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Chemical characterization, antioxidant properties and oxygen consumption rate of 36 commercial oenological tannins in a model wine solution

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ABSTRACT

The chemical composition (CC), antioxidant capacity (AC) and oxygen consumption rate (OCR) of 36 different commercial tannins were measured. The CC was analyzed by total polyphenol index, Bate-Smith, methyl-cellulose, Folin-Ciocalteu, OIV official method and phloroglucinolisis. The AC was measured by different methods (ABTS, CUPRAC, DPPH, FRAP, ORAC) using Trolox as standard. The OCR was measured using a non-invasive method based on luminescence. The results indicate that it is possible to obtain differentiation between procyanidins/prodelphinidins, profisetinidins/prorobinetidins, gallotannins and ellagitannins by PCA based on their CC data. It is also possible to separate condensed from hydrolysable tannins by PCA based on their AC data. The results show that ellagitannins are the fastest oxygen consumers of the various oenological tannins, followed in descending order by condensed tannins and finally gallotannins. The combination of CC, AC and OCR analyses enable to classify tannins according to their effectiveness in protecting wines against oxidation.

1. Introduction

There is in fact a wide range of oenological tannins in the market which differ in chemical structure (condensed and hydrolysable tannins), botanical origin (grape seed or grape skin, oak wood, exotic wood) and/or preparation process. These include hydrolysable tannins from nut galls, tara, oak and chestnut, and condensed tannins from grape seeds and skins and other plant sources, such as quebracho, mimosa and acacia (Versari, du Toit & Parpinello, 2013).

Their use in winemaking has become common practice worldwide, but so far, they are only authorized by the International Organization of Vine and Wine (OIV) (OIV, 2015) to facilitate the fining of wines and musts. Nevertheless, they are also used for other purposes because of their interesting and varied properties. These properties, as demonstrated by various authors, can be classified into different groups: "impact on oxygen/metals", "impact on colour/pigments", "protein interaction", "sensory/mouthfeel properties" and "bacteriostatic effects". The first group includes antioxidant capacity (protection of wine against oxidation) (González-Centeno, Jourdes, Femenia, Simal, Rossello & Teissedre, 2012; Magalhaes, Ramos, Reis & Segundo, 2014), antioxidasic activity (anti-laccase activity) (Obradovic, Schulz & Oatey, 2005), the ability to scavenge superoxide radicals (Farhadi, Esmaeilzadeh, Hatami, Forough & Molaie, 2016), the prevention of oxidative damage mediated by Fenton-based reactions (Perez, Wei & Guo, 2009), the ability to chelate iron (Karamać & Pegg, 2009) and the direct consumption of dissolved oxygen (Navarro et al., 2016; Pascual et al., 2017). The second group includes colour improvement and stabilization of red wines (Canuti et al., 2012; Trouillas et al., 2016), copigmentation effect (Neves, Spranger, Zhao, Leandro & Sun, 2010) and the direct formation of new pigments (Versari et al., 2013). The third group is related to their ability to interact with wine proteins and their use in preventing protein haze (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006) caused by over-fining when white wines are treated with gelatin (Mierczynska-Vasilev & Smith, 2015). The fourth group involves their impact on sensory/mouthfeel properties. In this regard, oenological tannins are used to improve wine structure and mouthfeel (astringency and bitterness) (Preys et al., 2006) and to eliminate reduction odors (Vivas, 2001). Finally, the bacteriostatic effects of oenological tannins (Lempereur et al., 2002) have been also described.

Tannins are usually classified into two families: hydrolysable and

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condensed tannins. Hydrolysable tannins are classified into two subfamilies, gallotannins and ellagitannins. Gallotannins are polymers formed by esterification between D-glucose and gallic acid. Tannic acid is the commercial name for gallotannin extract comprising mixtures of polygalloyl quinic acid ester or polygalloyl glucoses (Pascual et al., 2017). The main sources of commercial gallotannins are nut galls and tara.

Ellagitannins are polymers of ellagic, gallic and/or hexahydroxidiphenic acids (Versari et al, 2013). To be more precise, a nonahydroxyterphenoyl unit (NHTP) is esterified in positions 2, 3 and 5 with a C-glycosidic bond, while an open-chain glucose is esterified in positions 4 and 6 with a hexahydroxydiphenoyl unit (HHDP) forming the chemical structure of ellagitannins (Quideau et al., 2004). They constitute one of the most important families of tannins with many biological features, such as antioxidant capacity (Hosu, Cristea & Cimpoiu, 2014). The main sources of commercial ellagitannins are oak and chestnut.

Condensed tannins, also known as proanthocyanidins, come from different botanical origins, such as grapes, quebracho, mimosa and acacia. They differ mainly in regards to the monomer released after acidic cleavage, the degree of polymerization (mDP), and their levels of galloylation and ramification (Versari et al., 2013). Grape-skin tannins are composed of procyanidins and prodelphinidins because their acidic cleavage gives cyanidin and delphinidin, whereas grape-seed tannins are composed only of procyanidins. Grape-skin tannins have a high mDP and a low level of galloylation, while grape-seed tannins have a lower mDP and a high level of galloylation (Souquet, Cheynier, Brossaud & Moutounet, 1996). Quebracho tannins are profisetinidins, because their acidic cleavage gives fisetinidin, and they have a high level of ramification, while mimosa tannins are prorobinetidins because they release robinetinidin (Celzard et al., 2015). Less is known about acacia tannins, but it seems they are composed of a mixture of profisetinidins, prorobinetidins and prodelphinidins (Hoong, Pizzi, Tahir & Pasch, 2010). Condensed tannins as a whole are called proanthocyanidins.

