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Title: Sensory variability associated with anthocyanic and tannic fractions isolated from red wines

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Abstract: Tannins and anthocyanins are important modulators of the intrinsic quality of red wines, playing a major role in consumer preference and appreciation. Tannins are chiefly responsible for the astringency in wines although their role in eliciting different astringent subqualities is still relatively unknown. On the other hand, the sensory contribution of anthocyanic fractions is even less clear. The main aim of the present study was to assess whether anthocyanic fractions from red wine elicit specific mouthfeel and taste attributes that differ from their tannin counterparts, and to evaluate the contribution of anthocyanic and tannic fractions to taste and mouthfeel of red wines. Isolation of tannin (Ftannin) and anthocyanin (Fantho) fractions from 20 wines involved reversed-phase semipreparative liquid chromatography followed by solid phase extraction. The 40 derived fractions subsequently underwent sensory characterisation using a labelled sorting task and a rate-K attributes method. Bitterness and dryness were the salient attributes differing among the sensory spaces of both Fantho and Ftannin. Likewise, other independent and non-correlated mouthfeel dimensions differed for both Fantho ("grainy" and mouthcoating") and Ftannin ("gummy"). A significant linear model predicting wine dryness from the "dry" intensity of Fantho and Ftannin was obtained, with tannic fractions presenting a higher contribution than anthocyanic fractions. These results not only confirmed that tannins have a major implication in red wine dryness but also unequivocally demonstrated a relevant implication of certain anthocyanins in this attribute. In contrast, bitterness of the original wines could not be directly related to the bitterness perceived in any of the two groups of fractions. The addition of an extremely bitter anthocyanic fraction to wines only increased bitterness in certain wines, suggesting that bitterness in wines may result from perceptual interactions and that some wines contain strong bitterness suppressors.

Highlights

- Tannin and anthocyanin fractions were isolated from a diverse set of 20 red wines
- Sensory analysis of fractions was conducted with sorting task and rate-*K* attributes
- “Bitter” and “dry” were salient attributes differing among anthocyanic fractions
- Anthocyanic fraction contributes to orosensory cues more than previously thought
- Red wine was proposed to contain strong bitterness suppressors

1 Sensory variability associated with anthocyanic and tannic fractions isolated from red
2 wines

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Abstract

Tannins and anthocyanins are important modulators of the intrinsic quality of red wines, playing a major role in consumer preference and appreciation. Tannins are chiefly responsible for the astringency in wines although their role in eliciting different astringent subqualities is still relatively unknown. On the other hand, the sensory contribution of anthocyanic fractions is even less clear. The main aim of the present study was to assess whether anthocyanic fractions from red wine elicit specific mouthfeel and taste attributes that differ from their tannin counterparts, and to evaluate the contribution of anthocyanic and tannic fractions to taste and mouthfeel of red wines. Isolation of tannin (F_{tannin}) and anthocyanin (F_{antho}) fractions from 20 wines involved reversed-phase semipreparative liquid chromatography followed by solid phase extraction. The 40 derived fractions subsequently underwent sensory characterisation using a labelled sorting task and a rate- K attributes method. Bitterness and dryness were the salient attributes differing among the sensory spaces of both F_{antho} and F_{tannin} . Likewise, other independent and non-correlated mouthfeel dimensions differed for both F_{antho} (“grainy” and mouthcoating”) and F_{tannin} (“gummy”). A significant linear model predicting wine dryness from the “dry” intensity of F_{antho} and F_{tannin} was obtained, with tannic fractions presenting a higher contribution than anthocyanic fractions. These results not only confirmed that tannins have a major implication in red wine dryness but also unequivocally demonstrated a relevant implication of certain anthocyanins in this attribute. In contrast, bitterness of the original wines could not be directly related to the bitterness perceived in any of the two groups of fractions. The addition of an extremely bitter anthocyanic fraction to wines only increased bitterness in certain wines, suggesting that bitterness in wines may result from perceptual interactions and that some wines contain strong bitterness suppressors.

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1. Introduction

Polyphenols are important bioactive molecules present in grapes and wines, with red wines being especially rich in these compounds. Their significance is based on their effect on human health (antimicrobial, antiviral, anti-inflammatory and antioxidant activity) (Arranz et al., 2012; Nash et al., 2018) as well as on their ability to modulate intrinsic quality of red wines (colour, aroma, taste and mouthfeel) (Soares, Brandão, Mateus, & de Freitas, 2017), thus consumer preference and appreciation. In this context, the most relevant polyphenols are tannins (oligomers and polymers of flavan-3-ols, >dimers) and anthocyanins (and their derivative pigments).

Tannins can be classified as hydrolysable, such as those coming from oak wood or oenological tannin addition, or condensed (i.e., proanthocyanidins, PAs), coming from grape skin and seed and extracted during fermentation. The concentration and structure of PAs in wine are dependent on the grape variety, degree of ripening and interventions during winemaking (Harrison, 2018): researchers still seek to understand how these variables influence the composition and sensory perception of red wines. In a recent study (Sáenz-Navajas et al., 2017), the sensory properties of an isolated PA fraction (mean degree of polymerisation (mDP) in the range of 3-10), obtained from three red wines that differed in mouthfeel, were described with terms such as “coarse”, “grainy”, “dry on the tongue” and “dry on the palate”. Interestingly, in another study of four wines with very different mouthfeel properties (Sáenz-Navajas et al., 2018), it was determined that the mouthfeel characteristics of the PA fraction isolated as per the previous study were more diverse, appearing to resolve into three types of sensory-active fractions: 1) “silky”, “sweet” or “greasy”, 2) “sticky” and “coarse”, and 3) “dry”, “granular” and “coarse”. These fractions were characterised by measuring the usual chemical parameters linked to astringent mouthfeel sensations: concentration and activity of tannins (WatreLOT, Byrnes, Heymann, & Kennedy, 2016), mean degree of polymerisation (mDP), and % of galloylation (Kennedy & Jones, 2001). However, the analysed chemical variables were not able to explain such important sensory differences. This might be attributed to the low number of assessed fractions (four) hindering the calculation of significant statistical correlations or to the limited

