#### **REVIEW ARTICLE**



# Spray-dried Ancellotta red wine: natural colorant with potential for food applications

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#### Abstract

Ancellotta red wine (*Vitis vinifera* L.) was encapsulated by spray-drying (inlet and outlet temperatures were 145 °C and 70 °C, respectively) to obtain a wine powder with a low water activity (aw) using maltodextrin DE10 as an encapsulating agent. The retention of total monomeric anthocyanins (TMA) in the wine powder was found to be greater than 80%. Anthocyanin profiles of Ancellotta liquid wine and wine powder were characterized by using HPLC–DAD and 33 compounds were identified. The wine powder was stored under two different water activity values (aw 0.25 and aw 0.33). Furthermore, the TMA (pH-differential method), total anthocyanins and malvidin-3-glucoside were determined by HPLC–DAD for up to 90 days' storage at 38 °C. Total anthocyanins and malvidin-3-glucoside decreased very slowly during storage. The stability of anthocyanins and color differences ( $\Delta E^*_{ab}$ ) in 1% wine powder solution at different pHs and temperatures were evaluated. These results indicated that Ancellotta wine powder has the potential to be used as a food colorant in low pH and low water activity foods.

Keywords Ancellotta · Red wine · Spray-drying · Food colorant · Anthocyanins

# Introduction

It is common knowledge that humans are strongly influenced by color. In fact, color is the first notable characteristic of a food or a beverage and often predetermines the expectation of flavor and taste [1]. In recent years, there has been an increased awareness and interest around the potential impact of foods on health. For this reason, there is an increasing demand for natural ingredients in place of synthetic and/or artificial ingredients. As public concern about synthetic food

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colorants has increased, consumers and food manufacturers are looking for colorants from natural sources [2, 3].

Anthocyanins are natural pigments found in flowers, vegetables, fruits and foods. Examples can be seen in tea and wine with an extensive range of colors including red, blue and purple hues [4, 5]. Anthocyanins are also beneficial to health as they act as antioxidants that scavenge free radicals and decrease the oxidative effect of the blood by donating protons to highly reactive radicals [4]. Research found that regular intake of anthocyanins may decrease the potential of contracting cancer, cardiac diseases, Alzheimer's disease, and diabetes [3, 6, 7].

Due to the enormous potential of natural anthocyanins as healthy pigments, there is an increasing number of reports in the literature regarding their purification and separation from plant tissues [4, 8].

Utilization of anthocyanins as food colorants have two main drawbacks: (a) in aqueous medium such as foods, anthocyanins undergo reversible structural transformations that are pH dependent, with concomitant changes in color [8-10]; (b) the thermal instability of anthocyanins during food processing and storage acts as an impediment to their use. For this reason, the anthocyanins are encapsulated to retain their color and improve stability [11].

It is well known that red wines have a significant amount of anthocyanins responsible for color [12], and cv. Ancellotta stands out among them for its extremely high concentration of anthocyanins. The red-skinned variety of Ancellotta is typically grown in northwest Italy. Outside Italy this variety is cultivated in Brazil, in the southeast of Switzerland and in Argentina; because it produces wines of very good color suitable for blending. In Argentina the surface of Ancellotta registered in 2017, by Department of Statistics and Market Studies of INV (National Institute of Viticulture), a total of 1313 ha cultivated, which represents 0.6% of the total vine of the country. The number of hectares of Ancellotta throughout the country has increased by 824% (+1171 ha) in the period 2008–2017. The province of Mendoza has the largest number of Ancellotta in the country, reaching 1103 ha (84%) in 2017 [13].

Spray-drying is a technique used in the encapsulation of various bio-products. During the process, the "active" materials are trapped within a protective matrix of the encapsulating agent. This technique has been widely used for drying heat-sensitive foods and pharmaceutical products [14], due to the rapid evaporation of water from the droplets formed [15, 16]. Encapsulation plays a key role in maintaining the stability of bioactive compounds, therefore, improving their shelf life.

