Highlights

- Significant effects of grape maturity on astringency, fruity and oxidation wine aromas
- Oxidation aromas appeared in wines elaborated with grapes prematurely harvested
- Oxidation aroma is positively correlated to the concentration of Strecker aldehydes
- Lower levels of aldehyde-reactive polyphenols are related to higher oxidation nuances
- Astringency is positively correlated to ethanol, tannin and anthocyanin-derivatives

Effect of grape maturity on the sensory and chemical features: The case –of Moristel wines

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Abstract

Among the different grape factors involved in wine quality, the present work is focused on evaluating the effect of grape maturity on wine flavour and how these sensory effects are related to wine chemical composition.

Moristel grapes were collected from two vine blocks, with *a priori* maximal variability in terms of grape quality, at 4 and 3 points of maturation, respectively. Wines were elaborated in triplicate yielding 21 wine samples. Sensory characterisation of samples was carried out by a panel of trained panellists following the rate-all-that-apply method. Volatiles and non-volatiles with known sensory impact on wines were quantified.

Grape maturity generated significant sensory effects on wine astringency and fruity aroma including raisin, black and red fruit. Interestingly, a significant effect on oxidation nuances revealed a general pattern in the appearance of higher oxidation aromas in wines elaborated with grapes prematurely harvested. This attribute is related to free acetaldehyde, methional, phenylacetaldehyde and isoaldehydes and aldehyde-reactive polyphenols content. The presence of raisin aroma is linked to β-damascenone, which is suggested to be formed during the on-vine dehydration process. Astringency is related to ethanol content, tannin activity (measured as the interaction of tannins with a hydrophobic surface) and the content in anthocyanin-derivative compounds.

Keyword: wine; aroma; oxidation; astringency; tannin activity

1. Introduction

Grape composition is an important factor influencing sensory characteristics of wines (Niimi, Boss, Jeffery, & Bastian, 2017). Thus, selecting the optimal point to harvest berries with the greatest potential to yield wines with desired sensory properties is a major issue for winemakers. The measurement of the basic chemical parameters of grapes (such as pH, total acidity, colour intensity, phenolic content) to determine ripeness prior to harvest is a standard industry practice. However, these conventional measurements are not enough to predict wine features (Pérez-Magariño & González-San José, 2006). Phenolic compounds together with sensory-active volatile compounds are generally considered to be major determinants of the quality of red wines (Sáenz-Navajas et al., 2015). However, a clear relationship between aroma precursors and the phenolic composition present in grapes, and wine sensory characteristics including aroma, taste or chemesthesic sensory properties (including thermal, pain-related or astringency-related sensations) has not been yet established. Concerning the potential aromatic quality of grapes, it is a factor poorly understood. Winemaking grapes present mostly neutral aroma, which is the result of the presence of very low quantities of a long list of aromatic compounds such as furaneol, β-damascenone, terpenols, benzenoids or phenols among others. Besides these molecules, grapes contain a complex series of specific aroma precursors. These nonvolatile molecules, known as precursors, can generate an aromatic molecule by 1) the break of chemical bonds (including glycoside, S-derivatives of cysteine or glutathione or S-methionine and other precursors of dimethyl sulphur) and/or 2) spontaneous molecular reassemble (by pH effect or esterification) (Parker, Capone, Francis, & Herderich, 2018). These precursors play an essential role in wine aroma, but the effect of grape maturity on aroma grape potential is far from being clear. Firstly, because the analytical tools to quantify these precursors are still being developed and secondly because precursor concentration in juices is not directly correlated to the aroma compounds found in wines (Alegre, Ferreira, & Hernández-Orte, 2019).

Regarding phenolic compounds, tannins (proanthocyanidins) and anthocyanins constitute the most abundant classes in grapes. Anthocyanins are released from grape skins, whereas proanthocyanidins are released from both skins and seeds. Accumulation of anthocyanins set in at *véraison* and decline during overripening. Proanthocyanidins mainly accumulate before *véraison* (Fournand et al. 2006). The ripeness of the grapes has an important effect on the kind and extractability of phenolic compounds into the wine. The extractability of proanthocyanidins from seeds decreases with ripeness, probably due to oxidation phenomena and gradual seed lignification that hinder their extraction. Differently, the extractability of skin phenolics increases with ripening, which is attributed to the action of enzymes by degrading the wall of skin cells (Gil et al., 2012).

Hence, grape maturity represents an important factor determining grape composition and consequently composition and sensory properties of wines and hence wine quality.

In terms of grape cultivars, Moristel is a minor variety suggested to originate from Aragon (north-east Spain), where it is basically found in the Somontano region (Robinson, Harding, & Vouillamoz, 2012). This is a cultivar with reasonably good resistance to drought, pests and diseases, presenting a late ripening with the onset of anthocyanins taking place at low sugar levels (García, Zheng, Balda, & Martinez De Toda, 2017). These make Moristel an interesting alternative cultivar to be grown in warm climates, however scarce scientific literature can be found about its potentiality.

In this context, the aim of the current study was to determine the effect of ~~Moristel~~

grape maturity on the sensory attributes of final wines and to relate these sensory changes with chemical composition considering Moristel variety as case study.

2. Material and Methods

2.1. Site location and winemaking

The experiment took place in Barbastro situated in Somontano region (Huesca, Spain) during 2017 harvest. Two vineyard blocks (BLA and BLB) with *a priori* maximal diversity in quality were selected based on historical data and criteria derived from the commercial system Dyostem® (Vivelys, France). According to commercial information, this tool monitors sugar loading and changes in the colour of the fruit to classify grape quality and determines the optimal harvest date. Moristel grapes were handpicked at four points for BLA (BLA_1; BLA_2; BLA_3 and BLA_4) and at three points for BLB (BLB_1; BLB_2; BLB_4), each point separated by one or two weeks. According to the commercial system, the second point of maturity (BLA_2, BLB_2) was the optimal point to harvest, thus it was decided to harvest one week before (BLA_1, BLB_1) and one (BLA_3) and/or two (BLA_4, BLB_4) weeks after to have grapes with different maturity levels and thus with *a priori* maximal variability in chemical composition. One hundred and fifty kilograms of fruit were collected at each harvest date. Grapes were processed (destemmed/crushed) the same day, and the fruit was divided into three separate lots. Wines were elaborated in 75-litre stain-less steel tanks, in triplicate. To each tank (total of 21), sulphur dioxide was added to get a total concentration of 50 mg L^{-1}. The following day of harvest all tanks were inoculated with Lalvin ICVD 254 (Lallemand) at 10^6 cells ml^{-1} and pectolytic enzyme at 0.8 mL Hl^{-1}. Alcoholic fermentations (FOH) took place on skins for 10 days, in average. Once alcoholic fermentation was finished wines were inoculated with malolactic bacteria (Oenococcus oeni) strain Lalvin VP41 (Lallemand). Wines were bottled ca. 3 months after FOH (free SO_2 adjusted to 30 mg L^{-1}). Wines were bottled and closed with natural cork closures.

2.2. Sensory analysis

2.2.1. Participants

Seventeen panelists from Instituto de Ciencias de la Vid y del Vino (ICVV) and Universidad de La Rioja (Spain) participated in sensory description. They were mainly last-year oenology students and oenologists (60% women, ranging from 22 to 34 years of age, average = 28).

