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Research Article

Development of Semiliquid Ingredients from Grape Skins and Their Potential Impact on the Reducing Capacity of Model Functional Foods

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Grape skins (GS), which can be considered as reusable coproducts of winemaking, were processed to develop semiliquid ingredients for functional foods, as an alternative to powdered GS, which needs high energy input for drying. Processing of semiliquid GS ingredients included blanching, dilution to obtain dispersions with 2% or 10% of dry solids, milling, homogenization, and pasteurization. The individual phenolic contents and *in vitro* ferric ion reducing capacity (FRAP) of semiliquid GS ingredients were compared with those of air-dried and freeze-dried GS. With respect to freeze-dried GS, the recovery of FRAP values was ~75% for both air-dried GS and 2% GS dispersion and 59% for 10% GS dispersion. The average particle size diameters of solids in semiliquid GS ingredients were similar to those observed in commercial apple skin products. Possible applications of GS semiliquid ingredients to increase the reducing capacity of food 10 times include formulation into beverages and ice-type desserts and use in bakery products.

1. Introduction

Bioactive compounds such as phenolics present in winemaking by-products have displayed interesting health promoting activities both *in vitro* and *in vivo* [1] and thus the reuse of phenolic-rich grape skin (GS) in the food chain has been proposed. The recovery of phenolic-rich GS includes drying and milling, drying and extraction of phenolic fractions, or drying, extraction, and encapsulation of phenolic compounds [2–5]. Food applications described so far have included uses in meat and fish-based products [6, 7], bread and bakery products [8, 9], dairy products [10], and fruit purees [4, 11].

No information is present in the literature regarding the possibility of processing GS into semiliquid ingredients, in order to avoid an energy- and time-consuming step such as drying and/or to open up new applications. For this purpose, blanching aimed at polyphenol oxidase (PPO) and peroxidase (POD) deactivation, homogenization, and pasteurization should be applied to achieve product stability. Regarding the energy input for processing dry products, it is worth considering that drying is one of the most energy-consuming operations in food technology, with 3200–11,500 kJ consumed per kilogram of water evaporated, depending on the dryer and conditions used [12]. Conversely, for liquid products, blanching and pasteurization are energy-consuming operations, and their transportation costs, which depend on process logistics, are higher than for dried products [12]. Hence, the availability of both dried and liquid GS ingredients could offer the means to minimize the energy demand relative to a specific food process and plant logistic.

This research focused on the study of the effects of GS processing into semiliquid micronized ingredients on the phenolic profile and reducing capacity compared to

air-drying and freeze-drying. Potential applications of these ingredients in a wide array of foods were then analyzed in terms of the resulting increase of the reducing capacity of the target foods.

2. Materials and Methods

2.1. Chemicals. Standards of flavanols, flavonols, and anthocyanins were purchased from Extrasynthese (Lyon, France). All other chemicals were purchased from Sigma-Aldrich Italia (Milan, Italy).

2.2. Grape Skins (GS) and Commercial Fibers. Red grape pomace of the Barbera variety was provided by a winery located in Northern Italy. At the winery, grape pomace was sieved (with a 5 mm sieve) to separate the skins from the seeds and frozen. The frozen GS were transported to the laboratory. GS (20% dry weight, d.w.) was thawed and subjected to steam blanching for 1 and 2 min, respectively, with the vapor released during water heating at 100°C and then quickly cooled at 4°C in ice to ambient temperature (25°C). The samples subjected to 2 min blanching showed no residual PPO and POD activities and hence were further processed, in parallel with unblanched GS as control. Blanched and unblanched GS were diluted with 8.0 mM potassium citrate buffer, pH 3.0, at 1 : 10 (2% d.w.) or 1 : 2 (10% d.w.) to allow for easier wet milling. The diluting buffer was chosen since anthocyanin stability is maximum at pH 3.0 [13]. Wet milling was performed with a Waring Blender for 1 min at 1,700 rpm. After wet milling, the unblanched GS were not processed further, while the blanched GS were homogenized and pasteurized. The blanched 10% GS were further homogenized by prolonging milling in the Waring Blender for 3.5 min. The blanched 2% GS were homogenized with Ultra-Turrax for 1 min at 15,000 rpm. After that, both 2% GS and 10% GS were pasteurized to achieve 6-decimal (6D) reductions of the target microorganism *Alicyclobacillus acidoterrestris* as described previously [11].

