Volatile and Sensory Characterization of Xarel.lo White Wines

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ABSTRACT

A comprehensive study based on the profiling and quantification of the volatile composition and the application of descriptive sensory analysis to twenty-five commercial monovarietal white wines (*var. Xarel.lo*) from different vintages and from representative wine cellars along the Penedés region (Catalonia, Spain) was performed in order to characterize representative wines that are being commercialised under the O.D. Penedés. In addition, relationships between the instrumental (volatiles) and sensory variables were found through the application of partial least square regression. The results showed great differences between younger wines and wines that underwent the *crianza* (or aging) process. The first ones were characterized by a marked *fruity* and *floral* odor and *fresh* taste, while the second group of wines was characterized by more complex sensory attributes such as *toasted*, *spicy* and *compote* odour attributes. These differences in sensory characteristics were related to a higher content of higher alcohol acetates and ethyl and methyl esters of fatty acids in wines included in the first group, while the second group was characterized by a lower concentration of esters, but higher concentration of compounds related to wine aging, such as furfural, 5-methylfurfural and vitispiranes.

Keywords: *Xarel.lo* white wines, volatile compounds, descriptive sensory analysis, partial least square regression (PLS).

INTRODUCTION

In recent years, the wine industry has made a great effort to improve autochthonous grape varieties to produce varietal wines with distinctive characteristics, which will diversify the current wine market, and the recovery of native grapes. In this sense, the sensory and chemical characterization of monovarietal wines seems to be an outstanding task in order to find peculiar and distinctive characteristics between wines.

Penedés is an important viticultural and oenological area on the northeast coast of Spain, where some white native grape varieties such as Muscatel, Malmsey, Xarel.lo and Macabeo are grown ^[1]. Among them, the Xarel.lo variety has been traditionally preferred, together with other white grapes varieties for the production of base wines for Cava (Spanish sparkling wine produced by the *traditional* method) ^[2]. In fact, there are several studies in the literature that have focused on the influence of this variety on the chemical and foaming characteristics of Cava wines ^[3-7].

Currently, Xarel.lo is the white grape variety most cultivated in the Penedés (www.dopenedes.es) and the number of monovarietal Xarel.lo wines produced by using different winemaking technologies and commercialized under the Origen Denomination (O.D.) Penedés has greatly increased. However, little is known about its chemical and sensory characteristics. López-Tamames and co-workers ^[4], showed differences in the free and bound volatile composition of musts from typical red and white Spanish grapes, including two Xarel.lo musts from Penedés. However, in the case of wines, besides the work performed by Campo and collaborators ^[8] which included two Xarel.lo wines, only De la Presa and Noble ^[9] and De la Presa and co-workers ^[1], respectively, performed the sensory and chemical characterization of wines from this variety. In the latter works, the authors showed sensory and chemical differences in wines from this variety compared to white wines from other typical grapes from Penedés such as

Macabeo and Parellada also used for Cava production. However, the rather small number of samples employed in these previous studies (two wines of each variety) may not be enough to represent the sensory and chemical characteristics of the Xarel.lo wines from different winemaking technologies currently on the market.

Therefore, the aim of the present study is to characterize representative monovarietal Xarel.lo wines that are being commercialised under the O.D. Penedés using both descriptive sensory and volatile analyses. The final goal will be to find relationships between the instrumental and sensory variables, which may helps in the development of winemaking and viticultural practices that lead characteristic sensory profiles.

MATERIALS AND METHODS

Wine samples

Twenty-five commercial monovarietal white wines (*var. Xarel.lo*) from representative wine cellars from the Penedés region (Catalonia, Spain) and different vintages were analysed. All the wines were selected by the Institut Català de la Vinya y el Vi (INCAVI) and represent the majority of the Xarel.lo wines from the Penedés region available on the market. The wines used in this study along with their respective vintages and global composition are shown in **Table 1**. All of them showed an adequate composition which fits the regulations of the Penedés O.D.

Chemicals and Reagents

Ethyl hexanoate and ethyl decanoate were provided by Merck (Darmstadt, Germany); acetaldehyde, ethyl acetate, methanol, 1-propanol, isobutanol, isoamyl alcohols (2- and 3-methyl-1-butanol), ethyl lactate, 3-pentanol (IS), isoamyl acetate, ethyl butanoate, hexyl acetate, 1-hexanol, (Z)-3-hexen-1-ol, ethyl octanoate, furfural,

linalool, diethyl succinate, α -terpineol, β -damascenone, 2-phenylethanol, phenylethyl acetate, methyl nonanoate and ethanol HPLC grade were from Sigma Aldrich; α -limonene, 5-methylfurfural, ethyl dodecanoate were from Fluka; hexanoic acid, octanoic acid and decanoic acid were supplied by Scharlau (Barcelona, Spain).

Analysis of major volatile compounds

Analysis of the major volatile compounds was performed by direct injection of 1 μ L of wine spiked with the internal standard (0.06 g L⁻¹ of 3-pentanol in ethanol 10 % v:v) in an Agilent 5890 (Agilent, Palo Alto, CA) gas chromatograph under the following conditions: Carbowax 20M fused-silica capillary column (30 m x 0.25 mm I.D), coated with a stationary phase of 0.25 μ m of thickness (Quadrex, New Haven, USA); split/splitless injector; FID detector; injector and detector temperature were 220 °C. The initial oven temperature was 40 °C (10 minutes hold). The temperature gradient was 7 °C/min to 150 °C, 30 °C/min to 210 °C (2 minutes hold). The carrier gas was helium (12.5 psi, split 1/15). The compounds determined by this method were acetaldehyde, ethyl acetate, methanol, 1-propanol, isobutanol, 2-methyl-1-butanol, 3-methyl-1-butanol and ethyl lactate. Quantitative data were obtained by calculating the relative peak area in relation to that of the internal standard (3-pentanol). For quantification purposes calibration curves (five levels of concentration covering the concentration ranges expected in wines) of each standard compound in synthetic wines were made and analysed under the same conditions as the samples.