2.2.2. Panel training and generation of sensory attributes

Participants attended a total of 6 training sessions (1h30 each session) over three weeks. During this period, panellists worked in two subgroups following the same guidelines. The first session was devoted to generate aroma terms differing among samples. Therefore, participants were presented simultaneously with the 21 wines of the study and were asked to sort them based on their aroma similarity according to a sorting task. Once groups were built, they described them with two or three descriptive aroma terms (avoiding hedonic terms). Terms generated were gathered and grouped in categories according to semantic similarities. This process was performed individually by three experienced researchers, who through a triangulation task (Abric, 2003) achieved a final consensual list of 12 terms that included: fresh vegetables (green pepper), red fruit (strawberry, cherry, raspberry), white fruit (apple, pear), black fruit (blackberry, blackcurrant), dried fruit (raisin, prune), fresh grass, oxidation (acetaldehyde, boiled potato, honey, overripe apple), roasted/smoky, reduction (cauliflower, rotten eggs), spicy (black pepper, nutmeg, clove), undergrowth (mouldy, mushroom) and alcohol (ethanol, spirit-like). During the following training sessions, reference standards (prepared at Laboratorio de Análisis del Aroma y Enología of Universidad de Zaragoza) representative of the 12 selected aroma terms as well as of 3 taste (sweet, sour, bitter) and 4 chemesthesic (astringency, alcoholic feeling, viscosity/body) terms were presented. For in-mouth terms, solutions containing different concentrations of table sugar (0-7 g L^{-1}) for sweetness, tartaric acid (0-~~–~~3 g L^{-1}) for acidity, quinine sulphate (0-~~–~~40 mg L^{-1}) for bitterness and potassium, aluminium sulphate (0-~~–~~5 g L^{-1}) for astringency, absolute alcohol (0-15% v/v) for alcoholic feeling and carboxymethylcellulose (0-1.5 g L^{-1}) for viscosity/body stimuli, were prepared. During a typical training session, panellists were presented with references illustrating the different aroma, taste and chemesthes~~t~~ic terms and 2-4 wines were firstly individually described and then ratings were discussed until achieving consensus.

2.2.3. Wine description

The 21 wines (7 different wines elaborated in triplicate) were described in duplicate during four sessions (replicated samples were presented in different sessions). Each session was split into two parts (45 min each) (5-6 samples per part), which were separated by an imposed pause of 10 min. Participants were asked to taste and rate the intensity of exclusively those terms (out of 18) that applied to the sample on a seven-point scale according to Rate-all-that-apply (RATA) methodology (Ares et al. 2014). Terms that did not apply to the sample were allocated a value of zero when collecting data. To avoid bias due to order of presentation, terms in the list appeared in different and randomised order for each assessor. The use of a sip (rinsing solutions: water and 1 g L^{-1} pectin solution) and spit protocol between each sample was imposed as described elsewhere (Colonna, Adams, & Noble, 2004). All participants evaluated the 21 in duplicate samples in a sequential monadic manner. Twenty-mL samples were served in dark wine glasses labelled with 3-digit random codes and covered with plastic Petri dishes according to a random arrangement, different for each participant. Samples were served at room temperature and evaluated in a ventilated and air-conditioned tasting room (at around 20 ºC).

2.2.4. Sensory data analysis

A three-way ANOVA for each of the sensory attributes evaluated involving wines (W), judge (J) and replicate (R) as fixed factors and all first order interactions was calculated to confirm panel performance with the 21 wines (in duplicate) of the study. The replicate effect was only significant (P=0.033) for the term roasted/smoky, indicating a global consistent assessment of attributes and reflecting the reproducibility of the panel. Thus, the average data between replicated samples was calculated and considered in further analyses. The wine-by-judge interaction (WxJ) was significant for white fruit, roasted/smoky, undergrowth, reduction, oxidation and body/viscosity. A PCA run on these attributes (judges in columns and wines in rows) revealed that judges' projections were spread over the loading plot for white fruit, undergrowth, reduction and body/viscosity, while they were grouped together for the other two attributes. This indicates that there are differences in the use of the scale for roasted/smoky and oxidation. Differently, for white fruit, undergrowth, reduction and body/viscosity there are differences in their interpretation, which suggests that assessors may need more training with respect to these four attributes. These terms were not considered in subsequent analysis.

Then, to find discriminant sensory attributes for the wines a two-way ANOVA (panellists as random and wines as fixed factors) was calculated for each of the remaining 14 terms of the list. Then, for discriminant terms, pair-wise comparison test (Fischer test) was applied (5% risk) for significant effects. All statistical analyses were performed using XLSTAT (2018).

2.3 Chemical analysis

2.3.1. Conventional oenological parameters

Grapes: Sugar content in grapes was analysed by Infrared Spectrometry with Fourier Transformation with a WineScanTM FT 120 (FOSS®, Barcelona, Spain), which was previously calibrated with the official OIV methods.

Wines: Total polyphenol index (TPI) was estimated as absorbance at 280 nm (Ribéreau-Gayon, 1970) and colour intensity (CI) as the sum of absorbance at 420, 520 and 620 nm (Glories, 1984). For TPI determination, the abs at 280 nm of samples diluted 1:100 in deionised water was measured in 1-cm-quartz cuvettes. Reducing sugars, ethanol content, pH, malic and lactic acid as well as titratable and volatile acidities were analysed by Infrared Spectrometry with Fourier Transformation with a WineScanTM FT 120 (FOSS®, Barcelona, Spain), which was previously calibrated with the official OIV methods.

2.3.2. Chemical characterisation of non-volatile compounds

2.3.2.1. Determination of anthocyanin-derived pigments

Determination of monomeric (MP), small polymeric pigments (SPP) and large polymeric pigments (LPP) in wines and fractions was carried out as described elsewhere (Harbertson, Picciotto, & Adams, 2003). MPs were the group of compounds bleachable with bisulphite, while SPP and LPP were resistant to bisulphite bleaching. SPP did not precipitate with ovoalbumin, different to LPP. Levels of MP, SPP, and LPP were expressed as absorbance at 520 nm.

2.3.2.2. Mean degree of polymerisation (mDP) of tannins

Acid-catalysed degradation in the presence of toluene-α-thiol was performed according to the method described by Labarbe et al. (1999) but with some modifications as described by Gonzalo-Diago, Dizy, & Fernandez-Zurbano (2013). Quantification was done in the negative mode from the extracted ion chromatogram (EIC) for flavan-3-ols and in the positive mode for malvidin-3-O-glucosi~~y~~de. The area under the peaks of malvidin-3-O-glucosi~~y~~de and flavan-3-ol monomers (terminal units) before and after thiolysis as well as toluene-α-thiol adducts (extension units) released from the depolymerisation reaction were integrated. Calibration curves were established with malvidin-3-*O*-glucosi~~y~~de, (+)-catechin, (−)-epicatechin, (−)-epicatechin-3-*O*-gallate, and (−)-epigallocatechin. In the absence of the standards of the thiol derivatives and considering the fact that the thiolytic derivatives were shown to have similar response factors as the correspondent monomeric units, their concentrations were calculated from the respective monomer calibration curves. The mean degree of polymerisation (mDP) was calculated as the ratio of total units (extension + terminal) to terminal units (calculated as the difference between before and after thiolysis). The percentage of tannins linked to malvidin-3-*O*-glucosi~~y~~de (%T-M) was calculated as the molar ratio of malvidin-3-*O*-glucosi~~y~~de linked to tannins (calculated as the difference before and after thiolysis) to the sum of total units of terminal malvidin-3-*O*-glucosi~~y~~de and extension + terminal units of (+)-catechin, (−)-epicatechin, (−)-epicatechin-3-*O*-gallate, and (−)-epigallocatechin (i.e. total units of tannins). The percentage of procyanidins (%PC) was calculated as the ratio of total units (extension and terminal) of catechin and epicatechin to total units of tannins. The percentage of prodelphinidins (%PD) and galloylated (%G) units as the ratio of total units of PD and G to the total units of tannins, respectively.

