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Cherry fibers isolated from harvest residues as valuable dietary fiber and functional food ingredients

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ABSTRACT

Residues discarded at cherry fruit harvesting were extracted with ethanol from 'Chelan', 'Brooks' and 'Sunburst' varieties to obtain cherry fibers constituted by the cell wall polysaccharides, applicable as functional food ingredients, additives and/or dietary fibers. Powder properties were evaluated. The highest specific volume, directly related to sample porosity, corresponded to 'Brooks' fibers. These results matched the best hydration properties showed by 'Brooks'. Chemical composition may indicate a hydrogel microstructure for cherry fibers. 'Chelan' and 'Sunburst' powders showed the highest total phenolics content, 40–63% of which were bound. The FRAP-antioxidant activity determined in water was lower than that expected from the total phenolics content determined after alkaline or acid hydrolysis. Cherry fibers stabilized oil-in-water (ϕ = 50%) emulsions and showed foaming capacity. Beyond some differences observed between varieties, cherry harvesting residues constitute valuable sources of biopolymers and antioxidant compounds potentially useful as functional food ingredients and dietary fiber.

1. Introduction

Cherry is a fleshy stone fruit of perennial trees of some species of the genus *Prunus*. Sweet cherries (*Prunus avium* L.) are commercially cultivated in more than 40 countries, with a world production forecasted for 2011/2012 at 1.9 million metric tons. The Southern hemisphere (mainly Chile, South Africa, Australia and Argentina) contributes to only 3.5% of the world production (USDA, 2011). In spite of this small proportion, it is important economically for local development because of harvest and counter-season marketing advantages (Cittadini, 2007). 'Chelan', 'Brooks' and 'Sunburst' are among the cherry varieties grown in Argentina (Cittadini, 2007).

Size, absence of misshapen fruit, freedom of cracks, green fleshy stems together with high soluble solids and red surface color, are the main quality attributes of fresh cherries (Mattheis and Fellman, 2004). The demands of the international markets about cherry quality, mainly size, notably increased. In seasons with less favorable climate and in areas with an excess of cherry charge per tree, up to 30% of the total production of Argentina can be discarded only due to smaller sizes. This proportion can increase to 50% due to cracking and bruising (M.D. Raffo, unpublished results).

Cell walls removed from vegetables and fruits discarded at harvesting or from residues developed after processing are renewable and valuable sources of biopolymers which can be applied to pharmaceutical (Beneke et al., 2009) and food (Willats et al., 2006) formulations as well as to materials science (John and Thomas, 2008). Upgrading of vegetable wastes add value to the commodities production (Laufenberg et al., 2003). Fiber-rich by-products may be incorporated into food products as inexpensive, low-caloric bulking agents for partial replacement of flour, fat or sugar, as enhancers of water and oil retention and to improve emulsion or oxidative stabilities (Elleuch et al., 2011). Natural functional ingredients can be applicable to food formulation (Kohajdová et al., 2012; de Escalada Pla et al., 2013) but also useful as dietary fiber (de Escalada Pla et al., 2012). Hence, the functional properties of the CW biopolymers are relevant in the upgrading of vegetable by-products and functional characterization contributes to predict the potential usefulness of the biopolymers extracted. This work aims at isolating fibers from the residues of 'Chelan', 'Brooks', and 'Sunburst' cherry harvesting in order to be evaluated as potential functional ingredient for food formulation and dietary fibers. Their chemical composition and functional characterization is reported.

2. Materials and methods

2.1. Plant material

Small, bruised, cracked and overripe fruits, residues of 'Chelan', 'Brooks' and 'Sunburst' cherry fruit harvesting, obtained from trees

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located in the Río Negro Upper Valley, Argentina (39°01′32″S, 67°44′22″W, 240 m above sea level) were used. Ca. 4.0 kg of the harvesting residues of each variety were separately collected.

2.2. Isolation of cherry fibers

After removal of stone and peduncle, for each cultivar, 1500 g of fruit was put into 2 L of 80% (v/v) ethanol and homogenized in a Warring blender and in an Omni Mixer homogenizer. The homogenate was boiled for 30 min, cooled, and filtered through glass filter paper (Whatman GF/C). The retentate was thoroughly washed with 95% (v/v) ethanol. The insoluble material yielded the cherry fibers (alcohol insoluble residue, AIR), which was air-dried, lyophilized and grounded. Samples were stored at −18 °C until usage.