Analysis of minor volatile compounds

Analysis of minor volatile compounds was performed by HS-SPME-GCMS. Eight mL of wine was placed in a 20 mL headspace vial that was sealed with a

PTFE/Silicone septum (Supelco, Bellefonte, PA). Samples were left in a water bath at 40 °C for 10 minutes. Before the analysis, 50 µL of a solution of methyl nonanoate in absolute ethanol at a concentration of 5 mg L⁻¹ was added to the wine to be used as an internal standard. The extraction was performed with the exposure of a StableFlex 85 µm carboxen-polydimethylsiloxane, CAR-PDMS fibre (Supelco) to the headspace of the sample for 20 minutes at 40 °C and constantly stirring (500 rpm). After the extraction, the fibre was removed from the sample vial and desorbed in the GC injector port in splitless mode for 10 minutes. All the analyses were performed in duplicate.

An Agilent 6890N GC system with a split/splitless injector and interfaced with an Agilent 5973N mass spectrometer was used for sample analysis. The injector was set at 280 °C. Agilent MSD ChemStation Software (D.01.02 16 version) was used to control the system. For separation, a Carbowax 10M fused silica capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness) Quadrex Co. (Woodbridge, CT) was used. Helium was the carrier gas (7 psi). The oven temperature was programmed as follows: 40 °C as initial temperature, held for 10 minutes, then increased to 250 °C at 4 °C/min, then held for 10 minutes.

For the MS system, the temperatures of the transfer line, quadrupole and ionization source were 270 °C, 150 °C and 230 °C respectively; electron impact mass spectra was recorded at 70 eV ionization voltages and the ionization current was 10 µA. The acquisitions were performed in Scan mode (from 35 to 450 amu). Peak identification was carried out by comparison of retention times and mass spectral data with those of reference compounds. Compounds, for which it was not possible to find reference volatiles, were tentatively identified by comparison of their mass spectra with the mass spectral data in Wiley 6.0 and NIST libraries and by comparison of the calculated retention index with those published in the literature.

Quantitative data were obtained by calculating the relative peak area (or TIC signal) in relation to that of the internal standard (methyl-nonanoate). For quantification purposes, calibration curves (five levels of concentration covering the concentration ranges expected in wines) of each standard compound in synthetic wines were made and analysed under the same conditions as the samples. A semi-quantitative analysis assuming that component response factors were the same as the response factor of the internal standard was performed for the compounds in which no reference compound was available.

Descriptive sensory analysis (DA)

Descriptive sensory analysis was performed by a trained panel (12 people) which regularly participates in the Origin Denomination Penedes and, therefore, they had a large experience in the evaluation of Xarel.lo wines. Previously, the descriptive attributes most representative of the wines were defined in the first tasting seasons. To do so, the moderator suggested some terms and few wines from different years were tasted by the panel. After an open discussion of the results, the attributes were chosen to better reflect the differences among the wines. Statistical evaluation of performance of the panel was done by one-way ANOVA in order to discard attributes scores from judges not consistent with the whole panel for the subsequent sessions. From these preliminary tests 16 terms related to the odour (*white flower, white fruit, stone fruit, citric, tropical, fresh grass, dry grass, compote, spicy, toasted and lactic*), taste (*fresh taste, texture, persistence*) and colour (intensity and tonality) were selected.

Following the International Organization for Standardization ISO 5492, wine samples were evaluated in triplicate in three formal sessions that were held on different days. Each evaluation was conducted in individual tasting booths at room temperature (22 ± 1

°C). In each case, wines (20 mL) were served at 13 ± 2 °C in coded, tulip shaped wineglasses covered by glass Petri dishes. Samples were presented in random order. Still mineral water was provided for rinsing between wines. The intensities of the 16 descriptors were rated on a scale of 0 to 9; a score of zero indicated that a descriptor was not perceived and a score of 9 indicated the highest intensity. The mean scores awarded by the assessors for each of the attributes evaluated in the wine samples were used for subsequent statistical processing.

Statistical analysis

The statistical methods used for the data analysis were: one-way ANOVA and Scheffe test for mean comparisons; principal component analysis (PCA) (from correlation matrix) was used to examine the relationship among the variables and between samples; cluster analysis (Ward's method, from standardized data) was used to discover natural groupings of the samples; and partial least square regression (PLS) was applied to predict the sensory attributes of the wines based on the chemical composition. STATISTICA program for Windows, version 7.1 (StatSoft Inc., Tulsa, OK 74104, USA, www.statsoft.com), and THE UNSCRAMBLER program, version 9.6 (CAMO Software AS, Nedre Vollgate 8, N-0158 OSLO, Norway, www.camo.no) was used for data processing.