2.3.2.3. Tannin concentration and activity

Concentration and activity of tannins were estimated by a UHPLC-UV-Vis method following the method proposed by Revelette, Barak, and Kennedy (2014). Tannin activity is related to the thermodynamics of interaction between tannins and a hydrophobic surface (polystyrene divinylbenzene HPLC column).

2.3.3. Chemical characterisation of volatile compounds

2.3.3.1. Determination of Total Odour-Active Carbonyls

The determination by headspace-SPME-GC-MS of total (free plus bound) forms of different odour-active carbonyls such as isobutyraldehyde, 2-methylbutanal, isovaleraldehyde, methional, phenylacetaldehyde, and diacetyl in wine was carried out as is described in the method proposed by Bueno, Zapata, and Ferreira (2014).

2.3.3.2. Determination of major volatile compounds

Major volatile compounds were isolated by liquid-liquid extraction and analysed in a gas chromatograph with flame ionization detector (GC-FID) following the method described by Ortega, López, Cacho, and Ferreira (2001) but with some modifications.

2.3.3.3. Determination of trace aroma compounds

Trace aroma compounds were isolated through solid-phase extraction (SPE) and analysed by gas chromatography coupled to a mass spectrometry detection system (GC-MS) as explained by López et al. (2002).

2.3.3.4. Determination of alkylmethoxypyrazines

Alkylmethoxypyrazines were quantified using stir bar sorptive extraction (SBSE), followed by thermal desorption gas chromatography coupled with mass spectrometry (TD-GCxGC-MS) (Wen, Ontañon, Ferreira, & Lopez, 2018). Stable isotope dilution analysis was used for quantification (with selective mass fragments). The compounds analysed were 2-isobutyl-3-methoxypyrazine (IBMP), 2-isopropyl-3-methoxypyrazine (IPMP) and rotundone.

2.3.4. Data analysis of chemical data

Quantitative data of the 72 volatile compounds were transformed into Odour Activity Values (OAV), by dividing by their corresponding sensory thresholds (ST) (tabulated in Table 1). In the case of concentrations below detection (DL) or quantification (QL) limits, OAV was calculated as DL/ST or QL/ST, respectively. In order to rank compounds in accordance to their discriminatory ability, the quotients between the maximum and minimum OAV were worked out for each compound (OAV minimum < 0.2, this value was arbitrary used for avoiding quotients with no sense from a sensory point of view, especially when OAVmin are zero).

In order to facilitate the correlation of chemical and sensory spaces, the chemical space of volatile molecules was simplified by creating aroma vectors. Aroma vector is defined as "*a perceptual unit constituted by one or several molecules with similar aroma descriptors, which altogether and in an integrated form, are responsible for a specific set of sensory features of a type of products; wine in our case*" (Ferreira, Sáenz-Navajas, & de La Fuente, 2019). Aroma vectors are built by grouping aroma compounds with similar chemical structure and odour properties based on Ferreira, Sáenz-Navajas, and de La Fuente (2019). Therefore, the individual OAV for each compound belonging to each vector is firstly calculated and aroma vectors are the sum of OAVs of compounds within each vector. Table 1 shows the 13 aroma vectors built. Another 11 compounds with known sensory impact were studied individually: β-damascenone (baked apple, dry plum), β-ionone (violets, berry), ethyl dihydrocinnamate (sweet, balsamic), *Z*-3-hexenal (leaf, grassy), diacetyl (buttery, milky, yogurt), methional (potato, oxidised, overripe), phenylacetaldehyde (honey, oxidized), acetaldehyde (green apple, oxidized), isoamyl acetate (fruit, banana), phenylethyl acetate (floral, rose, sweet) and *t*-whiskylactone (oaky, coconut).

Discrimination ability of individual compounds and vectors among wines was evaluated by calculating the ratio OAVmax/OAVmin. Only values >2 were considered to have the ability to discriminate among wines. Besides, only compounds or vectors with OAV> 1 in at least one wine were considered to have a potential sensory impact.

For compounds with OAVmax/OAVmin >2 and OAV>1 in at least one wine, one-way ANOVA (wines as fixed factors) was calculated to find compounds and vectors able to explain the aroma properties of the wines. Pair-wise comparison test (Fischer test) was applied (5% risk) for significant effects. All statistical analyses were performed using XLSTAT (2018).

Finally, a principal component analysis (PCA) was calculated with the mean sensory scores (of the 17 panellist) of the significant sensory aroma terms as active variables and with significant volatile compounds or vectors as supplementary variables. All analyses were carried out with XLSTAT (2018 version).

2.4. Colour measurement

The absorbance spectra of this set of wines were measured. Measurements were carried out in a Shimazdu UV-1800 (Shimadzu Corporation, Tokyo, Japan), using 0.2-cm path-length crystal cuvettes. Measurements were taken every 1 nm between 380 and 780 nm. Wine samples had been previously clarified by passing wine through 0.45 µm filters. From the spectra, the colour coordinates were calculated using the CIE method, with the CIE 1964 10º standard observer and the illuminant D65, according to the OIV. The values correspond to the degree of wine lightness (L_{10}*) and the degree of red (when a_{10}*>0), green (when a_{10}*<0), yellow (when b_{10}*>0), and blue (when b_{10}*<0) colour.

3. Results and discussion

3.1. Effect of grape maturity on conventional parameters of grapes and wines

Grapes from block A, BLA, reached higher levels of sugars (267±3 g L^{-1}) than block B (250±6 g L^{-1}). Significant effects ($P<0.05$) of the maturity point (i.e. harvest point) on sugar content were observed on both blocks, presenting later points of harvest (BLA_4 and BLB_4) the highest levels in both cases (Table 2). These data are well correlated with the ethanol content present in the final wines (Table 2), which reached maximal values (15.8 and 13.7%, v/v, in BLA_4 and BLB_4, respectively) at these points. Interestingly, there is a relatively ample variation (3.4 %, v/v) of ethanol content among the studied wines, which is significantly correlated with total polyphenol index (TPI) ($r=0.97$; $P<0.001$). This fact can be related to the higher capacity of ethanol to extract polyphenolic compounds.

A significant effect of titratable acidity on maturity point was observed in both blocks, presenting the initial harvest points (BLA_1, BLB_1) the highest levels (Table 2). This parameter ranges from 5.8 to 6.7 g L^{-1} (expressed as tartaric acid) in the studied wines, which is within the normal values found in Spanish wines (Sáenz-Navajas, Avizcuri, Ferreira, & Fernández-Zurbano, 2012; Sáenz-Navajas, Fernandez-Zurbano, Tao, Dizy, & Ferreira, 2010). Differently, no significant effect of grape maturity on pH nor volatile acidity of wines was observed for neither of the two blocks studied. Interestingly, the variety object of study shows low pH values (range: 3.2-3.3) in comparison with other Spanish wines elaborated with more common varieties such as Tempranillo, Grenache, Cabernet Sauvignon or Syrah among others, which are reported to range between 3.3 and 4.0, while acetic acid, that ranges from 0.3 to 0.5 g L^{-1} (expressed as acetic acid), is within values reported in literature for Spanish wines (Sáenz-Navajas et al., 2010, 2012).

