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Chemo-sensory characterization of fractions driving different mouthfeel properties in red wines

María-Pilar Sáenz-Navajas [a,*], José-Miguel Avizcuri [a], Sara Ferrero-del-Teso [a], Dominique Valentin [b], Vicente Ferreira [a], Purificación Fernández-Zurbano [c]

[a] Laboratorio de Análisis del Aroma y Enología (LAAE), Department of Analytical Chemistry, Universidad de Zaragoza (UZ), Instituto Agroalimentario de Aragón (IA2) (UNIZAR-CITA), Associate unit to Instituto de las Ciencias de la Vid y del Vino -ICVV- (UR-CSIC-GR), Zaragoza, Spain
[b] Centre des Sciences du Goût et de l'Alimentation, AgroSup Dijon, CNRS, INRA, Univ. Bourgogne Franche-Comté, F-21000 Dijon, France
[c] Instituto de Ciencias de la Vid y del Vino -ICVV- (Universidad de La Rioja, CSIC, Gobierno de La Rioja), Carretera de Burgos Km. 6, Finca La Grajera, 26007 Logroño, La Rioja, Spain

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ABSTRACT

The absence of reference materials with defined mouthfeel properties makes it difficult to progress in finding the chemical compound or group of compounds responsible for such properties in complex foods or beverages such as wine. The present work aimed at developing a chemo-sensory strategy providing different odorless fractions with consistent mouthfeel properties. Three wines with different mouthfeel properties were separated in six different odorless fractions per wine by semipreparative liquid chromatography and Solid-Phase Extraction (SPE). Fractions were sensory analyzed by sorting task, repertory grid, triangulation and Rate-All-That-Apply (RATA) with wine experts. In parallel, fractions were chemically characterized by spectrophotometrical strategies, UPLC-MS and MALDI-TOF-MS.

A list of 23 terms related to in-mouth properties (18 to mouthfeel) was generated and successfully employed in the description of wines and fractions by RATA analysis. Fractions containing oligomers of flavanols (from tetramers up to decamers) were mainly *coarse*, *grainy*, *dry on the tongue* and *dry on the palate*. More surprising was the sensory properties of a fraction containing anthocyanin-derivative pigments, which was especially *dry*, *bitter* and *persistent* as was the original wine. This fraction did not contain either oligomers or polymers of flavanols or flavanol-anthocyanin pigments, but a series of trimers of anthocyanins tentatively identified by MALDI-TOF MS. Further separation strategies are being developed to isolate anthocyanin-derived compounds to further confirm their sensory impact in wines.

1. Introduction

Flavor of food products is driven by color, aroma, taste and mouthfeel. In complex systems, the formation of mouthfeel is overall the least understood. This fact is especially true for the case of complex beverages such as wine. In the scientific literature, the few papers that relate quality perception and mouthfeel properties are limited to a reduced number of terms such as astringency, hot sensation, body or viscosity (Hopfer & Heymann, 2014; Sáenz-Navajas et al., 2016; Varela & Gambaro, 2006). However, based on anecdotal beliefs, it seems that there is a wide range of mouthfeel terms driving wine quality perceived by consumers with different levels of expertise. This is especially important for winemakers as they usually claim to base most of their technical decisions on grape and wine mouthfeel properties. Based on declarations of experts, high quality wines are positively related to in-mouth sensations such as *balance*, *volume/body*, *round/smooth tannins* or *soft tannins*, while negatively to *unbalance*, *light/short*, *green sensations*, *coarse/dry tannins* or *green tannins among others* (Sáenz-Navajas et al., 2016). Mouthfeel properties seem also to be important quality drivers for wine communicators as they usually mention different subqualities of mouthfeel in their wine descriptions and judgements. For example, they use positive terms such as *full*, *rich*, *supple*, *smooth* or *full texture* and negative such as *thin*, *limp*, *watery*, *angular*, *harsh*, *aggressive*, *rough* or *angular*. Mouthfeel terms (e.g., *rough*, *dry*, *strong*, *astringent*, *harsh*, *body*, *hard* or *tannin*) are also included in less experienced consumer vocabulary for describing wines in Spanish language. (Vidal, Giménez, Medina, Boido, & Ares, 2015). However the valence or hedonic role (positive or negative) of these terms has not been established.