As an alternative treatment, part of the thawed GS was air-dried at 50–55°C for approximately 3.5 h until the residual moisture content was <5% and then milled in the Waring Blender for 3.5 min (AD). The powder obtained was sieved using the Octagon Digital sieve shaker (Endecotts Ltd., London, UK), with a certified sieve (500 μm). A ground freeze-dried sample (processed by the Edwards Minifast MFD 01 freeze-drier, UK) was analyzed as a reference sample (FD) to calculate the recovery of phenolic compounds and reducing capacity in the other GS samples. Two commercial apple skin fiber samples were obtained from the market.

2.3. Moisture, Dietary Fiber, Protein, Carbohydrate, and Fat Content. The moisture content of wet GS was determined by drying in a vacuum oven at 70°C for 18 h. The pH was determined with a pH meter (Sartorius, Ravenna, Italy). Protein, fat, carbohydrate, and dietary fiber content was measured on the freeze-dried GS according to the Association of Official Analytical Chemists (AOAC) official methods of analysis [14]. Glucose and fructose were determined as described previously [15].

2.4. Particle Size Determination. The analysis of particle size distribution (PSD) of GS samples and commercial apple skin fiber was performed according to the specifications reported in the international standard ISO 13320 [16] using a Malvern 2000 Laser granulometer (Malvern Instruments Ltd., Malvern, UK) equipped with a single laser source at $\lambda = 633$ nm. The samples were diluted with deionized water (1 : 500 ratio). Calculations for PSD and its descriptors were made assuming a spherical particle shape with enhanced calculation sensitivity.

The descriptors considered were the surface-weighted mean diameter (μm), that is, $D[3,2]$, also called Sauter mean diameter, and the volume moment-weighted mean diameter (μm), or $D[4,3]$, defined as

$$D[3,2] = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2},$$
$$D[4,3] = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3}, \quad (1)$$

where d_i is the ith diameter class and n_i is the respective number of particles per unit volume. The width of the distribution (i.e., span) is defined as

$$\text{Span} = \frac{(d0.9 - d0.1)}{d0.5}, \quad (2)$$

where $d0.1$, $d0.9$, and $d0.5$ are 10, 50, and 90% quantiles, respectively.

2.5. Determination of Polyphenol Oxidase (PPO) and Peroxidase (POD) Activities. Prior to determining PPO and POD activities, 50 g of GS (20% d.w.) was added to 500 mL of McIlvaine buffer at pH 6.5, 1 M sodium chloride, and 5% (w/w) polyvinylpolypyrrolidone. The mixture was homogenized with a Waring Blender for 1 min at 1,700 rpm and then centrifuged (10,000 xg for 10 min). Fresh apple was used as a control. The enzymatic activities were evaluated in the supernatant. PPO activity of GS was determined following the methods of Alvarez-Parrilla et al. [17] and expressed on a fresh weight basis as arbitrary units, that is, $\Delta A_{400\,\text{nm}} \cdot g^{-1} \cdot \text{min}^{-1}$. POD activity of GS was determined following the methods of Ahn et al. [18] and expressed on a fresh weight basis as nmol of guaiacol$\cdot g^{-1} \cdot \text{min}^{-1}$ (extinction coefficient of guaiacol at 470 nm: 26.6 $\text{mM}^{-1}\,\text{cm}^{-1}$).

2.6. Phenolic Extraction and HPLC Characterization. Phenolic extraction with methanol : water : HCl (80 : 20 : 0.1, v/v/v) and HPLC characterization were performed as described previously [4]. Duplicate extractions were performed for each sample. Results were expressed as milligram per kilogram of product or as percent recovery with respect to freeze-drying.

2.7. Total Phenolic Content, Soluble Proanthocyanidin Content, and Ferric Ion Reducing Antioxidant Power (FRAP) Assay. The Folin–Ciocalteu assay and FRAP assay were performed as described previously [4]. Total phenolics were expressed as grams of gallic acid equivalents (GAE) per

Table 1: Percent recovery of soluble proanthocyanidins, monomeric flavanols, anthocyanins, flavonols, total phenolics, and FRAP values after GS processing, considering the freeze-dried GS as a reference.*