Based on the content in reducing sugars, which ranged from 1.6 to 2.6 g L^{-1}, it can be confirmed that alcoholic fermentation was properly carried out yielding dry wines in all cases (<5 g L^{-1}). Noteworthy is that wines elaborated with grapes from block B, BLB, underwent malolactic fermentation, providing wines with an average of 0.5 g L^{-1} of lactic acid. Differently, wines from block A had difficulty to finish malolactic fermentation, showing low levels of lactic acid (<0.3 g L^{-1}in all cases).

3.2. Effect of grape maturity on polyphenolic composition and colour coordinates of wines

Table 3 shows variables related to the characterisation of wine polyphenolic compounds and colour coordinates. The values of tannin activity, which is measured as the enthalpy of interaction between polyphenols and a hydrophobic surface (Revelette et al., 2014), range between 854 and 2751 –J mol^{-1}, which are relatively low in comparison with other studies with Cabernet Sauvignon (1430-4820 –J mol^{-1}) (Watrelot, Byrnes, Heymann, & Kennedy, 2016) or Merlot wines (3170-4060 –J mol^{-1}) (Sáenz-Navajas et al., 2018). This property has shown to decrease with both barrel ageing and microoxygenation (Watrelot et al., 2016; Sáenz-Navajas et al., 2018) attributed to tannin oxidation (Yacco, Watrelot, & Kennedy, 2016). Concerning tannin concentration and pigmented tannins, which range from 1993 to 4188 mg L^{-1} and 618-1138 mg L^{-1}, respectively in the studied wines, are significantly lower ($P<0.01$) than values found in Cabernet Sauvignon (2750-6160 mg L^{-1}) and Merlot wines (4390-4940 mg L^{-1}) (Watrelot et al., 2016; Sáenz-Navajas et al., 2018) for tannins and in oaked aged Cabernet Sauvignon for pigments (8300-12700 mg L^{-1}). These data show that the Moristel wines studied present relatively low levels of polyphenols in comparison with other common varieties such as Cabernet Sauvignon or Merlot. The relatively low concentration of tannins seem to be the responsible for the low b_{10}* values (which measures yellow colour) and high values of the L* coordinate (measures wine luminosity, being higher in clearer wines) in comparison with other young Spanish red wines (Soto Vázquez, Río Segade, & Orriols Fernández, 2010). Differently, the red colour of these wines, measured by the a_{10}* coordinate is relatively high (a_{10}*=37-59) in comparison with reported young Mencía wines (a_{10}*=39-46), which could be in part related to the lower pH (average pH=3.3 vs 3.8) of Moristel wines. To this concern, lower pH values favours the presence of flavylium cation species, which contributes to red colour.

Significant effects of maturity level on all the variables studied are observed for block A, while ~~. Differently,~~ for block B, only tannin activity, and coordinate L*, changed significantly. Interestingly, tannin activity is inversely correlated with tannin concentration, pigmented tannins and mean degree of polymerisation (mDP) in block A, while in block B, it decreases with maturity point, when the rest of polyphenolic measurements do not experiment any significant change. These results suggest that tannin activity is a very interesting parameter that can help controlling grape maturity, especially because it is independent from other polyphenolic chemical variables including concentration of tannins or pigments and mean degree of polymerisation.

In general, it is observed that the evolution of the parameters measured are block dependent and no generalisation concerning the effect of grape maturity can be drawn.

3.3. Effect of grape maturity on wine sensory properties

Figures 1a and 1b show the flavour (aroma, taste or mouthfeel) descriptors that present significant differences among wines elaborated with grapes harvested at different points of maturation for the two blocks studied: BLA and BLB, respectively. Significant effects of grape maturity are observed on raisin (F=3.41; P<0.05) and oxidation (F=2.93; P<0.05) aromas as well as on astringency (F=6.90; P<0.01) for block A. For block B significant effects on oxidation aromas (F=12.5; P<0.001) and fruity nuances including raisin (F=3.39; P<0.05), red fruit (F=4.32; P<0.05) and black fruit (F=4.82; P<0.05) as well as on astringency (F=4.05; P<0.05) are observed. It is ~~interesting~~ important to note that the sensory effects of grape maturity on most flavour attributes, including fruity aromas as well as astringency, are block dependent. Interestingly, in

Figure 2, a general pattern of appearance of oxidation nuances in wines elaborated with grapes harvested at earlier points, such as BLA_1, BLB_1 and BLB_2, is observed. These oxidation nuances, change~~move~~ to fresh fruits (black or red fruit) in wines elaborated with grapes harvested latter in both blocks (BLA_3 and BLB_4), and finally, overripe grapes obtained in BLA generated raisin-like aromas.

Considering that young red quality is positively linked to fruity aromas and negatively to oxidation and dried fruit nuances (Sáenz-Navajas, Gonzalez-Hernandez, Campo, Fernández-Zurbano, & Ferreira, 2012), results suggest that the optimal point of harvest would be BLA_3 for Block A and BLB_4 for Block B. This result differs from the commercial system employed as it suggested earlier points of maturity: BLA_2 and BLB_2 as optimal points.

To gain insights into the sensory-active compounds driving such sensory differences, further relationships between sensory and chemical variables were explored.

3.3. Relationship between sensory and chemical variables

3.3.1. Aroma properties

The study of the volatile composition of the twenty-one wines has provided quantitative data for 72 compounds (Table 4). Part of these compounds were grouped into 13 aroma vectors as detailed in Table 1, while other eleven compounds with known sensory impact by themselves were individually considered. Among these 24 variables, only 13 of them were expected to explain the aroma differences perceived among the 21 wines studied (Table 5). Firstly, because they were above their sensory threshold (OAV >1) and secondar~~il~~y because the difference in odour activity among wines was important enough to induce sensory differences (measured as the ratio of OAVmax/OAVmin). Figure 2 shows the PCA with these 13 volatile-related parameters projected as active variables and four aroma-related variables (raisin, red and black fruit and oxidation) projected as illustrative variables. As can be seen in the plot, the first principal component (PC1), explaining 75% of the total variance, confronts samples with black and red fruity aromas (projected on the right side of the plot) to wines projected on the left part of the plot with dried fruit (BLA_4) notes and oxidised nuances (BLA_1 and BLA_2; BLB_1 and BLB_2). These fresh fruity aromas are positively correlated to the isoamyl acetate compound (with banana-like aroma), which has been described to be an undeniable contributor to fruity nuances in young red wines (Ferreira et al., 2002). Different ethyl ester profiles are suggested to be the responsible for the appearance of specific red (higher levels of linear ethyl esters) or black (higher levels of branched ethyl esters) fruit aromas (Pineau, Barbe, Van Leeuwen, and Dubourdieu, 2009). However, such differences are not observed in the studied wines. Differently, sample BLA_1, with the highest level of ethyl esters, present outstanding oxidation nuances that are also present in samples BLB_1, BLB_2 and BLA_2. These oxidation notes can be easily explained in terms of aldehydes including phenylacetaldehyde, and isoaldehydes, free acetaldehyde and methional. This suggests a possible masking/suppressor effect generated by the aldehydes (Culleré, Cacho, & Ferreira, 2007) as well as the acetic acid vector (San Juan, Ferreira, Cacho, & Escudero, 2011) on the fruity character of ethyl esters, specially of BLA_1.