Gawel, Oberholster, and Francis (2000) already developed a mouthfeel wheel based on a hierarchical classification with the main aim of facilitating the communication among wine consumers. However this wheel has not been generalized and less experienced consumers seem not to understand most of the terms (Vidal et al., 2015). This suggests that there is still a lack of understanding among wine audience when describing wine mouthfeel properties. The main reason could be that

* Corresponding author.
E-mail addresses: masaenn@unizar.es, maria@saenz.info (M.-P. Sáenz-Navajas).

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compounds present in wine and generating different mouthfeel properties are still unknown, resulting in a lack of reference materials illustrating such mouthfeel properties, and consequently a lack of adequate lexicon, which makes it difficult to interpret of vocabulary.

There is a wide range of scientific publications aimed at exploring the compounds eliciting different mouthfeel sensation, especially phenolic compounds such as phenolic acids, anthocyanins, polymers of flavanols or flavonols among others (Ferrer-Gallego, García-Marino, Hernández-Hierro, Rivas-Gonzalo, & Escribano-Bailón, 2010; Ferrer-Gallego, Gonçalves, Rivas-Gonzalo, Escribano-Bailón, & De Freitas, 2012; Ferrer-Gallego, Hernández-Hierro, Rivas-Gonzalo, & Escribano-Bailón, 2014; Gonzalo-Diago, Dizy, & Fernandez-Zurbano, 2013; Hufnagel & Hofmann, 2008; Sáenz-Navajas, Fernandez-Zurbano, Ferreira, & Dizy, 2010; Vidal, Meudec, Cheynier, Skouroumounis, & Hayasaka, 2004). The researches described in these publications are usually carried out by chemists, resulting in impeccable methodologies able to isolate compounds or group of compounds. However, the step involving the sensory characterization of such molecules is usually restricted to the use of a limited and predetermined number of mouthfeel terms such as *body/viscosity*, *astringency*, *velvety*, *puckering* or *tannic intensity*.

In this context the main challenge in this field is to find the compound or groups of compounds responsible for mouthfeel properties, which will help to develop references illustrating mouthfeel attributes and further develop a homogeneous and well-defined mouthfeel vocabulary.

Our main hypotheses are that 1) in order to build vocabulary it is of paramount importance to have isolated fractions showing specific mouthfeel-related properties and 2) the subsequent chemical characterization of these fractions will help to identify the chemicals driving such mouthfeel properties. In this context, the specific aims of the present work were 1) to develop a semi-preparative fractionation method for isolating groups of compounds displaying different sensory properties, 2) to use these fractions to generate a wide vocabulary related to mouthfeel properties able to characterize fractions and wines, 3) to chemically characterize fractions and 4) to establish relationships between sensory and chemical composition.

2. Material and methods

2.1. Chemicals

Bovine serum albumin (V powder), tartaric acid, catechin, epicatechin, *trans*-aconitic acid, *cis*-aconitic acid, syringic acid, myricetin, kaempferol, vanillin, protocatechuic acid ethyl ester, gallic acid, *trans*-caffeic acid, and quercetin were purchased from Sigma-Aldrich (St. Louis, MO). Malvidin-3-*O*-glucoside, syringetin-3-*O*-glucoside, quercetin-3-*O*-glucoside, quercetin-3-*O*-galactoside, quercetin-3-*O*-glucuronide, isorhamnetin-3-*O*-glucoside, epicatechin gallate, epigallocatechin, gallate, epigallocatechin, syringetin-3-*O*-galactoside, isorhamnetin-3-*O*-glucoside, ferulic acid, and *p*-coumaric acid were provided from Extrasythese (Genay, France). Vanillic acid was supplied by Fluka (Buchs, Switzerland). Purity of chemical standards was over 95% in all cases and most of them over 99%. Glacial acetic acid, HPLC-grade acetone, HPLC–MS-grade acetonitrile and formic acid, methanol, diethyl ether and absolute ethanol all of them of reagent grade were obtained from Scharlab (Sentmenat, Spain), and potassium metabisulfite from Panreac (Madrid, Spain). Deionized water was purified with a Milli-Q water system (Millipore, Molsheim, France) prior to use.

