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Spray drying encapsulation of red wine: Stability of total monomeric anthocyanins and structural alterations upon storage

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Abstract

Wine *C. Sauvignon* was encapsulated by spray drying to obtain a wine powder having a low water activity (a_w). Maltodextrin DE_{10} was added to wine before atomization. The retention of Total Monomeric Anthocyanins (TMA) in the wine powder was found to be above 83%. Wine powder was stored under various relative humidities, and TMA concentration was determined up to 120 days at 38 °C. Anthocyanins decreased steadily during storage and increasing RH% enhanced the losses. Results stressed the importance of a_w (or RH%) as a key control parameter for anthocyanins stability during storage. Encapsulated wine collapsed when exposed few days to 58% RH and 38 °C; this was investigated by spray drying wine model systems containing various nonvolatile components of the dry extract, namely glycerol, organic acids, and monosaccharides. Structural alterations of encapsulated wine were attributed to glycerol, main component of dry extract and which has a very low glass transition temperature.

Practical applications

The main practical application of this work is that it allows the wine to be transformed into a freely flowing powder by the addition of maltodextrin before the atomization stage in spray drying. The encapsulated wine contains 5 times the concentration of anthocyanins than that in liquid wine (both expressed in mg/100 g). This is the first published work on spray drying of red wine.

1 | INTRODUCTION

Red wine, as a consequence of its polyphenolic content can be considered a useful raw material for making a number of different healthy food and drink products (Di Giacomo & Taglieri, 2012; Rocha-Parra, Lanari, Zamora, & Chirife, 2016). Wines are rich in compounds as flavonoids (catechins, flavonols, and anthocyanins) which are implicated in health benefits. Like resveratrol, quercetin, and catechins, anthocyanins also have high antioxidant capacity and are researched for their possible effects for reducing the risk of cancer and for fighting against cardiovascular disease and aging (Nistor, Dobrei, Camen, Mălăescu, & Prundeanu, 2015; Rocha-Parra et al., 2016). Epidemiological evidence has indicated that a moderate consumption of red wine reduces the incidences of coronary heart disease, atherosclerosis, and platelet aggregation (Li, Wang, Li, Li, & Wang, 2009).

In recent years, Sanchez, Baeza, Galmarini, Zamora, and Chirife (2013), Galmarini et al. (2013), and Rocha Parra et al. (2016) reported results on the freeze drying encapsulation of red wine with maltodextrin, or maltodextrin plus arabic gum, obtaining a powder with low alcohol (≤ 1%). Water and almost all alcohol were removed during freeze drying and the use of appropriate amount of carriers led to encapsulation of dry extract components (polyphenols among them). Very recently, Wilkowska, Ambroziak, Adamiec, and Czyżowska (2016) and Wilkowska, Czyżowska, Ambroziak, and Adamiec (2017) studied spray drying of chokeberry juice and chokeberry wine (fermented chokeberry juice) using different carriers (maltodextrin, arabic gum and hydroxypropyl-β-cyclodextrin). They reported anthocyanins stability during storage at 8 and 25 °C as well as the antioxidant and antimicrobial activity of fruit wine microencapsulated using the different carriers.

Spray drying can be used as an encapsulation method when it entraps "active" materials within a protective matrix. The spray-drying technique has been widely used for drying heat-sensitive foods and pharmaceuticals (Masters, 1991), because of the rapid water evaporation from the droplets. (Mahdavi, Jafari, Ghorbani, & Assadpoor, 2014; Tonon, Brabet, & Hubinger, 2010). Compared to other conventional microencapsulation techniques, it offers the attractive advantage of producing microcapsules at lower cost than freeze drying, in a simple and continuous operation. Carrier agents are usually employed as an aid in the spray drying process. Several substances can be used as carriers to microencapsulate anthocyanins (Fang & Bhandari, 2012; Osorio et al., 2010; Souza, Thomazini, Balieiro, & Fávaro-Trindade, 2015) namely maltodextrins, arabic gum, starch, and so forth. Maltodextrin of low dextrose equivalent has been widely use because of their good water solubility, low viscosity at high concentrations, low cost, and the ability to increase the glass transition temperature (T_g) of the system (Cai & Corke, 2000; Desobry, Netto, & Labuza, 1997; Wagner & Warthesen, 1995).

The objective of this work was to study the feasibility of spray drying to encapsulate red wine in a maltodextrin matrix to obtain a powder which can be used as ingredient for the food and/or pharmaceutical industries. The storage stability of Total Monomeric Anthocyanins (TMA) in encapsulated red wine stored at different relative humidities (RH%) was monitored. Structural alterations experimented by encapsulated wine when exposed to selected RH% and temperature were investigated by spray drying wine model solutions.

No previous studies on spray drying encapsulation of red wine have been previously reported in literature.