The appearance of oxidation nuances in wines elaborated with grapes harvested at earlier points can be explained in terms of higher levels of oxidation-related aldehydes. Interestingly, this observed wine oxidation seems to be related to the presence of lower polyphenolic contents. More specifically, the levels of both the isoaldehyde vector and phenylacetaldehyde present significant ($p < 0.05$) negative linear correlations with total polyphenol content (TPI) ($r=-0.886$, $r=-0.843$), tannin concentration ($r=-0.782$, $r=-0.791$) and not precipitable anthocyanin-derivative pigments (MP+SPP) ($r=-0.810$, r=-

0.772). This result is well in line with models predicting accumulation of oxidation-related aldehydes calculated by Bueno et al., (2018). In these models, the accumulation of these compounds was negatively correlated to the content in different polyphenolic compounds (anthocyanins and tannins), which were denominated aldehyde-reactive polyphenols (ARPs). Thus, the lower levels of polyphenolic compounds acting as ARPs found in wines elaborated with prematurely harvested grapes could explain the higher OAVs values observed for both the isoaldehyde vector and phenylacetaldehyde compound, and thus the appearance of oxidation nuances in these wines.

Sample BLA_4 presents a specific raisin aroma, which could be related to the presence of higher levels of β-damascenone (San Juan et al., 2011). Interestingly, higher levels of this norisoprenoid have been found in wines elaborated with dehydrated grapes in comparison with fresh grapes (Bowen & Reynolds, 2012; Genovese, Gambuti, Piombino, & Moio, 2007). This is well in accordance with studies that observed the formation of β-damascenone in grapes during the on-vine dehydration process (Lan et al., 2016). This could be the case of sample BLA_4, which was elaborated with the ripest grapes and probably overripe.

3.3.2. Astringency

Astringency scores range between 0.53 and 3.6 (being 7 the maximum possible score) and highly significant differences among wines (F=18.17; P<0.00~~0~~1) are observed. Table 6 shows 14 variables with potential to be involved in the formation of astringency perception. All of them are significantly different (P<0.001) among the 21 wines studied.

Astringency scores present significant (p<0.001) positive linear correlations with six out of the 14 chemical variables studied, such as ethanol content and polyphenolic-related variables, including total polyphenol index, tannin activity and anthocyanin-derivative pigments (such as monomeric and large polymeric pigments).

The role played by ethanol content in astringency perception is contradictory since there are works that show a reduction of astringency with increasing ethanol content (Vidal et al. 2004), which is attributed to a decrease of the strength of interaction between tannin and protein in presence of increasing levels of ethanol (McRae et al. 2015). Contrary to these reports, and in accordance with the presented results, there is a wide range of papers (Watrelot et al. 2016, Sáenz-Navajas et al. 2010, 2012) that report significant positive effects of ethanol on astringency perception. Thus, it cannot be ruled out that certain astringent-related sensations are driven by other mechanisms different from polyphenol-protein interactions.

Regarding anthocyanin-related compounds, both bleachable anthocyanins (or monomeric anthocyanins, MP) and non-bleachable (or polymeric pigments, SPP+LPP) present significant positive correlations with astringency (Table 6) (r =0.76; p<0.00~~0~~1 and r =0.79; p<0.00~~0~~1 respectively). To this concern, recent works suggest that certain anthocyanins could be involved in the modulation of taste and/or mouthfeel properties (Ferrer-Gallego et al., 2015; Paissoni et al., 2018; Sáenz-Navajas et al., 2017, 2018b).

Interestingly, tannin activity is highly correlated (r =0.91; p<0.01) with astringency, this is the first time that this variable, that measures the affinity of tannins to a hydrophobic surface (polystyrene divinylbenzene HPLC column), is related to sensory perception. To this concern, same grape variety from similar origin and processed with the same winemaking protocol, could have helped to establish such interesting linear relationship between tannin activity and sensory astringency, in contradiction with other studies in which not significant correlation could be found, which was attributed to a possible effect of aroma or even other non-volatile components on astringent perception (Watrelot et al., 2016).

Conclusions

In the present work, the effect of Moristel grape maturity on wine sensory and chemical composition was studied. This variety is shown as an interesting minor variety to be cultivated under warm climates. Under the presented experimental winemaking protocol Moristel grapes yielded wines with relatively low pH values, high red colour with relatively low tannin activity, tannin and pigmented tannin concentrations that harvested at optimal point is able to yield wines with fresh fruity aroma and a moderate astringency. Interestingly, it was observed in the present work that Moristel grapes prematurely harvested yield oxidation aroma nuances. This attribute is related to free acetaldehyde, methional, phenylacetladehyde and isoaldehydes as well as to low levels of aldehyde-reactive polyphenols (tannins, and anthocyanins that do not precipitate with ovaoalbumin: MP and SPP). Contrary, grapes suffering on-vine dehydration, induce the ~~appearance~~ development of raisin aroma in wines, which is suggested to be due to the formation of β-damascenone already in grapes. Astringency is related to ethanol content, tannin activity (measured as the interaction of tannins with a hydrophobic surface) and the content in anthocyanin-derivative compounds.

At present, further studies are being carried out to find the grape precursors that yield aldehydes in wines, this would help to control grape quality and define the optimal point of harvest. Besides, it would be interesting to perform similar studies in other grape varieties to elucidate if this tendency to generate oxidised wines with unripe grapes is a general tendency or on the contrary is cultivar-dependent.

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Figure captions

Figure 1. Sensory attributes (expressed as the average of three tanks, error bars are the standar deviation among the three tanks) that present significant effects of grape maturity in wines elaborated with grapes of a) Block A harvested at four different points (BLA_1, BLA_2, BLA_3, BLA_4) and Block B harvested at four different points (BLB_1, BLB_2, BLB_4).

Figure 2. Principal component analysis plot calculated with the 7 different wines elaborated, chemical aroma parameters as active variables and sensory attributes as supplementary variables.

Table 1

Table 1. Aroma vectors built by grouping volatile compounds with similar chemical and aroma description according to Ferreira, Sáenz-Navajas, and de La Fuente (2019).

Vector	Compounds in the vector	Aroma description
Acetate vector	isobutyl acetate, butyl acetate	Fruity, pear
Acetic vector	ethyl acetate, acetic acid	Glue, vinegar
Branched acid vector	3-methylbutyric, 2-methylpropanoic acids	Cheese, sweaty
Ethyl ester vector	ethyl proponoate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl isobutyrate, ethyl 2-methylbutyrate, ethyl isovalerate, ethyl lactate, diethyl succinate	Fruity, apple, strawberry
Ethyl phenol vector	4-ethylguaicol, 4-ethylphenol	Animal, leather
Isoaldehyde vector	isobutanal, 2-methylbutanal, 3-methylbutanal	Malty, yeasty
Higher alcohol vector	isobutanol, isoamyl alcohol, β-phenylethanol, 1-butanol, methionol, benzylic alcohol, 1-penten-3-ol, 1-hexanol, z-3-hexenol, t-2-hexenol, t-3-hexenol, 1-octen-3-ol	Harsh, spirit, solvent
ɣ-Lactone vector	γ-nonalactone, γ-butyrolactone	Peachy
Linear fatty acid vector	butyric, hexanoic, octanoic, decanoic acids	Cheese, soapy
Methoxyphenol vector	guaiacol, eugenol, isoeugenol, 4-vinylguaiacol, 2,6-dimethoxyphenol, 4-allyl-2,6-dimethoxyphenol, 4-vinylphenol, o-cresol, m-cresol	Clove, smoky
Methoxypyrazine vector	3-isopropil-2-methoxypyrazine (IPMP), 3-isobuthyl-2-methoxypyrazine (IBMP)	Green, earthy, green pepper
Terpenol vector	geraniol, β-citronellol, α-terpineol, linalool	Jasmine, muscat, orange blossom
Vanilla vector	vanillin, acetovanillone, ethyl vanillate, methyl vanillate	Vanilla, nutmeg

Table 2

Table 2. Conventional oenological parameters of wines and grapes (sugar content) expressed as the average (among replicated tanks) ± standard deviation. Different letters within the same block (BLA or BLB) indicate significant differences (P<0.05 according to pairwise Fischer test) among the maturity points (BLA1-BLA4 or BLB1-BLB3).

