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Condensed tannins extraction from grape pomace: Characterization and utilization as wood adhesives for wood particleboard

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ABSTRACT

The extraction of condensed tannins from grape pomace was examined using water medium in the presence of NaOH, Na_2CO_3, $NaHCO_3$ eventually in the presence of Na_2SO_3. The tannin fractions reactivity towards formaldehyde was studied by gel time analysis and thermomechanical analysis in bending and it was demonstrated that despite of their lower phenolic contents, some of these extracts displayed promising properties for adhesive applications. A resin formulation in which the total content of tannin is 75% of the total resin solids content gave good results and was employed for the elaboration of the first grape pomace based-wood particleboard which passed relevant international standard specifications for interior-grade panels.

1. Introduction

The recovery of byproducts from agricultural industries to be converted into value-added products has attracted great interest in the past several years. Grape is one of the world's largest fruit crops and this production generates a substantial volume of solid organic by-product. Grape pomace (consisting mainly of skins, but also of seeds and stems) is approximately 20% (w/w) of the harvested grapes after pressing (Laufenberg et al., 2003). Only small amounts of these by-products are up-graded or recycled; a part of it is destined for distillation but this allows recovery of a minimum amount of ethanol. Seeds and anthocyans can also be recovered in the distilleries but in most of the cases, the pomace is used for animal feed or compost, without any pre-treatment. The remaining solid residues retain high levels of condensed tannins because of low extraction during winemaking. Thus pomace is composed for a large part of proanthocyanidins, consisting of flavonoid units which have undergone varying degrees of condensation. The proanthocyanidins are composed by procyanidin and prodelphinidin units that are linked together by a C4–C8 bond in grapes (Pizzi, 1993, see Fig. 1). This high polyphenolic content is a disadvantage for their use as animal feed and poses potentially pollution problems when it is used as soil fertilizer (Morthup et al., 1998). On the other hand, since the first observations of the "French paradox" (Renaud and De Lorgeril, 1992), grapes extracts are reported to exert favourable effects on human health. The main interest on polyphenolic compounds was due to their protective effect against some diseases as to their capacity for preserving foods (Makris et al., 2007; Bonilla et al., 1999; Negro et al., 2003). Several purification techniques to obtain high-purity fractions from pomace have been reported for cosmetic, pharmaceutic and food applications (Guerrero et al., 2008; Ruberto et al., 2007; Spigno and De Faveri, 2007; Monrad et al., 2010; Pinelo et al., 2005, 2007; Vatai et al., 2009).

Condensed tannins–formaldehyde wood adhesives have been used industrially since 1970s for interior and exterior wood bonding of products such as particleboard and plywood (Tondi and Pizzi, 2009; Lei et al., 2008; Pichelin et al., 2006; Pizzi, 2003, 2006). They are obtained by hardening of polymeric flavonoids by polycondensation with formaldehyde involving their more reactive A-ring according to Fig. 1. Thus, it was demonstrated that condensed tannins are both chemically and economically interesting for the preparation of adhesives and that they could be successfully used as substitutes for phenol in the production of resins. Condensed tannins used in the previously described studies are generally extracted from the bark of various trees like mimosa, quebracho or pine (Fradinho et al., 2002; Panamgama, 2007; Vazquez et al., 2000). Although many different methods of tannin extraction from vegetable material can be employed in the laboratory scale, the industrial techniques are simple procedures, using water as solvent, at temperature between 70 °C and 100 °C, usually in the presence of a base (carbonate, soda) and of sodium sulfite or metabisulfite (Pizzi, 2003). Sulfitation of tannins is one of the most

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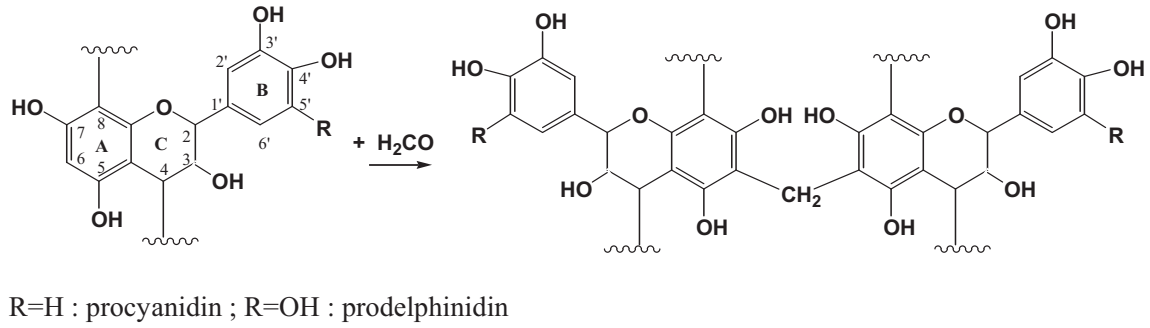

R=H : procyanidin ; R=OH : prodelphinidin

Fig. 1. Chemical structure of proanthocyanidins and reaction with formaldehyde.

useful reactions in flavonoid chemistry to increase tannin extraction yield from tree barks (Hoong et al., 2009; Pizzi, 1994). As an example, starting from pine bark, the best industrial tannins extraction yield in water medium in the presence of sulfite is 13% to 15% (w/w) (Von Leyser and Pizzi, 1990). However, the ability of green adhesives to make significant impact as a substitute for polymeric materials depends on the availability of low-price and high-quality tannin fractions in large quantities.