2 | MATERIALS AND METHODS

2.1 | Reagents

Glycerol, fructose, and glucose were purchased from CICARELLI (Santa Fe, Argentina). Tartaric acid and gallic acid from ANEDRA (Buenos Aires, Argentina). Malic acid from MERCK, Germany. Sodium carbonate, potassium carbonate, and sodium bromide were purchased from Biopack, (Buenos Aires, Argentina).

2.2 | Samples preparation

Wine *Cabernet Sauvignon*, "Postales del Fin del Mundo" (2015) from Neuquen, Argentina. Alcohol content was 14.1% (v/v) and pH 3.7. Maltodextrin used for encapsulation had DE_{10} and was purchased from Ingredion, S. A, Argentine. Salts (reagent grade) used for relative humidity (RH%) control were: magnesium chloride (33%), potassium carbonate (43%), and sodium bromide (58%).

2.3 | Spray drying

A mixture of 13.5% (w/w) maltodextrin DE_{10} and 86.5% (w/w) wine was prepared and spray-dried with a mini spray dryer Buchi model B-290 (Büchi Laboratoriums Technik, Switzerland) under the following operating conditions: feed flow rate 600 g/hr; drying air inlet temperature, 135–170 °C; flow meter spraying air (rotameter) 30 mm, 0.23 bar pressure drop, and 439 L/hr actual volume flow (at standard temperature and pressure).

2.4 | Storage conditions

Spray dried wine powder in small opaque glass flasks was stored in a constant temperature oven kept at 38 °C in one or the other of the following conditions, (a) in hermetically sealed flasks to preserve its initial moisture condition ($a_w = 0.19$) during 120 days; (b) in open flasks placed over one or the other of the following saturated solutions: MgCl (33% RH) during 120 days, K_2C0_3 (43% RH) during 115 days, and NaBr (RH 58%) during 21 days. Temperature 38 °C is representative of accelerated shelf life studies (Labuza, 1982). Samples were periodically removed from storage and analyzed at selected times.

2.5 | Water activity and moisture content

Water activity (a_w) was measured using a dew point hygrometer "Aqualab Series 3" (Decagon Devices) previously calibrated. Moisture content was determined gravimetrically (2 g sample) in a forced convection constant temperature oven at 90 °C during 6 hr, cooled for 1 hr in a glass dessicator and reweighted.

2.6 | Scanning electron microscopy

Scanning Electron Microscopy (SEM), morphological analysis was performed by SEM using a FEI, Quanta 200 microscope (Netherlands). The spray dried red wine samples were placed in a carbon support and coated with a layer of gold (40–50 nm) and examined using an acceleration voltage of 5 kV.

2.7 | Wine dry extract

Ten g of each wine sample were weighed in glass containers and dried in a constant temperature convection oven for 2 hr at 105 °C, and then cooled for 1 hr in glass dessicator.

2.8 | Solubility

One g of wine powder was dissolved in 100 ml of distilled water and mixed for 5 min in a magnetic stirrer. The solution was centrifuged at 3,000 g for 5 min and 25 ml of supernatant were transferred into glass containers. The samples were dried in a constant temperature oven for 5 hr at 105 °C. The percentage of solubility was calculated according to AOAC (1995).

2.9 | Chromatic characteristics

A 1% m/v solution was prepared with 1 g of wine powder and 100 ml of distilled water. The spectrophotometric measurements were taken with UV-Vis spectrophotometer (T60 – PG Instruments, UK) using quartz cells (1 cm path length) and distilled water as reference liquid to set the zero on the absorbance scale at the wavelengths of 420, 520, and 620 nm. Measurements were made by triplicate and the average is reported.

2.10 | Total monomeric anthocyanin by the pH-differential method

Monomeric anthocyanin content was measured following the method described by Giusti and Wrolstad (2001). One g of wine powder was diluted in 8 g of distilled water and 100 µl of this solution were added into a tube containing 4,900 µl of 0.025 M potassium chloride buffer, pH 1.0. One hundred µl of the initial solution were added into a tube containing 4,900 µl of 0.4 M sodium acetate buffer, pH 4.5. The tubes were equilibrated for 15 min at room temperature, and then the absorbance was measured both at 700 and 520 nm in a UV-Vis spectrophotometer (T60 – PG Instruments) using quartz cells (1 cm path length). Absorbance was calculated as $A = (A_{520\text{nm}} - A_{700\ \text{nm}})_{\text{pH}1.0} - (A_{520\text{nm}} - A_{700\text{nm}})_{\text{pH}4.5}$, and the results were expressed as mg cyanidin 3-glucoside equivalents g^{-1} of powder, using a molar extinction coefficient of 2.69×10^4, and a molecular weight of 449.2 for cyanidin 3-glucoside.