Recently, Alvarez et al. [17] showed that a powder of red wine from cv. Cabernet sauvignon might be obtained by spray-drying leading to a free-flowing product with a good storage stability of anthocyanins, as long as the water activity of the powder remained low.

The objectives of the present study were to obtain a spraydried encapsulated Ancellotta wine from Mendoza (Argentina) and evaluate its potential use as a colorant in food. The anthocyanins profile of the wine powder was evaluated using HPLC–DAD and the stability of the powder during storage was also monitored. Additionally, the color behavior of powder solutions at different pH, temperatures, and times was evaluated. As far as we know, there is no published article to date about spray-drying of Ancellotta wine and the potential use of wine powder as a natural colorant in food.

# **Materials and methods**

#### Reagents

The encapsulating agent used for spray-drying was maltodextrin DE10 (dextrose equivalent 10-MD10) (Ingredion S.A, Argentina). The salts (analytical grade) used to control the relative humidity (RH %) were magnesium chloride (33%), potassium carbonate (43%), sodium bromide (58%), sodium chloride (75%), and ammonium sulfate (80%), purchased from Biopack (Argentina). The Folin–Ciocalteu reagent was obtained from Merck (Darmstadt, Germany). Standards of gallic acid [149-91-7] and malvidin-3-glucoside chloride [7228-78-6] were supplied by Sigma Aldrich (St. Louis, USA). Formic acid (98%), chromatography grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). All reactive chemicals were analytical grade or superior. Ultra-pure water was obtained from a RiO/Elix3-Sinergy185 purification system (Millipore, Sao Pablo, Brazil). Cellulose filters (3 µm pore size) and (0.45 µm pore size) nylon membrane were supplied by Microclar (Buenos Aires, Argentina).

#### **Red wine**

Ancellotta experimental wine (2015 harvest) from La Consulta (Mendoza, Argentina), produced by Experimental Agricultural Station Mendoza, National Institute of Agricultural Technology (INTA), was used as a raw material (pH 3.95, dry extract 3.15% (w/w), alcohol 14.8% (v/v), total acidity 5.3 g tartaric acid/L).

## Spray-drying

A mixture of 13.5% (w/w) maltodextrin DE10 and 86.5% (w/w) red wine was prepared and resulting solution was 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/h; drying air inlet temperature 145 °C, and outlet temperature (average) 70 °C; flow meter spraying air (rotameter) 30 mm; 0.23 bar pressure drop; and 439 L/h actual volume flow (at standard temperature and pressure). The yield of spraydrying was  $59 \pm 3\%$ .

#### **Storage conditions**

The spray-dried wine was stored in small opaque glass flasks in a constant temperature oven at 38 °C, in the following conditions: (a) in hermetically sealed flasks to preserve its initial moisture condition (aw 0.25); (b) in open flasks placed over a saturated solution of magnesium chloride (aw 0.33). Temperature 38 °C is representative of accelerated shelf life [18]. Samples of both systems were periodically removed from storage and analyzed at selected times.

#### Water activity and moisture content

Water activity (aw) was measured using a dew point hygrometer Aqualab Series 3 (Decagon Devices, USA), previously calibrated against standard saturated salt solutions [19]. Moisture content was determined gravimetrically (1.5 g sample) using a forced convection constant temperature oven at 105 °C for 3 h, then cooled for 1 h in a glass desiccator and finally re-weighed to calculate water loss.

#### 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.

#### **Dry extract**

Ten (10) g of each wine sample were carefully weighed in tared glass containers and dried in a constant temperature convection oven for 2 h at 105 °C. Then, were cooled for 1 h in a glass desiccator and re-weighed to calculate the dry extract content.

#### Solubility

One (1) 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 3000g for 5 min and 25 ml of supernatant were transferred into tared glass containers. The samples were dried in a forced convection constant temperature oven for 5 h at 105 °C. The percentage of solubility was calculated according to AOAC [20].