number of chemical parameters currently available for characterising polymerised flavan-3-ols isolated from wine. Nonetheless, the studies revealed the existence of an array of astringent sub-qualities arising from PA fractions obtained from different wines, which gives insight into further studies that are required to better understand the mouthfeel phenomenon of red wines. As for the other important class of polyphenols in red wines, anthocyanins present as monomers, oligomers and polymers are conventionally thought to be responsible exclusively for the colour of red wines (i.e., had no taste or mouthfeel properties). This understanding is based on studies carried out with grape anthocyanins (containing mainly anthocyanin glucosides along with their monoglucoside acetate and coumarate counterparts) (Vidal, Francis, et al., 2004). The authors concluded that free anthocyanins, like the coloured tannin-like polyphenolic compounds from red wine and pomace, do not contribute astringency nor bitterness to wine. The same authors found in other work that grape anthocyanins could contribute to fullness, chalkiness and coarseness when assessed in model wine (Vidal, Courcoux, et al., 2004). However, they questioned their results and concluded that such sensory properties were attributed to other phenolics present in the studied fraction. Most recently, in their review of astringency perception, García-Estévez, et al. (García-Estévez, Ramos-Pineda, & Escribano-Bailón, 2018) summarised that the effect of anthocyanins was indirect because they hinder the interaction between proteins and other phenolics such as flavanols, which are thought to be chiefly responsible for astringency in wines. However, these authors rightfully acknowledged the lack of research and inconclusive understanding of the role of anthocyanins in the development of astringency in relation to protein interactions. Indeed, new studies correlating surface plasmon resonance response and wine composition have suggested that anthocyanins are important drivers of pigmentation and mouthfeel properties (Guerreiro, Teixeira, De Freitas, Sales, & Sutherland, 2017), and they have also been implicated in bitterness (Soares et al., 2013). This proposition regarding the mouthfeel properties of anthocyanins is supported by studies demonstrating the formation of complexes of malvidin-3-*O*-glucoside (Ferrer-Gallego et al., 2015) and pyranoanthocyanins (García-Estévez et al., 2017) with proteins, combined with knowledge of the sensory activity of certain anthocyanic fractions

(Sáenz-Navajas et al., 2018; Sáenz-Navajas et al., 2017). The sensory variability of a discrete anthocyanin-containing fraction obtained from red wines pertained to descriptions such as “sour”, “dry”, “bitter”, “persistent” and “coarse” for three wines or “sticky” and “coarse” for a fourth wine (Sáenz-Navajas et al., 2018). In another set of three wines, the corresponding fraction was “dry”, “bitter”, and “persistent” for two wines and “silky” for the third. These results reinforced the uncertainty about the sensory role of anthocyanic fractions, and it is of paramount importance for the production of quality wines to better understand the sensory impact of different classes of wine polyphenols.

Having highlighted the lack of knowledge about the sensory variability associated to both red wine tannins and anthocyanins (and derived pigments), the main aim of the present study was to identify taste and mouthfeel dimensions related to red wine polyphenols, particularly in relation to tannins and anthocyanins. Specifically, the work tested the hypotheses that 1) the anthocyanic fractions present a sensory variability that differs from the tannic fractions, and 2) both the anthocyanic and tannic fractions contribute taste and mouthfeel properties of the original wines. In this context, a previously developed chemosensory strategy (Sáenz-Navajas et al., 2017) was used to isolate a wide range of fractions, mainly containing tannins and anthocyanins, from wines differing largely in their taste and mouthfeel properties, and then to characterise their sensory properties using both nonverbal (sorting task) and verbal (rate-*K* attributes) sensory strategies. The sensory activity of specific fractions and the impact of introducing an anthocyanic fraction back into wine were also evaluated.

2. Material and methods

2.1. Chemicals

Solvents used for isolation of fractions: HPLC-grade acetonitrile, ethanol and methanol were obtained from Scharlab (Sentmenat, Spain). Formic acid (98-100%), acetone and ethyl acetate of reagent grade were purchased from Scharlab (Sentmenat, Spain). Deionised water was purified with a Milli-Q water system (Millipore, Molsheim, France) prior to use.

Chemicals for reconstitution of fractions: food-grade potassium metabisulfite (E224), L (+)-tartaric acid (E334) and ascorbic acid were obtained from Enartis (Trecate, Italy). Gradient-

grade absolute ethanol for liquid chromatography was purchased from Merck (Darmstadt, Germany).

2.2. Selection of wines

Twenty wines with a wide difference in taste and mouthfeel properties were selected from an original sample set of 42 red wines characterised by rate- K -attributes methodology in previous work (Sáenz-Navajas, Ferrero-del-Teso, Jeffery, Ferreira, & Fernández-Zurbano, 2020). Principal component analysis (PCA) was calculated with the correlation matrix of mean scores ($n = 18$ participants) of the 42 wines for significant ($P < 0.05$) and close to significant ($P < 0.1$) mouthfeel and taste attributes. Further hierarchical cluster analysis (HCA) with the Ward method was calculated on all dimensions derived from PCA. The number of clusters was constrained to 20 to have the maximal number of wines with the widest possible sensory variability and to coincide with the number of samples in the subsets of fractions being evaluated in the subsequent sensory tests. From each of the 20 clusters, one wine was selected and further PCA was calculated followed by HCA with the Ward method with all dimensions of the PCA. The clusters identified by truncating the tree diagram were consolidated by aggregation around mobile centres. The terms that best characterised each of the clusters were identified by using the test-value parameter (Lebart, Morineau, & Piron, 1995). All analyses were carried out with XLSTAT (19.3 version) and SPAD (version 5.5, CISIA-CESRESTA, Montreuil, France) software.