2.11 | Wine model systems

Model systems (A and B) resembling red wine composition (with added maltodextrin), were prepared by mixing predetermined quantities of water, ethanol, maltodextrin DE_{10}, glycerol, tartaric acid, malic acid, fructose, and glucose. These models were spray dried at 145 °C inlet temperature and resulting powders used in rehumidification experiments described elsewhere. Composition of model systems (before spray drying) was as follows. Model A: hydroalcoholic solution 14% v/v (84.99%), maltodextrin DE_{10} (13.5%), glycerol (0.80%), tartaric acid (0.38%), malic acid (0.26%), fructose (0.07%), and glucose (0.03%). Model B: hydroalcoholic solution 14% v/v (85.79%), maltodextrin DE_{10} (13.5%), tartaric acid (0.38%), malic acid (0.26%), fructose (0.07%), and glucose (0.03%).

2.12 | Rehumidification experiments

Wine powder and spray dried wine models were poured (2 g) in 4 cm diameter plastic holders kept over saturated solution of NaBr (RH 58%) and placed at 38 °C ± 1 °C. At selected times (6, 21, 30, 43, 51, 69, 74 y 92 hr) the radial shrinkage of the powders was measured and photographs were taken.

2.13 | Sorption isotherms

A sorption isotherm (in a limited range of RH%) was determined. One and half g of wine powder spray dried at different temperatures were exposed at different RH% at 38 °C until equilibrium was noted. Samples were made by triplicate and the average is reported.

3 | RESULTS AND DISCUSSION

3.1 | Spray drying of red wine

Total Monomeric Antocyanin (TMA) content and dry extract of liquid red wine were determined to be, 171 ± 7 mg/L (as cianydin-3-glucoside) and 2.27% (w/w), respectively. The value of TMA is in good agreement with results reported by Fanzone et al. (2012) for red wines from Argentine.

It is well known that spray drying of fruit juices is difficult due to the presence of low molecular weight sugars and acids with low glass transition temperature (T_g) (Bhandari, Datta, & Howes, 1997; Bhandari, Senoussi, Dumoulin, & Lebert, 1993). These components which are present in fruit juices in high proportion and have low T_g, can stick on the dryer chamber wall during drying, leading to low product yield. Moreover, structural alterations, such as agglomeration and caking may occur in these amorphous food powders when stored at temperatures above the T_g. Part of these problems can be solved by the addition of carrier agents, like maltodextrin and arabic gum, to the product before being atomized.

It was early noted in this study that spray drying of red wine also had problems of sticking to the walls of the dryer and agglomeration of powder during storage under certain conditions of RH% and temperature. In previous trials, it was found that maltodextrin addition below 13.5% resulted in poor process yield and stickiness, and for this reason this maltodextrin concentration was adopted. The dry extract of present red wine is 2.27%, thus, addition of 13.5% maltodextrin leads to a ratio maltodextrin/wine dry solids of about 6. Table 1 shows the results of spray drying of red wine added with 13.5% (w/w) maltodextrin, at different inlet air temperatures, and for each one TMA retention and % solubility.

Outlet air temperatures were in the range 75–79 °C (Table 1) and in all drying runs a free-flowing powder having a_w below 0.20 was obtained. Due to simultaneous elimination of water and ethanol during spray drying, the concentration of total anthocyanins in the wine powder was increased to five times greater than in the original liquid wine. Solubility was very close to 100% and was practically independent of

TABLE 1 Spray dried encapsulation of red wine with different inlet air temperatures

Inlet air temperature (°C)	Outlet air temperature (°C)	Water activity (a_w)	TMA mg / 100 g of powder*	TMA retention %	Solubility %
135	75	0.139	87 ± 3^b	91	98.3 ± 0.3
145	75	0.194	95 ± 2^c	99	97.7 ± 0.3
155	76	0.135	83 ± 2^a	86	98.9 ± 0.1
170	79	0.183	80 ± 5^a	83	98.7 ± 0.2

*Means with the same letter are not significantly different according to the Tukey test ($p > .05$).

inlet air temperatures. At all temperatures the retention of TMA was high ($>$ 83%) indicating that spray drying allows a good anthocyanin retention. Silva, Stringheta, Teófilo, and de Oliveira (2013) performed a simultaneous optimization of different carrier agents (maltodextrin and arabic gum) and temperatures (140–180 °C) for the production of jaboticaba extracts by spray-drying microencapsulation. They also found that anthocyanin retention was high in all of the experimental conditions with retention values above 80%. Bernstein and Noreña (2015) also reported that anthocyanins retention during spray drying encapsulation of a red cabbage extract using 10% arabic gum as encapsulating agent, yielded high anthocyanins retention in the range 83–91% for inlet air temperatures of 140–160 °C. Wilkowska et al. (2016) spray dried black chokeberry (*Aronia melanocarpa*) juice and wine using maltodextrin, a mixture of maltodextrin with arabic gum and hydroxypropyl-β-cyclodextrin as coating materials. They followed degradation kinetics of polyphenols and antioxidant stability in microencapsulated juice and wine preparations from chokeberry over 12 months under storage at 8 and 25 °C. Wilkowska et al. (2016) reported that the type of encapsulant proved to have a significant effect on the storage stability of polyphenol microencapsulates. Microcapsules of maltodextrin showed a loss of 25% in total anthocyanins after 12 months storage at 25 °C. They did not report the effect of moisture content (or a_w) on anthocyanins stability during storage. Wilkowska et al. (2017) also spray dried different fruit wines (chokeberry, blackcurrant, and blueberry) using hydroxypropyl-β-cyclodextrin and inulin as encapsulants and followed the structural, physicochemical, and biological properties of the spray-dried wine powders over 12 months of storage in darkness under refrigeration (8 °C).

