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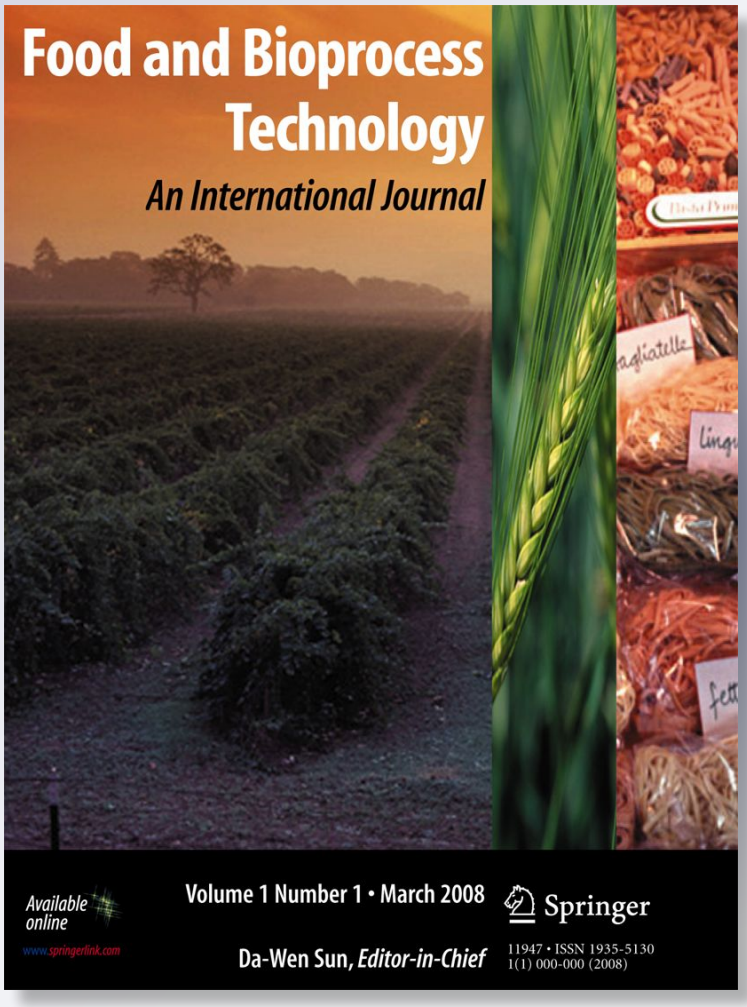

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COMMUNICATION

Freeze-Drying Encapsulation of Red Wine Polyphenols in an Amorphous Matrix of Maltodextrin

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Abstract Maltodextrin DE $_{10}$ was added to Argentine red wine (Cabernet Sauvignon) in a 20% concentration (total weight basis), and the resulting solution was freeze-dried. Water and almost all ethanol were eliminated during freeze-drying leaving an amorphous glassy maltodextrin microstructure (i.e., "wine powder"), containing the red wine's polyphenols (as well as other non-volatile constituents of the dry extract). Almost no loss of total polyphenols was found in the freeze-drying process. Upon milling, the maltodextrin microstructure yielded a free-flowing powder, and its glassy nature was confirmed by measuring its glass transition temperature (T_g). After 15 days, storage at 38 °C total polyphenols content in the "wine powder" remained practically unchanged. This free-flowing powder contained 3.7 times the concentration of polyphenols in red wine, while only containing less than 1% ethanol. This might be added to other powdered foods as a source of wine polyphenols.

Keywords Polyphenols · Red wine · Encapsulation · Freeze-drying · Glass transition temperature · Maltodextrin

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Introduction

Regular and moderate wine consumption is one of the mostly evoked facts for explaining the low incidence of cardiovascular events in France (the so-called French paradox) compared with other industrialized countries (Soulat et al. 2006; Nikfardjam Pour et al. 2006; Gorelik et al. 2008). It has been suggested that the phenolic compounds highly abundant in red wine might be responsible for this improvement in health in the French population. Although the mechanisms of action are yet not fully understood, it is well-known that these molecules behave as radical scavengers and antioxidants. It has also been demonstrated that they can protect cholesterol in the low-density lipoprotein species from oxidation (Brouillard et al. 1997; Cioroi and Musat 2007). The relationship between in vitro antioxidant capacity and polyphenol total content of red wines has been documented (Cioroi and Musat 2007; Avalos Llanos et al. 2003) accounting for the in vivo effect (Camussoni and Carnevali 2004).

However, there are some clear drawbacks associated with the ingestion of alcohol present in the wine: (a) consumption must be moderate (i.e., one to two glasses per day) in order to avoid alcohol-related diseases, and (b) ethnical, social, or religious reasons may prevent certain sectors of the population from consuming wine.

