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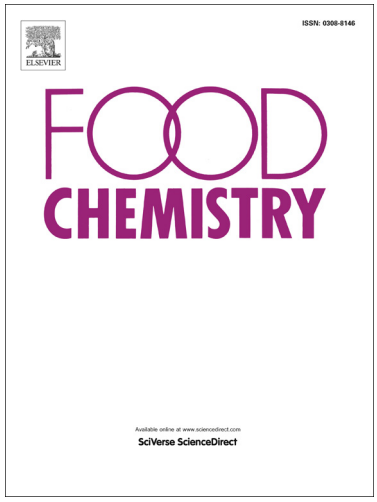

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Abstract

Unripe grapes (UGs) from thinning are an unexploited source of phenols useful as functional ingredient. However, phenols may negative affect sensory quality of food. Chemical and sensory properties of UG phenols in plant-based foods were not investigated before.

With this aim, an extract from UGs, obtained by a green extraction technique, was used to fortify three plant-based food models: carbohydrates/acidic pH/sweet - beetroot purée, proteins/neutral pH/sweet - pea purée and starch/neutral pH - potato purée.

Functional and sensory properties of phenol-enriched foods varied as a function of their composition and original taste. The amount of UG phenols recovered from potato purée was higher than that recovered from beetroot and pea purée, while the antioxidant activity detected in beetroot purée was higher than that in potato and pea purée. Significant variations of sourness, saltiness, bitterness and astringency were induced by UG phenols added to food models. Beetroot purée resulted more appropriate to counteract the negative sensations induced by UG phenols.

Keywords: functional food; unripe grapes; polyphenols; antioxidant activity; sourness; sweetness.

1. Introduction

By-products of the wine industry are rich in phenols and other valuable elements for the human diet such as mineral salts, fibres and vitamins. There are emerging evidences of the potential preventive effects of grape polyphenols towards cardiovascular diseases, diabetes, and degenerative diseases such as cancer (Guilford & Pezzuto, 2011; Mihaylova, Popova, Alexieva, Krastanov & Lante, 2018). The role of phenols from grapes in the prevention of various diseases associated with oxidative stress is primarily related to their antioxidant properties (Guilford & Pezzuto, 2011; Villaño, Fernández-Pachón, Moyá, Troncoso, & García-Parrilla, 2007; Rasines-Perea & Teissedre, 2017).

The sustainability of the winemaking process could be improved by the recovery of high-value bioactive compounds from by-products. Indeed, extensive studies have been made of the biological properties, extraction techniques and applications in the food system of phenols from grape pomace, the main by-product of the wine industry (Beres et al., 2017; Yu & Ahmedna, 2013).

Unripe grapes (UGs) discarded during thinning are an undervalued by-product of vineyard management for the production of high-quality wine (Gatti, Bernizzoni, Civardi, & Poni, 2012; Keller, Mills, Wample, & Spayd, 2005; Ough Cs, 1984). In unripe berries, the most important classes of grape antioxidants (phenolic acids, flavan-3-ols, flavonols, anthocyanins, stilbenes and glutathione) are present to variable extents in function of some factors such as variety, maturity level and season (Adams, 2006) but their anti

oxidant activity and potential application have received scarce scientific attention (Fia, Gori, Bucalossi, Borghini, & Zanoni, 2018; Tinello & Lante, 2017). Low-quality unripe grapes are processed into various traditional juices and sauces with a low pH and variable levels of antioxidant activity ((Dupas de Matos, Magli, Marangon, Curioni, Pasini & Vincenzi, 2018; Öncül & Karabiyikli, 2015). The added value of thinned grapes is higher than the one of other by-products of wine industry that were largely studied and proposed as source of antioxidants. That is because, the thinned grapes have not been exploited to make wine and therefore contain an intact complex of bio-active compounds. Recently, a green extraction technique (i.e. performed without solvents and preservatives) was patented (Fia & Gori, 2016) and applied at an industrial level with the aid of a patented oenological machine (Gori, C., Menichetti, S., & Fia, G. 2014) to obtain an extract from unripe grapes.

Functional food is essentially a marketing term with different definitions and regulations depending on the country (Henry, 2010). Recently in Europe, there has been a growing interest in functional foods. A scientific consensus document was drafted to develop a science-based approach for the emerging concepts in functional food (Europe, 1999). Foods that have been modified by enrichment with bioactive substances are included in the functional food categories and the health benefits of

phenols, beyond basic nutritional values of plant-based food and beverages containing phenols, are reported in a recent review (Shahidi & Ambigaipalan, 2015).

Phenols from plant by-products have been proposed as ingredients for functional foods and beverages preparation to improve their nutritional characteristics (De Toffoli et al., 2019; Torri et al., 2015; Nirmala, Bisht, Bajwa, & Santosh, 2018; Świeca, Gawlik-Dziki, Sęczyk, Dziki, & Sikora, 2018). Some examples of functional food enriched with phenols from tea and Guava are already included in the "food for specified health uses" (FOSHU) and regulated as functional food in Japan (Iwatani & Yamamoto, 2019).

In developing a phenol-enriched functional food, two main aspects need to be investigated: the first concerns the phenols' stability after their addition to the food system, affecting the preservation of their biological activities; the second concerns oral sensations, such as astringency, bitterness and sourness, which can arise after the addition of phenols to food and impair the acceptability of the product to consumers.