2.3. Fractionation procedure

The 20 wines selected (see Table A.1. of the Supporting Information) via sensory analysis underwent a two-step protocol (Sáenz-Navajas et al., 2017) to isolate anthocyanic (F_{antho}) and tannic (F_{tannin}) fractions. Accordingly, a first preparative fractionation approach was followed to obtain two fractions (F1 and F2, see Fig. A.1 of the Supporting Information) based on previous work (Remy, Fulcrand, Labarbe, Cheynier, & Moutounet, 2000). To begin, four-hundred millilitres of wine were freeze-dried (Coolsafe freeze-drier, Labogene, Denmark) and the residue was redissolved in 40 mL of hydroalcoholic solution (12% ethanol, v/v). The entire 40 mL was injected into a preparative column packed with Toyopearl gel (HW 50F) in a Millipore

(Bedford, MA) Vantage L column (280 mm × 44 mm id). F1 was eluted with ethanol/water/formic acid (55:44:1, v/v/v) during 255 min at a flow rate of 10 mL min⁻¹. F2 (F_{tannin}) was eluted with 840 mL of acetone/water (60:40) at a flow rate of 14 mL min⁻¹. Fractions were evaporated under vacuum (8 mbar, 28 °C, 30 min) with a rotary evaporator (KNF, Freiburg, Germany) to remove ethanol and acetone, then they were further freeze-dried (yielding 0.06-1.01 g from 400 mL of original wine) and stored at 5 °C until SPE fractionation of F1 and sensory analysis of F2.

F1 was subsequently reconstituted in 400 mL of hydroalcoholic solution (12%, v/v) and submitted to solid-phase extraction (SPE) using an extraction unit (VAC ELUT 20 Station from Varian, USA). SPE cartridges filled with 500 mg of Bond Elut LRC-C18 resin (Agilent Technologies, USA) were firstly conditioned by passing 5 mL of methanol followed by 10 mL of an aqueous solution of tartaric acid (5 g L⁻¹) adjusted to pH 2.5 with 0.1 M NaOH. Reconstituted F1 (5 mL) was then loaded and eluted with 5 mL of ethyl acetate. This eluate, which contains sugars, organic acids, flavanols, flavonols and hydroxycinnamic acids, was discarded. F_{antho} was recovered with 10 mL of methanol. Cartridges were re-conditioned and re-used a maximum of five times (with being allowed to dry out in between uses). The SPE procedure was repeated until the 400 mL of F1 were extracted. Recovered F_{antho} (recoveries of >80% in relation to malvidin-3-*O*-glucoside) was evaporated under vacuum (8 mbar), freeze-dried (yielding 0.20-1.25 g from 400 mL of original wine) and stored at 5 °C until sensory analysis.

The day before sensory evaluation tasks, proportionate amounts of the target fractions (F_{antho} and F_{tannin}) were redissolved in a hydroalcoholic solution (4 % ethanol, v/v and 50 mg L⁻¹ of SO₂; 80 mg L⁻¹ of ascorbic acid as antioxidants) based on natural mineral water (Acquajet, Tomares, Spain) to obtain samples that were twice as concentrated as the original wine, to facilitate the sensory characterisation of fractions. Fractions were deemed to be odourless, and the total absence of solvents was confirmed by headspace solid-phase micro extraction (Carboxen/PDMS 75 µm at 30 °C × 10 min) and analysis with a GCMS-QP2010 system (Shimadzu, Tokyo, Japan) having an overall system detection limit of 1 ng/injection.

2.4. Sensory characterisation of fractions

Reconstituted wine fractions (20 each for F_{antho} and F_{tannin}) were evaluated following two different sensory strategies during four sessions held on separate days during two weeks at the Instituto de Ciencias de la Vid y el Vino. Sessions 1 (20 fractions of F_{antho}) and 2 (20 fractions of F_{tannin}) were devoted to nonverbal characterisation (i.e., sorting task) and sessions 3 (20 fractions of F_{antho}) and 4 (20 fractions of F_{tannin}) to sensory characterisation by rate- K attributes methodology. The order of presentation of samples was different for each participant attending to a randomised order and in a monadic manner. Five-mL samples were served in normalised (German Institute for Normalisation, DIN) dark wine glasses (Sensus, Schott Zwiesel, Germany) labelled with 3-digit random codes. Participants were instructed to take a small sip of the sample (reserving some to describe groups in the labelled sorting task and to re-evaluate if necessary) and to gently distribute it throughout the oral cavity (as a mouthwash) to reach the entire surface of the mouth (including the mouth wall, gums, back palate and tongue). After expectorating the sample, panellists had to wait one minute before grouping or rating the sample. Finally, they followed the rinsing protocol described by Colonna, Adams, and Noble (2004) with mineral water and pectin (1 g L^{-1} , Sosa, Barcelona, Spain) before tasting the next sample. Fractions were served at room temperature and evaluated in individual booths in a ventilated and air-conditioned tasting room (at around 20°C) under ambient light. Participants were aware that samples were not commercial wines but fractions obtained in the laboratory, and their informed consent was gained prior to undertaking the sensory testing. They were not informed about the objective of the study nor paid for their participation.

2.4.1. Nonverbal characterisation by wine experts: Sorting task

Participants. Twenty winemakers from Rioja area, Spain (16 women and 4 men, ranging from 28 to 57 years of age, average = 40) participated in the study.

Procedure. Working with F_{antho} (session 1) and F_{tannin} (session 2), participants were presented in the separate sessions with the 20 samples simultaneously and asked to sort them on the basis of mouthfeel and taste properties by arranging wine glasses on the table. Participants could form as many groups as they wished (minimum of two) and groups could contain from 1 to 19 samples.

Upon completion, panellists recorded the three-digit codes of the samples of each group on a sheet of paper and were asked to describe the groups they formed with their own words (maximum of two terms per group). At this stage, participants were allowed to taste again, but not to modify the groups they had already established.

Data analysis. For each participant, results were encoded in an individual similarity matrix (wines $\times$ wines), in which 1 stands for two samples allocated in the same group and 0 for different groups. The three-way distance table was analysed by DISTATIS methods (Abdi, Valentin, Chollet, & Chrea, 2007). The quality and the reliability of representations were evaluated by Shepard diagrams and Kruskal's stress value. HCA with the Ward criterion was performed on the matrix consisting of wines x-coordinates of the retained DISTATIS dimensions. DISTATIS analyses were carried out with R software (version 3.6.0 for Windows) with the additional R packages DistatisR and FactoMineR. HCA was undertaken with XLSTAT (19.3 version).