Freeze-drying has been proved to be the most suitable method for drying thermosensitive substances, minimizing thermal degradation reactions. It has also been used to encapsulate delicate biomaterials in amorphous carbohydrate microstructure matrices (Heldman and Hartel 1997; Roos 1995). Fang and Bhandari (2010) recently reviewed technologies for polyphenol encapsulation, including freeze-drying; however, they did not consider the direct encapsulation of wine's dry extract (having its associated

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polyphenols). Maltodextrin (MD) is the most common carbohydrate matrix used for encapsulation stability, i.e., protecting against undesirable physical (stickiness and collapse) and/or chemical changes, such as oxidation of encapsulated material (Roos 1995; Galmarini et al. 2009).

Present work reports preliminary results on the freeze-drying encapsulation of red wine's dry extract (which contains its polyphenols) in an amorphous MD matrix, while simultaneously eliminating the water and alcohol. Some physical characteristics and polyphenol content of the dry powder so obtained were determined.

Materials and Methods

Materials

The wine used was Cabernet Sauvignon, "Postales del Fin del Mundo" (*Bodega Fin del Mundo*) from a cold climate wine growing region (Neuquén, Argentina); alcohol content was 13.7% (*v*/*v*) (10.29 g ethanol/100 g wine). Maltodextrin DE $_{10}$ was from Productos de Maíz S.A., Buenos Aires, Argentina.

Wine's dry extract was determined by evaporation of a thin layer of wine in a forced air circulation oven at 97–102 °C during 2.5 h: four replicates were made and the average is reported. The pH of the wine was measured using a previously calibrated glass electrode.

Encapsulation Procedure

Maltodextrin DE $_{10}$ was dissolved in wine to 20% concentration (total weight basis) and freeze-dried to encapsulate the polyphenols (and associated constituents of the wine's dry solids) in an amorphous microstructure of MD. The wine containing the dissolved MD was poured into a stainless steel tray (round tray of 20 cm diameter; depth of sample 1 cm), and freeze-dried at room temperature in a FIC Ll-I-E300-CRT freeze dryer (Buenos Aires, Argentina) operated with a freezing plate and condenser at −40 °C and a vacuum below 200 μmHg. Freeze-drying time was of 40 h at room temperature (22±3 °C).

The freeze-dried sample of glassy aspect, was milled in a domestic grain coffee grinder, resulting in a free-flowing powder (i.e., "wine powder") resembling red wine's color. This powder was placed in a hermetically sealed opaque plastic flask and stored up to 15 days in a constant temperature oven at 38±0.2 °C representative of an accelerated storage test.

Moisture Content

Moisture content of the "wine powder" was determined using the Karl Fischer (KF) method. KF titration was carried out at 25±1 °C with a Karl Fischer titrator DL 31 from Mettler-Toledo, applying the one-component technique with Hydranal Titrant Composite 5 (from Riedel-de Haën, Germany). A methanol/formamide mixture (1:1) was used as solvent (purchased from Merck, Darmstadt, Germany). Standard deviation for moisture determination using KF titration was determined to be about ±0.04% moisture.

Water Activity

Water activity (a_w) was determined using an electronic dew-point water activity meter Aqualab series 3 (Decagon Devices, Pullman, Washington, USA). The equipment was calibrated with saturated salt solutions in the water activity range of interest (Favetto et al. 1983). The error in a_w measurement was found to be about ±0.004.

Determination of Thermal Transitions

Glass transition of MD-added wine powder and regular red wine were determined by differential scanning calorimetry (DSC; onset values) using a DSC 822e 104 Mettler Toledo calorimeter (Schwerzenbach, Switzerland). The instrument was calibrated with indium (156.6 °C), lead (327.5 °C), and zinc (419.6 °C). All measurements were performed at a heating rate of 10 °C⁄min. Hermetically sealed 40-μL medium pressure pans were used (an empty pan served as a reference). In order to obtain the glass transition temperature (T_g), the thermograms were evaluated using Mettler Stare program; the onset temperature of the T_g was reported (Roos and Karel 1991).

Determination of Residual Ethanol in Wine Powder

A sample of MD-added freeze-dried "wine powder" was dissolved in water (20 g of powder with 80 g of distilled water). This solution was then distilled (simple distillation) and water added to the distillate to restore the original volume; a solution containing only volatile compounds from the wine was obtained in this way. The ethanol concentration in this solution was determined using an enzymatic kit provided by Cobas Roche, Argentina, based on Bucher and Redetzki (1951). The resulting ethanol concentration was then expressed as gram ethanol/100 g powder. Determination was done in duplicate.