RESULTS AND DISCUSSION

Volatile Composition

The wines considered for this study were a group of 25 wine samples from the same grape variety (Xarel.lo) and from the same geographical origin but with differences in their vintage and winemaking techniques. In addition, some of them were

submitted to an aging process (*crianza*) during their production. The volatile composition of all the wines was determined, as this is the main fraction involved in their aroma. **Table 2** lists, the volatile compounds identified in the samples and the average and range of concentrations calculated in order of compound elution. The table also shows the percentage of wines in which a specific volatile compound was found. As can be seen, in spite of the fact that 59 volatile compounds were identified in the samples, not all of them were present in all the wines analysed. Only 24 of them were detected in most of the Xarel.lo wines (in more than 90 % of the wines). Among them, all the major volatile compounds (acetaldehyde, ethyl acetate, methanol, 1-propanol, isobutanol, isoamyl alcohols: 2- and 3-methyl butanol and ethyl lactate), were present in all the samples. Although individually, because of their high sensory threshold, the contribution of major volatile compounds to wine aroma could be considered minor, depending on their concentration and on their combinations in wines, they may positively or negatively impact wine aroma ^[10]. For instance, ethyl acetate might be responsible for some off flavours at levels of 150-200 mg L⁻¹ ^[11]. However, the average values determined in the wines of this study were above 62 mg L⁻¹ that has been associated to fruity notes in wines ^[12]. On the other hand, the average concentration of isoamyl alcohols (189 mg L⁻¹) (**Table 2**), was well below the concentration described that may produce negative nuances in wines (400 mg L⁻¹) ^[13]. The concentration of other higher alcohols identified in the wines (1-propanol and isobutanol) were also within the range previously described in Cava base wines ^[6, 7]. The values of ethyl lactate, were very low (9 mg L⁻¹) and similar to those reported for other white wines ^[12], showing that most of the wines did not undergo malolactic fermentation.

Other minor volatile compounds also detected in most of the wines were mainly esters and specifically higher alcohol acetates and ethyl esters of fatty acids. Among the

first group, isoamyl, hexyl and phenylethyl acetates were identified in all the wines (Table 2). Some of them, such as isoamyl acetate, were found in slightly lower concentrations (2.3 mg L^{-1}) than what was previously reported for Albariño wines (above 7 mg L^{-1})^[12], although some of the Xarel.lo wines in this study also reached these values. Hexyl acetate was found at minor concentrations (0.50 mg L^{-1}), and with similar values as those reported in base wines for cava^[7]. All of these compounds are important contributors to the fruity and flowery aroma of wines^[14] and they have shown very high Odour Activity Value (OAV >100) in some white wines, such as Albariño^[12]. Moreover, several ethyl esters of fatty acids (ethyl butanoate, hexanoate, octanoate, decanoate, 9-decenoate and diethyl succinate) were also found in all the wines (Table 2). These compounds have been associated to *fruity* and *soapy* odours^[15]. For instance, ethyl 9-decenoate has been associated to quince aroma in wines^[16]. Among them, ethyl hexanoate and ethyl octanoate were found at the highest concentrations (on average 10.4 and 4.3 mg L^{-1} respectively). These two esters together with ethyl decanoate have been shown to be the most abundant in base wines from Penedés^[7].

In addition to the above mentioned esters, 1-hexanol and 2-phenylethanol were the only alcohols found in all the samples (Table 2). The latter, has been associated to floral nuances in wines^[13], and in the wines under study was found at lower concentrations (average 6 mg L^{-1}) than in other Spanish wines such as Albariño^[12]. Although this compound is mainly produced by yeast metabolism, López-Tamames and co-workers^[4] also identified it in Xarel.lo grapes. It is interesting to notice, that besides 1-hexanol that was found in all the wines and (Z)-3-hexen-1-ol that was found only in 56 % of the wines, no other alcohol and/or aldehyde of six carbon atoms were detected. This is in agreement with the results of López-Tamames and collaborators^[4] who

showed the low amount of these carbonyl C6 volatile compounds, usually associated to grassy or herbaceous odors, in Xarel.lo grapes compared to other Spanish white grape varieties.

The three medium chain volatile fatty acids hexanoic, octanoic and decanoic acids also were detected in all the wines (**Table 2**). All of them were present at concentrations ranging between 3 and 10 mg L⁻¹, far below the concentration of 20 mg L⁻¹ that has been associated to off-flavours in wines ^[17]. Finally, three other compounds, ethyl 3-methylbutanoate, methyl octanoate and isoamyl octanoate were also found in most of the wines and although their presence in Cava wines has been previously reported ^[18], their involvement on wine aroma has not yet been described.

Linalool, α -limonene and α -terpineol were the only terpenic compounds detected in the wines, and in general, they appeared at very low concentrations (**Table 2**). Although α -limonene was found in a higher number of wines (44 %), linalool was the terpenic alcohol found at higher concentrations (average of 50 μ g L⁻¹). The latter, has been related to floral nuances in wines ^[19]. The low concentration of terpenes in grape juices from some Mediterranean white grape varieties compared to other Northern Spanish varieties (e.g Albariño) has been previously shown ^[4, 12]. Bosch-Fusté et al. (2007) were also unable to identify terpenic compounds in control Cava wines (0 days of aging) using a DVD-CAR-PDMS SPME fibre for the analysis. However, it has been shown that the polymeric composition of the fibre can greatly influence the extraction of these compounds from wines ^[20].

