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Degradation kinetics of encapsulated grape skin phenolics and micronized grape skins in various water activity environments and criteria to develop wide-ranging and tailor-made food applications

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ABSTRACT

Micronized grape skin powder (GS) and maltodextrin-encapsulated grape skin phenolics (eGSP) were recovered from winemaking byproducts as potential food ingredients. Hygroscopicity was higher in eGSP than in GS. Both eGSP and GS had intense color and less fermented odor than the wet GS. Phenolic content, antioxidant activity and inhibitory effectiveness towards enzymes related to hyperglycemia damage were ~ double in eGSP than in GS. During storage, the rate of phenolic degradation diminished with decreasing a_w from 0.75 to 0.11. Anthocyanins and proanthocyanidins were less stable than monomeric flavanols and flavonols. The rate of decrease in antioxidant activity was lower compared to the extent of phenolic degradation. At a_w 0.11 no degradation was observed in eGSP, while anthocyanin and proanthocyanidin contents slightly decreased in GS ($k * 10^3$ in the range 0.69–2.94 d^{-1}). Criteria for GS and eGSP storage were defined in relation to their final uses.

Industrial relevance: The conversion of winemaking by products into value added products is considered the unique strategy to overcome the cost of not recycling, including waste disposal and decontamination of affected areas. As winemaking is a seasonal activity, long-term stability of recovered byproducts is needed for their further utilization. GS and eGSP represent potential value-added food ingredients for wide-ranging applications (antioxidant, colorant, phenolic sources) and tailor-made functionalities (inhibitors of enzymes related to hyperglycemia). The results obtained led to the definition of criteria for GS and eGSP storage, which depend on their final use in foods, as illustrated by two discussed scenarios.

1. Introduction

Wine production is one of the most important agricultural activities throughout the world, causing the generation of large amount of byproducts including grape skins, seeds and stems. The management of all of the aforementioned byproducts poses serious environmental concerns because these residues have a low pH, high organic matter content and may exert phytotoxic effects if applied to crops or wetlands. Byproduct recovery and conversion into value added products is considered to be the unique strategy to overcome the cost of not recycling, including waste disposal and decontamination of affected areas (Devesa-Rey et al., 2011).

Grape skins (GS) are potential sources of dietary fiber and phenolics, particularly, flavonols, flavanols, anthocyanins and proanthocyanidins (Perez-Jimenez et al., 2008; Teixeira et al., 2014). Hence, a great deal of interest has been expressed in the possibility to convert GS into value-added food ingredients due to their ability to provide advanced technological properties and/or health claims, to the final product (Galanakis, 2015). In some applications, GS are dried and micronized to obtain the "antioxidant dietary fiber (ADF)", a product that delivers fiber along with soluble and insoluble antioxidants. Grape ADF was demonstrated to have a positive effect in the prevention of cardiovascular diseases (Perez-Jimenez et al., 2008). Alternatively, GS are extracted using conventional or emerging technologies such as ultrasonics, high hydrostatic pressure, pulsed electric fields (Corrales, Toepfl, Butz, Knorr, & Tauscher, 2008) and high voltage electrical discharges (Boussetta et al., 2012) to recover soluble phenolics. Phenolic extracts

Abbreviations: C, catechin; Cy-glc, cyanidin 3-O-glucoside; Dp-glc, delphinidin 3-O-glucoside; EC, epicatechin; GAE, gallic acid equivalents; K, kaempferol; Mv-glc, malvidin 3-O-glucoside; Mv-*pc*-glc, malvidin *p*-coumaroyl glucoside; Pn-glc, peonidin 3-O-glucoside; Pt-glc, petunidin 3-O-glucoside; Q, quercetin; Q-glc, quercetin 3-O-glucoside; Q-gln, quercetin 3-O-glucuronide; ADF, antioxidant dietary fiber; a_w, water activity; k, rate constant; eGSP, grape skin phenolics encapsulated into maltodextrins; GS, grape skins; GSP, grape skin phenolics; $t_{1/2}$, half-time; M_o, monolayer moisture content; T_g, glass transition temperature.