From a sensory point of view, it is well documented that phenolic compounds contribute to the bitter and astringent oral sensation of food and beverages (Hufnagel & Hofmann, 2008) and this significantly affects the preference and choice of phenol-rich vegetable foods (Dinnella, Recchia, Tuorila, & Monteleone, 2011). Monomeric and polymeric phenols have been widely studied because of their contribution to wine sensory perception. Monomeric flavan-3-ols, procyanidin dimers and trimers seem to be involved in the perception of astringency and bitterness in red wine (Peleg, Gacon, Schlich, & Noble, 1999). Several authors have studied the bitterness of polyphenols in red wine, demonstrating that larger molecules tend to be less bitter and more astringent (Peleg et al., 1999). More recently, in reconstruction studies it was observed that the puckering astringent offset was caused by a polymeric fraction exhibiting molecular masses above >5 kDa and it was found to be amplified by organic acids (Hufnagel & Hofmann, 2008). Some factors such as pH, acidity, carbohydrate content and saliva characteristics could affect oral sensations (Dinnella,

Recchia, Fia, Bertuccioli, & Monteleone, 2009; Fia, Dinnella, Bertuccioli, & Monteleone, 2009; de Freitas & Mateus, 2012).

To mitigate functional phenol's bitter and astringent potential, the naturally occurring interactions phenols/biopolymers in vegetable foods (Zhang et al., 2014) are an effective strategy (De Toffoli et al., 2019). Plant biopolymers can act as a physical barrier for the phenol stimuli utilized, thus hindering their interactions with sensory receptors and saliva. Many factors affect phenol/biopolymer binding, including pH and reagent features such as chemical compositions, structure, and hydrophobic/hydrophilic characteristics (Kroll, Rawel, & Rohn, 2003). Furthermore, several studies have investigated the chemical features of phenol/biopolymer interactions and their consequences on sensory attributes (Jakobek, 2015).

The health effects of phenols depend on the consumed amount and on their bioavailability. The bioavailability of phenols may vary depending on their bioaccessibility, referred as the release from the food matrix, their stability against several biochemical factors, and their later intestinal absorption (Sengul, Surek & Nilufer-Erdil, 2014). The bioavailability of phenols from many different vegetable sources, including grapes, was systematically studied by Manach, Scalbert, Morand, Rémésy, & Jiménez (2004). In humans, among the most well absorbed phenols there are gallic acid, catechins and quercetin glucosides (Manach et al., 2004). Recently, a phenol extract from grape pomace was included in the diet of Wistar rats by Olivero-David et al., (2018). The same authors observed a partial bioavailability of the phenol extract and an improvement in lipid metabolism of rats.

During food processing, bioactive compounds may undergo chemical degradation and lose their activities. Thermal processing and long-term storage can lead to a decrease in both polyphenol content and antioxidant activity (Yu & Ahmedna, 2013). Other factors such as pH and interactions with other macromolecular food constituents can affect the chemical stability and antioxidant

activity of phenolic compounds (Jakobek, 2015). It is emerging that the bioaccessibility and bioavailability of phenolic compounds are affected by interaction with other macromolecules such as proteins, carbohydrates and lipids. These interactions could give phenolic compounds protection from oxidation during their passage through the gastrointestinal tract (Saura-Calixto, 2011). On the other hand, phenol/protein interactions can lead to a loss of nutritional values due to protein precipitation and enzyme inactivation (Rohn, Petzke, Rawel & Kroll, 2006).

Variations in chemical composition, antioxidant activity and sensory profiles in food-base vegetables with added phenols from unripe grapes have never been investigated before.

This paper explores the chemical and sensory properties of phenols extracted from UGs and the consequences of phenol/biopolymer interactions on the chemical and sensory properties of plant-base foods. With this aim, three food models with variable macro-compositions in which different phenol/biopolymer interactions might occur were functionalised with an extract from unripe grapes (UGs).

2. Material & Methods

2.1. UG extract and UG-water solutions preparation

The unripe grapes (UGs), cv Merlot, were hand-picked in August 2017 in a commercial vineyard located in Velletri, Rome, Italy. To obtain the UG extract, maceration was performed as previously described by Fia et al. (2018), with some modifications (**Fig. S1**). After decantation and filtration of the liquid extract, sugar was eliminated by ultrafiltration, using a spiral wound configuration membrane, with a molecular weight cut-off of 2500 Dalton (General Electrix, Boston, Massachusetts, United States). The liquid extract was dehydrated by lyophilization with the addition of arabic gum (2% w/v) (Nexira Food, Rouen Cedex, France) as a support and stored in polyethylene pouches under vacuum, in a desiccator, at room temperature, protected from the light.

The UG extract (334 g) was diluted in distilled water to a total volume of 1L. This suspension was centrifuged at 1646 *g*, for 10 min, to eliminate the excess arabic gum. The phenol concentration in the supernatant UG stock solution (SS) was 6.81 g/L. The SS was daily prepared and used to prepare UG-water solutions at different phenol concentrations to be added to the plant-based food models (**Fig. S1**).

