Z)-8-hydroxylinalool	a	2302	8.2	2.8	17.2	2.3	25.1	12.5	123.7	28.6	111.5	90.8
geranic acid	a	2342	3.7	1.7	4.5	0.9	6.1	2.8	14.9	1.0	9.3	6.1
<i>p</i> -1-menthen-7,8-diol	a	2517	6.7	3.4	13.1	1.0	tr		1.8	0.1	0.8	0.4
total			103.4		196.8		94.0		250.2		248.4	
C₁₃-norisoprenoids (15)												
3,4-dihydro-3-oxo-actinidol I	a	2428	tr		1.0	0.5	0.6	0.7	0.9	0.3	1.0	1.0

3,4-dihydro-3-oxo-actinidol II	<i>a</i>	2463	1.1	0.9	3.8	1.3	1.6	0.6	2.0	0.6	2.1	1.9
3,4-dihydro-3-oxo-actinidol III	<i>a</i>	2466	2.0	0.9	6.8	1.2	2.2	0.9	2.5	0.8	3.2	2.8
3-hydroxy- β -damascone + 3,4-dihydro-3-oxo-actinidol IV	<i>a</i>	2529	9.1	3.8	15.3	1.5	12.6	3.1	21.3	1.6	16.4	10.9
3-hydroxy-7,8-dihydro- β -ionone	<i>a</i>	2553	2.1	2.0	8.8	1.8	tr		1.9	0.1	0.4	0.5
megastigm-7-ene-3,9-diol	<i>b</i>	2568	2.0	0.2	5.0	0.5	1.5	0.9	5.0	2.0	4.9	3.8
3-oxo- α -ionol	<i>a</i>	2628	22.0	11.3	48.1	4.9	24.1	9.4	47.3	14.2	53.3	39.2
3-hydroxy-7,8-dihydro- β -ionol	<i>a</i>	2654	6.6	3.3	21.7	1.5	1.6	0.7	4.2	2.2	3.4	2.4
4-oxo-7,8-dihydro- β -ionol	<i>a</i>	2673	4.5	2.9	9.0	0.4	2.5	0.4	4.2	0.5	2.7	0.5
3-oxo-7,8-dihydro- α -ionol	<i>a</i>	2702	3.7	2.7	7.9	2.2	7.0	0.8	11.7	1.6	12.4	10.1
3-hydroxy-5,6-epoxy- β -ionone	<i>a</i>	2721	<i>tr</i>		1.0	0.1	<i>tr</i>		0.2	0.0	<i>tr</i>	
3-oxo- α -retroionol	<i>a</i>	2735	<i>tr</i>		1.1	0.4	<i>tr</i>		0.7	0.1	0.5	0.1
3-hydroxy-7,8-dehydro- β -ionol	<i>a</i>	2742	3.8	1.9	7.1	0.7	6.4	1.8	8.6	1.6	7.8	6.9
vomifolol	<i>a</i>	3139	20.3	8.7	34.3	8.2	14.4	5.6	19.2	1.0	21.1	9.6
total			77.2		170.9		74.5		129.7		129.2	

Volatile phenols (14)

methyl salicylate	<i>a</i>	1770	1.5	1.2	2.3	0.7	1.2	0.4	1.9	0.3	2.2	1.5
guaiacol	<i>a</i>	1852	1.0	0.2	0.7	0.1	0.9	0.4	0.3	0.1	0.9	0.2
<i>o</i> -cresol + phenol	<i>a</i>	2005	0.8	0.4	1.7	0.4	0.9	0.4	1.4	0.1	0.8	0.8
<i>p</i> -cresol	<i>a</i>	2085	0.2	0.1	0.6	0.1	0.3	0.1	0.5	0.2	0.5	0.5
<i>m</i> -cresol	<i>a</i>	2093	0.2	0.1	0.3	0.2	0.2	0.1	0.3	0.2	0.2	0.1
eugenol	<i>a</i>	2165	0.9	0.1	1.7	0.6	1.7	0.8	3.2	0.1	2.5	1.9
vanillin	<i>a</i>	2560	<i>tr</i>		<i>tr</i>		<i>tr</i>		<i>tr</i>		<i>tr</i>	
methyl vanillate	<i>a</i>	2601	0.4	0.2	<i>tr</i>		<i>tr</i>		0.8	0.1	0.7	0.3
3,4-dimethoxyphenol	<i>a</i>	2759	<i>tr</i>		0.8	0.2	0.6	0.2	0.8	0.2	0.8	0.5
zingiberone	<i>a</i>	2805	<i>tr</i>		<i>tr</i>		<i>tr</i>		<i>tr</i>		<i>tr</i>	
2-(4'-guaiaicyl)-ethanol	<i>a</i>	2844	0.7	0.9	3.5	0.5	0.5	0.1	0.9	0.2	1.0	0.3
3,4,5-trimethoxybenzyl alcohol	<i>a</i>	2879	1.8	1.7	3.0	1.5	4.0	2.7	2.8	0.1	3.0	2.6
3,4,5-trimethoxyphenol	<i>a</i>	3060	2.7	1.4	5.5	1.0	2.0	1.5	3.9	0.2	3.0	1.9
total			10.2		20.1		12.3		16.8		15.6	