The antioxidant capacity attributed to oenological tannins is probably one of the main reasons they are widely used in wineries. It is generally accepted that they are very useful in protecting grape juice and wine against oxidation and avoiding browning (Nichols-Orians, 1991; Versari et al., 2013). On this subject there are quite a few references about the antioxidant properties of commercial tannins (Laghi et al., 2010; Magalhaes et al., 2014) using diverse antioxidant assays (ABTS, CUPRAC, DPPH, FRAP, ORAC, …). However, Magalhaes et al. (2014) have shown that different antioxidant assays produce different and sometimes contradictory results. More recently, Pascual et al. (2017) measured the oxygen consumption rate (OCR) of two hydrolysable tannins and three condensed tannins.

Given the wide range of commercial tannins present in the market and their great chemical diversity, the main goal of this research is to carry out an exhaustive study to determine their chemical characterization, antioxidant properties and oxygen consumption rates using a large number of samples. A classification of their efficiency according to their chemical composition is then proposed.

2. Materials and methods

2.1. Chemicals and equipment

All samples and standards were handled without exposure to light. 2,2′azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS), (±)-6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid 97% (Trolox), 2,2-azobis(2-methylpropionamidine) dihydrochloride (AAPH), gallic acid, copper (II) sulfate pentahydrate, iron (III) chloride hexahydrate, 2,2-diphenyl-1-picrylhydrazyl (DPPH), copper (II) chloride dihydrate, neocuproine, Folin-Ciocalteu reagent, L(+)-tartaric acid, sodium hydroxide, sodium carbonate, potassium persulfate, sodium phosphate monobasic, phosphate buffer solution, polyvinylpolypyrrolidone (PVVP), methyl-cellulose, ascorbic acid, phloroglucinol, ammonium sulfate and ammonium acetate were purchased from Sigma-Aldrich (St. Quentin, Fallavier, France). Fluorescein, sodium acetate and 2,4,6-triazine-s-tripyridyl (TPTZ) were from Fluka Analytical (Munich, Germany). Sodium dihydrogen phosphate, disodium hydrogen phosphate, ethanol (HPLC grade) and methanol (HPLC grade) were supplied by VWR Prolabo Chemicals (Fontenay-sur-Bois, France). Acetic acid (HPLC grade) and hydrochloric acid (HPLC grade) were obtained from Fisher Scientific (Illkirch, France).

The equipment used was the following: a spectrophotometer UV–Vis Helios Alpha™ (Thermo Fisher Scientific Inc., Waltman, MA, USA); an HPLC-UV Agilent 1200 series™ (Agilent Technologies, Santa Clara, CA, USA); an Xterra RP18 (100 × 4.6 mm, 3.5 µm) column (Agilent Technologies, Santa Clara, CA, USA); a 96-well microplate reader (FLUOstar Omega, BMG Labtech, Germany); a NOMASense™ O2 Trace (Nomacorc SA, Thimister-Clermont, Belgium); and a CB Standard Balance (COBOS, Barcelona, Spain).

2.2. Commercial tannins

Thirty-six commercial tannins were considered in this study. Specifically, the following were analyzed: 17 proanthocyanidins comprising 9 procyanidins/prodelphinidins (3 from grapes, 4 from grape seeds and 2 from grape skin) and 8 profisetinidins/prorobinetidins (2 from acacia and 6 from quebracho), and 19 hydrolysable tannins comprising 8 gallotannins (4 from nut galls and 4 from tara) and 11 ellagitannins (8 from oak and 3 from chestnut). They were provided by eight different companies: Laffort (Floirac, France), Agrovin (Ciudad Real, Spain), Sofralab (Magenta, France), Institut Oenologique de Champagne (IOC) (Epernay, France), Esseco (Trecate Novara, Italy), AEB (Brescia, Italy), Erblsöh (Geisenheim, Germany) and Vason (Verona, Italy).

2.3. Determination of polyphenol and tannin contents

All the oenological tannins were characterized using the analytical methods described below to determine their richness. Solutions of 2 g/l of each tannin were prepared in a synthetic model wine solution (12% v/v ethanol, 4 g/l tartaric acid adjusted to pH 3.5 with sodium hydroxide). All the analyses were carried out at least in triplicate.

2.3.1. Total polyphenol index

The total polyphenol index (TPI) was analyzed by measuring the 280 nm absorbance of a 1:100 dilution of tannin solutions with a spectrophotometer, using a 10 mm quartz cuvette and multiplying the absorbance value by 100 as described by Ribéreau-Gayon et al. (2006). The tannin richness (g of tannin/100 g of commercial product) of the different oenological tannins was estimated by interpolating the TPI in two different calibration curves according to tannin type and with regard to the original weight of the sample. Fig. 1 shows the A280 nm calibration curves for (-)-epicatechin, gallic acid, ellagic acid and tannic acid. These clearly indicate that gallic acid, ellagic acid and tannic acid have similar absorptivity coefficients (expressed in $l.mg^{-1}.cm^{-1}$), whereas that of (-)-epicatechin is around four-fold lower. Proanthocyanidins were therefore interpolated in a (-)-epicatechin calibration curve because this is the main subunit of condensed tannins. In contrast, gallotannins are composed mainly of glucose and gallic acid and should therefore be interpolated in a gallic acid calibration curve or, even better, a tannic acid calibration curve, since this tannic acid is available at a high purity level. Ellagitannins, on the other hand, are composed mainly of glucose and ellagic acid and consequently should be interpolated in an ellagic acid calibration curve. The impossibility of obtaining commercial vescalagin or another pure ellagitannin in sufficient quantity and the poor solubility of ellagic acid led us use tannic acid as standard for ellagitannins too.