	% recovery					
	Proanthocyanidins	Monomeric flavanols**	Anthocyanins**	Flavonols**	Total phenolics	FRAP values
Semiliquid GS, 2% d.w.						
UM	$51^{e} \pm 3$	$82^{f} \pm 5$	$54^{d} \pm 1$	$71^{f} \pm 3$	$66^{ef} \pm 3$	$78^{bc} \pm 5$
BM	$51^{e} \pm 1$	$167^{b} \pm 8$	$80^{b} \pm 6$	$123^{c} \pm 5$	$71^{cde} \pm 3$	$77^{bc} \pm 4$
H	$50^{e} \pm 2$	$204^{a} \pm 1$	$81^{b} \pm 1$	$128^{c} \pm 1$	$76^{cd} \pm 1$	$85^{b} \pm 5$
P	$37^{f} \pm 4$	$120^{d} \pm 6$	$63^{cd} \pm 5$	$179^{a} \pm 8$	$66^{ef} \pm 6$	$75^{bcd} \pm 2$
Semiliquid GS, 10% d.w.						
UM	$46^{ef} \pm 5$	$25^{g} \pm 2$	$50^{d} \pm 1$	$70^{f} \pm 3$	$54^{g} \pm 3$	$46^{f} \pm 5$
BM	$59^{d} \pm 2$	$23^{g} \pm 2$	$81^{b} \pm 4$	$130^{c} \pm 7$	$70^{def} \pm 2$	$70^{cde} \pm 3$
H	$67^{c} \pm 4$	$28^{g} \pm 1$	$95^{a} \pm 1$	$131^{c} \pm 4$	$77^{cd} \pm 3$	$78^{bc} \pm 3$
P	$49^{e} \pm 4$	$30^{g} \pm 1$	$63^{cd} \pm 6$	$158^{b} \pm 11$	$63^{ef} \pm 3$	$59^{e} \pm 4$
Dried GS						
AD	$80^{b} \pm 2$	$142^{c} \pm 8$	$70^{bc} \pm 2$	$92^{de} \pm 2$	$85^{b} \pm 1$	$85^{b} \pm 3$
FD	$100^{a} \pm 8$	$100^{e} \pm 5$	$100^{a} \pm 6$	$100^{d} \pm 6$	$100^{a} \pm 3$	$100^{a} \pm 5$

*Values represent mean ± SE. **Sum of compounds identified by HPLC. Different letters in the same column indicate significant differences (LSD, $p < 0.05$). UM: unblanched and milled; BM: blanched and milled; H: homogenized; P: pasteurized; AD: air-dried; FD: freeze-dried.

kilogram of product. The FRAP values were expressed as mmol of Fe(II) sulfate equivalents per kilogram of product. Soluble proanthocyanidin was measured as described previously [4]. Briefly, 1 mL of the sample extract diluted with methanol : water : HCl (80 : 20 : 0.1, v/v/v) was added to 6 mL of *n*-butanol : HCl (95 : 5, v/v) and 0.2 mL of 2% $NH_4Fe(SO_4)_2 \cdot 12H_2O$ in 2 M HCl. Hydrolysis was carried out at 95°C for 40 min. The reaction mixtures were cooled and the absorbance was recorded at 550 nm by a Jasco UVDEC-610 spectrophotometer (Jasco Europe, Cremella, Italy) against a blank made as the sample but incubated at room temperature. For each sample extract, 2–4 dilutions were assessed in duplicate. Soluble proanthocyanidin amount was expressed as grams per kilogram of product. These values were also expressed as percent recovery with respect to freeze-drying.

2.8. Statistical Analysis of Data. Experimental data were analyzed by one-way ANOVA using the least significant difference (LSD) as a multiple range test and by linear regression analyses using Statgraphics 5.1 (STCC Inc., Rockville, MD). Results are reported as average ± standard error (SE).

3. Results and Discussion

3.1. Major Components of Grape Skins. The major components of wet GS recovered from winemaking (20% of dry solids, d.w.) were dietary fiber, 112 ± 2 g/kg; protein, 18 ± 1 g/kg; ash, 18 ± 1 g/kg; fat, 15 ± 1 g/kg; and soluble carbohydrates, 7.4 ± 0.2 g/kg. Proanthocyanidins were the prevalent antioxidant class, with a content of 3.5 ± 0.2 g/kg. The contents of monomeric flavanols, anthocyanins, and flavonols (calculated as the sum of compounds identified by HPLC) were 61 ± 1, 130 ± 20, and 110 ± 2 mg/kg, respectively.