The UG-water solutions were filtered through a membrane (Ø 0.45 μm) and the phenolic compounds were purified using a C18 Sep-pak cartridge (1 g) (Waters, Milan, Italy) before the evaluation of the total polyphenol content.

2.2 Food models

Three food models were selected on the basis of their composition (**Table S1**) and taste: beetroot purée (BP) characterized by high carbohydrate content, acidic pH and sweet taste; pea purée (PeP) characterized by high proteins content, neutral pH and sweet taste; potato purée (PoP) characterized by high carbohydrates content and neutral pH. Canned or powdered ingredients produced by large food companies were used to prepare the food models, since they are not subject to seasonal restriction and their composition is constant. Purées of beetroot, pea and potato were prepared as following: a) 500 g of peeled and steamed beetroots were blended at maximum speed, for about 1 min, using a Kenwood FDM 780 mixer (Kenwood, Treviso, Italy), until it was obtained a homogeneous product; b) 310 g of steamed peas were rinsed under cold water for 30 sec and drained for 30 sec to eliminate the water, then 7 g of water were added and the mix was blended at maximum speed for 2 min in a mixer Kenwood; c) 75 g of dehydrated potatoes were added to 340 g of water brought to 80°C and the product was mixed until it became homogeneous, then it was cooled for 30 min before using. Each food model was prepared at five levels of phenol concentration (0.00, 0.21, 0.44, 1.11 and 1.93 g/kg) (**Fig. S1**).

2.3. Chemicals

All solvent and reagents were supplied from Sigma-Aldrich (Milan, Italy), except for methanol and ethanol which were supplied by Carlo Erba (Milan, Italy). Ultrapure water was obtained using a Milli-Q Gradient water purification system (Thermo Scientific, Waltham, Massachusetts, USA).

2.4. Physical-chemical analysis

2.4.1 General analysis

Total acidity and pH were evaluated according to the methods recommended by the International Organization of Vine and Wine (OIV) (International Organization of Vine and Wine Website, 2014).

2.4.2. Moisture content and water activity

The powder moisture content was determined gravimetrically by drying in a vacuum oven, at 70°C, until a constant weight was reached (A.O.A.C. , 1990) . Powder water activity (A_w) was measured using a Rotronic Hygroskop *DT* hygrometer (Michell Italia Srl, Milan, Italy).

2.4.3. Solubility

Water solubility was determined according to (Cano-Chauca, Stringheta, Ramos, & Cal-Vidal, 2005). A volume of 100 mL of distilled water was transferred into a blender jar. The sample (1g, dry basis) was carefully added to the blender while operating at high speed for 5 min. The solution was centrifuged at 3000 *g* for 5 min. An aliquot of 25 mL of the supernatant was transferred to pre-weighed Petri dishes and immediately oven-dried at 105°C for 5 h. The solubility (%) was calculated by weight difference.

2.4.4. Hygroscopicity

Hygroscopicity was evaluated following the method described by Callahan et al. (1982), with some modifications. The equilibrium moisture content (EMC) of the samples (1 g, dry basis) was evaluated following storage in desiccators containing saturated salt solutions with a relative humidity ranging from 8% to 84% at 25°C until a constant weight was reached (approx. 21 days). The hygroscopicity was expressed as g of adsorbed water per 100 g of dry matter (g/100g dm).

206 *2.4.5. Phenol extraction*

207 Extracts were obtained from the food models (FMs) following the method described by Turkmen,
208 Sari, & Velioglu (2005). For each food matrix, 1 g was homogenized and extracted twice with 4.5
209 mL of 80% aqueous methanol solution in a mechanical shaker, for 2 h. The mixture was centrifuged
210 at 13440 *g*, for 15 min, at room temperature, and the supernatant decanted into polypropylene tubes.
211 The supernatant was filtered through Whatman No.1 filter paper. The extraction procedure was
212 performed in triplicate.

213 *2.4.6. Total polyphenol*

214 The total polyphenols (TP) were quantified according to the Folin-Ciocalteau method (Singleton,
215 Rossi Jr., & Rossi J A Jr., 1965). A Perkin Elmer Lambda 10 spectrophotometer (Waltham, MA,
216 USA) was used to measure the absorbance of the reaction mixture at 700 nm. A standard curve was
217 obtained with (+)-catechin solutions at concentrations ranging from 5 to 500 mg/L. The TP was
218 expressed as mg of (+)-catechin equivalents/L of the UG-water solution or kg of the food model
219 extracts.

220 *2.4.7. Antioxidant activity*

221 Antioxidant activity was evaluated by 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay (Brand-
222 Williams, Cuvelier, & Berset, 1995). Trolox standard solutions were prepared daily in absolute
223 ethanol at concentrations ranging from 10 to 600 µmol/L. Antioxidant activity was expressed as
224 µmol of Trolox equivalent antioxidant capacity (TEAC)/L of the solution or kg of the food model
225 extract.

226 *2.4.8. LC-HRMS analysis*

227 Analysis of the phenolic compounds and glutathione was performed via liquid chromatography –
228 high-resolution mass spectrometry (LC-HRMS), according to Fia et al. (2018) using an Accela
229 1250 (Thermo Fisher Scientific) coupled with an LTQ OrbitrapExactive mass spectrometer
230 (Thermo Fisher Scientific) equipped with an electrospray ionization (ESI) source in negative mode.
231 The standards were purchased from Sigma-Aldrich (Milan, Italy), except for the quercetin 3-O-

glucoside which was supplied by Analytik GmbH (Rülzheim, Germany). Coumaric and ferulic acids were used as standards for coutaric and fertaric acids due to the lack of reference materials. Data were expressed as mg of phenols/kg of the UGs or food models.