	GRAPES	**WINES**							
	sugar content (g L^{-1})	**pH**	**volatile acidity (g L^{-1} acetic acid)**	**titratable acidity (g L^{-1} tartaric acid)**	**reducing sugars (g L^{-1})**	**malic acid (g L^{-1})**	**lactic acid (g L^{-1})**	**ethanol content (%. v/v)**	**TPI* (a.u.)**
BLA_1	251±3b	3.2±0.0	0.5±0.0	6.7±0.0a	2.0±0.1c	0.6±0.0b	0.2±0.1	14.8±0.2b	45.2±0.0b
BLA_2	254±5b	3.3±0.0	0.5±0.0	6.0±0.0b	2.3±0.0b	0.3±0.0c	0.2±0.1	14.9±0.2b	45.6±0.0b
BLA_3	250±11b	3.3±0.0	0.4±0.0	6.1±0.0b	2.6±0.1a	0.4±0.0c	0.3±0.0	14.4±0.3b	43.8±0.1b
BLA_4	267±3a	3.3±0.0	0.4±0.0	5.8±0.0c	2.5±0.0a	0.8±0.0a	0.1±0.0	15.8±0.0a	53.0±0.0a
BLB_1	224±9b	3.2±0.1	0.5±0.0	6.4±0.1a	1.6±0.0b	0.3±0.1b	0.5±0.0	12.4±0.2b	22.1±1.7b
BLB_2	227±12b	3.2±0.0	0.3±0.0	6.0±0.0b	1.6±0.0b	0.5±0.1a	0.5±0.1	12.7±0.3b	24.2±1.0a
BLB_4	250±6a	3.2±0.0	0.4±0.0	6.0±0.2b	1.9±0.0a	0.3±0.0b	0.5±0.0	13.7±0.2a	25.7±0.6a

*TPI: total polyphenol index

Table 3

Table 3. Chemical characterisation of polyphenolic composition and colour coordinates (a_{10}*, b_{10}*, L*) in wines expressed as the average (among replicated tanks) ± standard deviation. Different letters within the same block (BLA or BLB) indicate significant differences (P<0.05 according to pairwise Fischer test) among the maturity points (BLA1-BLA4 or BLB1-BLB4). Numbers marked in bold are the highest values within a block

	tannin activity (-J mol^{-1})	**tannin concentration** (mg L^{-1})	**pigmented tannins** (mg L^{-1})	**mDp**[1]	**a***	**b***	**L***
BLA_1	2751±19a	2926±71c	778±25b	1.4±0.1c	**58.6±0.2a**	8.7±0.1b	44.5±0.2b
BLA_2	**2689±96a**	3051±67c	841±120b	1.3±0.0c	56.6±0.1c	8.8±0.2b	45.0±0.1b
BLA_3	1811±15b	**4188±73a**	**1138±160a**	**2.8±0.2a**	46.7±0.1d	0.9±0.4c	**47.0±0.1a**
BLA_4	**2673±32a**	3472±40b	854±80b	1.9±0.0b	57.8±0.1b	**12.5±0.4a**	43.9±0.1c
BLB_1	**1044±47a**	2071±199	618±79	1.6±0.2	42.2±0.6a	0.4±0.1	64.3±0.0b
BLB_2	933±90b	1993±163	646±69	1.7±0.2	43.6±2.0b	1.4±0.9	63.9±2.3b
BLB_4	854±61c	2066±111	687±51	1.8±0.2	36.7±0.6a	0.4±0.4	**70.4±0.4a**

[1] mean deagree of polymerisation

Table 4

Table 4. Limit of detection (LOD), odour thresholds, concentration ranges and median values of volatiles found in the set of the 21 wines (all expressed in micrograms per litre). Maximum to minimum odour activity value rate (OAV $_{MAX}$/ OAV $_{MIN}$). Compounds found in at least one wine at concentrations above their sensory threshold are marked in bold. Based on sensory impact of compounds, part of them are grouped into aroma vectors (they act in a concerted way), and other 11 are individually presented.

compounds	LOD	odour threshold[a]	concentration range	median	OAV $_{MAX}$/ OAV $_{MIN}$
β-ionone	**0.33**	**0.09[5]**	**0.393-0.752**	**0.499**	1.91
diacetyl	**1.59**	**100[3]**	**244-12245**	**1996**	50.1
acetaldehyde (free)	**115**	**500[3]**	**<LD-5437**	**815**	47.3
β-damascenone	**0.187**	**0.05[3]**	**<LD-2.69**	**0.682**	14.4
isoamyl acetate	**18**	**30[3]**	**80.9-301**	**163**	3.72
phenylacetaldehyde	**1.67**	**1[15]**	**6.68-22**	**13**	3.3
***z*-3-hexenal**	**0.059**	**0.12[22]**	**15.1-24.9**	**18.3**	1.65
ethyl dihydrocinnamate	0.026	1.6[5]	<LD-0.491	0.375	1.53
phenylethyl acetate	0.019	250[3]	2.51-8.35	4.88	0.167
t-whiskylactone	0.09	790[2]	<LD-0.796	0	0.005
vectors	**LOD**	**Odour threshold[a]**	**Concentration Range**	**Median**	**OAV $_{MAX}$/ OAV $_{MIN}$**
acetate vector					
butyl acetate	0.167	1800[2]	1.8-15.9	3.39	0.044
isobutyl acetate	0.158	1600[1]	5.42-16	6.73	0.05
acetic vector					
acetic acid	**240**	**300000[3]**	**270496-746363**	**449652**	2.76
ethyl acetate	**10**	**12300[4]**	**1062-81907**	**49833**	33.3
branched acids vector					
isobutyric acid	**101**	**2300[6]**	**2029-3004**	**2574**	1.48
isovalerianic acid	**28**	**33[5]**	**60-3731**	**2211**	62.2
ethyl ester vector					
ethyl propanoate	50	5500[9]	<LD-228	0	0.207
ethyl butyrate	**26.3**	**125[9]**	**46-157**	**102**	3.42
ethyl hexanoate	**34.2**	**62[9]**	**145-490**	**277**	3.38
ethyl octanoate	12	580[2]	50.9-173	120	1.49
ethyl decanoate	**17.2**	**200[5]**	**<LD-409**	**33.6**	10.2
ethyl isobutyrate	**0.495**	**15[5]**	**79.9-164**	**106**	2.06
ethyl 2-methylbutyrate	**0.33**	**18[5]**	**10.3-20**	**16.6**	1.94
ethyl isovalerate	**0.33**	**3[5]**	**13.7-61.4**	**20.1**	4.48
ethyl lactate	100	154000[2]	10675-69951	33465	2.27
diethyl succinate	3	200000[2]	1137-8994	7714	0.225
ethylphenol vector					
4-ethylguaiacol	0.018	33[5]	<LD-0.289	0.09	0.044
4-ethylphenol	0.023	35[9]	<LD-1.5	0.175	0.215
isoaldehyde vector					
isobutanal	**0.495**	**6[15]**	**16.5-43.4**	**30.8**	2.63
2-methylbutanal	0.176	16[15]	5.97-14.9	9.45	2.5
3-methylbutanal	**0.206**	**4.6[15]**	**6.85-55.4**	**21.2**	8.1
higher alcohol vector					
benzylic alcohol	10	200000[7]	44.1-468	199	0.012
1-butanol	2	150000[2]	876-1885	1144	0.063
1-hexanol	14	8000[3]	2556-3348	2921	1.31
t-2-hexenol	0.739	15000[21]	<LD-16.6	3.02	0.006
t-3-hexenol	0.166	1000[20]	33.8-86.1	59.7	0.43
z-3-hexenol	12.2	400[3]	27.9-168	48.4	2.11
isoamyl alcohol	**19**	**30000[3]**	**219088-289686**	**259247**	1.32
isobutanol	**24.3**	**40000[3]**	**28890-40186**	**32461**	1.39
methionol	**26**	**1000[5]**	**169-3882**	**993**	19.4
1-octen-3-ol	3.85	40[18]	8.73-35.2	16.4	4.03
1-penten-3-ol	7.81	400[19]	<LD-294	97.2	3.68
β-phenylethanol	**5**	**14000[5]**	**2946-43218**	**32360**	14.7
γ **-lactone vector**					
γ -butyrolactone	18.3	35000[12]	1071-17501	10821	2.5
γ-nonalactone	**0.064**	**25[14]**	**9.93-25.1**	**17.1**	2.52
linear fatty acid vector					
butyric acid	**100**	**173[5]**	**162-1170**	**678**	7.24
hexanoic acid	**10**	**420[5]**	**177-1992**	**1546**	11.3
octanoic acid	**10**	**500[5]**	**729-1561**	**975**	2.14
decanoic acid	27	1000[5]	<LD-909	474	4.55
methoxyphenol vector					
guaiacol	**0.05**	**9.5[5]**	**<LD-21.5**	**5.67**	11.3
eugenol	0.019	6[5]	1.23-2.99	1.61	2.43
4-vinylguaiacol	0.039	40[3]	5.75-24.7	11	3.09
isoeugenol	**0.073**	**6[12]**	**1.04-14.3**	**3.46**	11.9
2,6-dimethoxyphenol	0.048	570[10]	4.16-23.9	8.65	0.21
4-alyl-2,6-dimethoxyphenol	0.33	1200[6]	1.78-6.15	2.96	0.026
o-cresol	0.33	31[2]	<LD-1.05	0.828	0.17
m-cresol	0.003	68[11]	<LD-0.68	0.078	0.05
4-vinylphenol	0.055	180[13]	6.03-52.4	14.1	1.46
methoxypyrazine Vector					
2-isopropyl-3-methoxypyrazine (IPMP)	**0.00007**	**0.0003 [17]**	**<LD-0.00138**	**0.00007**	19.6
2-isobutyl-3-methoxypyrazine (IBMP)	**0.00002**	**0.002[17]**	**0.00087-0.00222**	**0.00157**	2.56