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are then used as such or after encapsulation with various carriers that improve their solubility in alcohol-free water (Souza et al., 2014). Many studies have shown that phenolic can act as antioxidants and inhibitors of enzymes involved in oxidative stress, type-2 diabetes, hypertension and inflammation (Apostolidis, Kwon, & Shetty, 2007; Teixeira et al., 2014).

Hence, both GS and GSP have been proposed for wide-ranging applications in various food products. In meat- and fish-based products GS and GSP have been applied as antioxidants (Sáyago-Ayerdi, Brenes, & Goñi, 2009; Sanchez-Alonso, Jimenez-Escrig, Saura-Calixto, & Borderias, 2008; García-Lomillo, González-SanJosé, Skibsted, & Jongbergb, 2016) and antimicrobials (García-Lomillo, González-SanJosé, Del Pino-García, Rivero-Pérez, & Muñiz-Rodríguez, 2014). In beverages and gel products, GS and GSP have been proposed as natural colorants (Maier, Fromm, Schieber, Kammerer, & Carle, 2009; Lavelli, Sri Harsha, & Spigno, 2016a) and texturizing agents (Lavelli, Sri Harsha, Mariotti, Marinoni, & Cabassi, 2015). In dairy products, GS and GSP have been used to increase fiber and/or phenolic contents (Tseng & Zhao, 2013; Marchiani, Bertolino, Ghirardello, McSweeney, & Zeppa, 2015); moreover their effect on curd microstructure has been investigated to modulate cheese rheology (Han et al., 2011). In bakery products, GS and GSP have been used as fortifying agents to improve phenolic and fiber contents (Walker, Tseng, Cavender, Ross, & Zhao, 2014; Sant'Anna, Christiano, Marczak, Tessaro, & Thys, 2014). GS and GSP have also been utilized for specific functionality. In fact, they have been found to decrease the level of N-(carboxymethyl)lysine, an advanced glycated end-product related to health risk (Mildner-Szkudlarz, Siger, Szwengiel, & Bajerska, 2015), to increase the antiglycation activity of foods (Lavelli, Sri Harsha, Torri, & Zeppa, 2014) and to inhibit starch digestion enzymes, thus leading to food that could address the needs of diabetic people (Lavelli, Sri Harsha, Ferranti, Scarafoni, & Iametti, 2016b).

It is worth considering that winemaking is a seasonal activity and thus byproduct accumulation is typically concentrated to a limited time frame. Hence, long-term stability of GS and GSP is needed for further utilization. Previous studies have pointed out that GSP in the liquid form lack in long-term stability, as the half-life of anthocyanins is about 30 d at 20–25 °C (Cardona, Lee, & Talcott, 2009; Souza et al., 2014). The freeze-dried GSP showed higher anthocyanin stability; moreover, encapsulation of the GSP with maltodextrins further increased anthocyanin stability (Souza et al., 2014). The stability of foods in the dry and intermediate moisture state is critically dependent on the water activity level (a_w). In fact, progressive decrease in a_w slows down the rates of microbial growth, microbial production of toxins, and enzyme activities. Moreover, at low a_w levels, water limits reagent mobility and becomes unavailable as a solvent to support chemical reactions (Lavelli & Vantaggi, 2009). With decreasing a_w, the glass transition temperature (T_g) increases. T_g is the temperature below which a soft, rubbery material will transform into hard amorphous solid (glassy state). This leads to a marked increase in viscosity and a decrease in molecular mobility. Foods are often considered very stable below their T_g, as compounds involved in deterioration reactions take many months or even years to diffuse over molecular distances and approach close enough to each other to react (Roos & Karel, 1991; Nurhadi, Roos, & Maidannyk, 2016).