2.5. Sensory evaluations

The present data were collected as part of a larger study aimed at investigating factors affecting the acceptability of health foods (PRIN 2015: Individual differences in the acceptability of health foods: focus on phenol and fat content). This multisession study consisted of a home questionnaire session and one-on-one testing in a sensory laboratory across two days. This paper will only present a selection of these data. The sensory tests are further detailed in De Toffoli et al. (2019). Two respondent groups were recruited to evaluate the UG extract (Group 1: n=29; 59% females; mean age 27.5 ± 7.1) or functionalized food prototypes (Group 2: n=27; 70% females; mean age 31.5 ± 9.4). The participants received a gift to compensate for their time. The respondents gave their written informed consent at the beginning of the test according to the principles of the Declaration of Helsinki. In brief, training was performed as described by Monteleone et al., (2017) using the general Labelled Magnitude Scale - gLMS (0: no sensation-100: the strongest imaginable sensation of any kind) (Green et al., 2007). Eight water solutions of UG extract were prepared as sensory stimuli with increasing phenol concentration: 0.14, 0.21, 0.30, 0.41, 0.59, 1.11, 1.27 and 1.93 g/L of phenol (**Fig. S1**). The data were collected using Fizz software (ver.2.51. A86, Biosystèmes, Couternon, France).

2.6. Data analysis

A one-way ANOVA model was used to assess the storage effect on the variation of phenol content and antioxidant activity of the UG extract. Two-way ANOVA models were used to assess the effect of both phenol concentration and replicates on the antioxidant activity in the UG solutions and to

assess the effect of both the amount of phenol added and replicates on the recovery of UG phenols from food models.

The UG phenols recovered (recovery %) from the functionalized food samples were calculated as the difference between the total phenol content of the functionalized food and that of the non-functionalized food, then it was expressed as percentage of the phenols added. Two-way ANOVA models were used to assess the effect of phenol concentration on the intensity of the target sensations in UG solutions and food prototype samples (phenol concentration were used as fixed factor; subjects were considered as random factor). Three-way ANOVA were used to assess the effect of the food matrix on the perceived intensity of the target sensations models (fixed factors: food matrix and phenol concentration; random factor: subjects and interactions). A *p*-value of 0.05 was considered as the threshold for statistical significance.

Data analysis was performed using XLSTAT statistical software package (Addinsoft - version 19.02).

3. Results

3.1. Physical-chemical characterization

3.1.1. UG extract

The solubility of the UG extract was 88.1 ± 1.2%. The moisture content of the UG extract, at 25°C, was 8.1 ± 0.3% and the water activity was 38.7 ± 0.1%. The adsorption isotherm of the UG extract at 25°C was determined (**Fig**. S**2**). The experimental data for water activity (A_w) as a function of the moisture content fitted well with the Halsey model (Okos et al., 1992), as follows:

$$A_w = exp\left(-\frac{B}{{n_s}^A}\right) \qquad (r^2 = 0.98)$$

where n_s (g water/g dry matter), A = 0.039 and B = 1.461.

The powder displayed little hygroscopic behaviour up to A_w values < 0.80, while for A_w values greater than 0.85 the hygroscopicity increased exponentially.

The total phenol content of the UG extract was 20403 ± 943 mg/kg. The total phenol content of the UG extract was evaluated monthly until to nine months of storage. After this period, the UG extract displayed the same phenolic concentration as the outset. No significant differences (p = 0.05) were assessed among phenolic content values during storage.

The phenolic composition of the UG extract was analysed by LC-HRMS. Nineteen phenolic compounds were identified in the UG extract (**Table 1**). Phenolic acids were the most abundant class of phenolic compounds and they accounted for 89% of the amount of phenols identified in the UG extract. Caftaric acid accounted for 85% of the phenolic acid content. Flavonols, flavan-3-ols, procyanidins, trans-resveratrol and 2-S-glutathionyl fertaric acid accounted for the remaining 11% of the amount of phenols detected in the UG extract.

The antioxidant activity of the UG extract was 33829 ± 949 TEAC µmol/kg, and the specific activity of the phenols was 1.66 ± 0.04 TEAC µmol/mg. The antioxidant activity of the UG extract was evaluated monthly, up to nine months of storage. After this period, the antioxidant activity of the UG extract remained at 99.4%. No significant differences (p = 0.05) were assessed in the antioxidant activity values at different times of storage.

3.1.2. UG water solutions

The total phenol content of the stock solution was 6.81 ± 0.04 g/L. The stock solution was characterized for total acidity (7.6 ± 0.26 g/L as tartaric acid) and pH (3.21 ± 0.02). The solutions from the UG extract were tested for antioxidant activity at increasing phenol concentration levels (0.14, 0.21, 0.30, 0.41, 0.59, 1.11, 1.27 and 1.93 g/L) **(Fig. S3)**. The UG phenol concentration significantly affected the level of antioxidant activity of the water solutions ($p \leq 0.001$) while the

replicates were not significant ($p < 0.05$). A significant positive relationship ($r = 0.978$) was found between the total phenol content and the antioxidant activity of the UG water solutions.