Wilkowska et al. (2017) reported that spray drying of fruit wine at inlet temperature of 140 °C lead to a powder with less than 1% ethanol content; it is noteworthy that 140 °C is the same inlet temperature we used in present spray drying of red wine. Also, Sanchez et al. (2013) reported that freeze drying of red wine (*Cabernet Sauvignon*) added with maltodextrin resulted in a residual ethanol content of 0.8%. Thus, although we did not determine alcohol content in present spray dried wine powder, we may safely assume that it is a "low" ethanol content product (i.e., below 1%).

The high TMA retention % observed (Table 1) may be explained on the basis of the particular drying characteristics during spray drying of liquid foods. The following description of spray drying events is widely accepted in literature (Anandharamakrishnan, 2015; Huang, 2011; Ranz & Marshall, 1952). When a food solution (i.e., wine with dissolved maltodextrin) is fed to the atomizer the droplets formed are mixed with hot air and this causes the solvent (water and some ethanol) to evaporate, leading to formation of particulates. The drying of droplets containing the dissolved solid can be divided into two different stages known as constant rate period and falling rate period. In the first stage the droplet diameter decreases due to water evaporation from the wetted surface, whereas the mass fraction of the dissolved maltodextrin increases. In this period droplet evaporation rate is nearly constant and the droplet surface temperature (T_s) is also constant and may be represented by the wet bulb temperature (T_{wb}). This is strictly valid when the solvent is water; in wine, the solvent includes a small mass fraction of ethanol (water 89% w/w + ethanol 11% w/w) but it is not considered by now. Note that vapor pressure lowering effect of maltodextrin DE_{10} can be neglected due to its relatively high molecular weight (about 1,300); for example, a 14% (w/w) maltodextrin DE_{10} solution has a relative water vapor pressure, $p/p_o = 0.998$.

An important fraction of the available moisture in a droplet may be removed during the period of constant rate, thus protecting anthocyanins from degradation because $T_s = T_{wb}$. In a study of spray drying of proteins, Anandharamakrishnan, Rielly, and Stapley (2008) reported $T_{wb} = 44.5$ °C and 46.6 °C for inlet air temperatures as high as 160 °C and 180 °C, respectively. As more moisture is removed from the droplet, the maltodextrin dissolved in the liquid reaches a concentration beyond its saturation concentration and forms a shell at the droplet surface denominated "crust formation." This crust of maltodextrin in present work can be seen in SEM micrographs of spray dried wine. The beginning of crust formation is an important characteristic of spray drying since the evaporation rate is now dependent on the rate of water vapor diffusion through the dried surface shell. In this period, evaporative cooling is not sufficient to maintain $T_s = T_{wb}$ causing a gradual increase in T_s. Although the particle will begin to heat it is almost at the coolest part of the dryer, where the drying air is at or near the outlet temperature of the dryer. Consequently, the particles are never heated above the outlet temperature of the dryer (75–79 °C in Table 1). Red wine used contained 11% (w/w) ethanol and its possible effect on spray drying rates deserves some comments. Ethanol should somewhat facilitate the evaporation process during the constant rate period (as compared to water alone). However, at lower moisture contents (falling rate period) the diffusion coefficient of the solvent (water + ethanol) through the shell becomes the determining factor for evaporation rate. The molecule of ethanol, due to its molecular size larger than of water, may hinder diffusion in the dried matrix (Menting, Hoogstad, & Thijssen, 1970). Nevertheless, the overall effect, if any, on final a_w of powder did not appear to be important enough from a practical point of view.

3.2 | Sorption isotherms (in a limited range of RH%) of raw wine powder

Figure 1 shows the sorption isotherms (in a limited range of RH%) at 38 °C of wine powder spray dried at 135 °C, 155 °C, and 170 °C. The sorption isotherm was determined only up to a 43% RH because at 58% RH the structure of wine powder completely collapsed with release of typical red wine color.

The sorption isotherm of the powdered wine does not appear to be influenced by the temperature of previous drying. This is an indication that spray drying treatment did not produce modifications in the active sites available for water sorption in the substrate (Iglesias & Chirife, 1976); and may be considered also as an indicator of the mildness of spray dying treatment.