For the terms derived from the description of the groups, an initial list was built with all the terms elicited by participants. This list was first reduced by omitting words with hedonic or emotional character (e.g. pleasant, easy, classic, different...) and adverbs (e.g., very, barely, extremely...). For remaining words, a lemmatisation process was performed, i.e., words sharing the same lemma or root (e.g., sour, sourness) were grouped in the same category. Finally, all terms were grouped in categories according to semantic similarities. This process was performed individually by three experienced researchers, who through a triangulation task (Abrieu, 2003) achieved a final consensual list of terms. The frequency of quotation of each term was calculated and only terms cited by at least by 20% of the panel (>4 participants) were considered. Chi-square (χ^2) tests were applied for calculating significance differences ($P < 0.05$) for attributes among clusters. Marascuilo post-hoc pairwise comparison (95%) was carried out for significant effects.

2.4.2. Verbal characterisation by wine experts: Rate-K attributes

Participants. Seventeen winemakers from Rioja area, Spain (14 women and 3 men, ranging from 28 to 57 years of age, average = 37) participated.

Procedure. As with the procedure in Section 2.4.1, participants evaluated the 20 fractions of F_{antho} (session 3) and 20 fractions of F_{tannin} (session 4) on separate days using the rate- K attributes methodology described elsewhere (Sáenz-Navajas et al., 2020).

Data analysis. Two-way ANOVAs with assessors as random factors and fractions as fixed were calculated on the scores of each sensory attribute. For significant effects, Fischer post-hoc pairwise comparison (95%) test was performed.

Principal component analysis (PCA) was calculated with mean scores ($n = 17$) of the significant mouthfeel and taste attributes. Further HCA with the Ward method was calculated on all dimensions derived from PCA. The attributes best defining the resulting clusters were identified by calculating an ANOVA with clusters as fixed factors. For significant attributes ($P < 0.05$), the highest score for a given attribute among clusters was selected to be the attribute best defining the cluster(s). Analyses were carried out with SPAD software (version 5.5, CISIA-CESRESTA, Montreuil, France) and XLSTAT (19.3 version).

The degree of similarity between the sensory spaces of 1) fractions (F_{tannin} or F_{antho}) derived from both sorting tasks and the rate K -attributes analysis, and 2) wines (rate K -attributes) and fractions (rate- K attributes and sorting task), was assessed by calculating RV coefficients (Robert & Escouffier, 1976).

In order to evaluate the level of contribution of fractions to wine sensory spaces, Pearson correlation coefficients were calculated between 1) the scores of similar descriptors for wines (Table A.2. of the Supporting Information) and fractions (F_{antho} or F_{tannin}) (Tables A.3. and A.4. of the Supporting Information), 2) significant PCs derived from the PCA calculated with the significant wine and fraction attributes scored by the rate- K attributes method, and 3) significant PCs derived from the PCA calculated with the significant wine attributes scored by the rate- K attributes method and the significant factors derived from the sorting task of fractions. Partial least squares regression models (PLSR1) were calculated for each sensory attribute to predict wine scores from fraction scores. Analyses were carried out using Unscrambler (version 9.7).

2.5. Evaluation of the sensory activity of anthocyanic fractions (F_{antho})

2.5.1. Calculation of orosensory threshold of fractions

F_{antho} derived from two different wines ($F_{\text{antho}}\text{SM5}$ and $F_{\text{antho}}\text{SM25}$) was separately prepared at 6 concentration levels relative to the original wine: 1) twice the concentration (C1), 2) the same concentration (C2), 3) dilution 1:2 (C3), 4) dilution 1:4 (C4), 5) dilution 1:8 (C5), and 6) dilution 1:16 (C6). Weighed amounts of the lyophilised fractions were dissolved in an ethanolic solution (4% ethanol v/v, 50 mg L⁻¹ of SO₂, 80 mg L⁻¹ of ascorbic acid) to arrive at the desired concentrations.

Ten wine experts (two men and eight women, ranging from 27 to 55 years of age, average = 37) carried out six ascending forced choice triangle tests for each of the two fractions studied ($F_{\text{antho}}\text{SM5}$ and $F_{\text{antho}}\text{SM25}$), in duplicate. The samples (4 mL, 20 °C) assessed in each triangle test were the fraction at one of the six concentration levels (two identical samples) and the ethanolic solution used to prepare the samples. Testing was conducted in random order in coded black tulip shaped wine glasses under ambient light in individual booths in a ventilated and air-conditioned tasting room (20 ± 2 °C).

Each participant was presented with three glasses and asked to select the sample that presented different oral properties. The number of right answers was compared with tabulated values to evaluate the presence of significant sensory differences between ethanolic solution and reconstituted fraction at different concentration levels. If obvious differences were detected, panellists were asked to freely cite 2-3 descriptors inducing the sensory difference.

2.5.2. Effect of wine matrix on the sensory activity of fraction $F_{\text{antho}}\text{SM5}$

Five of the original wines were spiked with $F_{\text{antho}}\text{SM5}$ at the concentration present in the original wine (SM5). A total of ten wines (the five original wines: SM5, SM8, SM16, SM23, SM25, and the five spiked with $F_{\text{antho}}\text{SM5}$: SM5+ $F_{\text{antho}}\text{SM5}$, SM8+ $F_{\text{antho}}\text{SM5}$, SM16+ $F_{\text{antho}}\text{SM5}$, SM23+ $F_{\text{antho}}\text{SM5}$, SM25+ $F_{\text{antho}}\text{SM5}$) were described in duplicate by ten wine experts (two men and eight women, ranging from 27 to 55 years of age) according to the rate-*K* attributes methodology described previously while wearing nose clips (Sáenz-Navajas et al., 2020).

A three-way ANOVA was calculated for each attribute with judges as random factor and wine and type of wine (i.e., spiked or non-spiked) as fixed factors including “wine” x “type of wine” interaction.

3. Results and discussion

3.1. Sensory description of wines. Sample selection

From an expert assessment of 42 wines using rate- K attributes (Sáenz-Navajas et al., 2020), 8 of 23 descriptors were found to differ significantly according to two-way ANOVA (Table 1). They were “bitter”, “sweet”, “dry”, “dry on tongue side”, “dry on palate”, “unctuous”, “oily” and “watery”, together with another four (“sour”, “silky”, “burning” and “prickly”) when relaxing the criteria for significance ($P < 0.1$) to avoid missing a true difference. Based on these 12 attributes, the PCA scores plot in Figure 1 shows the projection of the 42 wines on the first two PCs, which explained 50% of original variance. From the 20 clusters derived from HCA, one wine was chosen at random from each with the aim of selecting the 20 most different wines in terms of both taste and mouthfeel. These wines included samples elaborated with 13 different varieties and from 12 different regions of origin.