2.3. Chemical analysis

The extracted cherry fibers were chemically analyzed. Cellulose, lignin, uronic acids and total carbohydrate determinations were performed as reported by Ng et al. (1998). Proteins were determined according to Lowry et al. (1951) and ashes through the AOAC's method (923.03, 1990). Ascorbic acid was spectrophotometrically determined in cherry fibers as indicated by Rojas and Gerschenson (1991).

Total phenolics determined after alkaline hydrolysis was performed as reported by Basanta et al. (2013), whereas those determined by acid hydrolysis (2 M HCl) were performed as indicated by Latorre et al. (2013). Results were expressed as mg of gallic acid per gram of AIR.

2.4. Particle size, apparent density, specific volume and true density

Particle size of the isolated cherry fibers was determined through light scattering (Malvern, USA) by suspending the isolated fiber in ethanol and the mass median diameter ($D_{(0.5)}$) was informed. Apparent density (g/cm^3) was determined according to Chau et al. (2007). Specific volume was calculated as the inverse of the apparent density. True density was measured with a He pycnometer (Accupyc 1330, Micromeritics, Australia) at a cell temperature of 20.0 °C, using at least 6 g of each cherry fiber sample. Mean values and standard deviation of ten measurements for each fraction were reported.

2.5. Physical and hydration properties

Swelling capacity (SC), water holding capacity (WHC), water retention capacity (WRC) and kinetics of spontaneous water absorption were determined for the extracted cherry fibers in triplicate, as reported by Basanta et al. (2013). Data of spontaneous water absorption were fitted to a power-law relationship for swelling according to Ritger and Peppas (1987):

$$q = k \cdot t^n \tag{1}$$

where k is a constant dependent on kinetic features and experimental conditions and n is the swelling exponent.

2.6. Water activity

Water activity (a_W) of cherry fibers was evaluated in triplicate at 25.0 °C through a Decagon AquaLab (Series 3 Water activity meter, USA). The true water activity (a_W^o) was then extrapolated from the calibration curve previously made in the equipment by measuring saturated solutions of known a_W: LiCl ($a_W^o = 0.110$), CH_3-COOK ($a_W^o = 0.220$), $MgCl_2$ ($a_W^o = 0.333$) and NaBr ($a_W^o = 0.577$) at 25.0 °C (Greenspan, 1977).

2.7. Color

Measurement of the cherry fiber color was performed in each sample employing a Minolta colorimeter (Minolta CM-508d) with an aperture of 1.5 cm-diameter. CIE L^*, a^*, and b^* color space parameters were measured using the D65 standard illuminant and the 2° standard observer (CIE, 1931). Data recorded were between $L = 0$ (black) and $L = 100$ (white or maximum) for lightness, $-a$ (greenness) and $+a$ (redness), $-b$ (blueness) to $+b$ (yellowness). Standard values considered were those of the white background. Each of three samples took from each kind of cherry fiber was put into a 20-mm-diameter transparent and colorless cell. Then, it was measured at ten different points across the sample surface. The average and standard deviation for the triplicates was reported.

2.8. Antioxidant capacity

The ferric reducing antioxidant power was determined through the FRAP assay according to Pulido et al. (2000), but using water as solvent. About 4.5 mg of each cherry fiber was separately soaked in the water volume (2.0 mL) required by this spectrophotometric assay. FRAP reagent was added and the reaction was monitored for up to 120 min as the increase in absorbance ($\lambda = 595$ nm). A calibration curve was constructed with $FeSO_4 \cdot 7\ H_2O$ aqueous solutions 2 μmol/mL.

2.9. Emulsifying properties

Emulsifying activity of cherry fibers was assayed by using the proportions reported by Prakongpan et al. (2002). For each experiment performed in a graduated (40.0 mL) cylindrical tube, 0.7000 g of fiber sample was suspended in 10.0 mL of deionized water and left for 18 h at 25 °C for fiber hydration. Afterwards, 10.0 mL of middle-chain triglyceride (MCT) oil volume was added and the initial total volume (V_{initial}) was measured. The mixture was emulsified using a homomixer (Ultra Turrax-T25, S25 N 25F dispersing tool, IKA Werke, Germany) at 9,500 rpm for 1 min. The total final volume (V_{final}) was measured and the foam capacity (F) was calculated as

$$F = \frac{(V_{\text{final}} - V_{\text{initial}})}{V_{\text{initial}}} \cdot 100 \tag{2}$$

The foam-emulsion system was submitted to dynamic assays.