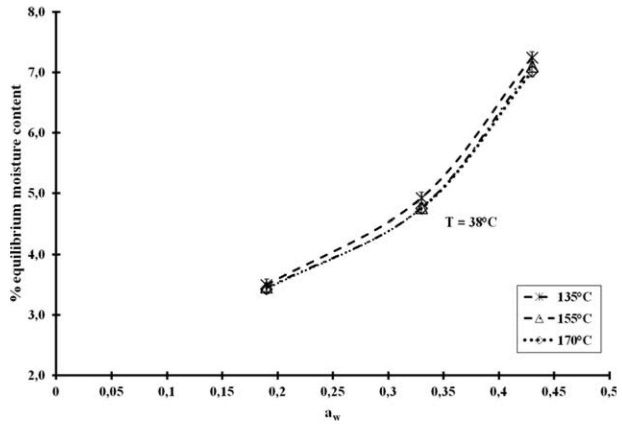

FIGURE 1 Sorption isotherm (for a limited range of RH%) of red wine powder spray dried at different air inlet temperatures. Error bar overlapped with data points

3.3 | Chromatic profiles and morphology of spray dried particles

The chromatic profile of red wines is formed by the participation of various phenolic compounds: anthocyanins, tannins, flavones, and phenolic acids. Anthocyanins are the polyphenolic substances with the most important role in the color of wines. The natural evolution of young red wine leads to changes of structures and chromatic properties of wine due to polymerization reactions, condensation, and oxidation (Vișan & Dobrinoiu, 2013). Similarly, spray drying may promote such chemical modifications leading to changes in the chromatic profile of reconstituted dried wine. Figure 2 shows the effect of inlet air temperature on the chromatic values of reconstituted spray dried red wine dried at different air inlet temperatures. The differences between the absorbance values of wines spray dried at different temperatures is very small and is mainly observed at 155 °C and 170 °C. Although a Tukey Test indicated a significant difference between absorbance values of wines dried at different temperatures, this may be due to the very small standard deviation values of present absorbance measurements. In practice, only wines dried at 155 °C and 170 °C seem to show difference with the dried ones at 135 °C and 145 °C. Present results are also an indication of mildness of spray drying of red wine under present experimental conditions.

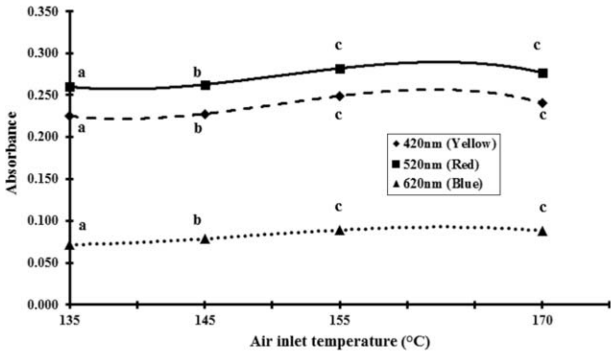

FIGURE 2 Chromatic values of reconstituted spray dried red wine at different air inlet temperatures. Error bars overlapped with data points and means with the same letter are not significantly different according to the Tukey test ($p > .05$)

The size of particles depends on the size of the droplets after atomization and the total solute concentration in the solution going to be spray-dried. However, not only the droplet size and the total solid content of the liquid feed but, also external drying conditions as well as the material and formulation properties have to be considered when discussing effects on particle morphology (Schiffter, 2005; Schiffter & Lee, 2007). Figure 3 shows the SEM microphotographs of the wine powders at 145 and 155 °C inlet air temperatures. The particles showed spherical shape and various sizes, which are typical of materials produced by spray drying, although most of the particles showed a shriveled surface. According to Alamilla-Beltrán, Chanona-Perez, Jimenez-Aparicio, and Gutierrez-Lopez (2005), when relatively low inlet air temperatures are used, the crust is more pliable and collapsed, while the use of higher drying temperatures results in a more rigid and porous crust.

3.4 | Stability of total monomeric anthocyanins during storage

Figure 4 shows the stability of TMA during storage (38 °C) of encapsulated wine as it comes out of the spray dryer (a_w about 0.19), and also exposed to RH%, 33%, 43%, and 58%. Anthocyanins concentration slowly decreased with time over a period of about 120 days and the rate of loss was increased by the increase in relative humidity. After 120 days storage anthocyanins loss amounted to 44% for the sample as it comes out of the spray dryer; at 43% RH (115 days) loss was 78% and it was associated with visible caking of the sample (Figure 5, forward). At 58% RH (21 days) total collapse was visually observed (accompanied by release of red wine color) this being related to the greatest rate of loss of anthocyanins.

These results are similar to those reported by Rocha-Parra et al. (2016) for the stability of total anthocyanins in a freeze-dried encapsulated (maltodextrin plus arabic gum) wine stored at 38 °C and various relative humidities. They also found that increasing RH% decreased the retention of anthocyanins in freeze-dried encapsulated red wine. Other authors also reported (Tonon et al., 2010) that anthocyanin stability in spray-dried encapsulated *acai* juice was negatively influenced by the increase of water activity. They attributed to the higher molecular mobility, which allows easier oxygen diffusion, thus accelerating the oxidation reactions.