In this study, we propose an economically and environmentally valuable utilization of grape pomace which retains high levels of condensed tannins and is currently underexploited. A few preliminary experiments have been recently reported in a preliminary short communication (Lan et al., 2011). Extraction of tannins from this resource was investigated in water medium using sodium hydroxide, sodium carbonate or sodium hydrogenocarbonate in the presence of sodium sulfite. The tannin extracts were characterized by ^{13}C NMR and we verified the possible use of these fractions as a component of a green adhesive formulation. Then, we prepared the very first grape pomace extract-based particleboards. One of them was good enough to pass relevant international standard specifications for interior-grade panels.

2. Materials and methods

The samples correspond to mixtures of by-products of the wine-making process of red grape variety (Vitis vinifera), growing in south-east of France and were provided by a French distillery (Franck Le Net, UDM). The air-dried grape pomace was composed by grape skin, seeds and stalks manually separated. It was stored at room temperature during the course of this study.

2.1. Tannins extraction

Twenty grams (oven-dry matter) of grape pomace was treated with an aqueous solution of sodium chemicals with a solid-to-liquid ratio of 1:8. The reaction mixture was heated at different extraction parameters (see Table 1 for treatment conditions). Concerning experiments conducted at atmospheric pressure (T = 70 °C and 100 °C), the treatments were carried out in a round bottle flask connected by water condenser. For reactions performed at 120 °C, the treatments were carried out in a reactor with a Parr 4836 temperature controller (Parr Instrument Company, Moline, IL) and the reaction mixture was heated at a rate of ~5 °C/min with continuous stirring. After heating, the pomace was cooled, washed and filtered through filter paper. The washed liquid was evaporated to a moderate concentration (rotary evaporator, temperature: 60 °C), then lyophilised to yield lyophilised tannins. A sample of each solid residue and lyophilised tannins was separated and stored in a freezer at −5 °C before analysis.

The kinetics of tannins extraction from pomace was studied by the measurement of tannin concentrations in the hydrolysates from the absorbance at 330 nm (UV-2500 PC series spectrophotometer). Results were given according to a calibration plot for a solution of procyanidins prepared by the method of hydroalcoholic maceration of grape seeds extracted with ethyl acetate in the laboratory.

2.2. Analysis of the raw material and solid residue

Moisture content was determined using KERN MRS 120–3 infrared moisture analyser.

Condensed tannins were calculated from the absorbance at 550 nm of polyphenolic solutions obtained after 5% HCl–BuOH treatment (100 °C, 3 h) of sample (Reed et al., 1982). Results were given according to the same calibration standard in the kinetics testing of tannins extraction. Sulfur and nitrogen elemental analysis were obtained on a Perkin Elmer 240C micoranalyser. The protein was calculated form the formula: protein (%) = Nitrogen (%) × 6.25.

Carbohydrate and lignin contents were measured on extractive-free material (soxhlet extracted with dichloromethane overnight), ground to pass a 40-mesh screen, according to the laboratory analytical procedure (LAP). Samples were hydrolysed with 72% sulfuric acid for 1 h and then autoclaved after being diluted to 3% sulfuric acid through the addition of distilled water. The autoclaved samples were filtered and the dried residue was weighed to give the Klason lignin content. Monosaccharide contents in the filtrate were quantified using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) (Pronto, 1998). The acid soluble lignin content was determined from absorbance at 205 nm (UV-2500 PC series spectrophotometer) according to Lin and Dence (1992). In brief, the lignin content was calculated from the following expression of Beer's law: Lignin (g/L) = Absorbance/110.

2.3. Characterization of tannins

Liquid phase ^{13}C NMR experiments were performed on a Bruker Avance-400 spectrometer operating at a ^{13}C frequency of 100.59 MHz. Tannins (100 mg) were dissolved in D_2O (0.5 ml) with slight heating. ^{13}C NMR spectra were acquired at 50 °C in order to reduce viscosity. 10,000 scans were collected with a pulse delay of 12 s. ^{13}C data were processed offline using XWinNMR processing software (Acorn NMR Inc.).

The Stiasny number reaction was used to determine the reactivity of tannins towards formaldehyde. According to Yazaki and Collins (1994) about 0.2 gm (oven-dry mass) of tannins sample, 5 ml of 37% aqueous formaldehyde and 5 ml of 10 M hydrochloric acid solution (HCl) were mixed together and heated under reflux for 30 min. At the end of this reaction, the mixture was filtered through a sintered glass filter (filter no. 3) while it was still hot. The precipitate was dried to a constant weight in an oven at 105 °C. The Stiasny number was determined as a percentage of the weight of the precipitate to the weight of the starting sample.