The aqueous phase of the emulsion was separately obtained following the same procedure described above, but without the addition of MCT oil. After homogenization, the aqueous system was allowed to rest for 15 min and centrifuged at 6000 rpm (6 °C) for 20 min in order to separate the cherry fiber pellet. The aqueous supernatant solution was submitted to a flow assay to determine its viscosity profile.

2.9.1. Rheological characterization

The assays were performed in triplicate with a controlled rheometer (Paar Physica MCR300, Germany) at a constant temperature of 20 °C (Viscotherm VT2 Physica, Germany), using a 25 mm-diameter parallel plate geometry (PP25/P2).

2.9.1.1. Oscillatory assays. An amplitude sweep assay was first performed at constant frequency (1 Hz) in order to determine the linear viscoelastic range of the foam-emulsion sample. Then, steady shear storage or elastic modulus (G') and strain were recorded against shear stress. A 1% constant strain was then selected from the linear viscoelastic range in order to record the mechanical spectra from a new sample of each cherry fiber foam-emulsion. Mechanical spectrum was obtained at 1%-constant strain by

recording steady G' and G'' moduli, as well as the tangent of the shift angle ($\tan\delta$) *vs* angular frequency (ω; 0.1–50 rad s^{-1}). The power law type model (Kim and Yoo, 2006) was used to fit the experimental data:

$$G'(\omega) = G'_0 \cdot \omega^A \quad (3)$$

$$G''(\omega) = G''_0 \cdot \omega^B \quad (4)$$

wherein A and B are the exponents related to the frequency dependence of the rheological parameters and G'_0 and G''_0 are the equilibrium moduli.

2.9.1.2. Flow assays. Flow curves were determined by recording the steady shear viscosity of the aqueous phase obtained as described in Section 2.9, in the 0.001–200 rad s^{-1} shear rate ($\dot{\gamma}$) range. The Cross model was considered (Basanta et al., 2013):

$$\eta_{app} = \eta_\infty + \frac{(\eta_o - \eta_\infty)}{1 + (\tau\dot{\gamma})^m} \quad (5)$$

wherein η_0 represents the zero-shear rate viscosity or Newtonian viscosity, τ is the time constant corresponding to the Cross model, and m is a dimensionless constant.

2.10. Statistical analysis

Results were reported as the average and standard deviation for n sample replicates. Results were analyzed through ANOVA ($p < 0.05$) followed by multiple comparisons evaluated through least significant difference test, using the Statgraphic package (Statgraphic Plus for Windows, version 5.0, 2001, Manugistic Inc., Rockville, MD, USA). Correlations and nonlinear regressions were respectively performed by using GraphPad Prism 5 (GraphPad Software Inc., USA, 2007) and OriginPro 7.5 SRO (OriginLab Corp., MA, USA, 2003).

3. Results and discussion

3.1. Chemical characteristics

The 80% ethanol-insoluble residue (AIR) of the cherry harvesting residues is expected to be constituted by cell wall (CW) biopolymers (Table 1). Cell walls are intended to be the main source of physiologically and/or functionally useful fibers (Guillon and Champ, 2000). These isolated cherry fibers contained 16–20% of cellulose, 32–37% of non-cellulosic carbohydrates (pectins, hemicelluloses) as well as 7–8% of lignin and 12–15% of proteins, leaving 3.2–3.9% of ashes. Pectins are determined through the uronic acid content (Table 1), which is included in the proportion of non-cellulosic carbohydrates. The drying processing used is intended for the retrieval of fiber fractions with high functional quality, mainly in relation to their hydration properties (de Escalada Pla et al., 2012). 'Chelan' cherry showed significantly higher fiber yield than the other varieties (Table 1).

3.2. Physical and hydration properties of fibers

Cherry fibers were dark purple. Those isolated from 'Chelan' showed the lowest lightness (L^*) as well as a^* and b^* values (yellowness and redness, respectively, Table 1). Water activity (a^o_W) varied between 0.253 and 0.285 (Table 1), which means that at this condition of storage the fibers obtained are stable as dehydrated powders in relation to lipid oxidation, hydrolytic reactions, non-enzymatic browning and microbial spoilage (Labuza et al., 1972). In the particle size distribution determined through light scattering, the mass median diameter ($D_{(0.5)}$) found in ethanol for the current fibers was ≅520 μm. At this particle size, flow becomes easy because inertial forces are larger than the interparticle forces (Merkus, 2009).