#### **Total polyphenols**

Total polyphenols of the raw red wines and wine powders were determined by the Folin–Ciocalteu (FC) method [21, 22]. All measurements were made in triplicate. Concentration was expressed as milligrams of gallic acid equivalents (GAE) per liter or per 100 g of powder.

#### Total monomeric anthocyanin (TMA) by the pH-differential method

Monomeric anthocyanin content was measured following the method described by Giusti and Wrolstad [23]. Pigment content was expressed as malvidin-3-glucoside, where molar weight was 493.441 g/mol; molar absorptivity  $\varepsilon = 28,000$ 1/M cm; and path length of the cell 1 cm. To express the TMA concentration in mg/g, the density of the diluted sample was taken into account.

#### Sorption isotherms

The equilibrium moisture of the wine powders was determined by means of the static gravimetric method [24]. For this purpose, 1.5 g samples of spray-dried wine powder was exposed at different saturated salt solutions that provide different values of relative humidity. The desiccators were placed in an oven at 30  $^{\circ}$ C and after reaching equilibrium the moisture content of the samples was determined using the gravimetric method. Each point of the different values of relative humidity was conducted three times.

#### **HPLC** analysis of anthocyanins

The chromatographic system employed was a Perkin-Elmer Series 200 high-performance liquid chromatograph equipped with a diode array detector, a quaternary pump, and an autosampler (HPLC-DAD; PerkinElmer, Shelton, CT). Separation was performed on a reversed phase Chromolith Performance C18 column (100 mm×4.6 mm I.D., 2 µm; Merck, Darmstadt, Germany) with a Chromolith guard cartridge (10 mm × 4.6 mm) at 25 °C. A gradient consisting of solvent A (water/formic acid, 90:10, v/v) and solvent B (acetonitrile) was applied at a flow rate of 1.1 ml/ min from 0 to 22 min and 1.5 ml/min from 22 to 35 min as follows: 96-85% A and 4-15% B from 0 to 12 min, 85-85% A and 15–15% B from 12 to 22 min, 85–70% A and 15–30% B from 22 to 35 min; followed by a final wash with 100% methanol and re-equilibration of the column. The samples were prepared by dissolving  $40.0 \pm 0.5$  mg of wine powder in 1 ml of hydroalcoholic solution (ethanol/water, 12:88, v/v) containing 5 g/L of tartaric acid. Both, the powder solutions or wines were filtered through a 0.45-µm pore size nylon membrane, and then 100 µl was injected into the column. Diode array detection was performed from 210 to 600 nm, and the quantification was carried out by peak area measurements at 520 nm. The anthocyanin amount was calculated by using malvidin-3-glucoside chloride as is standard for a calibration curve ( $R^2 = 0.99$ ). The results in wines were expressed as mg/L, and in powder solutions as mg per 100 g of powder. Identification and confirmation of anthocyanin pigments were performed by HPLC-DAD/ESI-MS as described by Blanco Vega [25].

#### **Color determination**

Color measurements over time in the two 1% wine powder solutions (pH 3.0 and pH 6.0) were evaluated using a MINOLTA CM-600d colorimeter (Konica-Minolta, Corp., USA), with the illuminant D65 and an observation angle of 2°. The measurement was made by placing 3 ml of the two solutions prepared at the different time intervals of the test in plastic containers with a white background. The values of  $L^*$  to  $b^*$  (CIELab) were recorded directly from the equipment. All measurements were made in triplicate. Color difference ( $\Delta E^*_{ab}$ ) was calculated as the euclidean distance between two points (1 and 2) in three-dimensional ( $L^*a^*b^*$ ) space.  $\Delta E^*_{ab} (L^*_1, a^*_1, b^*_1; L^*_2, a^*_2, b^*_2) = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ , where  $\Delta L^* = L^*_1 - L^*_2$ ,  $\Delta a^* = a^*_1 - a^*_2$ , and  $\Delta b^* = b^*_1 - b^*_2$ .