3.2. PPO and POD Activity. In wet GS, POD activity was 109 ± 9 nmol of guaiacol·g^{-1}·min^{-1}. Although the presence of POD in fermented GS is generally neglected, the observed POD activity fell in the range of the values found for the typical fruit affected by enzymatic browning, that is, apple, which is 39–599 nmol of guaiacol·g^{-1}·min^{-1} [18]. PPO activity of wet GS was 0.075 ± 0.001 $\Delta A_{400\,nm} \cdot g^{-1} \cdot min$, which was also similar to that of fresh apple used as a control. After milling of unblanched GS, there was a decrease in all phenolic classes (Table 1). In 10% GS, percent recovery of total phenolics was lower than in 2% GS, indicating that the oxidative reactions were accelerated by increased concentration of solids. Flavanols are substrates for both PPO and POD [19]. Flavonols can also be oxidized by both PPO and POD [20]. Conversely, proanthocyanidins are not substrates for PPO; however, these compounds can be oxidized by enzymatically generated *o*-quinones through coupled-oxidation mechanisms by which they are retransformed into the *o*-diphenolic substrate [21]. Moreover, their oxidation due to POD action cannot be ruled out [22]. Kader et al. [23] have shown that anthocyanins are also degraded through coupled-oxidation mechanisms by *o*-quinones generated by the PPO. Additionally, Movahed et al. [24] have demonstrated the role of POD in the degradation of grape anthocyanins.

3.3. Blanching. Upon 2 min blanching at 100°C, no residual PPO and POD activity was observed in GS. As shown in Table 1, in 2% GS, the recovery of soluble proanthocyanidins after 2 min blanching was the same as observed for the unblanched GS and it was only 50% with respect to the freeze-dried GS. This result suggests that wet milling could have promoted the formation of proanthocyanidin complexes within the GS matrix, causing a decrease in solubility. In fact, molecular interactions occur between high-molecular-mass proanthocyanidins and proteins, which is driven by hydrogen bonding or hydrophobic interaction and causes the formation of insoluble polyphenol–protein aggregates [4]. However, during blanching, partial proanthocyanidin

Table 2: Individual flavanol and flavonol contents (mg/kg) and relative abundance (% of total, in brackets) in GS after processing.*

	Flavanols				*Flavonols*			
	C		E		Q		Q-glc	
	mg/kg	(%)	mg/kg	(%)	mg/kg	(%)	mg/kg	(%)
Semiliquid GS, 2% d.w.								
BM	$6.0^{b} \pm 0.3$	(60)	$4.0^{b} \pm 0.2$	(40)	$5.3^{b} \pm 0.2$	(43)	$7.1^{a} \pm 0.3$	(57)
H	$7.5^{a} \pm 0.1$	(61)	$4.8^{a} \pm 0.1$	(39)	$5.4^{b} \pm 0.1$	(43)	$7.3^{a} \pm 0.1$	(57)
P	$4.5^{c} \pm 0.3$	(63)	$2.7^{c} \pm 0.1$	(38)	$10.3^{a} \pm 0.5$	(58)	$7.6^{a} \pm 0.3$	(42)
Semiliquid GS, 10% d.w.								
BM	$4.2^{b} \pm 0.5$	(58)	$3.0^{a} \pm 0.2$	(42)	$29^{ab} \pm 2$	(42)	$40^{ab} \pm 2$	(58)
H	$5.6^{ab} \pm 0.1$	(64)	$3.2^{a} \pm 0.1$	(36)	$20^{b} \pm 1$	(29)	$50^{a} \pm 1$	(71)
P	$6.3^{a} \pm 0.1$	(67)	$3.1^{a} \pm 0.1$	(33)	$43^{a} \pm 9$	(52)	$40^{b} \pm 3$	(48)
Dried GS								
AD	$262^{a} \pm 16$	(60)	$174^{a} \pm 10$	(40)	$116^{a} \pm 3$	(24)	$373^{a} \pm 10$	(76)
FD	$185^{b} \pm 10$	(60)	$122^{b} \pm 3$	(40)	$110^{a} \pm 8$	(21)	$424^{a} \pm 25$	(79)

*Values represent mean ± SE. For every sample group (semiliquid GS, 2% d.w.; semiliquid GS, 10% d.w.; and dried GS), different letters in the same column indicate significant differences among samples (LSD, $p < 0.05$). C: catechin; E: epicatechin; Q: quercetin; glc: glucoside; BM: blanched and milled; H: homogenized; P: pasteurized; AD: air-dried; FD: freeze-dried.

degradation also occurred. In fact, the content of monomeric flavanols (sum of catechin and epicatechin) was higher in blanched GS than in unblanched GS and more than 100%. This probably resulted from proanthocyanidin hydrolysis favored by heating under acidic conditions. It is worth noticing that, as shown in the previous paragraph, the amount of soluble proanthocyanidins in GS is ~60 times higher than that of monomeric flavanols. Hence, a moderate extent of proanthocyanidin hydrolysis would result in a considerable increase of monomeric flavanols. Conversely, in 10% GS, the recovery of soluble proanthocyanidins after blanching was moderately higher than that in unblanched GS, but the recovery of monomeric flavanols was very low in both blanched and unblanched GS. This result suggests that, in the concentrated medium, the extent of proanthocyanidin hydrolysis was lower than in the diluted medium. The percentages of relative abundance for catechin and epicatechin, equal to 61 and 39, respectively, were the same in blanched GS and freeze-dried GS (Table 2).