It is interesting to note that the observed reduction in the rate of anthocyanins degradation when moisture content/a_w is decreased, contributes to protect against the negative effect of droplets temperature increase following the constant rate period.

3.5 | Behavior of spray dried red wine stored at 38 °C at increasing RH%

It is known that structural changes (such as caking, collapse) in amorphous food powders are a time dependent phenomena and a function of (T–T_g) where T is storage temperature and T_g is glass transition

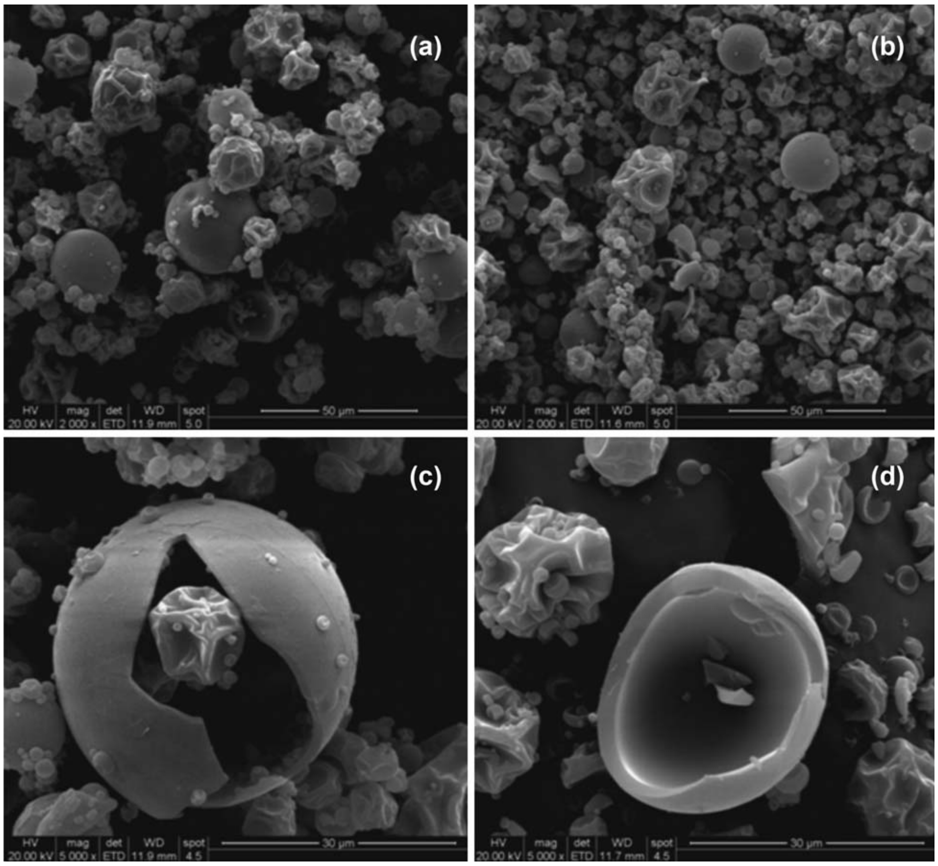

FIGURE 3 SEM micrographs of spray dried red wine added with MD DE10 (a) dried at 145 °C (×2,000); (b) dried at 155 °C (×2,000); (c) dried at 145 °C (×5,000); (d) dried at 155 °C (×5,000)

temperature (Roos & Karel, 1991). Figure 5 shows the behavior of red wine powder after six days storage at 38 °C under relative humidities of 33%, 43%, and 58%. At 43% RH caking of the powder is visually apparent (some color release is also observed) while at same time at 58% RH total structural collapse and release of wine color from the collapsed matrix, is evident. The moisture content for samples humidified at 33% and 43% were, 4.8% (w/w) and 7.2% (w/w), respectively. Observed caking/collapse behavior is attributed to the well known influence of moisture content on reduction of T_g with corresponding transition from a glassy to rubbery state (Roos, 1995). Therefore, in samples stored at 43% and 58% RH the structural changes visually observed indicated that the amorphous solid is in the rubbery state, and glass transition temperature of wine powder (T_{gm}) is below storage temperature; that is, T_{gm} is $<$ 38 °C. It is noteworthy that these structural alterations occurred despite the high ratio maltodextrin/dry extract wine (about ≈ 6).