#### Influence of pH, temperature and time on color and anthocyanin contents of the dissolved wine powder solution

Two 1% solutions of wine powder were added with 5% (w/w) sucrose, and pH was adjusted to two values pH 3.0 and pH 6.0. The solutions were fractionated in test tubes (5 ml of sample) and stored at 5 °C, 30 °C and 60 °C for different intervals of time. The color parameter ( $L^*$ ,  $a^*$ ,  $b^*$ ) and the concentrations of malvidin-3-glucoside and total anthocyanin were determined at different times.

#### **Statistical analyses**

All analyses were carried out in triplicate, and the statistical analysis was assessed with Statgraphics Centurion XVI software (StatPoint Technologies Inc., Warrenton, VA). All of the results of Table 3 are tested for homogeneity of variance using Cochran's test, and analyzed by one-way analysis of variance (ANOVA) and Tukey's honestly significant difference (HSD) test. A p < 0.05 was considered to be statistically significant.

#### **Results and discussion**

Table 1 shows general analytical parameters of cv. Ancellotta. A simple way to highlight the coloring power of Ancellotta wine was by comparing its total anthocyanin to a red wine of a traditional varietal. For example, total anthocyanins value found in this work for Ancellotta wine (581 mg/L) is dramatically higher than those reported by Fanzone et al. [26] for Cabernet sauvignon wines also from Mendoza area, which ranged between 105.5 and 158.7 mg/L.

Table 2 shows the characterization of Ancellotta wine powder obtained using maltodextrin (13.5% w/w) and dried with 145 °C inlet temperature and 70 °C outlet temperature (average).

 Table 1
 General analytical parameters of cv. Ancellotta

Parameter	Ancellotta
Dry extract (%, w/w)	$3.15 \pm 0.04$
pH	$3.95 \pm 0.01$
TMA* (mg malvidin-3-glucoside/L)	$581 \pm 15$
Total polyphenols (mg gallic acid/L)	$3889 \pm 117$

\*TMA (total monomeric anthocyanin by the pH-differential method)

 
 Table 2
 Characterization of Ancellotta powder obtained by spraydrying

Parameter	Ancellotta
TMA (mg malvidin-3-glucoside/100 g wine powder)	$348 \pm 10$
Total polyphenols (mg gallic acid/100 g wine powder)	$1958 \pm 286$
Water activity (aw)	$0.25\pm0.00$
Moisture (% w/w)	$4.5\pm0.05$
Solubility (%)	$99 \pm 0.20$

\*TMA (total monomeric anthocyanin by the pH-differential method)

It is to be noted that percent yield in samples of Ancellotta spray-dried with MD10 averaged  $59 \pm 3\%$ , which is similar to previous studies with Cabernet sauvignon wine [16]. The high solubility of the spray-dried Ancellotta wine (Table 2) is one important parameter regarding its potential application in liquid matrices.

Figure 1 shows the visual color of liquid and spray-dried Ancellotta wine. The high anthocyanin content of the Ancellotta variety is reflected in its intense coloration.

Figure 2 shows scanning electron micrographs (SEM,  $\times 10,000$ ) of Ancellotta wine powder encapsulated with DE10 maltodextrin (dried at 145 °C).

During the spray-drying process of Ancellotta wine, the maltodextrin forms a layer on the surface of the drop, which can be seen in scanning electron micrographs (SEM) of the spray-dried Ancellotta wine (Fig. 2). The SEM image shows that maltodextrin enabled the formation of homogeneous capsules and polyphenols were encapsulated by the MD within a typical morphology for microcapsules. They visually appear a little dented with a rounded outer surface at x10,000 magnifications. The formation of these indentations on the surface (of particles obtained by spray-drying) is usually attributed to particle shrinkage due to the drastic loss of moisture followed by cooling [27, 28].