Flavonol recovery after blanching was higher than 100% in both 2% and 10% GS products, most probably due to increased extraction of these compounds from the cell wall upon heat treatment. Comparing the relative abundance of flavonols, the aglycone quercetin, which was 21% of total flavonols in freeze-dried GS, increased to 43% after blanching, while quercetin glucoside decreased from 79% to 57%, indicating the occurrence of hydrolysis and/or increased extraction of the aglycone in both 2% and 10% GS (Table 2).

The recovery of total anthocyanins after blanching was 80%, both in 2% and in 10% GS, which was higher than in unblanched GS (Table 1). The relative abundance of the individual anthocyanins remained the same as in the freeze-dried GS (Table 3).

Total phenolics and FRAP values in 2% GS were ~70% those of freeze-dried GS, both in blanched and in unblanched GS. This probably resulted from the marked degradation of proanthocyanidins even when blanching was applied. In 10% GS, the recovery of total phenolics and FRAP value was also ~70%, while in unblanched 10% GS, the degradation of these parameters was significantly higher.

3.4. Homogenization. From a technological point of view, homogenization is necessary to improve ingredient dispersion in the food matrix. As shown in Table 1, homogenization of blanched GS did not change the recovery of phenolics, except for a moderate increase in the recovery of monomeric flavanols in 2% GS and anthocyanin and soluble proanthocyanidin in 10% GS, which did not affect FRAP values.

3.5. Pasteurization. Upon application of 6D treatment, phenolic compounds generally decreased in both 2% GS and 10% GS products, except for flavonols that increased, probably resulting from increased solubility (Table 1). Quercetin increased compared to quercetin glucoside (Table 2), suggesting increased extraction of the aglycone, as observed during blanching. The relative abundance of anthocyanins did not vary after the pasteurization treatment (Table 3), indicating that these compounds have similar thermal stability. For the pasteurized 2% GS, FRAP value was 75% that of freeze-dried GS (Table 1), corresponding to 4.1 ± 0.1 mmol Fe(II) eq/kg, which is in the range of that of fruit juices [25]. Although for the pasteurized 10% GS FRAP value was only 59% that of freeze-dried GS (Table 1), it was much higher than those of fruit juices, equal to 18 ± 1 mmol Fe(II) eq/kg. Hydroxymethylfurfural has been shown to have cytotoxic, genotoxic, mutagenic, and carcinogenic effects [26]. This compound is generally found in pasteurized fruit products, at levels in the range of 0.13–0.32 mg/L [27]. Conversely, it was not found in the GS samples (detection limit was 0.02 mg/L), probably due to its low level of reducing sugars in the fermented GS.

3.6. Drying. Air-drying of GS is commonly performed in the temperature range of 40–80°C [28]. In this study, air-drying

Table 3: Individual anthocyanin content (mg/kg) and relative abundance (% of total, in brackets) in GS after processing.*