Some C13-norisoprenoids were also identified in the Xarel.lo wines. In general, it has been shown that their occurrence in wines can be considered as a quality factor, since they seem to supply pleasant scents to the wines such as tobacco, fruity and tea ^[21]. Among them, β -damascenone was identified only in 20 % of the wines at

concentration above 9 $\mu\text{g L}^{-1}$ (**Table 2**). Because of the very low perception threshold of β -damascenone (45 ng L^{-1})^[22], this compound might have a great importance for wine aroma. β -Damascenone has been recently identified in some young Portuguese white wines such as Boal, Malvazia, Sercial and Verdelho^[22], and it has been shown to be an odour impact compound in Macabeo white wines^[23], with an OAV of 110; however, this is the first time its presence in Xarel.lo wines has been reported. Other important norisoprenoids that were identified in the wines, were the two vitispirane isomers and the 1,1,6-trimethylnaphthalene (TDN) (**Table 2**). The three were identified in more than 80 % of the wines. Vitispirane has been associated to *canphorous-eucalyptus* nuances, while TDN has been associated to the *kerosene petrol* like odour typical of aged Riesling wines^[13]. However, at high concentrations the latter can also be responsible for off-flavours^[21]. In addition, although both compounds have been found in young wines, their concentration considerably increases during wine aging because of the breakdown of the corresponding carotenoid precursors^[21]. It is because of this, that vitispirane and TDN have been claimed to be used as markers of aging in old Cava wines^[18].

Other compounds identified in the wines were some furfuryl compounds such as furfural, 5-methylfurfural, ethyl 2-furancarboxylate and 2-acetylfuran (**Table 2**). All of them have been previously identified in Cava wines^[18]. Among them, furfural was identified in the 80 % of the wines analysed and its concentration ranged between 0.3 and 1.8 mg L^{-1} . However, on the basis of its OAV, it has been shown that its importance for wine aroma seems to be rather low^[24]. It is a carbohydrate degradation product and it has been shown it can increase during the aging in the bottle^[13].

Sensory Characterization

For the sensory evaluation, the 25 wines were firstly submitted to descriptive analysis to evaluate 16 sensory terms that were found in preliminary sensory sessions as the most appropriate to characterize Xarel.lo wines. These descriptors and their intensity values (mean $\pm$ SD) are shown in **Table 3**. In the case of the odour-related attributes, the highest scores were obtained for *citric fruit*, *white fruit* and *tropical fruit* aromas (4.12, 4.05, 3.96 respectively). In addition, the descriptor *fresh* taste was highly rated (5.51). The wines also obtained high scores in texture, persistence and colour intensity and tonality. De la Presa-Owens and Noble (1995) ^[9] also found that some of these attributes, such as *tropical fruit and floral notes* were characteristic of Xarel.lo wines. In addition, they also found the descriptor *black pepper* as an important contributor in explaining the sensory characteristics of Xarel.lo wines. In our study, *spicy* aroma was also characteristic of these wines, although we found a high dispersion in this attribute between wines (**Table 3**), which could be due to differences in winemaking practices and vintage year. As a matter of fact, some other sensory attributes such as *white flower* and *toasted aroma* also seemed to have major differences between wines, as it is suggested by the high SD values in the intensity scores (**Table 3**). Interestingly, the intensity of the attribute *fresh grass*, which has often been related to vegetative off-flavours ^[13] was generally low in most of the wines.

Principal Component Analysis (PCA) was applied to determine the main causes of variation in the sensory profiles of the wines. From this analysis, two principal components, which explained 74 % of the total variation on the sensory data were obtained. The first principal component (PC1, 41.6 % of the total variance) was positively correlated with the descriptors *white flower*, *white fruit*, *stone fruit* and *fresh taste* (loadings > 0.8) and negatively with *compote*, *toasted*, *spicy*, *lactic* and *dry grass* (loadings < -0.8). The second principal component (PC2, 32.7 % of the total variance)

314 was negatively correlated with *citric* and *tropical* aroma, *persistence*, *colour* and
315 *tonality*. In **Figure 1** the scores of the wines in the four groups, and the loadings of the
316 sensory descriptors, are plotted on the plane defined by the two first principal
317 components. As can be seen, four groups of wines already noticed by cluster analysis
318 (data not shown) were distinguished by PCA analysis. Wines from group 1, were better
319 characterized by descriptors associated to the PC1, on the contrary, wines included in
320 groups 2 and 3 were very little characterised by them. The PCA also revealed a fourth
321 group of wines (group 4) that were negatively related with PC1 (on the contrary to the
322 wines from group 1). To better illustrate these differences, **Figure 2** shows the mean
323 intensity ratings for the 4 groups of wines on a cobweb plot using the 16 sensory terms.
324 The four groups might correspond to four styles of Xarel.lo wines. The style of the
325 wines from group 1 was characterized by a marked fruity and floral odour and fresh
326 taste. All the wines included in this group were young wines from 2008, thus they could
327 define the sensory characteristics expected for Xarel.lo young wines. These
328 characteristics seemed to be in agreement with previous sensory studies ^[8, 9]. However,
329 in this study three other styles of Xarel.lo wines were also found. Wines included in
330 group 4 were very different from group 1. They were characterized by a lower intensity
331 of flowery and fruity aromas and fresh taste, but for the presence of attributes such as
332 *dry grass*, *compote*, *toasted* and *spicy*, that were almost absent in wines from group 1. In
333 addition, some other sensory characteristics such as texture, persistence, and colour
334 intensity and tonality were also present at higher intensity in group 4 compared to wines
335 from group 1. Compared to previous works ^[8, 9], this seems to be an unusual sensory
336 profile for Xarel.lo wines, and even different to the sensory profiles described for white
337 wines from other North-Spanish regions such as Godello and Albariño white wines ^[25].
338 However, all the wines within group 4 were from 2006 and 2007 vintages and most