The true density (≈1.5 g/cm^3), which provides an estimate of the volume of the solid part of a sample, was non-significantly different in fiber powders (Table 2). The true densities of solid pharmaceutical samples should reflect the fundamental chemical properties (e.g., molecular weight, molecular formula, and unit-cell dimensions) of the materials. As drug substances and excipients are primarily organic materials, their true densities do not vary greatly, exhibiting values falling in the 1.2–1.6 g/cm^3 range (Hancock et al., 2003).

Apparent density is an increased bulk density attained after mechanically tapping a container with the powdered sample (World Health Organization, 2012). The highest apparent density was showed by 'Sunburst' fiber 0.578 g/cm^3 (Table 2), and the lowest one by 'Brooks' (0.34 g/cm^3). Hence, 'Brooks' fibers showed the highest specific volume (inverse of the apparent density) and 'Sunburst' the lowest one (Table 2). The specific volume suggests differences in capillary structure: the more porous the system is the greater amount of water should take up, assuming a constant chemical composition. The drying processing also shapes up the porosity of the dehydrated material (Vetter and Kunzek, 2003). 'Brooks' fiber showed not only higher SC values but also higher WHC values (Table 2). However, a non-significant difference in the WRC values was found with respect to 'Chelan' fibers. 'Sunburst' fiber showed a lower value of WRC (Table 2). Values for SC, WHC and WRC are not relevant for soluble polysaccharides; rather, they are attributes of the insoluble polysaccharides (Thebaudin et al., 1997). As previously determined by Basanta et al. (2013), less than 4% of the total polysaccharide content of cherry fibers was constituted by water-soluble polymers. They were principally high methoxyl pectins (degree of methylation = 65–77%) containing 50% of uronic acids and 28% of neutral sugars (mainly arabinan- and some arabinogalactan-side chains), together with a low proportion of water soluble galactoglucomannans. SC, WHC and WRC of cherry fibers were similar to those determined by Kohajdová et al. (2012) for a carrot pomace powder, and higher than those obtained from oat and rice brans treated with endoxylanase for development of dietary fiber enriched cakes (Lebesi and Tzia, 2012). SC indicates how much the fiber matrix swells as water is absorbed (Raghavendra et al., 2004). Loosely associated water is also being considered in this assay. Solubility and swelling are related properties: the first step of polysaccharide solubilization is swelling. The water moves into the matrix structure and produces relaxation of macromolecules (swelling) until they are completely dispersed (Thebaudin et al., 1997). On the other hand, WHC is defined as the water retained by the fibers without the application of any external force, except for gravity and atmospheric pressure (Raghavendra et al., 2004). Thus, this parameter also includes the proportion of water loosely associated to the fiber matrix. Also, strongly bound water has no effect on stool weight, whereas loosely associated water readily increases it (Cadden, 1987). WRC is defined as the water that remains into the hydrated fiber following the application of an external force such as centrifugation, being then related to strongly-bound water (Raghavendra et al., 2004). Cherry fibers showed a relevant proportion of strongly retained water (Table 2). WHC and WRC are hydration properties ascribed mainly to pectins and hemicelluloses in cherry (Basanta et al., 2013). Specific volume and SC were ascribed to cellulose. Hydration characteristics are relevant for the fiber functionality as ingredient, affecting the texture of the final product among other qualities (Biswas et al., 2011).

Knowledge of the water absorption kinetics can help in determining the time needed by the fibers to absorb water for rehydration of a food mix. Also, it allows knowing the amount of water

Table 1
Color parameters[a,b,c], water activity, yield and chemical composition[a,b] of the 'Chelan', 'Brooks' and 'Sunburst' cherry fibers.