	Anthocyanins											
	Dp-glc		Cy-glc		Pt-glc		Pn-glc		Mv-glc		Mv-*pc*-glc	
	mg/kg	(%)	mg/kg	(%)	mg/kg	(%)	mg/kg	(%)	mg/kg	(%)	mg/kg	(%)
Semiliquid GS, 2% d.w.												
BM	$17.0^{a} \pm 1.3$	(18)	$8.0^{a} \pm 0.6$	(8)	$20.2^{a} \pm 1.5$	(21)	$9.9^{ab} \pm 0.7$	(10)	$40.3^{a} \pm 2.5$	(42)	$1.07^{a} \pm 0.09$	(1)
H	$17.1^{a} \pm 0.1$	(18)	$8.2^{a} \pm 0.1$	(8)	$20.3^{a} \pm 0.2$	(21)	$10.2^{a} \pm 0.1$	(10)	$41.2^{a} \pm 0.4$	(42)	$1.11^{a} \pm 0.01$	(1)
P	$12.4^{b} \pm 1.1$	(16)	$6.6^{b} \pm 0.4$	(9)	$15.6^{b} \pm 1.2$	(21)	$8.0^{c} \pm 0.6$	(11)	$32.4^{b} \pm 2.1$	(43)	$1.01^{a} \pm 0.16$	(1)
Semiliquid GS, 10% d.w.												
BM	$88^{a} \pm 5$	(16)	$47^{ab} \pm 2$	(9)	$112^{ab} \pm 6$	(21)	$58^{ab} \pm 3$	(11)	$231^{ab} \pm 13$	(43)	$6.7^{b} \pm 1$	(1)
H	$84^{a} \pm 1$	(13)	$56^{a} \pm 1$	(9)	$134^{a} \pm 2$	(21)	$71^{a} \pm 2$	(11)	$280^{a} \pm 5$	(44)	$9.0^{a} \pm 0.2$	(1)
P	$56^{b} \pm 5$	(13)	$38^{b} \pm 5$	(9)	$87^{b} \pm 8$	(21)	$47^{b} \pm 5$	(11)	$183^{b} \pm 20$	(44)	$6.0^{b} \pm 0.7$	(1)
Dried GS												
AD	$723^{b} \pm 44$	(16)	$388^{b} \pm 10$	(8)	$984^{b} \pm 21$	(21)	$511^{b} \pm 13$	(11)	$1964^{b} \pm 39$	(42)	$56^{b} \pm 1$	(1)
FD	$1235^{a} \pm 66$	(19)	$581^{a} \pm 44$	(9)	$1412^{a} \pm 93$	(21)	$704^{a} \pm 52$	(11)	$2630^{a} \pm 160$	(40)	$83^{a} \pm 5$	(1)

*Values represent mean ± SE. For every sample group (semiliquid GS, 2% d.w.; semiliquid GS, 10% d.w.; and dried GS), different letters in the same column indicate significant differences among samples (LSD, $p < 0.05$). Dp: delphinidin; Cy: cyanidin; Pt: petunidin; Pn: peonidin; Mv: malvidin; glc: glucoside; *pc*: *p*-coumaroyl; BM: blanched and milled; H: homogenized; P: pasteurized; AD: air-dried; FD: freeze-dried.

of GS at 50°C for 3.5 h caused a decrease in total phenolic content, soluble proanthocyanidins, anthocyanins, and FRAP values, which showed percent recoveries of 85, 80, 70, and 85, respectively (Table 1). Monomeric flavanols increased with a percent recovery of 142, probably due to proanthocyanidin hydrolysis. The relative abundance of monomeric flavanols was the same as that for the freeze-dried GS. Conversely, the recovery of total flavonols was not significantly different from 100%. However, there was a slight increase in the relative abundance of quercetin compared to quercetin glucoside, suggesting the occurrence of hydrolysis which however was not as pronounced as that occurring during pasteurization (Table 2). Planinic et al. [28] found that drying of GS in the temperature range of 60–80°C for 1.5–3 h causes a decrease in total phenolic compounds, total flavonoids, total extractible proanthocyanidins, and antioxidant activity by 13.2%, 43.1%, 15.3%, and 21.0%, respectively. These values are in the range of the losses found in the present study. Higher antioxidant losses during GS drying at 60°C were observed by Torres et al. [29], especially for anthocyanins. However, the duration of the process was also longer (24 h). Drying of fruits promotes the Maillard reaction, which is evaluated by measuring hydroxymethylfurfural [30]. Hydroxymethylfurfural was not detectable in the air-dried GS. On the other hand, this compound was found in sun-dried raisins in the concentration range of 1.7–57 mg/kg [31]. This could be due to either the low sugar content in the fermented GS or the shorter process applied with respect to sun-drying.

3.7. Particle Size Distribution and Sedimentation Behavior. The PSD of GS samples was analyzed in comparison with that of commercial fiber-rich samples. The surface-weighted mean diameter, that is, $D[3,2]$, of both 2% and 10% GS was 23.8 μm, lower than that observed for the commercial apple skin products (Table 4). For commercial oat, wheat, apple, and bamboo fibers dispersed in water, $D[3,2]$ was in the range of 14.4–34.6 μm [32]. On the other hand, the moment weight mean diameter, that is, $D[4,3]$, of the 10% GS was 174 μm, slightly higher than that of the 2% GS, that is, 159 μm, falling in the range of commercial apple fibers. This result indicates that the 10% GS had higher amounts of large particles than the 2% GS. Indeed, the span was also higher for the 10% GS than for the 2% GS, indicating that homogenization led to the narrowest PSD in the most diluted GS sample (Figure 1).