importantly, they were submitted to *crianza* in which the wines spent at least 6 months aging in oak. Therefore, either the vintage and/or the *crianza* process provoked changes in the sensory characteristics of the wines, such as the loss, at least in part, of the fruity, floral and freshness sensory attributes, but the increase in more complex aromatic notes (*compote, spicy, toasted*, etc) that may be defined as an *aging bouquet*. This could be due to the release of aroma compounds from the wood into the wine or a masking effect of fruity and floral descriptors by typical sensory descriptors from wood, as it has been shown in some Chardonnay wines aged with toasted oak chips ^[26]. In addition, the wines from group 4 showed the highest scores in colour intensity and tonality descriptors, which is in agreement with the higher colour and tonality data instrumentally determined compared to the non-*crianza* wines (**Table 1**). This, might be related to the increase in oxidation phenomena because of the *crianza* process ^[26].

The other two styles of wines that we found in this work corresponded to groups 2 and 3. Both groups were very similar and had sensory characteristics between wines from group 1 and those from group 4 (**Figure 2**). Both groups included wines from all the vintages with or without *crianza*. Similarly to wines from group 4, they were characterized by *toasted, compote, dry grass* and *spicy aroma*, but in the case of wines from group 3 the sensory panel also found some fruity (*tropical, citric, stone* and *white fruit*) and white flower descriptors, in higher intensities, although the latter were very low or almost absent in wines from group 2 (**Figure 2**).

Correlation between sensory and chemical composition

Partial least squares regression (PLS) was applied to predict the sensory attributes of the wines based on the instrumental variables (volatile compounds). The

number of components in the model was selected by cross-validation procedure. Using this procedure, one component for each descriptor (*white flower*, *white fruit*, *stone fruit*, *tropical fruit* and *fresh taste*) was selected, except for *spicy* and *toasted* notes, for which two components were selected (**Table 4**). The size and sign of the values of the regression coefficients in the model for standardized predictor variables can be used to determine the variables that mostly contribute (positively or negatively) to the prediction of the sensory attributes. The PLS results, regression coefficients for the variables that mostly contribute to the prediction of specific sensory attributes, number of selected components and the determination coefficient (R^2), are shown in **Table 4**. In addition, the table shows (in brackets) the values, significantly different from zero ($p < 0.05$), of the correlation coefficients, between the instrumental variables and the sensory attributes. It is worth noticing the high similarity between the volatile compounds that have been selected because of their higher correlation with the flower and fruity attributes. In this sense, the similarities between the variables (volatiles) that better predict the sensory attributes *white flower* and *white fruit*, are even more evident. As we have previously shown, these attributes, seem to be important in defining the sensory characteristics of young Xarel.lo wines. This might be due to the difficulty to differentiate between both attributes by the sensory panel. In general, the selected variables that were positively related to both attributes were higher alcohol acetates (hexen-1-ol, acetate, phenylethyl acetate, hexyl acetate) and ethyl and methyl esters of fatty acids (methyl octanoate, methyl decanoate and ethyl decanoate). This is in agreement with the high involvement of these compounds in the characteristic fruity and flowery aroma of some young white wines^[13, 14]. In fact, 2-phenyl acetate has been found to be an odour impact compound in other Penedés white wines (e.g. Macabeo) described as flowery-like by GC-O^[23]. In addition, *white flower* and *white fruit*

attributes showed a relatively high correlation (0.77 and 0.78) (**Table 4**) with hexyl acetate. Although some previous sensory studies in Spanish wines from white varieties such as Gual and Verdello have suggested that floral aromas might be related to high levels of terpenes ^[27], in the Xarel.lo wines under the study, both sensory attributes seemed to be more correlated to the ester content.

On the other hand, and as it is shown in **Table 4**, compounds such as diethyl succinate, vitispirane and TDN, were negatively associated to all the fruity attributes. The first one has been shown as the only ester which increases during Cava aging ^[6, 18] while the other two compounds are mainly degradation products from carotenoids breakage during wine aging ^[21]. Therefore, the low correlation of the three volatile compounds with *fruity* and *flowery* attributes seems logical when taking into consideration that these attributes are mainly associated to young wines. In addition, it is interesting to underline that the attribute *fresh taste* followed a similar trend (**Table 4**) than that observed by the *fruity* and *floral* characteristics and it was also associated to the higher ethyl alcohol esters and higher alcohol acetates.

In general, esters did not show a contribution to the *spicy* and *toasted* sensory characteristics and even some of them such as 3-hexen-1-ol, acetate and isoamyl acetate were negatively correlated to both sensory attributes (**Table 4**). Interestingly, the only volatile compounds that seemed to contribute the most to both sensory characteristics were furfural to the *toasted* note and 5-methylfurfural to both *spicy* and *toasted* (**Table 4**). These compounds are carbohydrate degradation products and it has been shown they can increase with aging in the bottle ^[13]. In addition, they may have been released into the wines that underwent *crianza* process, since both volatiles may be produced by the degradation of polysaccharides during oak wood toasting ^[26].