The anthocyanin profiles of the Ancellotta liquid wine and the powder were determined by HPLC–DAD and the results are shown in Table 3. The Ancellotta wine samples



Fig. 1 Visual color of Ancellotta wine and spray-dried powder



Fig. 2 Scanning electron micrographs (SEM,  $\times 10,000$ ) of Ancellotta wine powder

were analyzed within the same year of production. As mentioned before, it has high levels of anthocyanins and, consequently, the formation of derivatives is promoted during the winemaking processes. There is little literature about phenolic composition of the Ancellotta variety and its relationship with other international red varieties, while in Argentina there are no published data. However, some studies have shown higher levels of anthocyanins in this variety compared to other Italian cultivars [29–31]. In the present study, the mean proportions of different families in wine samples were 63.2% for glucosylated, 17.4% for acetylated, 8.1% for cinnamoylated, and 11.4% for pyranoanthocyanins and adducts (flavanol–anthocyanins) (Table 3).

Additionally, the mean values obtained for the ratios  $\Sigma$ glucosylated/ $\Sigma$ acetylated,  $\Sigma$ glucosylated/ $\Sigma$ coumaroylated, and  $\Sigma$ acetylated/ $\Sigma$ coumaroylated were 3.6, 8.1 and 2.2, respectively. These results show a pattern similar to that of Malbec, a red cultivar very important for Argentinian wine industry and characterized previously by Fanzone [32]. The effect of spray-drying, the ratio of the concentration (100 g of powder/100 g of liquid wine) was calculated for each anthocyanin. The ratio observed for each individual compound ranged between 4.1 and 17.9, with an average value of about 7.2. It is noticeable, that the cyanidin and malvidin derivatives were the most concentrate compounds, 10.2- and 7.2-fold, respectively, in relation to the rest of compounds.

The water sorption isotherm of Ancellotta powder at 30 °C is shown in Fig. 3. Physical changes in the powder were observed with increasing the water activity level from aw 0.29 to aw 0.75. At low water activity the powder remains free-flowing; at aw 0.43 the powder formed lumps and at aw

0.58 and above it completely collapses. This behavior can be explained by considering that physical changes in the amorphous wine powder matrix depends on time and are a function of (T-Tg), where T is the storage temperature and Tg is the glass transition temperature [17]. Between water activity of aw 0.43 and aw 0.58 a small plateau was observed which could be attributed to crystallization of wine tartrates.

The stability of anthocyanins in Ancellotta wine powder during storage at 38 °C and two different water activities (aw 0.25 and aw 0.33) was examined and the results are presented in Fig. 4.

It is observed that after 90 days of storage at 38 °C the loss is only 20%, as compared to the initial concentration. This behavior is consistent with previous literature results indicating that maintaining a low water activity value is critical for anthocyanin retention during storage [33].

The afforded mentioned behavior of total monomeric anthocyanins during storage was also examined by HPLC–DAD (in total anthocyanins and malvidin-3-glucoside contents) analysis and the results are shown in Fig. 5.

The behavior of malvidin-3-glucoside and total anthocyanins during storage at 38 °C and water activity aw 0.25 and aw 0.33 is fairly similar to that previously shown (Fig. 4) using pH-differential method.

The total anthocyanins and malvidin-3-glucoside in the Ancellotta wine powder also decreased slightly with the time similarly to that observed with total monomeric anthocyanin.

The observed storage stability of total anthocyanins and malvidin-3-glucoside in the Ancellotta wine powder was associated with the protection afforded by powder matrix components; i.e., to act as a barrier to the permeation of detrimental substances like moisture and oxygen [34, 35].