Volatile fatty acids (5)

acetic acid	<i>a</i>	1453	6.6	2.8	3.5	3.1	7.7	2.5	5.0	0.3	4.8	1.6
butyric acid	<i>a</i>	1626	0.8	0.3	0.5	0.1	1.0	0.2	0.5	0.1	1.0	0.2
hexanoic acid	<i>a</i>	1841	8.6	0.4	10.5	2.7	11.0	4.0	9.8	0.5	19.4	9.1
octanoic acid	<i>a</i>	2057	8.7	4.6	11.6	1.3	11.0	2.2	9.4	0.0	12.6	7.0
hexadecanoic acid	<i>a</i>	2903	<i>tr</i>		<i>tr</i>		<i>tr</i>		<i>tr</i>		<i>tr</i>	
total			24.7		26.1		30.7		24.7		37.8	

Carbonyl compounds (1)

benzaldehyde	<i>a</i>	1517	0.5	0.2	0.9	0.3	0.5	0.3	0.3	0.1	0.5	0.2
total			0.5		0.9		0.5		0.3		0.5	

TOTAL 416.6 825.9 447.3 609.0 644.9

m, reliability of identification

*R*_I, linear retention index on column CP-Wax 52 CB

a, identified by comparing retention time and mass spectra with those of a pure standard

b, tentative identification: molecular weight = 212 g/mol; *m/z* (%) = 43 (100.0), 41 (42.8), 39 (30.9), 29 (25.2), 79 (20.4), 55 (18.2), 97 (18.0), 120 (16.6), 94 (15.4), 77 (14.4); other characteristic ions, *m/z* (%) = 212 (int, M⁺), 179 (int, M⁺-H₂O-CH₃), 161 (int, M⁺-2H₂O-CH₃)

*, levels were determined as 4-nonanol equivalents

—, not detected

tr, traces

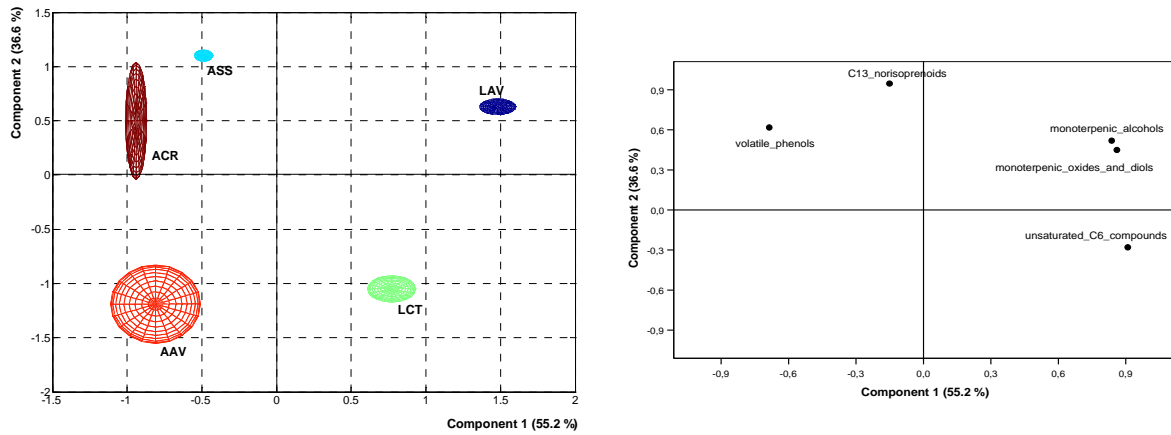


Figure 1. Discrimination of *Loureiro* and *Alvarinho* wines by principal component analysis applied to varietal compounds (by groups) of the free volatile fraction. Ellipsoids represent the 95 % confidence level.

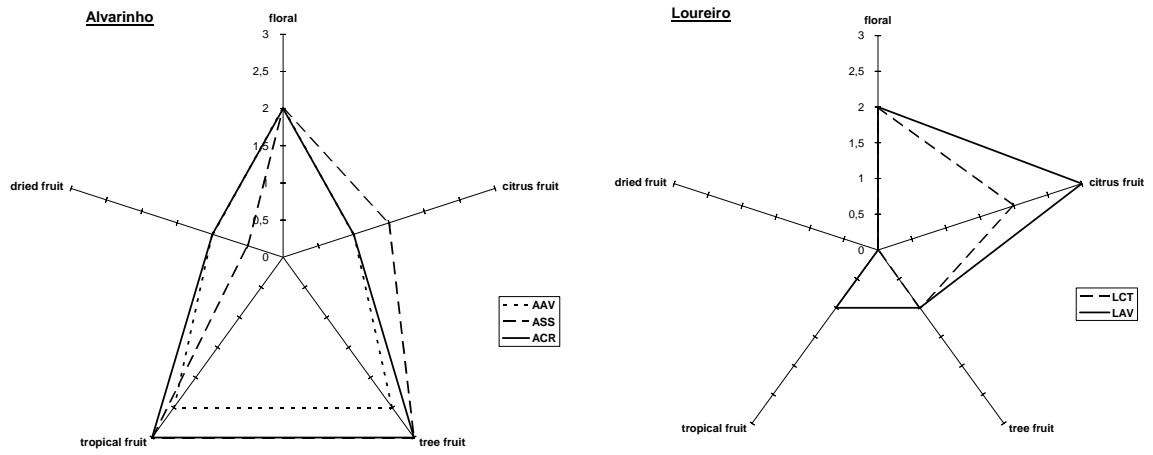


Figure 2. Aromatic descriptor intensity (median) for *Loureiro* and *Alvarinho* wines.