In summary, in this work that constitutes the first comprehensive study performed on the characterization of commercial Xarel.lo wines from the Penedés, four different styles of wines were found based on their sensory characteristics. Among them, two groups or styles were perfectly distinguishable: young wines, characterized by a marked fruity and floral odour and fresh taste and wines that underwent *crianza*, characterized by more complex sensory attributes such as *toasted*, *spicy* and *compote* odour attributes. The differences in the two styles seems to be related to a higher content of higher alcohol acetates and ethyl and methyl esters of fatty acids in wines included in the first style, while the second style was characterized by a lower concentration of esters, but higher concentration of compounds related with wine aging, such as furfural, 5-methylfurfural and vitispiranes. Therefore, this study contributes to the chemical knowledge of wines from the Xarel.lo variety and hence on the promotion of the use of autochthonous grapes varieties to produce high quality wines with distinctive sensory characteristics helping to diversify the current wine market.

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FIGURES CAPTIONS:

Figure 1. Plot of the wines in the four groups and the loadings of the intensity of sensory attributes on the plane defined by the first two principal components obtained from the PCA. Wine codes are explained in the Materials and Methods section.

Figure 2. Polar coordinate (cobweb) graph of the mean intensity ratings of sensory attributes for the 4 groups of Xarel.lo wines. At the origin, intensity=0; at the perimeter, intensity=9.

491 **Table 1.** Characteristics and Global composition of Xarel.lo white wines.

Code	Vintage	“Crianza” ^a	Ethanol (%) (v/v)	pH	TA ^b	Lactic acid (g L ⁻¹)	Malic acid (g L ⁻¹)	Glycerol (g L ⁻¹)	Gluc+ Fruct (g L ⁻¹) ^c	CI ^d	T ^e
w-01	2008	yes	12.75	2.95	6.9	0.1	1.5	6.1	0.9	0.09	5.66
w-02	2008	no	12.75	2.98	6.9	0.1	2.5	6.9	1.7	0.12	3.17
w-03	2006	yes	13.55	3.13	5.6	0.1	1.1	6.5	1.8	0.13	5.33
w-04	2007	yes	12.1	3.03	6.8	0.1	1.8	5.8	1.1	0.09	4.82
w-05	2007	yes	13.15	3.08	5.9	0.1	1.5	6	2.7	0.09	5.52
w-06	2008	yes	13.3	3.11	5.7	0.1	1.7	6.1	0.5	0.07	5.31
w-07	2008	no	12.35	2.97	5.9	0.1	1.6	5.7	3.5	0.07	4.80
w-08	2007	yes	13.65	3.08	5.7	0.1	1.1	7	4.5	0.14	4.73
w-09	2006	yes	13.66	3.21	5.2	0.2	1.5	3.5	1.7	0.15	4.60
w-10	2008	no	12.75	3.33	4.6	0.1	1.8	5.8	0.5	0.10	5.96
w- 11	2007	no	12.2	3.09	6.5	0.1	1.8	5.7	0.9	0.11	5.23
w-12	2007	no	12.45	3.04	6	0.2	0.9	6.7	1.6	0.11	3.94
w-13	2007	yes	12.7	3.22	6.2	0.1	1.7	7.2	0.1	0.13	4.24
w-14	2008	no	12.7	3.07	5.6	0.1	1.8	5.6	1.9	0.08	4.59
w-15	2007	yes	13.4	3.09	6.8	0.1	1.8	7	2	0.12	4.96
w-16	2008	no	11.55	3.08	6.2	0.1	2.5	4.7	1.5	0.09	5.70
w-17	2007	yes	13.35	3.16	6	0.5	0.4	6.4	1.2	0.18	4.86
w-18	2007	yes	13.45	3.07	6	0.2	1.2	6.8	1.5	0.17	4.73
w-19	2007	yes	11.75	3.2	5.1	1.1	0.4	6.8	2.1	0.10	5.19
w-20	2008	yes	13.3	3.21	5.7	0.1	2.3	5.5	1.2	0.08	4.86
w-21	2008	no	12.95	3.07	5.7	0.4	1.4	3.8	4.2	0.08	4.43
w-22	2004	yes	11.78	3.01	7.4	0.1	2.6	8	4.3	0.17	5.29
w-23	2005	yes	12.05	2.98	6.4	0.1	1.5	6.3	1.3	0.14	5.46
w-24	2005	yes	13.71	3.25	5	0.3	1.4	3.1	2.2	0.16	5.89
w-25	2008	yes	12.17	3.11	5.7	0.2	1.4	5	1.5	0.07	4.99

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493 ^a ‘Crianza’ means wines aged for 12 months in which at least 6 months correspond to aging in oak; ^b Titratable acidity (g L⁻¹ tartaric acid); ^c
494 Glucose + Fructose; CI ^d: colour intensity determined as the sum of A₄₂₀ + A₅₂₀; ^e T: Tonality determined as the ratio of A₄₂₀/ A₅₂₀. All the
495 analyses were performed according to the International Methods of the OIV (International Organization of Vine and Wine 1990)