PCA conducted with the 12 significantly different attributes for the 20 wines (Table A.2. of the Supporting Information) yielded four independent and non-correlated sensory dimensions (data not shown), which explained 79.3% of the original variance and were identified as significant according to the Kaiser criterion (eigenvalue ≥ 1). The first PC (35.3% explained variance) was positively contributed by the terms “unctuous” ($r = 0.73$), “oily” ($r = 0.50$) and “silky” ($r = 0.90$), and negatively by “dry” ($r = -0.85$) and “dry on palate” ($r = -0.85$). The second PC (22.8% explained variance) was positively contributed by “bitter” ($r = 0.71$), “dry on tongue sides” ($r = 0.61$), “burning” ($r = 0.62$) and “prickling” ($r = 0.57$), and negatively by “sour” taste ($r = -0.69$). The third dimension (11.7% explained variance) was mainly influenced by “sweet” taste ($r = 0.79$) and the fourth (9.5% of variance) by “watery” ($r = 0.68$). Table 2 shows the six main groups of wines identified by HCA. Cluster 1 was composed of four wines, including two Bobal from La Mancha, one Merlot from Somontano and one Gamay from Côte du Puy (France) (refer to Table A.1. of the Supporting Information), and was significantly described

with terms such as “sweet”, “dry on palate” and “dry” based on test-value (Lebart et al., 1995). Cluster 2 was the most numerous group, having five wines elaborated with four different varieties: Merlot, Cabernet Sauvignon, Mencía and Tempranillo all from the north of Spain. This is characterised with the terms “bitter”, “dry on the tongue side”, “burning” and “dry on palate”. Cluster 3 included four wines from very diverse origins (Argentina, France, Castilla and Bierzo) and varieties (Bonarda, Pinot Noir, Prieto Picudo and Mencía), and was mainly “watery” and “oily”. Cluster 4, formed by three wines elaborated in very close regions (DO Campo Borja and DOCa Rioja, Spain) but with different varieties (Grenache, Syrah, Tempranillo) was basically “sour”. Clusters 5 and 6 were formed by two wines each elaborated with four different varieties in four different regions. Cluster 5 was characterised with terms such as “silky”, “unctuous” and “sour”, and cluster 6 with “unctuous”, “burning”, “prickly” and “oily”. These results reflect the wide sensory variability in terms of taste and mouthfeel associated to the 20 selected wines (Figure 1) with very different origins and varieties (Table A.1. of the Supporting Information).

3.2. Sensory characterisation of anthocyanic fractions (F_{antho})

3.2.1. Sorting task

The number of groups formed by participants with the 20 F_{antho} samples ranged from 4 to 11, being 7 the average. The maximum number of times two samples were grouped together was 9 (45% of participants). The individual similarity matrices obtained from the sensory sorting task were submitted to DISTATIS and based on Kruskal’s stress, three dimensions were required to reach a Kruskal value < 0.2 , which indicated a good fit to the original data (Cox & Cox, 2000). Figure 2a shows the dendrogram derived from the cluster analysis calculated on the DISTATIS dimensions. Three main groups of F_{antho} samples with different sensory properties can be identified. Based on the verbal description of groups carried out after the sorting task, the most cited terms were “bitter” (maximum of 90% citations for $F_{antho}SM5$ and $F_{antho}SM25$) and “dry” (maximum of 55% citations for $F_{antho}SM37$), but only “bitter” was significantly different ($\chi^2 = 5.2$; $P < 0.05$) among the three clusters: cluster 3 was the most bitter (average of 67% of citations), followed by cluster 2 (43%) and cluster 1 (34%). These results show that the F_{antho}

fractions were mainly “dry” and “bitter”, and that participants grouped samples mainly based on their variability in terms of bitter intensity.

3.2.2. Rate-*K* attributes

According to sensory description following rate-*K* attributes methodology, “bitter” ($F = 11.4$; $P < 0.0001$), “persistence” ($F = 11.2$; $P < 0.0001$), “watery” ($F = 2.4$; $P = 0.001$), “sweet” ($F = 2.2$; $P = 0.04$), and “dry” ($F = 2.1$; $P = 0.006$) were the attributes presenting higher sensory differences among the F_{antho} fractions, followed by “grainy” ($F = 1.8$; $P = 0.025$), “sour” ($F = 1.8$; $P = 0.028$), “silky” ($F = 1.7$; $P < 0.033$), “mouthcoating” ($F = 1.6$; $P = 0.047$), and “unctuous” ($F = 1.6$; $P = 0.056$). PCA calculated on significant attributes showed that the first three dimensions (accounting for 73% of the original variance) presented eigenvalues higher than one and thus could be considered significant based on the Kaiser criterion. Of note, identifying three main independent and non-correlated sensory dimensions as represented by these three PCs highlighted the utility of the rate-*K* attributes sensory methodology. The first PC (43.7% explained variance) was significantly ($P < 0.05$) and positively correlated to “watery” ($r = 0.85$), “silky” ($r = 0.81$), “sweet” ($r = 0.68$) and “unctuous” ($r = 0.64$), and negatively to “bitter” ($r = -0.89$), “dry” ($r = -0.75$) and persistent ($r = -0.68$). The second PC (20% explained variance), was positively correlated to “grainy” ($r = 0.87$) and “mouthcoating” ($r = 0.66$), and the third PC (9.6% explained variance) was positively correlated to sour taste ($r = 0.68$).

HCA calculated on the PCA dimensions yielded five main clusters of F_{antho} fractions (Figure 2b). Cluster 1, formed by four samples, was significantly ($P < 0.05$) described as “watery” (average = 1.4), “silky” (average = 1.3) and “sweet” (average = 0.8), and cluster 2, which included only sample $F_{\text{antho}}\text{SM5}$, was the most bitter (score = 6.1), and most persistent (score = 4.8). Cluster 3 (3 samples) was characterised by the terms “mouthcoating” (average = 0.7) and “grainy” (average = 0.6), cluster 4 (7 fractions) was especially “bitter” (average = 3.0) and “dry” (average = 1.8), and cluster 5 was mainly “sour” (average = 0.7). Notably, “bitter” and “persistent” reached the highest scores by far for $F_{\text{antho}}\text{SM5}$ among the fractions studied, with values of 6.1 and 4.8, respectively, followed by “dry” with an average value of 2.7 for $F_{\text{antho}}\text{SM26}$ (Table A.3. of the Supporting Information). Further, considering the difference

between the maximum and minimum score for a given attribute as a discriminatory value, the highest discriminative ability was found for the terms “bitter” (max-min = 5.6) and “persistent” (max-min = 4.8) followed by “dry” (max-min = 2.4) for the 20 F_{antho} fractions studied (Table A.3.).

