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Contribution of low molecular weight phenols to bitter taste and mouthfeel properties in red wines

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ABSTRACT

The aim of this study was to explore the relationship between low molecular weight compounds present in wines and their sensory contribution. Six young red wines were fractionated by gel permeation chromatography and subsequently each fraction obtained was separated from sugars and acids by solid phase extraction. Wines and both fractions were in-mouth evaluated by a trained sensory panel and UPLC–MS analyses were performed. The lack of ethanol and proanthocyanidins greatly increased the acidity perceived. The elimination of organic acids enabled the description of the samples, which were evaluated as bitter, persistent and slightly astringent. Coutaric acid and quercetin-3-*O*-rutinoside appear to be relevant astringent compounds in the absence of proanthocyanidins. Bitter taste was highly correlated with the in-mouth persistence. A significant predictive model for bitter taste was built by means of PLSR. Further research must be carried out to validate the sensory contribution of the compounds involved in bitterness and astringency and to verify the sensory interactions observed.

1. Introduction

The comprehensive study of non-volatile compounds in red wine is of great interest due to the sensory properties of these compounds, such as sweetness, acidity, bitterness and different oral mouthfeel perceptions such as velvety, puckering and drying astringency, among others. The quality perception of a wine is driven primarily by the absence of defective aroma and secondarily to the presence of non-volatile components and more precisely to phenolic composition that is able to modulate quality perception (Sáenz-Navajas, Tao, Dizy, Ferreira, & Fernández-Zurbano, 2010).

The contribution of non-volatile molecules to wine sensory properties has been widely published (Arnold, Noble, & Singleton, 1980; Chira, Pacella, Jourdes, & Teissedre, 2011; Gawel, Francis, & Waters, 2007; Landon, Weller, Harbertson, & Ross, 2008; Peleg, Gacon, Schlich, & Noble, 1999; Preys et al., 2006; Sáenz-Navajas, Avizcuri, Ferreira, & Fernández-Zurbano, 2012; Sáenz-Navajas, Campo et al., 2012; Vidal, Courcoux et al., 2004) and most publications have studied in detail the compounds that contribute most to astringency perception (Chira et al., 2011; Gawel et al., 2007; Landon et al., 2008; Sáenz-Navajas, Avizcuri et al., 2012). With this purpose, Hufnagel and Hofmann (2008a) carried out reconstruction studies from the nonvolatile composition of a red wine, demonstrating that puckering astringency (using tannic acid as reference standard) is mainly caused by a polymeric fraction exhibiting molecular masses above 5 kDa, this oral sensation being amplified by acids such as caftaric acid, gallic acid and furan-2-carboxilic acid. Other study performed with the same goal (Sáenz-Navajas, Avizcuri et al., 2012) developed two models for predicting perceived astringency (using, in this case, potassium and aluminium sulphate as the reference standard for astringency). In both models, the concentration of proanthocyanidins, the presence of organic acids and also ethanol content once again accounted for perceived astringency. Monomeric phenols have been repeatedly described as astringent and bitter (Arnold et al., 1980; Hufnagel & Hofmann, 2008a; Peleg et al., 1999), although recent studies have shown that monomeric phenols are not present in concentrations above their sensory threshold, suggesting that these compounds might not play an important role in the sensory perception of red wines (Hufnagel & Hofmann, 2008a; Sáenz-Navajas, Avizcuri et al., 2012).

In contrast, few authors have focused on the study of bitter taste in red wines, with controversy surrounding the results obtained for the compounds eliciting bitter taste (Arnold et al., 1980; Hufnagel & Hofmann, 2008a; Kallithraka, Bakker, & Clifford, 1997; Peleg et al., 1999; Robichaud & Noble, 1990). Furthermore, some authors, despite training assessors specifically in bitter term, have reported differences in its interpretation (Sáenz-Navajas,

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Avizcuri et al., 2012), while other authors have reported a very significant sample effect for each attribute studied except for bitterness (Vidal et al., 2003). Several authors (Peleg et al., 1999; Robichaud & Noble, 1990) have studied the bitterness of polyphenol compounds, such as polymeric fractions of tannic acid and tannins, as well as flavan-3-ol monomers, dimers, and trimers, demonstrating that larger molecules tend to be less bitter and more astringent. Peleg et al. (1999) found that (−)-epicatechin was more bitter than the stereoisomer (+)-catechin and that both were more bitter than the procyanidin trimers, catechin-(4–8)-catechin-(4–8)-catechin and catechin-(4–8)-catechin-(4–8)-epicatechin, in contrast to Hufnagel and Hofmann (2008a) found that procyanidins dimers and a procyanidin trimer were more bitter than (−)-epicatechin and catechin. One study focused on white wines with and without pomace contact and with the addition of anthocyanins (Oberholster, Francis, Iland, & Waters, 2009), establishing that the score for bitterness attribute was correlated with the concentration of most phenolic compounds, but especially with proanthocyanidins and polymeric phenols, which also coincided with previous reports (Arnold et al., 1980). In contrast, Hufnagel and Hofmann (2008a) considered polymeric phenols (>5 kDa) as non-bitter compounds. On the other hand, studies carried out on white wines and model solutions have demonstrated that catechin elicits both bitterness and astringency (Arnold et al., 1980; Robichaud & Noble, 1990). Sáenz-Navajas, Ferreira, Dizy, and Fernández-Zurbano (2010) studying red wine fractions reported that bitterness might be explained by the presence of monomers such as catechin and epigallocatechin, phenolic acids such as coutaric and caftaric acid and flavonols such as myricetin. With the same goal in mind, Hufnagel and Hofmann (2008a) by means of taste reconstruction and omission experiments described as potential bitter compounds two flavan-3-ol monomers and four dimers, seven phenolic acids and eight amino acids. Although the concentration of these compounds was ten times below their threshold concentrations, Hufnagel and Hofmann (2008a) concluded that sub-threshold concentrations of phenolic acid ethyl esters and flavanols contribute to red wine bitterness. In spite of these inconsistencies, not enough is known about the bitter taste of polyphenol compounds that do not belong to tannin classes, such as anthocyanins.

