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Sensory interactions between six common aroma vectors explain four main red wine aroma nuances

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ABSTRACT

This work aims at assessing the aromatic sensory dimensions linked to 6 common wine aroma vectors (N, norisoprenoids; A, branched acids; F, enolones; E, branched ethyl esters; L, fusel alcohols, M, wood compounds) varying in their natural range of occurrence. Wine models were built by adding the vectors at two levels (fractional factorial design 2^{VI}) to a de-aromatised aged red wine. Twenty other different models were evaluated by descriptive analysis. Red, black and dried fruits and woody notes were satisfactorily reproduced. Individual vectors explained just 15% of the sensory space, mostly dependent on perceptual interactions. N influences dried and black fruits and suppresses red fruits. A suppresses black fruits and enhances red and dried fruits. F exerts a major role on red fruits. E suppresses dried fruits and modulates black fruits. L is revealed as a strong suppressor of red fruits and particularly of woody notes.

1. Introduction

One of the major challenges of today's aroma research is to understand the rationale determining the qualitative and quantitative characteristics of the sensory perception elicited by complex mixtures of odorants. As discussed by Francis and Newton (2005) wine aroma is not just the sum of individual constituents, but the result of complex interactions between a large number of chemical compounds. Odorants can interact, showing either additive or competitive effects, which may turn even into synergistic or antagonistic effects (Ferreira, 2012). Interactions that influence the aroma properties of wine have been the object of wine and psychophysics research for decades, although most of these studies have focused on aroma interactions of relatively simple mixtures (Atanasova, Thomas-Danguin, Langlois et al., 2005; Atanasova, Thomas-Danguin, Langlois, Nicklaus, & Etievant, 2004; Carmeleyre, Lytra, Tempere, & Barbe, 2015).

Selfridge and Amerine (1978) studied the effects of masking, addition, and synergism in an artificial wine medium containing ethyl acetate and diacetyl in various proportions and concentrations. They observed that even when the compounds were at concentrations below their detection thresholds in wine, an odour can be perceived as a result of perceptual synergism. More specifically, several works have highlighted the existence of perceptual interactions for woody *versus* fruity notes in wine, (Atanasova, Thomas-Danguin, Chabanet et al., 2005; Atanasova et al., 2004), proving that woody notes tend to dominate over the fruity ones in binary mixtures containing sub- and peri-threshold levels of woody odorants. Ethanol can change some of those effects and be itself masked (Le Berre, Atanasova, Langlois, Etievant, & Thomas-Danguin, 2007).

Other researchers focused their studies on fruity esters from red wines, developing omission and addition experiments in synthetic solutions (the ester pool). These authors suggested that branched esters are linked to black-berry aromas, while linear esters would be related to red-berry aromas (Pineau, Barbe, Van Leeuwen, & Dubourdieu, 2009). They have also shown that fruity aroma can be enhanced by ethyl 2-hydroxy-4-methylpentanoate and masked by a mixture of four fermentation compounds (Lytra, Tempere, de Revel, & Barbe, 2012) and that subthreshold esters can enhance the fruity character of the ester pool (Lytra, Tempere, Le Floch, de Revel, & Barbe, 2013). In a more recent research it has been demonstrated that blackcurrant odour can be produced by the interaction between dimethyl sulfide and the ester pool (Lytra et al., 2014). Other relevant work has highlighted the suppression effects

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exerted by oxidation-related compounds on the fresh fruity character elicited by 3-mercapto-1-hexanol (Coetzee et al., 2015). Recently, Carmeleyre et al. (2015) have shown the presence of perceptual interactions between the fruity aroma of branched ethyl esters and the solvent-like aroma of isoamyl alcohol.

While all these studies highlight important features about the perceptual interaction between odorants, some of them are using simple working schemes, such as synthetic solutions, simple wine models or single odorant solutions, which may limit the generalisation of their results. In addition, in most cases researchers have studied the interaction between two odours, when the fact is that in wine there are many odorants creating different odours and competing simultaneously. Finally, and to the best of our knowledge, there is no study in which major wine odour components have been systematically assessed for their contribution and interactions. In this context, a more ambitious chemo-sensorial approach would be necessary based on the recreation of complex models eliciting aroma features as close as possible to those of real wine and targeting the first main wine aroma vectors.