The stability and equilibria of total anthocyanins and malvidin-3-glucoside in Ancellotta wine powder were also studied in aqueous solution at different pH values. As shown in Fig. 6, the rate of total anthocyanins and malvidin-3-glucoside degradation increased up to its maximum value as temperature and pH increased from 5 to 60 °C and pH 3.0 to 6.0. It was observed that anthocyanin contained in 1% wine powder solution displayed their most intense red coloration at acidic pH 3.0 (data not shown), even holding a 1% wine powder solution at the acid pH values for a period as long as 47 h, the red color of the solution retained its high stability at 5 °C and 30 °C (around 95% of retention at 5 °C and 50% of retention at 30 °C to malvidin-3-glucoside and total anthocyanins, respectively). With increasing pH value of the solution up to 6.0, the red color greatly faded and almost appeared colorless even at a pH value of 3.0.

The stability of anthocyanins was markedly influenced by heat treatment and pH. The highest levels of the degradation for total anthocyanins and malvidin-3-glucoside were observed at pH 6.0 and 60 °C (90–100% degradation to malvidin-3-glucoside and total anthocyanins).

Table 3	Anthocyanins profile
(HPLC-	-DAD) of Ancellotta
liquid w	vine (mg/100 g) and
wine po	wder (mg/100 g)

Compounds	Ancellotta 2015 liquid wine	Ancellotta 2015 wine powder
Delphinidin-3-glucoside	$7.55 \pm 0.73a$	35.97 ± 2.34b
Cyanidin-3-glucoside	$1.24 \pm 0.12a$	$6.96 \pm 0.45b$
Petunidin-3-glucoside	$8.06 \pm 0.78a$	$39.10 \pm 2.55b$
Peonidin-3-glucoside	$3.94 \pm 0.38a$	$19.06 \pm 1.24b$
Malvidin-3-glucoside	$20.64 \pm 2.00a$	$108.21 \pm 7.05 \mathrm{b}$
Total non-acylated	$41.43 \pm 4.00a$	$209.30 \pm 13.64$ b
Delphinidin-3-(6"-acetyl)-glucoside	$2.62 \pm 0.25a$	$13.13 \pm 0.86b$
Cyanidin-3-(6"-acetyl)-glucoside	$0.91 \pm 0.09a$	$5.55 \pm 0.36b$
Petunidin-3-(6"-acetyl)-glucoside	$2.50 \pm 0.24a$	$12.44 \pm 0.81b$
Peonidin-3-(6"-acetyl)-glucoside	$0.74 \pm 0.07a$	$4.57 \pm 0.30b$
Malvidin-3-(6"-acetyl)-glucoside	$4.61 \pm 0.45a$	$22.78 \pm 1.48 \mathrm{b}$
Total acetylated	$11.38 \pm 1.10a$	$58.47 \pm 3.81b$
Delphinidin-3-(6"-p-coumaroyl)-glucoside	$0.85 \pm 0.08a$	$5.05 \pm 0.33b$
Cyanidin-3-(6"-p-coumaroyl)-glucoside	$0.13 \pm 0.01a$	$2.07 \pm 0.13b$
Petunidin-3-(6"-p-coumaroyl)-glucoside	$0.69 \pm 0.07a$	$3.44 \pm 0.22b$
Peonidin-3-(6"-p-coumaroyl)-glucoside	$0.82 \pm 0.08a$	$3.20 \pm 0.21$ b
Malvidin-3-(6"-caffeoyl)-glucoside	$0.16 \pm 0.02a$	$2.02 \pm 0.13b$
Malvidin-3-(6"-p-coumaroyl)-glucoside	$2.64 \pm 0.26a$	$9.94 \pm 0.65b$
Total cinnamoylated	$5.28 \pm 0.51$ a	$25.73 \pm 1.68 \mathrm{b}$
10-H-Pyranomalvidin-3-(6"-acetyl)-glucoside	$0.82 \pm 0.08a$	$5.52 \pm 0.36b$
10-Carboxy-pyranodelphinidin-3-glucoside	$0.46 \pm 0.04a$	$3.26 \pm 0.21b$
10-Carboxy-pyranopetunidin-3-glucoside	$0.74 \pm 0.07a$	$5.04 \pm 0.33b$
10-Carboxy-pyranopeonidin-3-glucoside	$0.60 \pm 0.06a$	$6.45 \pm 0.42b$
10-Carboxy-pyranomalvidin-3-glucoside	$1.11 \pm 0.11a$	$6.45 \pm 0.42b$
10-Carboxy-pyranomalvidin-3-(6"-acetyl)glucoside	$1.19 \pm 0.11a$	$6.90 \pm 0.45b$
Total vitisin-like pyranoanthocyanins	$4.92 \pm 0.48a$	$33.62 \pm 2.19b$
10-Hydroxyphenyl-pyranomalvidin-3-glucoside	$0.36 \pm 0.04a$	$2.20 \pm 0.14$ b
10-Hydroxyphenyl-pyranomalvidin-3-(6"-acetyl)-glucoside	$0.17 \pm 0.02$	ND
10-Hydroxyphenyl-pyranomalvidin-3-(6"-p-coumaroyl)-glucoside	$0.11 \pm 0.01$	ND
10-Methoxy-hydroxyphenyl-pyranomalvidin-3-glucoside	$0.23 \pm 0.02$	ND
Total hydroxyphenyl-pyranoanthocyanins	$0.87 \pm 0.08a$	$2.20 \pm 0.14$ b
Malvidin-3-glucoside-catechin	$0.36 \pm 0.03a$	$3.58 \pm 0.23b$
Malvidin-3-glucoside-ethyl-catechin	$1.34 \pm 1.34a$	$7.13 \pm 0.46$
Total flavanol-anthocyanin adducts	$1.69 \pm 0.16a$	$10.71\pm0.70\mathrm{b}$
Total anthocyanins	65.57 ± 6.34a	$340.02 \pm 22.15b$