3.3. Sensory characterisation of tannic fractions (F_{tannin})

3.3.1. Sorting task

The number of groups formed by participants with the 20 F_{tannin} samples ranged from 3 to 12, with an average of 6. The maximum number of times two samples were grouped together was 13 (65% of participants). The similarity/proximity of fractions evaluated by DISTATIS algorithms showed a Kruskal stress value lower than 0.2 for two dimensions. Attending to cluster analysis, three main clusters of F_{tannin} samples could be identified (Figure 3a). They were mainly described with the terms “dry” and “bitter”, with both terms differing ($P < 0.1$) among the three clusters ($\chi^2 = 4.5$ and 4.9, respectively). Clusters 2 and 3 were drier (average of 75% and 70% of citations, respectively) than cluster 1 (45%), and cluster 2 was most bitter (70%) followed by cluster 3 (50%) and cluster 1 (35%). These results showed that the F_{tannin} fractions studied were mainly “dry” and “bitter”, and that participants grouped samples based on the intensity of both perceptions.

3.3.2. Rate- K attributes method

Eleven out of the 23 evaluated attributes were significantly different among the fractions, which was comparable with the 10 significant attributes found for F_{antho} . The 11 attributes were “bitter” ($F = 8.2$; $P < 0.0001$), “watery” ($F = 3.6$; $P < 0.0001$), “dry on palate” ($F = 3.3$; $P < 0.0001$), “dry” ($F = 2.8$; $P = 0.000$), and “dry on the tongue side” ($F = 2.8$; $P = 0.000$), which were the most different, followed by “silky” ($F = 2.5$; $P = 0.001$), “persistence” ($F = 2.1$; $P = 0.005$), “sweet” ($F = 2.1$; $P = 0.006$), “oily” ($F = 1.8$; $P = 0.021$), “sticky” ($F = 1.6$; $P = 0.059$), and “gummy” ($F = 1.5$; $P < 0.077$).

PCA calculated with the 11 different terms yielded two significant PCs (77% variance explained) according to Kaiser criterion. Thus, two main independent and non-correlated sensory dimensions can be identified by the rate- K attributes methodology. The first PC (66.9%

explained variance) was composed of “bitter” (correlation coefficient between PC1 and “bitter”:
 $r = 0.95$), “dry” ($r = 0.87$), “dry on tongue side” ($r = 0.89$), “dry on palate” ($r = 0.95$), “sticky” ($r = 0.81$) and “persistent” ($r = 0.74$) to terms such as “sweet” ($r = -0.65$), “oily” ($r = -0.84$), “silky” ($r = -0.86$), and “watery” ($r = -0.89$). PC2 (10.1% variance explained) was positively correlated only to the term “gummy” ($r = 0.84$). Figure 3b shows the four clusters derived from HCA calculated on the PCA dimensions. Cluster 1, formed by eight fractions, was mainly described as “watery” (average among wines of the cluster = 1.1), “sweet” (average = 0.9), “silky” (average = 0.9) and “oily” (average = 0.5). Cluster 2, which included two fractions ($F_{\text{tannin}}\text{SM25}$ and $F_{\text{tannin}}\text{SM26}$), was mainly “bitter” (average = 4.2) followed by “dry” (average = 3.4), “persistent” (average = 2.2), “dry on palate” (average = 2.2), “dry on tongue sides” (average = 1.7), and “sticky” (average = 1.1). Cluster 3 (3 fractions) was characterised by the term “gummy” (average = 0.4), and cluster 4 (7 fractions) was mainly “sticky” (average = 1.0). Interestingly, “bitter” and “dry” reached the highest scores among the fractions studied with values of 4.5 and 3.8, for fraction $F_{\text{antho}}\text{SM25}$ and $F_{\text{antho}}\text{SM26}$, respectively (Table A.4 of Supporting information). Besides, similar to F_{antho} fractions, the term “bitter” seems to be the most discriminant among the studied fractions based on the difference between maximal and minimal values (max-min = 4.2 for F_{tannin} and 5.6 for F_{antho}), followed by “dry” (max-min = 2.9 for F_{tannin} and 2.4 for F_{antho}) (Tables A.3. and A.4. of Supporting information).

3.4. Comparison of the sensory spaces of F_{antho} and F_{tannin}

Following verbal and nonverbal approaches, bitterness followed by dryness arose as the salient attributes describing both groups of fractions. Besides, the RV coefficient calculated on the sensory spaces derived from both sensory tasks was significant, with a moderate value (RV = 0.448; $P < 0.01$) for F_{antho} and moderate to strong (RV = 0.640, $P < 0.001$) for F_{tannin} . These results suggested that both nonverbal (sorting task) and verbal (rate- K attributes) sensory techniques generated overall similar sensory spaces, especially for F_{tannin} fractions. This can be attributed to the fact that in both strategies, the differences among the most salient sensory properties were represented. In the sorting task, all samples were presented simultaneously and groups built based on similarity among samples, thus memory played an important role

(Valentin, Chollet, Lelievre, & Abdi, 2012), especially considering that there was a relatively high number of samples ($n = 20$). In this scenario, participants had to adopt a strategy that allowed them to compare among samples, and thus a reduced number of the most salient properties (dryness and bitterness) were selected to form the groups in both sample sets (F_{antho} and F_{tannin}). In the rate- K attributes approach, the number of selected and rated attributes was limited to five descriptors, which leads to underlining the salient attributes of the product (Valentin et al., 2012). Notwithstanding, even if both tasks yielded close sensory spaces, the rate- K attributes approach was able to find differences among samples based on less salient dimensions such as “grainy/mouthcoating” and “sour” taste for F_{antho} and “gummy” for F_{tannin} . In summary, the anthocyanic fractions (F_{antho}) could be represented by three independent and non-correlated dimensions in both sensory tasks, and for tannic fractions (F_{tannin}), the sensory space showed a relatively lower variability than F_{antho} , with two main sensory dimensions conforming the sensory space. In this context, the first hypothesis related to anthocyanic fractions presenting a sensory variability that differs from tannic fractions was demonstrated to be correct. This is a relevant result because until now, anthocyanic fractions of wines have been mainly reported to be involved in wine colour, and their sensory activity in terms of taste and/mouthfeel was far from clear (García-Estévez et al., 2018).