Wine has been described as a sensory buffer containing ethanol and major fermentation compounds which are able to counterbalance the addition or omission of several odorants without any significant change in the overall aroma (for a complete review see Ferreira, Escudero, Campo, and Cacho (2008)). This blend is slightly sweet, pungent, alcoholic and a little bit fruity, that is, it evokes the typical odour of alcoholic beverages that is often defined as vinous. Only certain "impact" compounds or families of compounds sharing chemical and odour properties can break the sensory buffer and hence transmit to the wine a specific aroma nuance, forming then an aroma vector. Only in some particular cases is it possible to find genuine impact compounds able to transmit to the product their primary odours such as for Spanish Verdejo (3-mercaptohexyl acetate) or Sauvignon Blanc (4-methyl-4-mercapto-2-pentanone) (Darriet, Tominaga, Lavigne, Boidron, & Dubourdieu, 1995; Mateo-Vivaracho, Zapata, Cacho, & Ferreira, 2010). However, in the most complex and most valuable products the aromatic profile is created by the concerted action of many molecules. Red wine is a good example of a complex matrix: there is a rich non-volatile matrix, a quite large amount of different active odorants, and most often no clear impact compounds. In this chemical environment the perception of the different notes is extremely complex.

Recent investigation carried out by our research group (Sáenz-Navajas, Gonzalez-Hernandez, Campo, Fernández-Zurbano, & Ferreira, 2012) has highlighted that an expert's quality perception of a set of Spanish premium wines (samples within the high price segment in the Spanish retail market) is not necessarily linked to intense explicit odour nuances, but rather to a large palette of many subtle odours. This suggests that complexity and harmony are essential dimensions related positively to judgments of high quality wine as shown by Charters and Pettigrew (2007). The study of the analytical composition of the abovementioned set of Spanish premium wines together with two other wine categories belonging to lower price segments: low- and medium-price (San Juan, Cacho, Ferreira, & Escudero, 2012) provided an extensive quantitative database and identified some relevant clues relating wine quality, odour notes and odorant composition. For the purpose of the present research, two major observations derive from such work. First, models for quality had a common structure based on the opposition of positive *versus* defective aroma compounds in all the wine categories, but the key compounds able to explain quality were characteristic of the price segment. For instance, branched acids turned to be positively related to quality in premium wines, while they were negatively related in the medium-price category. This could be due to the existence of perceptual interactions among aroma components specific of the wine category. Second, leaving aside some odour notes of the premium segment (San-Juan, Ferreira, Cacho, & Escudero, 2011), it was not possible to find satisfactory predictive models for most odour notes in the other wine categories (low and medium price segments). The failure in modelling can have multiple causes, among them the effects of the non-volatile matrix on the volatility of aroma compounds (Saenz-Navajas, Campo, Cullere et al., 2010) or the inadequacy of the linear models used in those works. In any case this implies that controlling perfectly compositional variables would be essential for increasing knowledge about aroma perception and thus wine quality. Hence, working with complex matrices such as wine models would be an interesting tool able to overcome the main limitations related to the understanding of aroma formation.

The present work aims at assessing the aromatic sensory dimensions linked to six common wine aroma vectors varying in their natural range of occurrence and at studying the sensory interactions between them. The six aroma vectors studied were norisoprenoids (N), branched acids (A), branched ethyl esters (E), major alcohols (L), enolones (F), and wood-related compounds (M); all of them were essential basic elements of the PLS models explaining quality of red wines (San Juan et al., 2012). A major concern in the study was to present "wine-like" samples to trained assessors, so that realistic interactions between components could be identified. Different wine models (WMs) will be prepared through a reconstitution-based protocol that provides close-to-real wine samples (Saenz-Navajas, Campo, Fernandez-Zurbano, Valentin, & Ferreira, 2010), which will be further submitted to sensory evaluation.

2. Materials and methods

2.1. Standards

2.1.1. Chemicals and reagents

The chemical standards were from Fluka (Buchs, Switzerland), Lancaster (Strasbourg, France); Panreac (Barcelona, Spain) and Firmenich (Geneva, Switzerland). Dichloromethane and ethanol of LiChrosolv quality were from Merck (Darmstadt, Germany). Pure water was obtained from a Milli-Q purification system (Millipore, Bedford, MA).

2.1.2. Nonvolatile extracts

Fifty-millilitre samples of wine (Muga Reserva 2004, D.O. Rioja, Spain) were lyophilised in 250-mL rounded flasks, and after this, samples were extracted with 3×10 mL of dichloromethane to remove remaining volatile compounds. Afterward, dichloromethane was completely eliminated by forcing a stream of pure nitrogen (*ca.* 50 mL min^{-1}) to pass through the sample for 20 min. The total absence of dichloromethane was assessed by headspace solid-phase microextraction (Carboxen/PDMS 75 μm at 30 °C for 10 min) and GC with electron capture detector (overall system detection limit = 1 ng/sample). The extract was then dissolved in flavourless low mineralisation water (Evian, Evian-les Bains, France) and brought to 10 mL (5 times concentrated). After this, a controlled stream of nitrogen was passed through samples, which were finally placed in vials with no headspace to avoid sample-oxygen contact and stored at 5 °C until sample preparation.

2.2. Wine models (WM)

2.2.1. Selection of models by factorial design

Six quantitative controllable variables (named aroma vectors) at two concentration levels (low and high) were considered for carrying out a preliminary screening test in a fractional design. Low