Total Polyphenols

Total polyphenols of red wine and carbohydrate-added freeze-dried "wine powder" were determined by the Folin–Ciocalteau method (Cioroi and Musat 2007; Camussoni and Carnevali 2004). The Folin–Ciocalteau reagent was from Merck KgaA Darmstadt, Germany, and concentrations were

expressed as gallic acid equivalent in milligrams per liter. Wine powders were first reconstituted with water to their original weight. Absorbance at 765 nm (spectrophotometer Shimadzu PharmaSpec UV-1700) of wine samples (diluted 1:10) were measured in duplicate, and polyphenol concentrations of samples were derived from a standard curve of gallic acid.

Results and Discussion

Dry Extract, pH, and Total Polyphenols Content of Red Wine

The dry extract, pH, and total polyphenols content of the Cabernet Sauvignon wine used were: 25.9±0.25 g/L; 3.7 and 2,345±89 mg/L gallic acid equivalent, respectively. The value of total polyphenols obtained in the present study is in agreement with literature values reported for red wines (Camussoni and Carnevali 2004; Simonetti et al. 1997). Total polyphenols represented 9.1% of the wine's dry extract.

Freeze-Drying of Red Wine with or without Maltodextrin Addition

Van Galde et al. (2003) used the technique of freeze-drying to remove alcohol and water in order to study the health effects of wine polyphenols separately without the influence of alcohol. Removal of alcohol (and water) by the freeze-drying technique leaves the "dry" extract of wine which is mainly comprised of glycerol, fixed organic acids, sugars, inorganic and organic salts, polyphenols, proteins, etc. It was observed here that after freeze-drying of Cabernet Sauvignon wine without the addition of MD, an amorphous rubbery mass (very difficult to handle) was obtained (Fig. 1; right side). However, when 20% (*w*/*w*) MD was added to wine before freeze-drying, an amorphous microstructure of glassy appearance was obtained which was easily milled into a free-flowing powder with the characteristic red wine's color (Fig. 1; left side).

Ethanol Retention in Freeze-Dried "Wine Powder"

The possibility that relatively small amounts of ethanol were entrapped in the amorphous MD microstructure was examined. In fact, entrapment of organic volatiles in amorphous carbohydrate regions has been largely studied in literature to explain aroma retention during freeze-d0rying of food solutions (Chirife and Karel 1973, Galmarini et al. 2010). For this reason, retention of ethanol in a recently freeze-dried sample was experimentally determined and found to be 0.80 g ethanol/100 g dry powder (average of duplicate determinations). This result indicated that almost all of the ethanol originally present in wine was eliminated during freeze-drying.

Fig. 1 Photograph showing the freeze-dried wine (*right side*) as compared to milled freeze-dried maltodextrin-added red wine (*left side*)

Physical Stability and Glass Transition Temperature of Wine Powder

It is well-known that freeze-dried carbohydrates and proteins may exist in an amorphous state with time-dependent physical properties, which affect their storage stability (Roos and Karel 1990, 1991). An amorphous material undergoes a change from a very viscous "glass" to a rubber at the glass transition temperature which may result in structural changes such as stickiness and collapse. Water strongly plasticizes the amorphous structure and T_g decreases with increasing moisture content.

The encapsulation of the wine's dry extract in an amorphous glassy matrix of MD was possible because of the high glass transition temperature (T_g) of MD as compared to the T_g values expected for the main constituents of wine's dry extract. Main constituents of red wine's dry extract are glycerol (range 7.0–12.8 g/L, Giurgiulescu 2008; Rizzon and Miele 1997), tartaric and malic acids (1.66–2.64 g/L for tartaric acid and 0.28–1.78 g/L for malic acid, Rizzon and Miele 2001), and fructose and glucose (range of about 2.2–2.7 g/L Rizzon and Miele 1997). Glass transition temperature for anhydrous MD DE_{10} is 160 °C (Galmarini et al. 2010), while those of anhydrous glucose, tartaric acid, fructose, malic acid, and glycerol are much lower, being 30, 18, 8, −21, and −85 °C (Roos 1995; Bhandari and Howes 2002; Talja et al. 2003). It may be estimated that the sum of glycerol, reducing sugars, tartaric and malic acid in a typical red wine may be as high as about 58% *w*/*w* of the dry extract. This is in line with present observation of an amorphous rubbery mass after freeze-drying of red wine without the addition of MD (Fig. 1; right side); and it is attributed to the low glass

transition temperature of the abovementioned compounds, mainly glycerol, which amounts (average several red wines) to about 35% weight of wine's dry extract.

This was confirmed by measuring the glass transition temperature of a sample of freeze-dried wine (without MD addition); the T_g of this plastic rubbery material was found to be, T_g=−58.0 °C, (at 9.2% moisture content) as shown in the thermogram of Fig. 2a. On the other hand, it could be observed (Fig. 2b) that the addition of MD before freeze-drying resulted in a much higher glass transition temperature.