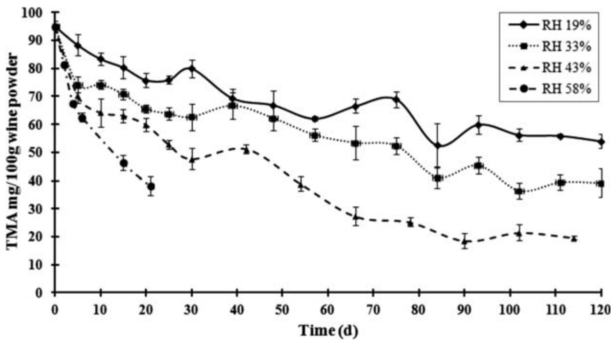

FIGURE 4 Stability of TMA in spray dried red wine stored at 38 °C and increasing relative humidities

To explain this phenomenon, the composition of dry extract of red wine was analyzed. Approximate concentration of principal compounds present in the dry extract of a typical red wine (data from Paladino, 2014) were (as % of dry extract): glycerol 37.4%, tartaric acid 17.8%, malic acid 12.1%, phenolic compounds 10%, minerals 6%, fructose 2.8%, citric acid 2.1%, sorbitol and mannitol 1.6%, glucose 1.2%. Thus, glycerol is by far, the main component of the red wine dry extract.

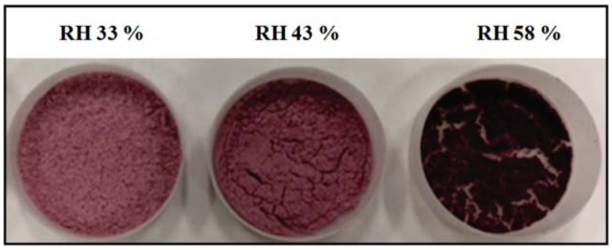

FIGURE 5 Caking and structural collapse in red wine powder stored (38 °C) during six days at increasing relative humidities at 38 °C

Several of these compounds have a low glass transition temperature (T_g), particularly glycerol whose T_g is well below values for the other constituents of the dry extract. Values reported for T_g of anhydrous glycerol ranged between −81 °C to −90 °C (Win & Menon, 2006; Zondervan, Kulzer, Berkhout, & Orrit, 2007). T_g values for the other constituents of the wine dry extract (also anhydrous state) are, tartaric acid = 16 °C, malic acid = −20 °C, glucose = 32 °C, and fructose = 8 °C (Bhandari & Roos, 2016; Rahman, 2009). Glycerol found in wine is mainly formed as a by-product of glicero pyruvic fermentation by wine yeasts: its amount is influenced by several factors such as yeasts strain, fermentation temperature, and addition of sulfur dioxide (Rankine & Bridson, 1971). As an example, representative Chilean red wines have between 5.2 and 12.2 g/L glycerol (Ureta & Brinkmann, 1986).

As mentioned before, structural changes in amorphous food powders are a time dependent phenomena and a function of (T–T_g) where T is storage temperature and T_g is the glass transition temperature (Foster, Bronlund, & Paterson, 2006; Roos, 1995; Roos & Karel, 1991). Instead of measuring the T_g of wine powder and wine models, an alternative approach was used. It consisted in observing and comparing the structural alterations that occurred in the different powders stored at identical temperature, RH%, and time. Experiments of rehumidification of the spray dried wine models, were performed and results are shown in Figure 6. It compares measured radial shrinkage during storage at 38 °C and 58% RH of spray dried wine Models (A and B). The results show that red wine powder and model with glycerol experimented a noticeable radial shrinkage as a function of time, but this was not observed in the model without glycerol, suggesting than glycerol plays a major role in the structural alterations of spray dried red wine powder. Maltodextrin DE_{10} is by far the main component in wine powder (ratio maltodextrin/wine dry extract = 6) and has an anhydrous T_g = 160 °C (Roos, 1995). It appears that glycerol is able to plasticize maltodextrin DE_{10}, with a concomitant reduction of T_g of red wine powder.

Interestingly, Enrione, Osorio, Pedreschi, and Hill (2010) were able to measure the effect of glycerol on the T_g for waxy maize and rice starch extruded-glycerol. They determined T_g by Differential Scanning Calorimetry (DSC) and reported that at 5% moisture content addition of 5% glycerol produced a reduction of about 27°C in the T_g of the maize matrix.

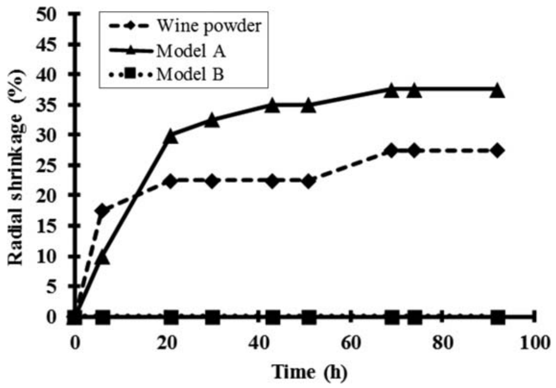

FIGURE 6 Radial shrinkage during storage at 38 °C and 58% RH of spray dried wine powder, and spray dried wine Models (A and B) formulated with and without glycerol

On spray drying of liquid foods, the powder particles stick to one another and to the walls of the dryer, leading to low product yield. This behavior was also studied using the wine models which were spray dried. The yield was determined in terms of percentage as the ratio of g of solids in the powder obtained in the cyclone to the g of solids in the feed. All components in the spray dried powders appeared to be well mixed and visual indication of some phase separation (i.e., glycerol) was not observed. The average (four replicates) yield was 52.9% for model with glycerol and 59.3% for model without glycerol (statistically different according to Tukey test values $p < .05$).