	Cherry fiber		
	'Chelan'	'Brooks'	'Sunburst'
L^{*c}	21.2 ± 0.2^{A}	35.14 ± 0.04^{B}	37 ± 1^{C}
a^{*c}	5.07 ± 0.07^{A}	9.37 ± 0.2^{B}	9.8 ± 0.1^{B}
b^{*c}	6.64 ± 0.04^{A}	15.8 ± 0.4^{B}	18.4 ± 0.4^{C}
Water activity (a_W^o)	0.253	0.255	0.285
Yield (g AIR[d]/100 g fresh tissue)	12.7	7.9	8
Proteins[a] (g/100 g AIR[d])	14.7 ± 0.9^{A}	12.24 ± 0.02^{B}	12.9 ± 0.5^{B}
Non-cellulosic carbohydrates[a] (g/100 g AIR[d])	32 ± 2^{A}	34 ± 4^{A}	37 ± 3^{A}
Uronic acids[a] (g/100 g AIR[d])	12.9 ± 0.6^{A}	13.52 ± 0.09^{A}	13.44 ± 0.08^{A}
Lignin[a] (g/100 g AIR[d])	7.3 ± 0.2^{A}	7.0 ± 0.2^{A}	8.4 ± 0.2^{A}
Cellulose[a] (g/100 g AIR[d])	16 ± 1^{A}	20 ± 2^{A}	17 ± 2^{A}
Ash content[a] (g/100 g AIR[d])	3.91 ± 0.01^{A}	3.42 ± 0.01^{B}	3.24 ± 0.03^{C}
Phenolic[a] (acid hydrolysis) (mg/g AIR[d])	3.72 ± 0.05^{A}	3.2 ± 0.4^{A}	4.5 ± 0.1^{B}
Total phenolics[a] (alkaline hydrolysis) (mg/g AIR[d])	10.1 ± 0.2^{A}	7.21 ± 0.06^{B}	9.33 ± 0.03^{A}
Bound phenolics[a] (mg/g AIR[d])	6.3 ± 0.05^{A}	4.0 ± 0.3^{B}	4.7 ± 0.02^{B}

[a] Mean and standard deviation ($n = 3$) are shown.
[b] Different capital letters in a row mean significant differences ($p < 0.05$).
[c] Hunter Lab color parameters L, a and b, which meaning can be seen in Section 2.7.
[d] AIR (dry mass) means "alcohol insoluble residue", which is synonym of cherry fiber.

Table 2
Physical and hydration properties[a,b] of the 'Chelan', 'Brooks' and 'Sunburst' cherry fibers.

	Cherry fiber		
	'Chelan'	'Brooks'	'Sunburst'
True density (g/mL)	1.52 ± 0.03^{A}	1.50 ± 0.04^{A}	1.48 ± 0.04^{A}
Apparent density (g/mL)	0.448 ± 0.002^{A}	0.34 ± 0.01^{B}	0.578 ± 0.008^{C}
Specific volume (mL/g)	2.23 ± 0.06^{A}	2.99 ± 0.2^{B}	1.73 ± 0.06^{C}
SC (mL/g)[c]	11.8 ± 0.4^{A}	13.7 ± 0.5^{B}	11.7 ± 0.4^{A}
WHC (g/g)[c]	9.4 ± 0.1^{A}	10.7 ± 0.1^{B}	9.04 ± 0.06^{A}
WRC (g/g)[c]	9.0 ± 0.2^{AB}	9.5 ± 0.2^{B}	7.9 ± 0.6^{A}
k (mL/g min^n)[c]	3.04 ± 0.07^{A}	2.96 ± 0.09^{A}	2.87 ± 0.08^{A}
n[c]	0.188 ± 0.006^{A}	0.200 ± 0.008^{A}	0.152 ± 0.007^{B}
R^2	0.917	0.894	0.883

[a] Mean and standard deviation ($n = 3$) are shown.
[b] Different capital letters in a row mean significant differences ($p < 0.05$).
[c] Swelling (SC), water holding (WHC) and water retention (WRC) capacity as well as the kinetics parameters of water absorption (k, n) and its R^2 of kinetic fitting.

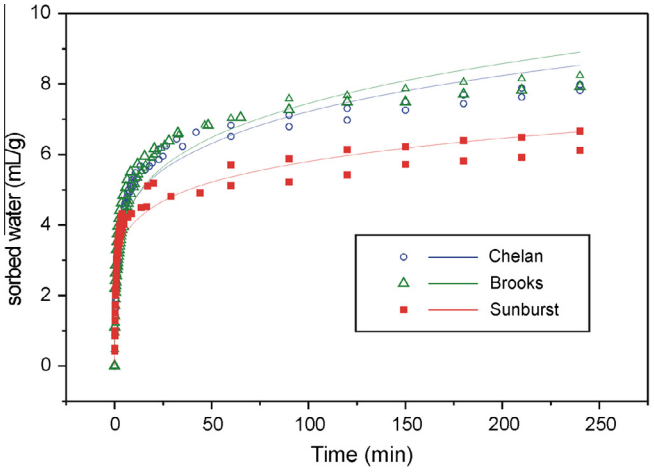

Fig. 1. Spontaneous water intake is shown for 'Chelan', 'Brooks' and 'Sunburst' cherry fibers as well as the fitted kinetic curves (continuous line).