3.1.3. Functionalized food models

After the addition of an increasing amount (0.00, 0.21, 0.44, 1.11 and 1.93 g/kg) of UG phenols to the food models, the phenol concentration in the FM extracts was determined (**Fig. 1A**). The non-functionalized food models showed different phenolic content, with the highest level detected in the beetroot purée and the lowest in the potato purée. The amount of phenols added to the food models significantly affected the concentration of phenols found in the FM extracts ($p \leq 0.05$).

The phenols recovered from food models significantly varied as a function of both the food model and the amount of phenols added. The recovered amount ranged from 27.7% to 81.3% in the beetroot purée, from 34.0% to 53.6% in the pea purée and from 52.7% to 86.4% in the potato purée. The mean phenol value recovered with the highest added amount of phenols was highest in the potato purée (68.7%), followed by the beetroot purée (57.8%), and the pea purée (43.3%). (**Fig. 1B**).

The food samples functionalized with the highest amount of phenols (1.93 g/kg) were extracted and the extracts analysed via LC-HRMS to evaluate their phenol composition. The FM extracts contained almost all of the phenolic compounds identified in the original UG extract, except for kaempferol-3-*O*-glucoside, quercetin-3-*O*-hexoside and 2-S-glutathionyl caftaric acid (**Table 1**). Caftaric acid was the most abundant phenolic compound assayed in the FM extracts of the three food models. Ferulic acid was not detected in the potato purée. The phenol profiles of the food model functionalized with 1.93 g/kg of UG phenols were compared to the profile of the UG extract (**Fig. 1C**). The relative amounts of each phenolic class in functionalized beetroot purée was similar to that observed in the UG extract, while slight differences were observed in the functionalized pea

and potato purees. Phenolic acids represented the most abundant class of phenols in the UG extract (90.3%) and the beetroot purée almost retained this same high percentage (88.9%), while in the pea and potato purées a slight loss was observed (80.6 and 83.9%, respectively). The proportion of other phenolic classes (flavonols, flavan-3-ols, procyanidins and stilbenes) was slightly higher in the pea and potato purées compared to the figure observed in the UG extract and the beetroot purée.

The antioxidant activity of the food models with an increasing added amount (0.00, 0.21, 0.44, 1.11 and 1.93 g/kg) of UG phenols was determined after extraction (**Fig. 2A**). The non-functionalized beetroot and pea purées had similar values of antioxidant activity while it was much lower in the potato purée. A significant increase in antioxidant activity was observed in the beetroot purée as function of the UG phenol concentration. No significant difference was observed between the antioxidant activity of the pea purée functionalized with 0.44 or 1.11 g/kg of UG phenols.
The difference between the antioxidant activity of functionalized food and that of food without added phenol was calculated to assess the contribution of UG phenols to the food models' final antioxidant activity. The relationship between the antioxidant activity of UG phenols in the water solution and in the FM extracts is shown in **Figure 2B**. The antioxidant activity was always significantly higher in the extracts of beetroot purée compared to that detected in the potato and pea purée extracts. The mean antioxidant activity was 3794 μmol/kg in the BP, 1722 μmol/kg in the PoP and 1127 μmol/kg in the PeP extracts.

3.2. Sensory evaluation

3.2.1. UG extract solutions

The phenol concentration of the UG solutions significantly affected the intensity of the target sensations (**Fig. 3A and Table S2**). According to the F values, the increase in phenol concentration had the strongest effect on sourness while it influenced the other target sensations much less. Significant intensity increases were observed in the samples with phenols from the UG extract

compared to the sample without added phenol (0.00 g/L). Sourness increased from weak to strong across the phenol concentration range. Bitterness, astringency and saltiness showed limited intensity increases, from barely detectable to weak.

Four concentration levels, which cover the whole range of significant variations of intensity of target sensations, were selected to fortify the vegetable matrices: 0.00, 0.21, 0.41, 1.11 and 1.93 g/L.

3.2.2. Functionalized foods

The intensity of target sensations significantly changed in all of the three vegetable prototypes as a function of the increasing phenol concentrations, the only exception being sweetness in the PoP (**Table 2**). Phenol concentration induced the strongest effect on sourness in all of the three food models as showed by F-values. The intensity of the other sensations was influenced by both the increase in phenol concentration and, to a lesser extent, by the macro-composition of the matrix. All of the sensations were barely detectable in the beetroot purée sample without added phenol, while in the rest of the samples, sourness increased from weak to strong, sweetness showed a significant decrease from moderate to weak, while saltiness, astringency and bitterness increased slightly from barely detectable to weak (**Fig. 3** B-Beetroot purée). The variation in intensity of the target sensation in the pea purée as a function of the phenol concentration was similar to that observed in the beetroot purée (**Fig. 3** C-Pea purée). The increase in sourness from barely detectable to moderate was associated with a significant decrease in sweetness, from moderate to weak, while the rest of the sensations were perceived at a weak intensity or even lower. In the potato purée sample without added phenols, all the sensations were rated at a barely detectable/weak intensity, while only sourness showed a remarkable increase from barely detectable to strong as the phenol concentration increased (**Fig. 3** D-Potato purée).