As for the semiliquid GS products, the air-dried GS were milled to allow for easier dispersion in the food matrix. $D[3,2]$ and $D[4,3]$ of the air-dried GS were higher than of the 2% and 10% GS, while the span was lower, indicating the narrowest PSD (Table 4, Figure 1). The semiliquid GS products formed a stable suspension in water, while the air-dried GS tended to precipitate fast (Figure 2). Thus, the semiliquid GS ingredients could be more suitable than the air-dried GS for use in semiliquid and gel-like food products.

3.8. Application Perspectives for the Ingredients Derived from Grape Skins. An array of potential applications for the GS ingredients are shown in Table 5, where the target foods are grouped into two clusters. Cluster 1 includes beverages and ice-type desserts, which have not been proposed as target foods for GS fortification previously. Within beverages, energy drinks with and without sugar, noncarbonated flavored drinking water, and drinks supplemented with vitamins have a very low or no detectable antioxidant activity [33]. All the products in Cluster 1 could reach the FRAP value of orange juice (0.4 mmol Fe(II)/kg) through formulation with the 2% GS ingredient. Cluster 2 includes bread and other bakery products, which have already been proposed as target foods for addition of dried GS [8, 9]. The addition of semiliquid GS product to dough instead of drying GS could be advantageous as a means of shortening the total processing time for the winemaking derived ingredient and decreasing

Table 4: Particle size distribution for the proposed dried and semiliquid food ingredients recovered from GS and for commercial apple skin fibers*.

	$D[3,2]$ μm	$D[4,3]$ μm	Span
Semiliquid GS, 2% d.w.			
P	$23.90^{a} \pm 0.19$	$159.24^{b} \pm 0.95$	$3.19^{b} \pm 0.02$
Semiliquid GS, 10% d.w.			
P	$23.82^{a} \pm 0.18$	$174.21^{a} \pm 2.16$	$4.16^{a} \pm 0.07$
Dried GS	-		
AD	$37.19^{b} \pm 0.20$	$231.94^{c} \pm 1.41$	$1.88^{c} \pm 0.01$
Apple skin fiber			
AF1	$39.86^{c} \pm 0.07$	$163.13^{b} \pm 0.76$	$2.51^{d} \pm 0.00$
AF2	$91.02^{d} \pm 0.38$	$298.02^{d} \pm 1.60$	$2.65^{e} \pm 0.01$

Results are reported as average ± SE. Different superscript letters within the same column (a–e) indicate significant differences (LSD, $p < 0.05$). P: pasteurized; AD: air-dried. AF1 and AF2 are two commercial apple skin fibers.