There is no detailed information on the effect of intermediate and low moisture levels (a_w in the range 0.75–0.11) on the stability of GS and encapsulated GSP (eGSP). Hence, in the current study micronized GS and eGSP were obtained from winemaking byproducts with the aims to: a) investigate some properties relevant for wide-ranging applications, namely: hygroscopicity, color, odor, phenolic composition and antioxidant activity, as well as a target functionality, such as inhibition of starch digestion enzymes; b) model the degradation kinetics of individual phenolic compounds as a function of a_w in the range 0.11–0.75 at 30 °C; and c) define criteria for GS and eGSP storage in relation to their final uses.

2. Materials and methods

2.1. Chemicals

Malvidin-, cyanidin-, delphinidin-, peonidin- and petunidin- 3-O-glucosides were obtained from Polyphenols (Sandnes, Norway). Catechin, epicatechin, quercetin 3-O-glucuronide, quercetin 3-O-glucoside, quercetin and kaempferol were purchased from Extrasynthese (Lyon, France). All other standards and chemicals were purchased from Sigma Aldrich (Milan, Italy).

2.2. Grape skins (GS) and grape skin phenolics encapsulated in maltodextrin (eGSP)

Grape pomace of the Barbera variety was kindly provided by a winery located in Northern Italy. At the winery, grapes were processed according to red vinification and the fermented pomace was recovered and sieved (with a 5-mm sieve) to separate the skins from the seeds. The seeds were also removed manually. Like all vegetable materials, the GS rapidly undergo spontaneous fermentation (Lavelli, Pagliarini, Ambrosoli, Minati, & Zanoni, 2006). Hence GS were put in a 1 cm-high steel plate and then frozen in a freezer at −20 °C. The frozen GS were transported to the lab and dried at 55 °C for approximately 3 h. After drying, GS were milled and sieved by using the Octagon Digital sieve shaker (Endecotts Ltd., United Kingdom), with a certified sieve (openings: 125 μm) for 10 min at amplitude 8. The sieved GS were stored under vacuum, in the dark, at 4 °C.

The eGSP were obtained as described previously (Lavelli et al., 2016a). Briefly, GS were extracted with 60% aqueous ethanol with continuous stirring for 2 h at 60 °C. The drying process was performed in a laboratory scale spray dryer (Buchi Mini Spray Dryer B-290, Switzerland), with the following operation conditions: 0.7-mm diameter nozzle, 4 mL/min feeding rate with 6.5% w/v maltodextrin (dextrose equivalence 12); 700 L/h drying air flow rate; 150 °C inlet air temperature.

2.3. Phenolic solubility at pH 3.5 and pH 6.5

An amount of 1.25 g of eGSP or GS was added to 15 mL of 0.15 M potassium citrate buffer, pH 3.5 or to 15 mL of 0.15 M potassium citrate buffer, pH 6.5. The mixtures were incubated in a water bath at 30 °C for 30 min and then centrifuged at 10000 × *g* for 20 min. The residues were discarded, while the supernatants were collected, and the total phenolic content was measured as described under Section 2.7. The amount of soluble phenolics extracted from GS and eGSP was evaluated in duplicate and expressed as milligrams of gallic acid equivalents (GAE) per litre of buffer.

2.4. Storage study

The powders were weighed into Petri dishes (6 cm diameter, 5.5 g of product in each dish). The dishes were placed inside airtight plastic chambers on wire-mesh racks situated above saturated salt solutions. The chambers were stored for 6 months at 30 °C in a thermostated cabinet. These time-temperature conditions were chosen as they resemble a practical handling for ingredients derived by winemaking byproduct. In fact, in the Mediterranean countries the winemaking season starts in August and ends in January. Hence, for a convenient management of these ingredients, stability for 6-months at room temperature should be advisable. Cold storage is not appropriate for byproduct since it is too energy-consuming, hence the effect of storage at lower temperatures was not investigated. To create different relative humidity environments, the following saturated salt solutions were used: LiCl (a_w = 0.113 ± 0.002), CH_3COOK (a_w = 0.216 ± 0.005), $MgCl_2$ (a_w = 0.324 ± 0.002), NaBr (a_w = 0.560 ± 0.004), and NaCl (a_w = 0.751 ± 0.001). Duplicate chambers were incubated for each a_w level. At five