Bitterness, astringency and saltiness were not further investigated since these sensations were marginally affected by addition of phenols and perceived at a weak intensity across the whole range of concentrations.

Sourness and sweetness perceived in the food functionalized at different UG concentration were compared to further explore the effect of food macro-composition on UG phenol sensory properties. While the vegetable matrix and phenol concentration significantly affected the intensity of sourness and sweetness, the vegetable matrix*concentration interaction was never significant (**Table S3**). Significant differences were found upon comparing sourness from the three matrices at phenol concentrations of 0.41, 1.11 and 1.93 g/L. The highest sourness intensity was rated in the PoP, whereas no significant differences were found between the BP and PeP (**Fig. 4-A**). Sweetness was rated as more intense in the BP and PeP than in the PoP across the 0.0 to 0.41 g/kg concentration range of spiked phenols. At the highest concentration levels, sweetness was perceived at the highest intensity in the BP (**Fig. 4-B**).

4. Discussion

Physical-chemical characterization was carried out to evaluate the attitude of UG extract towards rehydration and stability during storage, in terms of phenolic content and antioxidant activity. The solubility value of the UG extract was similar to those (86% - 88%) obtained by Kuck & Noreña (2016) on grape skin extracts lyophilized with arabic gum and partially hydrolysed guar gum as supports.

The moisture content and water activity value of the UG extract were in agreement with the results obtained on grape skin extracts by Kuck & Noreña (2016). The UG extract showed similar hygroscopic behaviour to the absorption isotherm of an aqueous solution of salts and simple sugars. Therefore, the powder has to be protected from humidity during storage to avoid water absorption, thus preserving the extract's stability.

The total phenol content of the UG extract was similar to that obtained by Kuck & Norena (2016) on aqueous extracts of grape skin microencapsulated with different agents while the antioxidant activity was slightly lower. In general, the phenol content and antioxidant activity of extracts vary mainly depending on the origin of grape by-products and extraction conditions (Trigo, Alexandre, Saraiva, & Pintado, 2019). Indeed, when ethanol or methanol were used for the extraction, the phenolic content and antioxidant activity of the extracts were higher than those detected in aqueous extracts (Trigo et al., 2019; Tournour, Segundo, Magalhães, Costa & Cunha, 2017). After nine months, the high percentage of both residual phenols and antioxidant activity in the UG extract indicated that the adopted storage conditions were suitable to protect the UG phenols from degradation.

When a different amount of the UG phenols was used to enrich the food models, the increase of phenol concentration in the FM extracts was expected. Similar results were obtained by other authors who studied the addition of phenolic extracts from different by-products to some food and beverages (Trigo et al., 2019). Chemical-physical characteristics of food models explored in these study significantly affect phenol recovery thus indicating clear reactivity differences between UG phenols and food components. The lowest amount of phenols was recovered from the protein-rich model (pea purée). A similar effect of the interaction phenol/biopolymers on the bioactivity of phenols from olive mill waste waters in plant-based food has already been observed by other authors (De Toffoli et al., 2019).

The formation of phenol/protein aggregates significantly lowers the phenol bio-activity both in terms of extractability from raw material and antioxidant activity (Ozdal et al., 2013). Proteins bind plant polyphenols through hydrophobic and hydrogen interactions; the preferred sites of interaction plant phenol/food protein in *in vitro* conditions are the proline-rich regions of leguminous proteins characterized by high basic-residue contents as well as open and flexible structures (Kroll et al., 2003; Zhang et al., 2014).

Phenol chemical structure, size and composition, including number of OH groups, play an important role in phenol/protein interactions, and phenolic compounds with a low molecular weight are inefficient to bond proteins (de Freitas & Mateus, 2012). It is known that upon extraction, the acidic condition of grape juice promotes the depolymerization of proanthocyanidins (Vidal, Cartalade, Souquet, Fulcrand, & Cheynier, 2002). However, these reactions begin during maceration and proceed slowly in wine, but they have never been highlighted in grape juice.

The quite high percentages of UG phenols recovered, mainly in the carbohydrate-rich potato and beetroot purée food models, indicated that moderate/weak chemical interactions take place among UG phenols and food components. These findings, associated with the significant increase in antioxidant activity detected in the functionalized food models after the addition of UG phenols, indicate that most of the potential biological activity and the extractability of UG phenols were maintained after blending.

Phenolic compounds can bridge or cross-link with polysaccharides, and a large fraction of the not extractable polyphenols consist phenol associated with polysaccharides (Pérez-Jiménez, Díaz-Rubio, & Saura-Calixto, 2013). The consequences of phenol/carbohydrate interactions on phenol biological activity depends on the chemical characteristics of both phenols and carbohydrates (Zhang et al., 2014).

Other authors have described a competition between the arabic gum and other carbohydrates and the proteins to bind to the tannin (Gonçalves, Mateus, & de Freitas, 2011). The mechanism was previously investigated by tasting the influence of several carbohydrates on the formation of polyphenols/protein complexes. Polygalacturonic acid, arabic gum and pectin prevented the association of procyanidin B3 with trypsin, and that of salivary proteins with grape seed procyanidins. The interruption of polyphenol-protein association by carbohydrates can prevent some of the negative effects of these complexes, such as enzyme activity inhibition, and it can influence the perceived astringency of some food products.