496 **Table 2.** Volatile compounds identified in the Xarel.lo wines.
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					Concentration (mg L ⁻¹)				
Compounds	RI _e ^(a)	RI _l ^(b)	ID ^(c)	% Wines ^(d)	Mean	SD	Min	Max	MQ ^(e)
Acetaldehyde			R	100	41.03	18.06	8.90	71.26	1
Ethyl acetate			R	100	62.01	19.49	25.31	95.75	1
Methanol			R	100	39.01	13.42	17.91	67.93	1
1-Propanol			R	100	22.78	16.31	1.89	57.93	1
Isobutanol			R	100	23.81	12.75	5.40	51.95	1
3-Pentanol (IS)			R						1
Isoamyl alcohols			R	100	189.53	51.77	97.29	293.64	1
Ethyl lactate			R	100	9.01	15.65	0.39	78.40	1
Ethyl butanoate			M, R	96	2.10	1.25	0.67	6.13	1
Ethyl 2-methylbutanoate			M	76	0.26	0.20	0.05	0.65	2
Ethyl 3-methylbutanoate			M	100	0.45	0.42	0.05	1.80	2
Isoamyl acetate	1113	1117	I, M, R	100	2.34	2.16	0.16	7.17	1
α-Limonene	1176	1180	I, M, R	44	0.9 10 ⁻³	2.06 10 ⁻³	0.1 10 ⁻⁴	6.81 10 ⁻³	1
Ethyl Hexanoate	1229	1230	I, M, R	100	3.66	1.11	1.56	6.03	1
Unknown	1264		M	7	4.52	7.40	0.09	13.06	2
Hexyl acetate	1267	1269	I, M, R	100	0.50	0.49	0.02	1.40	1
3-Hexen-1-ol, acetate	1301		M	44	0.17	0.07	0.10	0.30	2
Unknown	1313		M	7	0.23	0.12	0.10	0.34	2
Ethyl heptanoate	1324	1332	I, M	68	0.15	0.07	0.05	0.31	2
Ethyl 2-hexenoate	1333	1328	I, M	80	0.15	0.11	0.05	0.56	2
1-Hexanol	1351	1356	I, M, R	96	2.04	1.19	0.43	5.43	1
Heptyl acetate	1366	1366	I, M	4	0.15		0.15	0.15	2
2-Nonanone	1376	1386	I, M	72	0.15	0.08	0.06	0.33	2
Methyl octanoate	1379	1370	I, M	96	0.35	0.13	0.05	0.57	2
(Z)-3-Hexen-1-ol	1379	1370	I, M, R	56	0.06	0.13	0.00	0.64	1
Ethyl octanoate	1434	1431	I, M, R	100	4.32	1.46	0.00	7.19	1
Isopentyl hexanoate	1451	1453	I, M	64	0.83	0.24	0.25	1.23	2
Furfural	1462	1459 ^{bl}	I, M, R	88	0.77	0.49	0.32	1.83	1
Ethyl hexyl acetate	1468		M	24	0.16	0.10	0.07	0.33	2
Methyl nonanoate (IS)			R						1
Ethyl sorbate	1499		M	8	5.00	4.51	1.82	8.19	2
2-Acetylfuran	1502	1500 ^{bl}	M	7	0.14	0.02	0.13	0.17	2
Vitispirane-1	1504	1505	I, M	80	0.08	0.06	0.7 10 ⁻²	0.26	2a
Vitispirane-2	1504	1505	I, M	80	0.07	0.056	0.8 10 ⁻²	0.25	2a
Benzaldehyde	1510	1509	I, M	32	0.24	0.12	0.14	0.47	2
Ethyl nonanoate	1526	1541	I, M	56	0.21	0.28	0.08	1.15	2
Unknown	1529		M	7	0.18	0.06	0.11	0.23	2
Ethyl 2-hydroxy-4-methylpentanoate	1542	1547	I, M	12	0.12	0.06	0.07	0.19	2
Linalool	1547	1545	I, M, R	36	5 10 ⁻²	5 10 ⁻²	6.5 10 ⁻⁴	0.13	1
1-Octanol	1555	1530	I, M	56	0.11	0.05	0.05	0.24	2
2-Heptanol	1565	1307	I, M	4	0.15		0.15	0.15	2
5-Methylfurfural	1568	1559	I, M, R	52	0.21	0.13	0.12	0.58	1

Methyl decanoate	1587	1592	I, M	72	0.09	0.07	0.02	0.28	2
2-(2-Ethoxyethoxy)ethanol	1615	1579	I, M	52	0.14	0.05	0.07	0.25	2
Ethyl 2-furancarboxylate	1619	1621 ¹	M	60	0.16	0.12	0.05	0.57	2
Ethyl decanoate	1634	1634	I, M, R	100	0.74	0.18	0.46	1.17	1
Isoamyl octanoate	1650	1658	I, M	92	0.67	0.16	0.37	0.95	2
Diethyl succinate	1673	1694	I, M, R	100	3.22	2.40	0.55	7.56	1
Ethyl 9-decenoate	1680	1694	I, M	100	2.79	2.53	0.37	9.02	2
α -Terpineol	1689	1687	I, M, R	16	0.022	0.022	$3.2 \cdot 10^{-3}$	0.052	1
1,2-Dihydro-1,1,6-trimethylnaphthalene (TDN)	1723	1719 ^{b2}	M	84	0.031	0.03	$0.3 \cdot 10^{-2}$	0.106	2a
β -Damascenone	1807	1801	I, M, R	20	$4.8 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$6.9 \cdot 10^{-4}$	1
Phenylethyl acetate	1809	1805	I, M, R	100	0.23	0.02	0.20	0.27	1
Ethyl dodecanoate	1837	1833	I, M, R	100	0.20	0.01	0.18	0.23	1
Isoamyl decanoate	1854	1851	I, M	60	0.12	0.03	0.06	0.17	2
Hexanoic acid	1869	1826 ^{b1}	I, M, R	100	3.05	1.10	1.68	6.25	1
2-Phenylethanol	1910	1890	I, M, R	100	6.32	3.71	1.29	16.52	1
Octanoic acid	2083	1998	I, M, R	100	10.38	2.78	5.10	17.66	1
Decanoic acid	2295	2279	I, M, R	92	3.97	1.19	2.16	6.74	1