ND non-detected

\*Mean $\pm$ SD (mg/100 g, n=3). Different lowercase letters in the same row indicate significant differences between matrices (Tukey HSD test, p < 0.05)

# Color behavior of anthocyanins as a potential colorant

It is widely known that pH strongly influences the color of anthocyanins [36]. This effect was examined in a 1% wine powder solution in which pH was set at 3.0 and 6.0. Figure 7 shows the photographic record of color modification.

Depending on the pH of the medium, the red-colored flavylium cation coexists as an equilibrium mixture with other forms of anthocyanins: the blue–purple quinonoidal bases, the colorless hemiacetal B, and the pale-yellow chalcones. Therefore, the same anthocyanin solution may show a different color. It is also known that at pH 3.0 color is more stable than a higher pH [36, 37].

As mentioned before, utilization of anthocyanins as food colorants have two main drawbacks: (a) in aqueous medium anthocyanins undergo pH-dependent reversible structural transformations, with concomitant change in color [8–10]; (b) the thermal instability of anthocyanins during food processing and storage acts as an impediment to their use. These



**Fig.3** Adsorption isotherm at 30 °C of Ancellotta wine powder. Error bars overlapped with some data points. A few pictures were inserted to show the physical changes associated with water activity



**Fig. 4** Stability of total monomeric anthocyanin (TMA) in spraydried Ancellotta powder stored at 38 °C with two different values of water activity (aw 0.25 and aw 0.33)



**Fig.5** Stability of total anthocyanin and malvidin-3-glucoside in Ancellotta wine powder stored at 38 °C for two values of water activity (aw 0.25 and aw 0.33) determined by HPLC–DAD. Error bars overlapped with data points for malvidin-3-glucoside



**Fig. 6** Stability of total anthocyanin (**a**) and malvidin-3-glucoside (**b**) in 1% wine powder solution containing 5% sucrose and stored 47 h at 5  $^{\circ}$ C, 30  $^{\circ}$ C and 60  $^{\circ}$ C for pH 3.0 and pH 6.0. Error bars overlapped with some data points