The antioxidant activity of UG phenols was influenced by the food composition. The highest level of antioxidant activity was found in the carbohydrate-rich/acidic pH beetroot purée. The antiradical capacity of phenols depends on several factors such as their concentration and structures, and the physical-chemical characteristics of the solvent. The role of acidity in the kinetics of phenol/radical reactions was previously investigated by (Musialik, Kuzmicz, Pawcowski, & Litwinienko, 2009). In general, it is known that deprotonated flavonoids are more potent electron donors and are better radical scavengers than neutral molecules. However, the ability of phenols to scavenge reactive oxygen species such as peroxyl and hydroxyl radicals is still far from being fully understood. Valgimigli et al. (2009) described an unexpected dramatic acceleration of phenol-peroxyl radical reaction with the addition of acid. The best performance, in terms of antioxidant activity, of UG phenols when added to beetroot purée could be due to the acidic pH of the beetroot food model.

Sensory profiles of the three matrices were significantly affected by the addition of UG extracts. Sourness intensity increased as a function of the UG phenol concentration. The natural sweetness of the beetroot and pea purées was reduced by the spiked phenols due to the intermodal interaction between sour and bitter tastes, which induced the suppression of perceived sweetness as the sourness intensity increased (Keast & Breslin, 2002). The bitterness, saltiness and astringency intensities were significantly modified by the UG extract, but the extent of these effects appears marginal since these sensations are perceived at a weak intensity across the whole range of concentrations.

The different compositions of the vegetable matrices affect the UG phenols' contribution to sourness. Furthermore, the observed increasing intensity range differed across the series of samples indicating that their macro-component plays an active role in modulating the sensory impact of UG phenols.

5. Conclusions

An extract from unripe grapes showed suitable physical-chemical characteristics for its inclusion in plant-based foods. Food composition influenced the functional and sensory properties of phenols from unripe grapes. The strongest effect in terms of recovered phenol and antioxidant activity was observed in protein-based food. The use of matrices high in carbohydrates, with acidic pH and characterized by sweet taste appears a suitable strategy to counteract the impact of the negative sensory properties of added phenol on plant-based food. The use of phenolic extracts from unripe grapes can be useful to improve potential health benefits when formulating plant-based functional food.

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Figure legend

Figure 1. Total phenols (A) of food models, mean values of UG phenols recovered (B) from beetroot purée (BP), pea purée (PeP) and potato purée (PoP) functionalized with increasing amounts (0.00, 0.21, 0.44, 1.11 and 1.93 g/kg of food) of phenols and percentage of each phenolic class (C) detected in the UG extract (UG ext) and food models functionalized with 1.93 g/kg phenols from UG extract. The bars represent standard deviation. Different letters represent significant different values ($p \leq 0.001$).

Figure 2. Antioxidant activity (A) of beetroot purée (BP), pea purée (PeP) and potato purée (PoP) functionalized with increasing amounts of phenols (0, 0.21, 0.44, 1.11 and 1.93 g/kg of food) from UG extract and antioxidant activity (B) of UG phenols in water solution *vs* antioxidant activity in the FM extracts. The bars represent standard deviation. Different letters represent significant different values ($p \leq 0.001$).

Figure 3. Mean intensity of target sensations (A) in the UG solutions with increasing phenol concentration and food models (B, C and D) functionalized with increasing concentrations of phenols from UG extract. The bars represent standard error.

689 **Figure 4.** Effect of the vegetable matrix on the perceived intensity of sourness (A) and sweetness
690 (B) in foods spiked with different concentrations of phenols from UG extract. Different letters
691 represent significant different values ($p \leq 0.038$).
692

693 **Table 1.** Phenol profile of the UG extract and phenols detected in the FM extracts. Beetroot purée
694 (BP), pea purée (PeP) and potato purée (PoP) functionalized with 1.93 g/kg of phenols from the UG
695 extract.