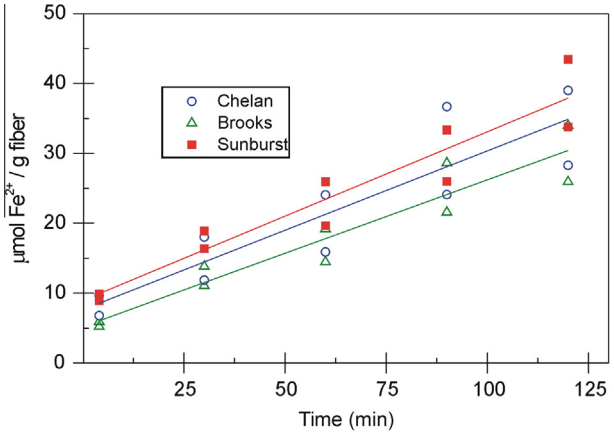

Fig. 2. The antioxidant activity of 'Chelan', 'Brooks' and 'Sunburst' cherry fibers measured over time, as the ferric-reducing power (FRAP assay).

compromised during hydration of a powder mixture (e.g. flour in bread making). Fig. 1 shows the curves obtained by fitting the experimental data to Eq. (1) during the spontaneous water uptake for a 240 min-assay. Fitting parameters are reported in Table 2. 'Brooks' and 'Chelan' fibers showed similar kinetic curves of water absorption, which were above that obtained from 'Sunburst' (Fig. 2). Parameters k and n were determined from Eq. (1), which is generally applied to determine the swelling power of hydrogels. The n-exponent is related to the mechanism by which water diffuses to produce swelling of polymeric samples (Jabbari and Nozari, 2000). For disk-shaped samples, n is 0.5 if the swelling occurs by Fickian diffusion of water whereas n is between 0.5 and 1.0 for non-Fickian diffusion. Fickian mechanism of swelling indicates that chain relaxation has little effect on the swelling rate. When chain relaxation contributes to the rate of swelling, the n value approaches 1.0. As determined in a previous work by Basanta el al. (2013), cherry AIRs were constituted by 30% of pectins and 53% of hemicelluloses, together with cellulose and lignin. Pectins covalently crosslinked at the arabinan side chains by diferulic esters constituted between 44% and 64% of the total pectin content (32–40%) of the cherry fibers As shown by the proportion of polysaccharides dissolved in the CDTA solution, Basanta et al. (2013) also determined that Ca^{2+} crosslinked homogalacturonans constituted ≈37% of the total pectin content of 'Chelan' and 'Brooks' fibers and 26% of the pectins of 'Sunburst' fibers. These materials may then be considered as hydrogels (Karadağ et al., 2002). More rapid water diffusion into the sample needs not only some degree of hydrophilicity but also adequate sample porosity. Absorption

kinetic constants (k) were not significantly different (Table 2). For the n-exponent, the lowest value (0.153) was obtained for 'Sunburst', but 'Brooks' and 'Chelan' fibers also showed a low one ($n \approx 0.190$). Thus, chain relaxation may have probably no effect on the swelling rate. SC and WHC results varied between fiber fractions in the same way as n (Table 2).

3.3. Phenolic content and antioxidant activity

Sweet cherries contain various phenolics, including anthocyanins, which contribute to the total antioxidant activity (Yanishlieva-Maslarova, 2001). Anthocyanins may appear red, purple, or blue depending on the pH. Through the Folin–Ciocalteu technique, Usenik et al. (2008) found a total phenolic content between 44.3 and 87.9 mg (expressed as gallic acid) per 100 g of fresh sweet cherry in the methanolic extracts. According to this data, the phenolic content determined in cherry fibers isolated in the present work either through acid or alkaline hydrolysis, was 5–10 times higher than in fresh tissue (Table 1). It has been reported that the total antioxidant capacity of cherry fruits measured through ABTS assay was positively correlated with the ascorbic acid content and total phenolics, and also with the anthocyanin concentration only from stage 8 of the fruit development (Serrano et al., 2005). As determined in the present work, non-detectable contents of ascorbic acid remained in cherry fibers after ethanolic extraction. Beyond this, cherry fibers exhibited a dark purple coloration (Table 1).