Another important aspect to take into account is the fact that human ability to taste bitterness is genetically dependent and approximately 30% of population is taste blind to the bitterness of bitter synthetic compounds such as phenylthiocarbamide (PTC) and 6-n-propylthiouracil (PROP) (Tepper et al., 2009). This genetic ability is probably linked to the presence of bitter-tasting compounds in sub-threshold concentrations, and both issues may be the key to understanding why bitter taste is still far from being understood.

It has also been reported that not only chemical composition but also molecular interactions among wine components play a determinant role in the chemical stability of wine, also affecting its sensory properties (Sáenz-Navajas, Campo, Fernández-Zurbano, Valentin, & Ferreira, 2010). It has been extensively reported that ethanol enhances perceived bitterness (Fischer & Noble, 1994; Noble, 1990; Oberholster et al., 2009; Vidal, Courcoux et al., 2004), masks it (Vidal, Francis, Noble et al., 2004) and can suppress the astringency of phenols (Noble, 1990; Vidal, Courcoux et al., 2004). An increase of 3% v/v of ethanol increases bitterness more (by nearly 50%) than the addition of 1400 mg L^{-1} of catechin to the same wine (which increased bitterness by only 28%) (Fischer & Noble, 1994). Increased acidity (and perceived sourness) increased the intensity of astringency (Kallithraka et al., 1997).

The possibility of identifying relationships between composition and sensory description will provide more information towards a better understanding of how interactions between chemical components may affect flavour perception. The general aim of this study was to advance in the knowledge of the effect of non-volatile low molecular weight phenolic compounds on in-mouth taste and feeling perceptions, especially bitterness and astringency. The specific aims of this study were: (1) to study correlations between in-mouth sensory properties and low molecular weight non-volatile compounds; and (2) to explore the role of low molecular weight non-volatile compounds in the bitter taste of red wines. To achieve both goals, six Spanish young red wines showing different total polyphenol index values and subsequently the fractions obtained from them were in-mouth sensory described by a trained panel selected for its ability to taste bitter. The non-volatile compounds were identified and quantified by UPLC–DAD–MS. The potential contribution of non-volatile molecules to bitter taste was studied using statistical tools.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals used were of analytical reagent grade. All chromatographic solvents were of HPLC grade. Ultrapure water was obtained from a Milli-Q purification system (Millipore, Molsheim, France). Spring water was purchased from Solán de Cabras (Cuenca, Spain). Methanol, formic acid, ethanol, acetonitrile, sulphuric and hydrochloric acid were purchased from Scharlab (Barcelona, Spain). Quinine sulphate dihydrate (98%) was obtained from Alfa Aesar (Karlsruhe, Germany). Potassium and aluminium sulphate and tannic acid were purchased from Panreac (Barcelona, Spain). L-Tartaric acid, L-malic acid, L-lactic acid, succinic acid, citric acid, *trans*-aconitic acid, *cis*-aconitic acid, syringic acid, 6-propyl-2-thiouracil, catechin, epicatechin, myricetin, kaempferol, vanillin, protocatechuic acid ethyl ester, protocatechuic acid, gallic acid, caffeic acid, resveratrol and quercetin were purchased from Sigma–Aldrich (St. Louis, MO, USA). Oenin-chloride, caffeic acid ethyl ester, quercetin-3-*O*-glucoside, quercetin-3-*O*-rutinoside, quercetin-3-*O*-galactoside, quercetin-3-*O*-glucuronide, kaempferol-3-*O*-glucoside, isorhamnetin-3-*O*-glucoside, myricetin, kaempferol, isorhamnetin, epicatechin gallate, epigallocatechin, procyanidins A2, B1 and B2, ferulic and *p*-coumaric acids were provided by Extrasynthese (Genay, France). Vanillic acid was supplied by Fluka (Buchs, Switzerland).

2.2. Wines

Six young red commercial wines were selected out of 35 wines from different Spanish Denominations of Origin and regions. The selection was made on the basis of differences in their total polyphenol index (TPI) values and also on the basis of different values given to bitterness and astringency attributes.

2.3. Sample preparation

2.3.1. Elimination of wine volatile compounds

Wines were de-alcoholized and de-aromatized according to Sáenz-Navajas, Campo et al. (2010) in order to obtain an odourless tastant fraction from each wine. The non-volatile extract obtained from 50 ml of wine was then re-dissolved in 2 ml of ethanol/water (13:87, v/v) in order to obtain the low molecular weight fractions as follows.

2.3.2. Isolation of low molecular weight compounds

TSK Toyopearl gel HW-50F (Tosohaas, Montgomery-ville, PA, USA) was suspended in miliQ water and, after swelling, it was packed in a Millipore (Bedford, MA, USA) Vantage L column