The Gordon and Taylor equation (Equation (1)) is used to calculate the T_g of a binary mixture of solids and water, and it reads (Roos, 1995)

$$T_g = \frac{x_s \, T_{gs} + k \, x_w \, T_{gw}}{x_s + k \, x_w} \qquad (1)$$

where T_g, T_{gs}, and T_{gw} are the glass transition temperatures of the mixture, solid, and water, respectively; x_s is the mass fraction of solid, x_w is the mass fraction of water, and k is the Gordon-Taylor parameter. Equation (1) is restricted to binary mixtures of solids and water. However, multicomponent systems may be also considered systems of solids and water and the use of multiple components with their individual mass factors may be used (Roos & Drusch, 2015). According to Goula and Adamopoulos (2008) the T_g of multicomponent solid mixtures such as maltodextrin-red wine mixture, may be determined using a mass weighted mean rule. The multicomponent mixture is assumed to be

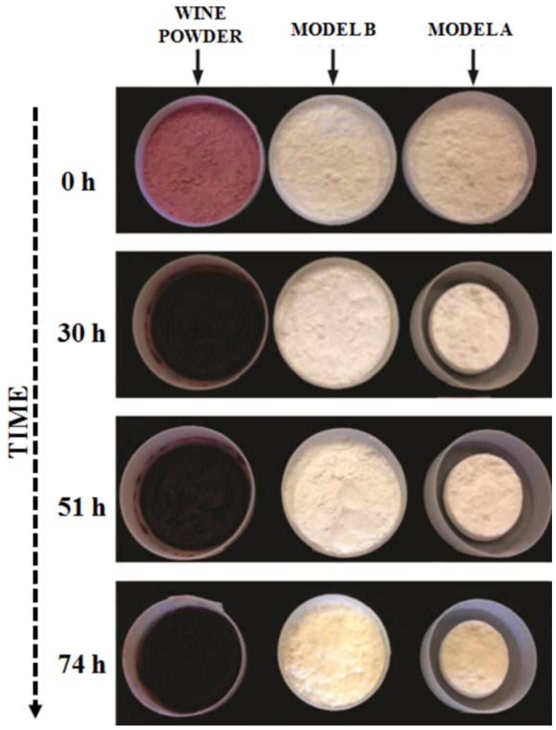

FIGURE 7 Structural changes in wine powder (left), spray dried wine Model B (center) and spray dried wine Model A (right) during storage at 38 °C and 58% RH

composed of *n* individual binary solid-water mixtures, where *n* is the number of solid components. First, the moisture dependence of T_g for each binary solid-water mixture is experimentally determined. Finally, the solids are assumed to be perfectly mixed and the T_g of the multicomponent mixture is computed as a mass weighted mean on a water free basis,

$$T_{gm} = \sum_{i=1}^{n} (Tg_i . x_i) \tag{2}$$

$$\sum_{i=1}^{n} x_i = 1 \tag{3}$$

where, T_{gm} represents the T_g for the multicomponent mixture including water, T_{gi} is the T_g of binary solid-water mixtures, (i.e., maltodextrin-water; tartaric acid-water, etc.), and x_i is the mass fraction of an individual solid component on a water free solids basis (Equation (3)).

Glycerol constitutes a high mass fraction of the dry wine, and as its T_g is very low (about $-83\,^{\circ}$C), it will have a dominant influence on the value of T_{gm} (Equation (2)) of wine dry extract. Adhikari, Howes, Bhandari, and Troung (2004) also assumed that T_g of multicomponent solid mixtures may be determined using a mass weighted mean rule.

A visual (qualitative) assessment of the collapse behaviour of spray dried models formulated with or without glycerol may be observed in Figure 7.

4 | CONCLUSIONS

Wine *C. Sauvignon* may be encapsulated by spray drying by previously adding 13.5% maltodextrin. An encapsulated wine powder having water activity (a_w) 0.19 was obtained, and the retention of TMA was very high ($>$ 83%). The wine powder was stored under various RH% and TMA determined up to 120 days storage at 38 °C. Anthocyanins decreased steadily during storage and increasing RH% enhanced the losses. The results stressed the importance of water activity (or RH%) as a key control parameter for anthocyanins stability during storage of spray dried encapsulated red wine.

The ease of structural collapse of red wine powder at certain relative humidities was mainly attributed to the presence of glycerol which is known to have a very low T_g and is also a major constituent of the dry extract of red wine.

In the case where it is desired to make a wine to be spray dried for use as an ingredient in the food and pharmaceutical industries, manipulation of the fermentation variables could result in a wine with a lower glycerol content and, therefore, more resistant to structural alterations during wine powder storage.

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