2.2. Wines

A set of three young wines (not aged in oak barrels) elaborated in the same winery was selected for the study (codes: W1, W2, W3). They underwent malolactic fermentation, being their L-malic acid concentration residual. Further sample information is provided in Table 1. The main criterion for their selection was based on having at least two samples with similar polyphenolic content (measured by absorbance at 280 nm −TPI) but displaying *a priori* different mouthfeel properties (based on an informal tasting carried out with the winemaker and three researchers of the research team). W1 and W2 had similar TPI but displayed different mouthfeel properties. The third wine, W3, was selected as it had *a priori* different mouthfeel properties and presented lower TPI than WI and W2, which allowed having wines in a relatively wide TPI range.

2.3. Preparation of wine fractions

A total of six fractions per wine were obtained by a two-step methodology.

In the first step, four fractions were collected by a preparative LC method adapted from Remy, Fulcrand, Labarbe, Cheynier, and Moutounet (2000) and Gonzalo-Diago et al. (2013). Therefore, the ethanol of two-hundred milliliters of wine was firstly removed in a rotary evaporator (15 min at 28 °C). Then, the sample was further freeze-dried in 500 mL-rounded flasks. The extract was redissolved in 20 mL of hydroalcoholic solution (12% ethanol, v/v) and the whole volume was injected into a preparative column packed with Toyopearl gel (HW 50F) in a HW-50F Millipore (Bedford, MA) Vantage L column (120 mm × 22 mm id; flow rate: 4 mL min^{-1}). A first fraction (F1) was eluted with 720 mL of ethanol/water/formic acid (55:45:1, v/v/v). The second fraction (F2.1) was recovered by elution with 80 mL of acetone (100%). The third (F2.2) and fourth (F2.3) fractions were eluted with 160 and 80 mL of acetone/water at rates of 80:20 and 60:40, respectively (see Fig. S1 in Supplementary material). Solvents present in the four fractions were evaporated under vacuum and samples were further freeze-dried.

In the second step, F1 was redissolved in 200 mL of hydroalcoholic solution (12%, v/v) and further 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 resins (Agilent Technologies, USA) were firstly conditioned by passing 5 mL of methanol and 10 mL of an aqueous solution at pH 2.5 (5 g L^{-1} of tartaric acid, pH adjusted to 2.5 with 0.1 M NaOH). After this, 5 mL of F1 were loaded and sugars and organic acids were washed with 10 mL of aqueous solution at pH 2.5. Then, F1.1 was eluted with 5 mL of diethyl ether, F1.2 with 5 mL of ethyl acetate and F1.3 with 10 mL of methanol. Each cartridge was used a maximum of 5 times. Finally, after F1.3 was eluted, ten-mL of acetonitrile were used as pre-conditioning solvent before conditioning to remove any impurities on the SPE tube. The SPE-procedure was repeated until the 200 mL of F1 were extracted. The extracts of F1.1, F1.2 and F1.3 were gathered in a round flask and further evaporated prior freeze-drying.

The total absence of solvents was assessed by headspace solid phase micro extraction (Carboxen/PDMS 75 μm at 30 °C × 10 min) and GCMS-QP2010 system (Shimadzu, Tokyo, Japan) with an overall system detection limit of 1 ng/sample.

The six freeze-dried fractions (F1.1, F1.2, F1.3, F2.1, F2.2, F2.3) were stored a maximum of one month at 4 °C prior sensory and/or chemical analysis. At that time, fractions (coming from 200 mL of original wine) were dissolved in 100 mL (concentrated twice) of hydroalcoholic solution (7% ethanol, v/v; 50 mg L^{-1} of SO_2; 80 mg L^{-1} of ascorbic acid) prepared with mineral water (Solan de Cabras®, Cuenca, Spain). The level of ethanol (7%) was selected in preliminary tests, in which the range from 5% to 11% was evaluated. This level fulfilled two criteria: 1) it did not induce a burning effect able to mask other sensations and 2) it was as similar as possible to ethanol content in real wines.

2.4. Chemical characterization of wines and fractions.

All chemical analyses were carried out in duplicate.