Fig.7 Effect of pH on visual color difference in 1% wine powder solution

In order to establish whether the observed changes in the CIELAB parameters were visually relevant, color variations between 1% wine powder solutions (containing 5% sucrose) at pH 3.0 (a) and 6.0 (b), during storage at 5 °C, 30 °C and 60 °C, were calculated and expressed as colorimetric differences  $\Delta E^*_{ab}$  (Fig. 8). Moreover, the figure shows the relative contribution of lightness, chroma and hue ( $\Delta L'$ ,  $\Delta C'$ ,  $\Delta H'$ ) to each color difference, what allows evaluating which color attribute was the most influenced. According to Martinez et al. [38],  $\Delta E^*_{ab}$  around 3 units indicates, the color differences detectable by the human eye (as an average observer). On this basis, the most perceptible color changes were produced when the pH and temperature were increased,

observing the highest  $\Delta E^*_{ab}$  values at 60 °C and pH 6.0, indicating greater color degradation (Fig. 8b). This data is also in agreement with the aforementioned results for phenolic compounds and total monomeric anthocyanins. As can be seen in Fig. 8a, at pH 3.0 and 60 °C the main difference was qualitative, evidenced by the significantly higher contribution of hue  $\%\Delta^2 H$  (87–93%), with respect to lightness  $\%\Delta^2 L$  or chroma  $\%\Delta^2 C$  (1–12% and 1–6%, respectively). On the other hand, at pH 6.0 (Fig. 8b) the quantitative color changes  $(\%\Delta^2 C)$  became more pronounced, especially for range time 0-47 h, and higher temperature values. Between time-lapse 0–29 and 0–47 h the chroma modifications  $\%\Delta^2 C$ (52% in both range time) were particularly more marked than hue  $\%\Delta^2 H$  ( $\approx 40\%$  in both range time) at 60 °C. Therefore, a wine powder solution at pH 3.0 and pH 6.0 maintaining at 60 °C promote a visual color change from brilliant red to more brownish hues. In contrast, samples kept at 5 °C maintained attractive colors even after 47 h of storage. Cevallos-Casals and Cisneros-Zevallos [39] reported that after 41 h

**Fig. 8** Color differences  $(\Delta E^*_{ab})$ , showing the relative contribution of lightness, chroma and hue  $(\Delta L', \Delta C', \Delta H')$ , in 1% wine powder solution containing 5% sucrose and pH values of pH 3.0 (**a**) and pH 6.0 (**b**)



in aqueous extracts of Andean purple corn and red-fleshed sweet potato, all quinonoidal structures decreased their absorbances significantly. The color of these unstable quinonoidal bases increasingly shifted towards brown and yellow with time. After 138 days, yellow colorless structures predominated for all extracts at pH > 4.0. Extracts at pH 1.0 and 3.0 were selected, due to their higher stability as determined previously.

Sensory analysis will be carried out in future to confirm the viability of Ancellotta powder as natural colorant in drinks powders.

# Conclusions

Ancellotta wine containing a fairly high amount of anthocyanins was spray-dried with maltodextrin to obtain a freeflowing powder having an intense color. The stability of anthocyanin compounds (determined by HPLC–DAD) in wine powder having water activity aw 0.33 or less was found to be remarkably good. Anthocyanins in 1% wine powder solution decreased with time in a temperature-dependent manner, with minimal loss at low temperature (5 °C) and higher loss at 60 °C. Moreover, if pH of solution increased the anthocyanins decreased with time. It does appear that Ancellotta powder could be used as a color of natural origin in products such as the popular "fruit drink powders", since they have a low water activity and a very favorable pH (3.0).

The present work is novel and provides important information about the feasibility of spray-drying to encapsulate Ancellotta red wine in a maltodextrin matrix to use as natural food colorant. In addition to contain a high concentration of anthocyanins and other phenolic compounds, the wine powder maybe useful in preparation of healthy foods since it would contain the polyphenols of red wine, but without the presence of alcohol.

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#### **Compliance ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

**Compliance with ethics requirements** This article does not contain any studies with human or animal subjects.

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