Total polyphenol content of the wine powder was measured immediately following freeze-drying, and a retention of 97.8% was found (average of duplicate samples) as compared to polyphenol content in the wine solution before freeze-drying.

The freeze-dried powder was analyzed for moisture content, a_w and T_g, and observed values were 1.53% (standard deviation±0.04% moisture), 0.050 (standard deviation±0.004 a_w), and 40.8 °C, respectively. A sample of the "wine powder" was then placed in a hermetically sealed opaque plastic flask and stored in a constant temperature oven at 38±0.3 °C for up to 15 days. The powder remained free-flowing during storage at this temperature, and this is explained because its T_g (40.8 °C) is higher than storage temperature (38 °C).

Table 1 shows total polyphenol content of freeze-dried wine powder samples, before and after storage at 38 °C; it can be seen that values remained essentially constant during the storage period here considered. The observed fluctuation is attributed to the uncertainty associated with the polyphenol determination as suggested by error bands in Table 1.

It is noteworthy that the "wine powder" contained after storage about 3.7 times the concentration of total polyphenols present in red wine (*polyphenol concentration in the powder/polyhenol concentration in liquid wine*—see Table 1), while containing only less than 1% of ethanol. This increased concentration of total polyphenols in the wine powder is the consequence of water and alcohol elimination and MD incorporation.

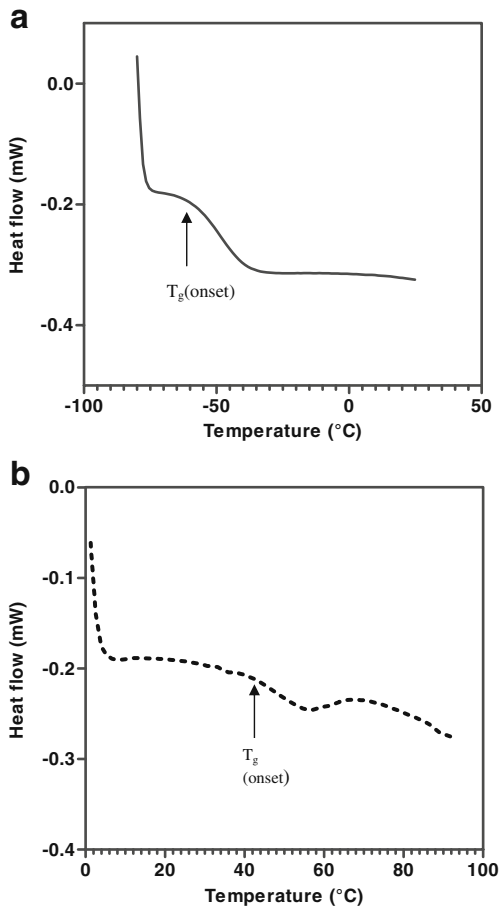

Fig. 2 Representations of thermograms, obtained using the Mettler Stare program, showing the glass transition temperature for **a** the freeze-dried wine with no added carbohydrates; **b** powder sample at 1.53% moisture

Conclusions

Red wine (Cabernet Sauvignon), previously added with 20% (*w*/*w*) MD DE_{10}, was freeze-dried allowing the simultaneous removal of water and most alcohol, while leaving an amorphous glassy microstructure which entraps the wine's dry extract, which includes its polyphenols. Since measured glass transition temperature of this powder is high enough (at controlled moisture contents), the freeze-dried product may be easily milled into a free-flowing powder which may be added to other powdered foods as a source of wine polyphenols. Polyphenols content of "wine powder" remained essentially constant during storage at 38 °C for the period here studied.

Table 1 Total polyphenol content of freeze-dried and stored (38 °C) "wine powder" made from red wine Cabernet Sauvignon and maltodextrin DE $_{10}$

Product	Polyphenols content (gallic acid equivalent, mg/100 g)
Red wine (*as is*) Cabernet Sauvignon	229.9±89
Freeze-dried wine + MD[a]	845.5±10.4
Freeze-dried wine + MD, stored for 6 days at 38 °C[b]	864.3±23.0
Freeze-dried wine + MD stored 15 days at 38 °C[b]	845.0±4.1

[a] Analyzed immediately after freeze drying

[b] "wine powder", T_g=40.8 °C

This powder might be useful to enhance some of the health-related advantages associated with red wine polyphenols, but avoiding the main disadvantage of wine, i.e., its alcohol content.

Future studies will deal with a detailed evaluation of storage stability of encapsulated red wine polyphenols (as well as their main individual constituents) at selected (and controlled) relative humidities and temperatures.

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