The content of total phenolics in cherry fibers was determined through the Folin–Ciocalteu method after alkaline treatment (Table 1). Many phenols and particularly the phenolic acids appear chemically bound, and thus they are released after alkaline hydrolysis (Robards, 2003). The highest content of total phenolics corresponded to 'Chelan' fibers and the lowest one to 'Brooks'. On the other hand, acid hydrolysis has been the traditional approach for measurement of phenolic aglycones from flavonoid glycosides and some phenolic acid esters (Robards, 2003). A lower proportion of phenolics was released by acid treatment from cherry fibers (Table 1). 'Chelan' and 'Brooks' showed similar amounts, whereas 'Sunburst' and 'Chelan' carried the same contents of total phenolics. Considering that acid hydrolysis releases mostly free (unesterified) phenolic compounds, significant higher amount of bound phenolics (63%) was shown by 'Chelan' fiber. This may be in part associated to diferulate ester cross linking the arabinan side chains of cherry pectins (Basanta et al., 2013). The phenolic content determined in cherry fibers by acid hydrolysis (Table 1) was similar to that determined by Tsao et al. (2005) for the dry residue of apple mesocarp (1.6–3.6 mg/g dry mass) and lower than the phenolic content determined by Bravo et al. (2007) for milled leaves of *Ilex paraguariensis* (80 mg/g), white wine (19 mg/100 mL) and an infusion of green tea (116 mg/100 mL), all expressed as gallic acid.

Phenolic content of the extracts is expected to be directly related to the antioxidant capacity (Bravo et al., 2007), which is an important quality for cherry fractions from the nutritional and functional point of view as dietary fibers, food additives and ingredients. The antioxidant activity of polyphenols of cherry fibers was determined as their ferric-reducing power using the FRAP assay. It was performed by swelling of cherry fibers in water, since water is the physiological as well as the food permitted solvent. At this condition, the antioxidant capacity that the polymeric matrix may really have if cherry fibers were used as food additives, ingredients or from a physiological point of view is being determined. Equivalent concentration was the antioxidant concentration liberated from fiber fractions with a reducing effect equivalent to 1 mmol/L of Fe(II) (Pulido et al., 2000). The equivalent of Fe(II), as μmoles per gram of cherry fiber sample, showed a linear increase with time up to 120 min of reaction (Fig. 2). Significant differences ($p < 0.05$) between the y-axis intercepts existed, being the highest antioxidant capacity for 'Sunburst' fiber and the lowest one for 'Brooks'. However, slopes were similar, with a value of 0.226 μmol Fe(II) min^{-1}/g fiber.

Studying the FRAP reaction, Pulido et al. (2000) determined that a 250 μmol/L-gallic acid aqueous solution showed a reducing FRAP value equivalent to 1281 μmol of Fe(II)/L, after 4 min of reaction. From this equivalence, the expected FRAP value was calculated from the phenolic contents expressed as gallic acid, shown in Table 1. It was observed that the antioxidant activity of every cherry fiber, even at 120 min of reaction (Fig. 2), was ≈6–8 times lower than the FRAP value calculated from the total phenolic content determined after alkaline hydrolysis (Table 1). On the other hand, the antioxidant activity reported in Fig. 2 was 3 times lower than the FRAP value calculated from the phenolic content determined after acid hydrolysis (Table 1). This may confirm that the antioxidant activity of cherry fibers determined in water, which is the natural solvent for food processing and formulation, was lower than that expected after alkaline hydrolysis of cell wall-associated phenolics. Though lower pH exists in the gut ≈8.2), higher proportion of the total phenolic content (Table 1) is then expected to be available during duodenal digestion from cherry fibers. The acid medium in the stomach (pH ≈ 1.4) may also contribute to phenolic extraction from cherry fibers before reaching the gut.

3.4. Emulsion stabilization

Cherry fibers were assayed in their capability to constitute emulsions which could also be stable for at least the first period of ingredient mixing for making food formulations. MCT oil was used because it is usually applied to dissolution of hydrophobic food additives. Oil-in-water emulsions with an oil volume fraction $\phi = 50\%$ were developed with cherry fibers. After shearing, these systems showed an associated foaming capacity of ≈128.7% (Eq. (2)), which did not permit to drain the emulsion formed for at least the first 48 h after constitution. Therefore, the foam-emulsion system obtained was studied through dynamic shear assays under linear viscoelastic condition. The rheological behavior of these emulsions containing cherry fibers showed a high elasticity since G' was always above G'' along the frequency range swept ($\omega = 0.1$–50 rad s^{-1}). G' and G'' experimental data respectively fitted to a power law type model (Eqs. (3) and (4)) and parameters are reported in Table 3. The emulsion made with 'Chelan' fiber showed the highest solid viscoelastic behavior because presented the lowest dependence of the elastic modulus on frequency, as shown by the A-exponent values. Although 'Chelan' and 'Brooks' emulsions showed higher G'_0 value than 'Sunburst' system

Table 3
Parameters[a] obtained by fitting the mechanical spectra data to the power law type model[b], obtained from the oil-in-water emulsions.