vectors	LOD	Odour threshold [a]	Concentration Range	Median	OAV_{MAX}/ OAV_{MIN}
terpenol vector					
linalool	0.045	25[5]	2.37-5.05	3.37	1.01
α-terpineol	0.048	250[5]	0.853-1.91	1.46	0.038
β-citronelol	0.779	100[2]	<LD-4.92	2.69	0.246
geraniol	0.33	20[12]	1.38-5.41	3.87	1.35
vanillin vector					
vanillin	0.076	995[12]	3.44-15	6.64	0.075
methyl vanillate	0.041	3000[10]	2.41-5.54	3.52	0.009
ethyl vanillate	0.059	990[10]	67.3-256	133	1.29
acetovanillone	0.136	1000[12]	32-78.1	53	0.391

[a] Odour thresholds. Reference in which the odour threshold value has been calculated is given in brackets. [1] Ferreira et al. (2002). [2] Etievant et al. (1991). [3] Guth (1997). [4] Escudero et al. (2004). [5] Ferreira et al. (2000). [6] Gemert (2003). [7] Aznar et al. (2003). [8] Peinado et al. (2004). [9] San Juan et al. (2012). [10] Lopez et al. (2002). [11] Ferreira et al. (2009). [12] Escudero et al. (2007). [13] Boidron et al. (1988). [14] Gemert (2003). [15] Cullere et.al (2007). [16] Cullere et.al (2016). [17] Hjelmeland et.al (2016). [18] Boutou et Chatonnet (2007). [19] Buttery et.al (1971). [20] Fariña et.al (2014). [21] Darici et.al (2014). [22 Sellami et.al (2018).

[b] For $OAV_{minimum} < 0.2$, this value is considered for calculating the quotient.

Table 5

Table 5. Individual aroma compounds and vectors with possible sensory impact (Odour Activity Values, OAV>1), with ability to differentiate ($OAV_{Max}/OAV_{Min} > 2$) and significantly different among the 21 studied wines. Maximum and minimum OAVs found in the set of wines. Significance (P-value): ****P<0.001; ***P<0.01; **P<0.05, *P<0.1) of the ANOVA (wines as fixed factors).

compounds	**OAV_{Max}**	**OAV_{Min}**	**OAV_{Max}/OAV_{Min}**	**significance P-value**
acetaldehyde (free)	10.9	0.23	47.3	**
branched fatty acid vector	114	2.96	38.7	****
β-damascenone	53.8	3.73	14.4	****
methoxypyrazine vector	5.61	0.666	8.42	****
methoxyphenol vector	5.4	0.853	6.33	****
acetic vector	8.19	1.81	4.53	****
isoaldehyde vector	19.5	5.17	3.77	****
isoamyl acetate	10	2.7	3.72	**
linear fatty acid vector	14	3.97	3.53	****
phenylacetaldehyde	22	6.68	3.30	***
γ-lactone vector	1.34	0.466	2.87	****
methional	55.8	22.5	2.49	*
ethyl ester vector	36.6	15.8	2.32	****

Table 6

Table 6. Conventional parameters and phenolic-related parameters analysed in the 21 wine samples of the study. Maximum, minimum, median, quotient of maximal and minimal level, and Pearson correlation coefficients (r) between sensory astringency and chemical variables (significance: *P<0.01). Chemical variables with significant lineal correlation with astringency are marked in bold.

	max	min	median	max/min	r (astringency)
pH	3.3	3.1	3.3	1.1	0.25
titratable acidity (TA) (g/L)	6.8	5.8	6.1	1.2	0.22
ethanol content (% v/v)	**15.8**	**11.8**	**13.4**	**1.34**	**0.69***
colour intensity (CI) (a.u.)	**14.0**	**4.30**	**6.40**	**3.26**	**0.79***
total polyphenol index (TPI) (a.u.)	**53.0**	**21.0**	**25.5**	**2.52**	**0.75***
tannin activity (TA) (-J/mol)	**2765**	**739**	**1007**	**3.74**	**0.83***
tannin concentration (TC) (mg/L)	4193	1794	2192	2.34	0.57
monomeric pigments (MP) (a.u.)	**0.96**	**0.26**	**0.42**	**3.7**	**0.76***
small and large polymeric pigments (SPP+LPP) (a.u.)	**0.60**	**0.17**	**0.25**	**4.1**	**0.79***
mean degree of polymerisation (mDP)	2.9	1.2	1.7	2.3	-0.17
% of procyanidins in tannins (%PC)	78.0	40.9	67.2	1.90	-0.27
% of galloylated tannins (%G)	2.33	0.639	1.21	3.64	0.39
% of prodelphinidins in tannins (%PD)	10.6	2.65	6.00	3.98	-0.22
% of malvidin in tannins (%M-T)	53.4	9.14	25.3	5.85	0.27