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499 (^a): Linear Retention Index calculated with an alkane mixture (C5-C30); (^b) From Flavornet
500 (<http://www.flavornet.org> –accessed Oct. 2009-) database, from NIST web chemistry book (2005)
501 (<http://www.webbook.nis.gov/chemistry>); (^{b1}): from Bosch-Fuste et al. (2007), (^{b2}): from Riu-
502 Aumatell et al. (2006) ; (^c) Identification based on the Wiley Mass Spectra Library (M), by
503 comparison of the experimental and literature retention index (I) and by comparison with reference
504 compounds (R); (^d): % of wines in which the volatile compound was detected, (^e) Quantification
505 method: 1=using calibration curves with the standard compounds, 2=semi quantification using the
506 response factor of the IS (methyl nonanoate), 2a= semi quantification using the response factor of
507 the β -damascenone.

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Table 3. Mean and Standard Deviation (SD) for intensity of sensory attributes in Xarel.lo wines

Sensory attributes	Mean	SD	Range
Odour			
<i>White Flower</i>	3.17	1.18	(1.50-5.20)
<i>White Fruit</i>	4.05	1.26	(2.3-6.33)
<i>Stone Fruit</i>	3.89	0.76	(2.2-5.4)
<i>Citric Fruit</i>	4.12	0.73	(3.13-5.83)
<i>Tropical Fruit</i>	3.96	0.90	(2.13-5.58)
<i>Fresh Grass</i>	3.00	0.71	(1.75-4.17)
<i>Dry Grass</i>	3.82	0.84	(2.25-5.33)
<i>Compote</i>	3.68	1.26	(0.5-6)
<i>Spicy</i>	2.98	1.13	(0.63-5.25)
<i>Toasted</i>	3.51	1.48	(0.38-6.25)
<i>Lactic</i>	2.94	1.10	(1-4.96)
Taste			
<i>Fresh taste</i>	5.51	0.96	(3.75-7.05)
<i>Texture</i>	6.12	0.64	(4.75-7.25)
<i>Persistence</i>	6.26	0.63	(4.60-7.33)
Colour			
<i>Intensity</i>	6.8	0.45	(5.88-7.58)
<i>Tonality</i>	6.72	0.53	(5.42-7.5)

513 **Table 4.** Regression coefficients from the PLS model for the variables that most contribute in the prediction of specific sensory attributes and
514 correlation coefficients (in brackets), which were significantly different from zero

Instrumental variables	Sensory Attributes						
	White Flower	White fruit	Stone fruit	Tropical fruit	Spicy	Toasted	Fresh taste
Diethyl succinate	-0.045 (-0.66)	-0.049 (-0.74)	-0.044 (-0.65)	-0.035 (-0.5)			-0.042 (-0.62)
Ethyl 2-methylbutanoate	-0.040 (-0.58)	-0.046 (-0.68)	-0.044 (-0.66)	-0.034 (-0.5)			-0.042 (-0.62)
Ethyl 3-methylbutanoate	-0.039 (-0.57)	-0.041 (-0.61)	-0.036 (-0.54)				
Vitispirane-1	-0.042 (-0.61)	-0.046 (-0.69)	-0.036 (-0.54)	-0.035 (-0.49)			-0.042 (0.59)
Vitispirane-2	-0.041 (-0.61)	-0.046 (-0.69)	-0.035 (-0.53)	-0.035 (-0.50)			-0.040 (-0.61)
TDN		-0.040	-0.035	-0.323			
Ethyl acetate						0.11 (0.6)	
Isoamyl alcohols			-0.038 (-0.57)	-0.034 (-0.49)			
2-Phenylethanol				-0.039 (-0.55)			
3-Hexen-1-ol, acetate	0.040 (0.59)	0.051 (0.77)	0.043 (0.65)	0.047 (0.50)	-0.066 (-0.49)	-0.075 (-0.58)	0.041 (0.60)
Methyl octanoate	0.036 (0.53)						0.037 (0.54)
Isoamyl acetate		0.042 (0.63)			-0.060 (-0.44)		0.036 (0.54)
Hexyl acetate	0.053 (0.77)	0.052 (0.78)	0.038 (0.6)	0.377 (0.53)		-0.06 (-0.54)	0.044
Phenylethyl acetate	0.042 (0.54)	0.042 (0.62)					
Methyl decanoate	0.044 (0.64)			0.037 (0.52)			
Isoamyl decanoate			0.034 (0.52)		-0.060		
Isopentyl hexanoate			0.037 (0.55)	0.065 (0.51)			
Ethyl decanoate	0.044 (0.65)	0.044 (0.66)	0.044 (0.66)	0.053 (0.75)			0.043 (0.64)
Decanoic acid				0.035 (0.49)			
Furfural						0.12 (0.62)	
5-Methylfurfural					0.117 (0.44)	0.11 (0.52)	
Linalool						-0.069 (-0.42)	
R²	0.63	0.70	0.62	0.57	0.77	0.74	0.60
Number of components	1	1	1	1	2	2	1

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