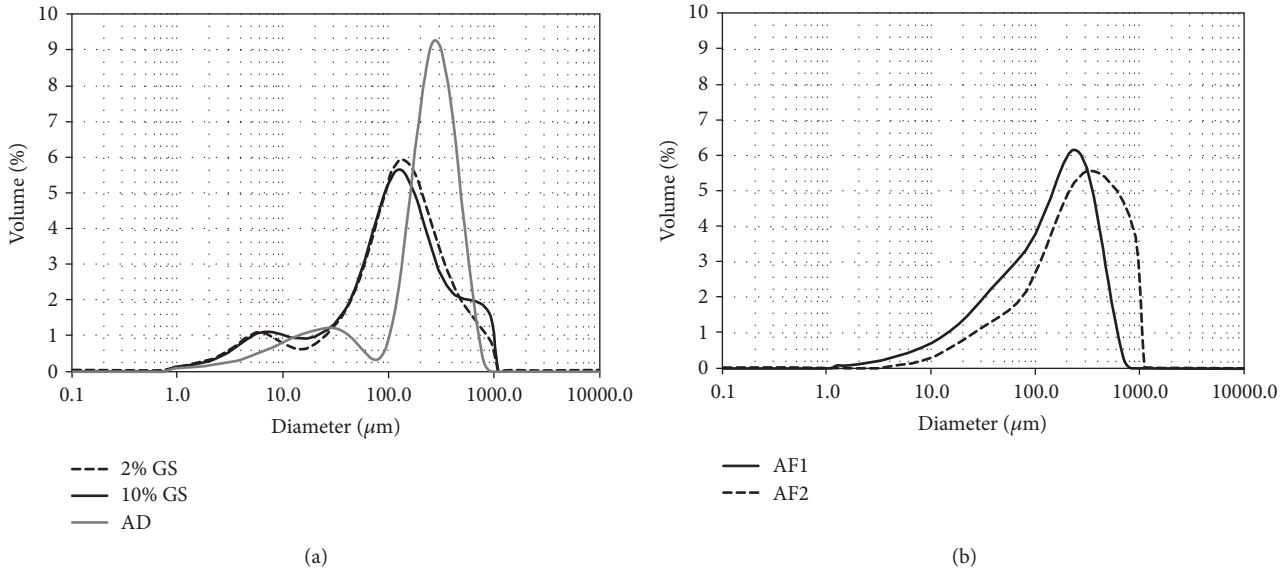

Figure 1: Particle size distribution of semiliquid 2% and 10% GS samples and air-dried GS [(a): 2% GS, 10% GS, and AD] and commercial apple skin samples [(b): AF1 and AF2].

the energy input. Bread and bakery products could increase their reducing capacity up to 10 times through addition of the 10% GS semiliquid ingredient.

4. Conclusion

The new processing scheme of GS based on blanching, pasteurization, and homogenization to obtain semiliquid ingredients, as well as the already proposed air-drying and milling process to obtain a dried ingredient, resulted in high antioxidant recovery with a decreased energy input compared to the addition of dried GS. The semiliquid GS products obtained could provide increased reducing capacity (up to 10-fold) to a wide array of food formulations, including beverages, ice-type desserts, and bread and bakery products.

Additional Points

Practical Applications. Grape skins (GS) recovered from winemaking can be considered as reusable coproducts, as they have very high phenolic and fiber contents. Various applications of GS as food ingredients have been proposed to develop fortified, added-value bakery, dairy, meat, and fish products. For this purpose, GS is dried and milled to obtain a powder. In this study, GS was processed into semiliquid ingredients in order to open up new food applications

Table 5: Potential ability of semiliquid food ingredients recovered from GS to increase the FRAP values (mmol Fe(II) eq/kg) of various foods*.

Food	GS ingredient	FRAP value (mmol Fe(II) eq/kg)
Cluster 1: beverages and ice-type desserts		
Energy drinks with or without sugar		
Unfortified	–	not detectable
GS-fortified (1 : 10)	2% GS	0.41
Noncarbonated flavored water		
Unfortified	–	not detectable
GS-fortified (1 : 10)	2% GS	0.41
Soft drink (Cola, Fanta)		
Unfortified	–	0.04–0.08
GS-fortified (1 : 10)	2% GS	0.44–0.48
Ice-type desserts		
Unfortified	–	0.00–0.09
GS-fortified (1 : 10)	2% GS	0.41–0.49
Cluster 2: bread and bakery products		
Bread		
Unfortified	–	0.31–0.53
GS-fortified (1 : 10)	10% GS	1.83–1.85
Waffles		
Unfortified	–	0.08–0.20
GS-fortified (1 : 10)	10% GS	1.87–1.98
Muffins		
Unfortified	–	0.37–0.46
GS-fortified (1 : 10)	10% GS	2.13–2.21
Biscuits		
Unfortified	–	0.01–0.33
GS-fortified (1 : 10)	10% GS	1.81–2.01

*FRAP values of conventional foods have been reported elsewhere [33]. FRAP values for 2% GS, and 10 % GS were 4.1, and 18 mmol Fe(II) eq/kg, respectively. FRAP values of the GS-fortified foods were calculated based on the above-reported values considering addition level 1 : 10 for both the 2% and 10% GS.

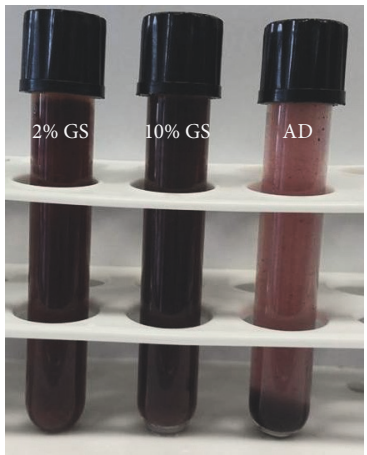

Figure 2: Sedimentation behavior of semiliquid GS, 2% d.w. (2% GS); semiliquid GS, 10% d.w. (10% GS); and air-dried GS (AD). The 2% GS sample was not diluted, while the 10% GS and AD samples were diluted with 8.0 mM potassium citrate buffer, pH 3.0, to achieve 2% of dried solids as for 2% GS.

in a sustainable perspective. While drying is one of the most energy-consuming operations in food technology, for liquid products, transportation costs can be high. Hence, the availability of both dried and liquid GS ingredients could offer the means to minimize the energy demand relative to a specific food process and plant logistic.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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