Figure

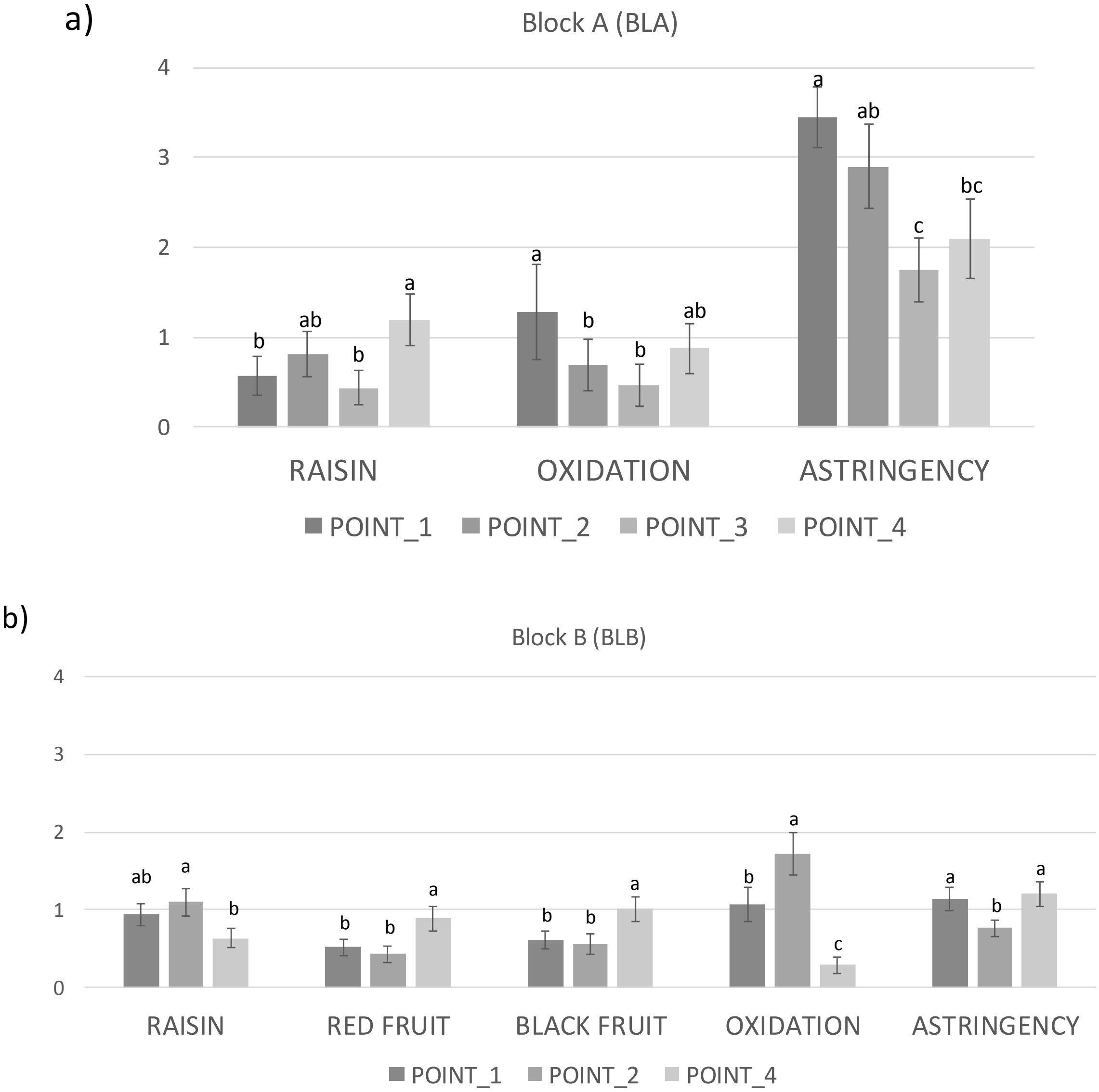
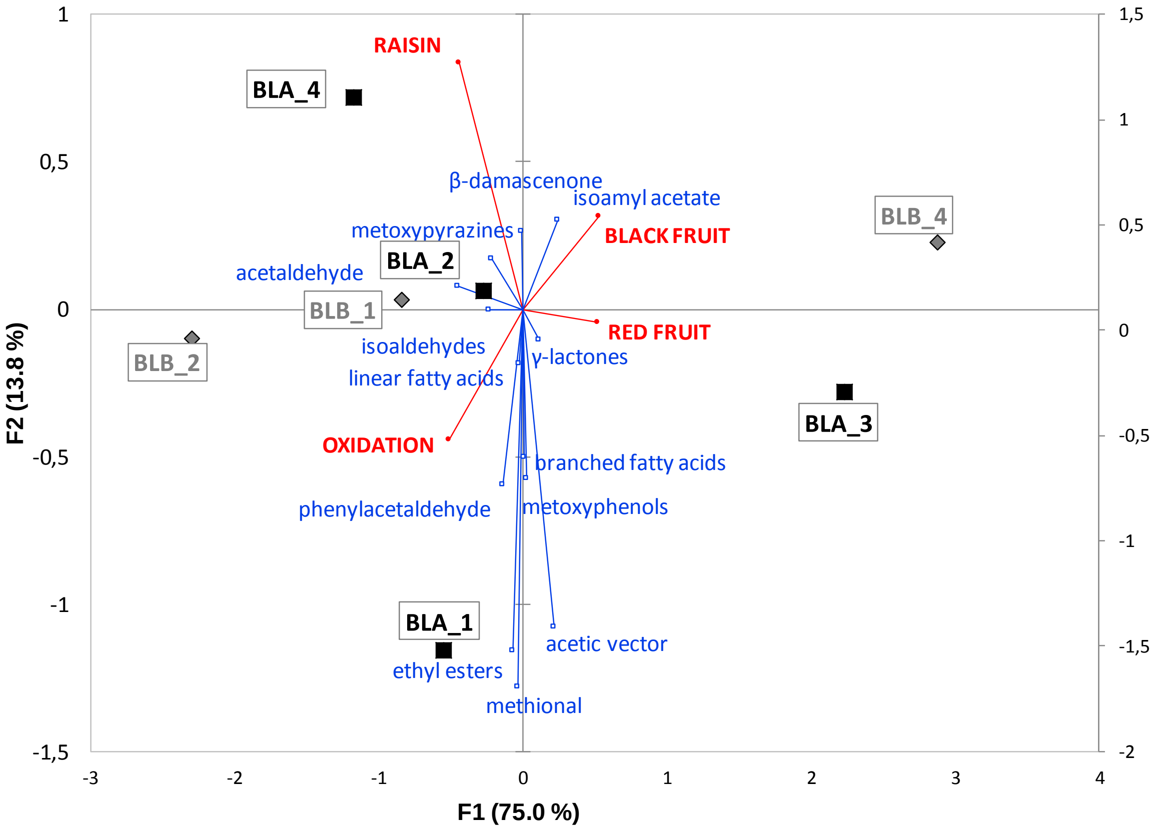


Figure 1



1
0,5
0
-0,5
-1
-1,5
1,5
1
0,5
0
-0,5
-1
-1,5
-2
-3
-2
-1
0
1
2
3
4
F1 (75.0 %)
F2 (13.8 %)
RAISIN
BLA_4
β-damascenone
isoamyl acetate
metoxypyrazines
BLACK FRUIT
BLB_4
BLA_2
acetaldehyde
BLB_1
BLB_2
isoaldehydes
RED FRUIT
γ-lactones
linear fatty acids
BLA_3
OXIDATION
branched fatty acids
phenylacetaldehyde
metoxyphenols
BLA_1
acetic vector
ethyl esters
methional

Figure 2