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Models based on ultraviolet spectroscopy, polyphenols, oligosaccharides and polysaccharides for prediction of wine astringency

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ABSTRACT

Astringency elicited by tannins is usually assessed by tasting. Alternative methods involving tannin precipitation have been proposed, but they remain time-consuming. Our goal was to propose a faster method and investigate the links between wine composition and astringency. Red wines covering a wide range of astringency intensities, assessed by sensory analysis, were selected. Prediction models based on multiple linear regression (MLR) were built using UV spectrophotometry (190–400 nm) and chemical analysis (enological analysis, polyphenols, oligosaccharides and polysaccharides). Astringency intensity was strongly correlated ($R^2 = 0.825$) with tannin precipitation by bovine serum albumin (BSA). Wine absorbances at 230 nm (A230) proved more suitable for astringency prediction ($R^2 = 0.705$) than A280 ($R^2 = 0.56$) or tannin concentration estimated by phloroglucinolysis ($R^2 = 0.59$). Three variable models built with A230, oligosaccharides and polysaccharides presented high R^2 and low errors of cross-validation. These models confirmed that polysaccharides decrease astringency perception and indicated a positive relationship between oligosaccharides and astringency.

1. Introduction

Astringency is a characteristic feature of phenolic compounds and especially of tannins. It is usually ascribed to the capacity of these molecules to bind salivary proteins, with subsequent formation of aggregates and precipitates and reduction of lubrication in the mouth (McRae & Kennedy, 2011; De Freitas & Mateus, 2012; Scollary, Pasti, Kallay, Blackman, & Clark, 2012). Wine astringency, elicited mostly by condensed tannins (i.e. flavan-3-ol oligomers and polymers), increases with their concentration but also depends on their structure, increasing with their mean degree of polymerization (mDP) and with the number of galloyl substituents. Moreover, astringency, as well as aggregation and precipitation of tannin complexes, is affected by the presence of other components. Aggregation and precipitation of tannin protein complexes increases with ionic strength and acidity and decreases as the ethanol content is increased. Astringency is also perceived as more intense at lower pH values regardless of the acid nature or concentration while it is little affected by ethanol concentrations in the range encountered in wine. In addition, astringency can be reduced by the presence of some polysaccharides, especially rhamnogalacturonan II (RGII) and mannoproteins which also impact aggregation properties of tannins (particle size of tannin aggregates) and of tannin protein complexes. Astringency is assessed by sensory analysis but repeatability is obtained only with a large panel of trained tasters, which is time-consuming and expensive. The development of alternative means to measure and predict astringency is thus an important challenge. Several approaches have been proposed to assess wine astringency. Methods based on precipitation with gelatin (Glories, 1984), bovine serum albumin (BSA) (Harbertson, Kennedy, & Adams, 2002), ovalbumin (Llaudy et al., 2004) or methylcellulose (MC) (Sarnekis et al., 2006), assuming that astringency is elicited by precipitated molecules, have been proposed. Other methods relying on the measurement of the turbidity resulting from interaction of tannins with mucins (Monteleone, Condelli, Dinnella, & Bertuccioli, 2004) or assay of salivary proteins precipitated by tannins (Saliva Precipitation Index) by SDS–PAGE electrophoresis (Rinaldi, Gambuti, & Moio, 2012) have also been proposed. High correlations reported between the values obtained using these methods and

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sensory scores (Kennedy, Ferrier, Harbertson, & Peyrot Des Gachons, 2006; Condelli, Dinnella, Cerone, Monteleone, & Bertuccioli, 2006) suggest that they are suitable to predict wine astringency. However, they are rather complex and time consuming. Simpler methods based on UV–visible spectrophotometry have thus been explored. A multiple linear regression approach (MLR) based on UV absorbance at five wavelengths (250, 270, 280, 290, and 315 nm) has been developed to predict the amount of tannins precipitated in the MC assay (Dambergs, Mercurio, Kassara, Cozzolino, & Smith, 2012), itself correlated to astringency intensity (Mercurio & Smith, 2008).

The experiments described hereafter were undertaken with two goals: propose a simpler method and improve our knowledge on the astringency mechanisms. Several spectral and chemical characterizations were performed on 21 wines, including UV spectroscopy, classical wine analysis, polyphenols, polysaccharides and oligosaccharides analysis. The resulting data were used to build models to predict astringency with these parameters.

2. Materials and methods

Twenty-one red wines, mainly from the South of France, from different vintages and made with different grape varieties were selected so as to cover a wide range of vintages and origins, grape varieties and astringency intensities.