3.5. Contribution of fractions to wine sensory properties

Results showed significant positive correlations between “dry” ($r = 0.72$; $P < 0.01$), “dry on palate” ($r = 0.65$; $P < 0.01$), and “silky” ($r = 0.51$; $P < 0.05$) terms scored for wines and F_{tannin} samples, and the term “dry” ($r = 0.40$; $P < 0.05$) for F_{antho} samples. RV coefficients calculated between the sensory spaces of wines derived from the rate- K attributes analysis and fractions obtained by both the rate- K attributes and sorting task showed significant correlations ($P < 0.001$) for wine and F_{tannin} sensory spaces ($RV = 0.520$ and 0.539 , for rate- K attributes and sorting task, respectively), but no significant correlation was observed with F_{antho} samples ($RV = 0.276$ and 0.200 for the sensory spaces derived from sorting and the rate- K -attributes method, respectively). A moderate negative correlation ($r = -0.5$; $P < 0.1$) was observed between PC1 derived from the sensory spaces of wine and Factor 1 derived from the sorting task of F_{antho}

samples. This result partially confirms our second hypothesis by highlighting the direct sensory importance of the F_{tannin} fraction on the final sensory properties of wines, contrary to the F_{antho} fractions, which is suggested to have a secondary role related to the overall dryness perception in wines.

In order to verify this hypothesis and considering that the terms “bitter” and “dry” were the most salient sensory properties differing among the 20 fractions of both F_{antho} and F_{tannin} , linear models to predict these sensations in wines were built. Interestingly, the dryness of wines could be predicted ($F = 11.41$; $P < 0.01$; $R^2 = 0.59$; $\text{RMSE} = 0.449$) from the “dry” scores of F_{tannin} and F_{antho} , with the tannic fraction contributing double that of the anthocyanic fraction (coefficients of 0.53 for F_{tannin} and 0.25 for F_{antho}). On the other hand, bitterness in wines could not be predicted from the bitter scores of any of the two fractions studied, even if they were especially bitter in isolation (especially F_{antho}). The reason the high bitterness of these fractions was not transmitted to wines could have two plausible explanations: 1) the sensory threshold of these fractions could have been below their concentration in wines, or 2) there were other wine components masking bitterness and acting as suppressors in wines.

The relative orosensory threshold of fractions F_{anthoSM5} and $F_{\text{anthoSM25}}$ (with scores for bitterness of 6.1 and 4.6, respectively, see Table A.3. of the Supporting Information) was estimated to further explore their sensory impact. These fractions were the most bitter among the 40 studied and the intensity of other sensory attributes such as dryness (1.5 and 2.2, respectively) were relatively low in comparison with bitterness, especially for F_{anthoSM5} . Figure 4a shows that for the F_{anthoSM5} , which was mainly “bitter”, the sensory threshold in model solution was slightly below the relative concentration of F_{anthoSM5} if wine SM5 was diluted four-fold. For $F_{\text{anthoSM25}}$, which was mainly “bitter” but also “dry” (2.2 ± 0.7), the sensory threshold was somewhat below the relative $F_{\text{anthoSM25}}$ concentration if wine SM5 was diluted two-fold (Figure 4b). These results confirmed the sensory activity of these fractions in isolation and suggested that they could be important contributors to the sensory profile of wines.

The presence of sensory interactions at either perceptual (cognitive or receptor level) or physicochemical level was investigated by assessing the impact of F_{anthoSM5} on wine sensory

properties in five of the original wines (SM5, SM8, SM16, SM23, SM25). Wine SM5 was included along with two pairs/groups of wines with different intergroup scores for bitterness but similar intragroup scores: SM23 and SM16 (average = 0.7) and SM8 and SM25 (average = 1.7). Besides, bitter scores for their respective F_{antho} varied largely intragroup. This selection was aimed at having wines with ample bitter scores and with different contributions of F_{antho} to the overall bitterness perceived in original wines. Five original wines and these same samples spiked with F_{antho} SM5 were described with the rate- K attributes approach. ANOVA showed a significant effect for bitter scores due to the spiking ($F = 5.05$; $P < 0.05$), whereby wines spiked with fraction F_{antho} SM5 presented significantly higher scores for bitterness (average = 3.5 ± 0.6 , 7-point scale) than non-spiked wines (average = 2.7 ± 0.5). This result confirmed the sensory contribution of F_{antho} to the sensory properties of wines. Interestingly, the increase in bitterness with F_{antho} SM5 was significant ($P < 0.05$) for three wines (SM8, SM5, SM23), whereas for wines SM16 and SM25, no sensory change was evident. This suggested that there were components in wines SM16 and SM25 that were able to mask the bitter perception associated with F_{antho} SM5, thus acting as bitterness suppressors.

It is important to remark that fractions were dissolved in a model solution with a minimal concentration of ethanol (4% v/v) and pH value of 6.5 ± 0.5 to avoid the saliency of burning sensations related to ethanol content and of sour taste due to the presence of acids needed to reach normal pH values found in wines. Ethanol is reported to have a significant effect on wine astringency, even if reported results are contradictory. On the one hand, there are authors that confirm that ethanol hinders protein-tannin interactions and consequently decrease “astringency” (Fontoin, Saucier, Teissedre, & Glories, 2008; McRae, Ziora, Kassara, Cooper, & Smith, 2015), but on the other hand, ethanol content is also suggested to increase this precept driven by other mechanisms different from tannin-protein interaction (Sáenz-Navajas et al., 2019; Watrelot et al., 2016). Concerning the effect of pH, it has been observed that decreases in pH can increase astringency (Fontoin et al., 2008; Luck et al., 1994; Sáenz-Navajas et al., 2020), attributable to decreases in saliva viscosity. This suggested that dryness perceived in the fractions of the present work could be drier at wine pH. In this context, it has to be considered

that differences in ethanol and pH between fractions and wines could be related to certain discrepancies between the sensory properties of both matrices.