Cherry fiber	G'			
	G'_0 (Pa)	A	R^2	$P<$
Chelan	167 ± 1	0.043 ± 0.005	0.836	0.01
Brooks	190 ± 1	0.094 ± 0.005	0.951	0.001
Sunburst	52.2 ± 0.2	0.081 ± 0.003	0.978	0.001
	G''			
	G''_0 (Pa)	B	R^2	$P<$
Chelan	103.8 ± 0.9	0.141 ± 0.007	0.965	0.001
Brooks	124.6 ± 0.6	0.194 ± 0.003	0.996	0.0001
Sunburst	35.1 ± 0.4	0.142 ± 0.006	0.970	0.001

[a] Mean and standard deviation ($n = 3$) are shown.
[b] Eqs. (3) and (4) (Kim and Yoo, 2006): A and B are the exponents related to the frequency dependence of the rheological parameters and G'_0 and G''_0 are the equilibrium moduli.

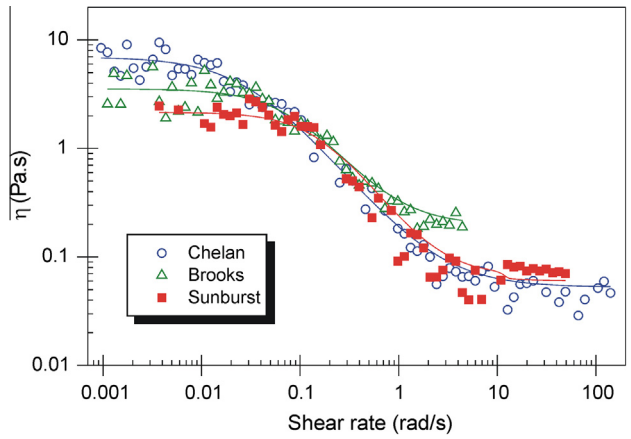

Fig. 3. Flow curves obtained from the emulsion aqueous phase developed from 'Chelan', 'Brooks' and 'Sunburst' cherry fibers. Continue lines show the cross' model fitted.

(Table 3), 'Brooks' and 'Sunburst' emulsions showed similar frequency dependence. As generally observed in this kind of viscoelastic systems, loss modulus was more frequency dependent (higher *B*-exponent values) than *G′* (Table 3).

Oil droplets are known to be susceptible to be linked by pectins solubilized in the water phase and concentrated at the oil–water interface. As previously mentioned, less than 4% of the total polysaccharide content of cherry fibers was water-soluble, mainly constituted by high methoxyl pectins (Basanta el al., 2013). The aqueous phase where cherry fibers swelled (pH = 6.5) was separately assayed, being viscous and pseudoplastic under the shear stress applied (Fig. 3). The upper Newtonian viscosity observed at the lowest shear rates was higher (7.0 ± 0.4 Pa s) for the polysaccharide solution obtained from 'Chelan' cherry fibers ($p < 0.05$) than from 'Brooks' (3.5 ± 0.2 Pa s) and 'Sunburst' (2.16 ± 0.08 Pa s) fibers, as determined by fitting to the Cross model (Eq. (5)). The adjusted model is shown as a continuous line for each curve (Fig. 3). The shear rate value at the onset of the shear-thinning or pseudoplastic region increases as the steady network is more fluid: Chelan < Brooks < Sunburst (Fig. 3). From the thickening effect observed, biopolymers of cherry fibers acted as stabilizers of the foam as well as of the oil-in-water emulsions. On the other hand, pectins can reduce the surface tension (Fissore et al., 2013) and proteins are responsible for the emulsifying capacity (Williams et al., 2005).

4. Conclusions

Fiber materials isolated through ethanolic treatment from 'Chelan', 'Brooks' and 'Sunburst' cherry fruits discarded at harvesting were constituted by the cell wall biopolymers. Fiber powders with a particle equivalent diameter of ≈520 μm and a true density of ≈1.50 g/cm^3 showed important hydration properties related to the sample porosity and chemical composition, as well as to cherry variety. Bioactive molecules such as phenolic compounds were found as an integral part of the isolated cherry fibers, which showed antioxidant capacity in water. Cherry residues of harvesting were upgraded as useful functional ingredient and dietary fiber able to deliver phenolics into the gut. As similar properties were found for the three cherry fibers, residues of the three varieties can be processed jointly, being economically convenient.

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