2.1. Sensory analysis

This analysis was conducted by an expert sensory panel, in individual testing booths. The twenty judges of the jury had been selected on the basis of their sensory performances and interest for descriptive sensory analysis of wines, according to the ISO 8586-1 norm (1993). To increase the homogeneity and repeatability of the jury, the panelists were trained with taste standards to understand and consistently use the astringency attribute. They were also familiarized with the product space. The wines were analyzed by time-intensity profile (Lee & Pangborn, 1986) with the following protocol. The judges sipped the 18 mL wine sample, which was then expectorated 15 s later. They continued to record their perception, during 60 to 120 s, on an unstructured linear scale, that is a cursor was moved along a line between low and high intensities. Thus the outputs of the judges were curves of astringency over time. The judges were then forced to wait 120 s between samples, and to rinse with a pectin solution (1 g/L citrus peel pectin). Ten wines were evaluated in monadic service, according to a random order (Latin square) minimizing carryover effects. They were served in 215 mL black wine glasses to ensure that visual perceptions did not influence analysis, identified with three digit random codes, different for each glass. No more than thirteen wines per day were proposed. One out of four wines were evaluated in duplicate, which was presented to the jury on two different days.

2.2. BSA precipitation assay

Tannins involved in astringency perception were evaluated using a test adapted from the Adams–Harbertson tannin assay (Harbertson et al., 2002) as follows. The wine (2 mL) was diluted 2-fold with a model wine buffer containing 12% ethanol and 5 g/L potassium bitartrate adjusted to pH 3.3 with HCl. Then it was added with 2 mL of a buffer solution at pH 4.9 (200 mM acetic acid, 170 mM NaCl) (control sample) or with 2 mL of the buffer solution at pH 4.9 containing 1 mg/mL BSA (test sample). Both samples were homogenized, incubated at room temperature for 15 min and centrifuged at 13,500 g for 5 min. Both supernatants were then diluted 10 folds in HCl 2%, and after 30 min, absorbance values (250–650 nm) were recorded. Tannins were estimated as the difference between the 280 nm absorbance measured on the control sample and that measured on the test sample.

2.3. Wine characterization

Classical oenology parameters, namely concentrations of ethanol, malic and lactic acids, total and free SO_2, glucose + fructose and glycerol, total acidity (TA), volatile acidity (VA), pH, were determined according to the CEE-2676/90 official methods of the European Union. The concentrations of anthocyanins, phenolic acids and flavan-3-ol monomers (catechin and epicatechin) were determined by HPLC-DAD analysis as described earlier (Wirth et al., 2010). Proanthocyanidin composition was analysed by HPLC-DAD after acid-catalysed depolymerisation in the presence of phloroglucinol (Ducasse et al., 2010a). The results yielded a matrix **C** of dimensions (21×16).

2.4. UV spectroscopy

UV spectra were acquired with 1 nm step, 1 cm path length, over the range 190–400 nm, after a 400× dilution with water operated by an autosampler. They yielded **A** of dimensions (21×211). Then a second matrix $\mathbf{A}_R$ of dimensions (21×42) was obtained by selecting one out of five wavelength from **A**. The information in $\mathbf{A}_R$ was almost the same as in **A**, but with fewer variables.

2.5. Complex sugars composition: oligosaccharides and polysaccharides

The complex sugars are classified into two groups: the lower molecular weight, or oligosaccharides, and the higher molecular weight, or polysaccharides. The polysaccharide and oligosaccharide fractions were isolated and analyzed as described earlier (Quijada-Morin, Williams, Rivas-Gonzalo, Doco, & Escribano-Bailon, 2014; Ducasse, Williams, Meudec, Cheynier, & Doco, 2010b; Doco, Quellec, Moutounet, & Pellerin, 1999). All sugars eluted after the RGII in gel permeation chromatography were attributed to the oligosaccharide group. The polysaccharide composition was estimated from the concentration of individual glycosyl residues determined by GC–MS after hydrolysis, reduction and acetylation as described elsewhere (Ducasse et al., 2010b). The isolated oligosaccharide fraction was submitted to solvolysis with anhydrous methanol containing 0.5 M HCl for 16 h at 80 °C, followed by per-O-trimethylsilylation of the methyl glycoside derivatives in order to determine the neutral and acidic composition (Ducasse et al., 2010b). Finally, the complex sugars composition was described by: the three main fractions of polysaccharides, i.e. mannoproteins (MPs), rhamnogalacturonan-II (RGII), polysaccharides rich in arabinose and galactose (PRAGs); the total of polysaccharides (PST) which is the sum (MPs + RGII + PRAGs); the total of oligosaccharides (OST); and the total of polysaccharides and oligosaccharides (POST = PST + OST). The results in mg/L were gathered in a matrix **S** of dimensions (21×6).

2.6. Data processing

The data were processed under Scilab with the Fact toolbox. Two matrices were built: **X** by merging **C**, **A** and **S**, then $\mathbf{X}_R$ by merging **C**, $\mathbf{A}_R$ and **S**. The dimensions were (21×233) and (21×64) respectively. Models with one to four variables were checked. For one variable, the model was the variable itself,