696

Compound	mg/kg			
	UG extract	BP*	PeP*	PoP*
Phenolic acid				
Caffeic acid	11.0 ± 0.4	1.04 ± 0.07 ^{c}	1.55 ± 0.14 ^{a}	1.28 ± 0.14 ^{b}
Caftaric acid	704 ± 33	48.7 ± 1.2 a	35.7 ± 6.5 b	36.5 ± 4.0 b
Coumaric acid	19.6 ± 0.6	1.80 ± 0.13 ^{b}	2.30 ± 0.12 ^{a}	1.79 ± 0.14 ^{b}
Coutaric acid	34.3 ± 1.1	2.31 ± 0.17 ^{a}	2.03 ± 0.18 ^{ab}	1.81 ± 0.15 ^{b}
Ferulic acid	4.63 ± 0.59	2.51 ± 0.04 ^{a}	0.44 ± 0.03 ^{b}	nd
Fertaric acid	52.0 ± 2.0	3.44 ± 0.10 a	3.54 ± 0.28 a	3.71 ± 0.19 a
Gallic acid	1.63 ± 0.03	0.03 ± 0.01 ^{b}	0.24 ± 0.02 ^{a}	0.05 ± 0.01 ^{b}
Flavonols				
Isorhamnetin	1.41 ± 0.03	0.05 ± 0.01 ^{b}	0.09 ± 0.01 ^{a}	0.06 ± 0.02 ^{b}
Kaempferol	0.78 ± 0.04	0.06 ± 0.01 ^{a}	0.06 ± 0.01 ^{a}	0.07 ± 0.01 ^{a}
Kaempferol-3-*O*-glucoside	0.54 ± 0.03	nd	nd	nd
Myricetin	3.79 ± 0.11	0.39 ± 0.03 ^{b}	0.47 ± 0.04 ^{a}	0.45 ± 0.03 ^{ab}
Quercetin	14.0 ± 0.4	1.26 ± 0.11 ^{b}	1.48 ± 0.13 ^{ab}	1.57 ± 0.14 ^{a}
Quercetin-3-*O*-hexoside	1.32 ± 0.08	nd	nd	nd
Flavan-3-ols				
(+)-Catechin	13.6 ± 0.8	1.23 ± 0.07 ^{c}	2.28 ± 0.12 ^{a}	1.51 ± 0.11 ^{b}
(-)-Epicatechin	8.23 ± 0.29	0.70 ± 0.03 ^{c}	1.09 ± 0.08 ^{a}	0.83 ± 0.05 ^{b}
Procyanidins				
Procyanidin B1	4.55 ± 0.19	0.44 ± 0.04 ^{b}	0.56 ± 0.04 ^{a}	0.47 ± 0.06 ^{ab}
Procyanidin B2	9.74 ± 0.37	1.13 ± 0.05 ^{c}	1.66 ± 0.05 ^{a}	1.33 ± 0.07 ^{b}
Stilbenes				
Trans-resveratrol	31.3 ± 1.6	2.18 ± 0.13 ^{b}	3.33 ± 0.48 ^{a}	2.36 ± 0.36 ^{b}
2-*S*-Glutathionyl caftaric acid	16.8 ± 0.6	nd	nd	nd

697 Data are expressed as mean ± standard deviation (n=3); nd, not detected. Different letters represent
698 significant different values ($p \leq 0.001$) among the columns.

699

Table 2. Two-way ANOVA mixed model (random effect: assessors): phenol concentration effect on intensity of target sensations in food models. Mean, F and p values.

			Concentration of phenols from UG (g/kg)				
			0.00	**0.21**	**0.41**	**1.11**	**1.93**
	F	**p**					
Bitterness							
Beetroot Purée	4.92	0.0011	0.97 b	1.34 b	0.62 b	1.34 b	3.31 a
Pea Purée	6.78	< 0.0001	1.28 b	1.31 b	1.41 b	3.72 a	5.28 a
Potato Purée	2.53	0.0445	2.61 b	3.00 b	3.25 b	4.11 ab	5.46 a
Sourness							
Beetroot Purée	26.22	< 0.0001	2.38 c	3.07 c	4.41 c	13.86 b	21.86 a
Pea Purée	39.02	< 0.0001	3.48 b	3.34 b	5.62 b	16.31 a	19.72 a
Potato Purée	48.39	< 0.0001	3.07 e	8.54 d	13.46 c	20.43 b	27.68 a
Saltiness							
Beetroot Purée	4.85	0.0012	1.17 b	1.38 b	2.38 b	2.86 ab	4.55 a
Pea Purée	3.63	0.0081	4.52 c	4.31 c	5.79 bc	7.24 ab	8.55 a
Potato Purée	5.78	0.0003	2.29 bc	1.96 c	3.89 bc	4.00 b	6.14 a
Sweetness							
Beetroot Purée	3.07	0.0194	16.31 a	17.79 a	15.21 ab	13.83 ab	11.28 b
Pea Purée	10.01	< 0.0001	12.72 a	13.69 a	11.41 a	7.31 b	5.52 b
Potato Purée	1.56	0.1865	4.18	3.21	3.43	2.36	2.54
Astringency							
Beetroot Purée	4.64	0.0017	4.31 bc	4.07 c	3.31 c	7.38 a	6.34 ab
Pea Purée	4.16	0.0035	5.48 bc	3.72 c	3.97 bc	6.76 ab	8.72 a
Potato Purée	6.01	0.0001	2.86 c	4.93 bc	6.86 ab	7.64 a	8.43 a

Different letters indicate significantly different values ($p \leq 0.05$).

Highlights

- A strategy was outlined for the exploitation of high-quality unripe grapes
- The food composition affected both the phenol recovered and antioxidant activity
- The highest recovery of phenols was from the starch/neutral pH food model
- The highest antioxidant activity was from the carbohydrates/acidic pH food model
- The models' sensory properties are modulated by phenol content and food composition

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Ginevra Bucalossi: Investigation, Visualization
Giovanna Fia: Writing- Original draft preparation
Caterina Dinnella: Conceptualization, Methodology, Writing - Review & Editing
Erminio Monteleone : Conceptualization, Methodology, Funding acquisition
Alessandra De Toffoli: Investigation, Visualization
Valentina Canutia: Investigation
Bruno Zanoni: Writing - Review & Editing
Maurizio Servili: Investigation
Ella Pagliarini: Investigation
Tullia Gallina Toschi: Investigation