4. Conclusions

The present work has successfully described the sensory space of two families of wine polyphenols, namely anthocyanins and tannins isolated from a sample set of 20 wines that exhibited distinct variability in terms of taste and mouthfeel properties. The anthocyanic (F_{antho}) and tannic (F_{tannin}) fractions of these 20 wines underwent sensory evaluation by nonverbal (sorting task) and verbal (rate- K attributes) sensory techniques, with both approaches generating overall similar sensory spaces as determined by RV values, especially for F_{tannin} fractions. Results showed that the sensory space of the F_{antho} studied could be represented by three independent and non-correlated dimensions in both sensory tasks, and related to taste and mouthfeel related terms, with “bitter” and “dry” appearing as the most salient and differential sensory properties among both groups of fractions.

Interestingly, dryness of wines was satisfactorily predicted from “dry” intensity of F_{antho} and F_{tannin} , which confirmed that tannins have a major role in the perception of dryness, and more importantly, unequivocally demonstrated a relevant implication of certain anthocyanins in the “dry” attribute. In contrast, bitterness of the wines could not be directly related to the bitterness perceived in any of the two fractions. Furthermore, the addition of extremely bitter anthocyanic fractions to wines increased bitterness only in certain wines, purportedly due to the presence of masking agents in wines.

The results contribute to the understanding of red wine taste and mouthfeel perception by suggesting that the anthocyanic fraction contributes to orosensory properties more than previously thought. Gaps in knowledge regarding the fractions and wines will involve comprehensive chemical characterisation by both targeted and untargeted metabolomics to identify the specific molecules and groups of molecules involved in “sour” and especially “bitter” tastes, as well as in the different mouthfeel dimensions identified.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodres>.

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FIGURE CAPTIONS

Figure 1. PCA scores plot calculated with the average scores ($n = 20$) of 12 significant taste and mouthfeel attributes derived from the sensory characterisation of 42 wines by rate- K attributes using nose clips. The 20 wines selected for fractionation and sensory characterisation of their anthocyanic and tannic fractions are marked in bold. The three letters going with sample code correspond to the abbreviation of the wine variety

Figure 2. Dendrograms showing the sensory clusters of the 20 F_{antho} derived from hierarchical cluster analysis calculated on dimensions of a) DISTATIS obtained by sorting task and b) PCA derived from rate- K attributes. Attributes describing each cluster are those with significantly higher scores in the given cluster (significant differences in the frequency of citation for the term “bitter” are expressed as follows: bitter < bitter⁺ < bitter⁺⁺).

Figure 3. Dendrograms showing the sensory clusters of the 20 F_{tannin} derived from hierarchical cluster analysis calculated on dimensions of a) DISTATIS obtained by sorting task and b) PCA derived from rate- K attributes. Attributes describing each cluster are those with significantly higher scores in the given cluster (significant differences in the frequency of citation for the terms “bitter” and “dry” are expressed as follows: bitter < bitter⁺ and dry < dry⁺).

Figure 4. Percentage of correct responses ($n = 20$) derived from triangle tests comparing wine model to wine model spiked with different concentrations of the F_{antho} obtained from wines a) SM5 and b) SM25. Lines indicate the 5% (lower) and 1% (upper) significance criterion, respectively.

Figure 1.

Figure 2.

a)

b)

Figure 3.

Figure 4.

Table 1. Two-way ANOVA (participants as random factors, wine as fixed factor) calculated to evaluate the effect of wine on taste and mouthfeel sensory properties (F values; P-significance: *P<0.1, **P<0.05, ***P<0.01, ****P<0.001)

attributes	F	P
salty	0.987	ns
bitter	1.754	***
sweet	1.426	**
sour	1.384	*
dry	2.225	****
dry on tongue side	1.539	**
dry on palate	2.410	****
sticky	1.233	ns
dusty	1.093	ns
grainy	1.104	ns
sandy	0.961	ns
coarse	1.100	ns
unctuous	1.692	***
oily	1.791	***
fleshy	0.929	ns
mouth coating	1.129	ns
silky	1.324	*
gummy	0.882	ns
watery	1.486	**
burning	1.366	*
hot	1.190	ns
prickly	1.348	*
persistent	1.188	ns

Table 2. Clusters yielded by HCA calculated with the 20 selected wines and 12 significant sensory terms. See Table A.1. of the Supporting Information for details of the wines.

cluster	wines	attributes
1	SM42_BOB†, SM23_MER, SM41_BOB, SM1_GAM	sweet, dry on the palate, dry
2	SM26_CS†, SM25_MER, SM10_MEN, SM35_TEM, SM31_MER	bitter, dry on tongue side, burning, dry on palate
3	SM6_BON†, SM12_PN, SM16_PP, SM4_MEN	watery, oily
4	SM29_GRE†, SM30_SY, SM37_TEM	sour
5	SM15_CAR†, SM7_MEN†	silky, unctuous, sour
6	SM5_MAL†, SM8_GAM†	unctuous, burning, prickly, oily

†Wines closest to the centre of gravity of the cluster. Attributes contributing most to the building of the cluster (test-value ≥ 1.96 ; $P < 0.05$) and wines belonging to each cluster are listed.

Supplementary material for online publication only

[Click here to download Supplementary material for online publication only: Appendix A. Supporting Information_070220.docx](#)

20 red wines with very different **orosensory** properties

Obtention of **two fractions** by preparative Liquid Chromatography and SPE

Sensory characterisation by:
1. Sorting task
2. Rate-K attributes

20 tannic fractions (F_{tannin})

20 anthocyanic fractions (F_{antho})

Credit authorship contribution statement

M.P.S.N.: Conceptualization, Methodology, Writing - review & editing, Writing - original draft, Investigation, Formal analysis. **S.F.d.T:** Investigation, Writing - review & editing. **A.S.:** Investigation. **D.W.J:** Conceptualization, Writing - review & editing. **V.F.:** Conceptualization, Writing - review & editing, Project administration, Funding acquisition. **P.F.Z:** Project administration, Funding acquisition, Writing - review & editing.