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Polyphenol Characterization and Antioxidant Activity of Grape Seeds and Skins from Sicily: A Preliminary Study

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Abstract: The interest in the consumption of health-promoting foods has led to identifying derivatives of the wine industry as products to increase the functional properties of different foods or to design new functional foods**.** The main goal of this study is to characterize and valorize byproducts and wastes of Sicilian grapes as new sources of bioactive components, from the perspective of a circular economy and a biorefinery approach. In particular, this research investigated: 1. the total phenolic content and antioxidant activities and 2. the phenolic profiles of free and bound fractions of defatted grape seeds and red grape skins from Sicily. Defatted grape seeds (DGS) and red grape skins (RGSK) are rich in phenolic compounds. Twenty biophenols were found in the defatted seeds and red grape skins. Particularly interesting were the results obtained after basic hydrolysis, which allowed the release of biophenols from the matrix. The degreased grape seeds showed p-coumaric acid levels at 4641.65 μg g^{-1}, gallic acid at 2649.23 μg g^{-1}, and caffeic acid at 1474.13 μg g^{-1}, along with appreciable quantities of myricetin, epicatechin, and quercetin. As a sustainable approach, the reuse and the value added of the byproducts and wastes of grapes grown in Sicily is shown, which makes possible new applications in different fields, i.e., nutraceuticals.

Keywords: winemaking waste; grape seeds; grape skins; phenolics; anthocyanins; radical scavenging activity; waste valorization

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1. Introduction

In recent years, interest in and studies aimed at the composition of agrifood industry waste have increased, both for environmental and economic reasons. In the European economy, viticulture has an important role, with a market dominated by Italy, France, and Spain [1]. The main product of the oenological sector is wine, and a great amount of waste and byproducts, i.e., grape skin, pulp, seeds, pomace and others, are produced during grape processing.

Alternative uses for these byproducts are being studied, considering factors such as improving the environmental aspects, reducing production costs, and offering new ways to diversify production [2,3]. Recent trends show the potential interest in non-extracted products such as pomace and grape seed flours to exploit the wide range of bioactive molecules. Lucarini et al. [4] reported an updated picture of the utilization of byproducts and wastes from the wine industry as a source of bioactive components following the

biorefinery model; winemaking byproducts have great added value in a wide range of different applications.

The most useful portions of the waste products of wine processing for the recovery of bioactive substances are the grape skins and seeds obtained after sieving the pomace [5–12]. Among the bioactive molecules recovered from wine waste, the most interesting are cell wall polysaccharides, polyunsaturated fatty acids (PUFAs), pigments, proteins, phenolic compounds and vitamins [13–15].

Grape seeds represent a highly studied raw material and contain bioactive components. The oil extracted from grape seeds shows great nutritional value, widely used in the industrial, cosmetic, and food fields. Polyphenols in grapes are mainly reported in the seeds, in the range between 60% and 70% of the total extractable polyphenols. Among the active metabolites that play a very important role are phenols, tannins, resveratrol, quercetin, flavonoids and anthocyanins [16].

Several studies describe the antioxidant, antimicrobial, anti-inflammatory, and anticancer effects as well as the cardiovascular protection and diabetes management provided by the biomolecules from grape byproducts and wastes [16–21].

On the other hand, the use of *Vitis vinifera* L. seed flour allows a more complete reuse of the byproducts; foods fortified with these flours would have an additional supply of fiber, minerals, proteins, and polyphenols, thus increasing the nutritional and potential beneficial properties of the final product [22]. Furthermore, since extraction is not required, the process to obtain these powdered products is cheaper and a more sustainable approach, with a lower environmental impact [23].

The market for natural products has been increasing as well, and the utilization of byproducts, i.e., the grape pomace, could represent a good alternative to meet this demand. In recent years, the utilization of grape seeds and pomace has been inefficient and a large amount of these byproducts has been discarded in fields, leading to environmental concerns [3,24]. In this context, this preliminary study aimed to explore new sources of functional components from the perspective of a circular economy and a biorefinery approach. Grapeseed and grape skin flours from Sicilian grapes were investigated from a nutraceutical point of view. The radical scavenging activities and total phenolic content (TPC) of both the flours (defatted grape seeds and red grape skins) were also investigated.

2. Materials and Methods

2.1. Chemicals and Reagents

Formic acid, methanol, sodium hydroxide, hydrochloric acid, ethanol, sodium carbonate, gallic acid, Folin-Ciocalteu's phenol reagent, DPPH (2,2-diphenyl-1-picrylhydrazyl), and solvents, all analytical grade, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Trolox (6-hydroksy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was obtained from Fluka (Buchs, Switzerland).

2.2. Material for Analysis and Sample Preparation

Red grapes used to produce wine were harvested in September 2020, from the "Sangiovese" variety grown in western Sicily (Italy), from organic cultivations in sunny conditions, mild temperatures, and with moderate ventilation.

The grapes were harvested at technological maturation and pressed to obtain the juice for the production of wine. The waste products of the processing consisted of pomace, seeds and grape stems. The mixture was sieved with a large mesh net to obtain the grape pomace (grape seeds and red skins). The grape seeds were separated from the red grape skins manually.

The grape seeds were dried at a temperature of 24 °C for a period of four days in order to reduce the humidity and then were put gradually into an oil automatic cold press apparatus (Cgoldenwall CAN-684) for oil extraction. The defatted grape seeds (DGS) were

ground to obtain a fine powder. The red grape skins (RGSK), on the other hand, were dried at 55 °C until completely dry (two days) and blended to obtain a fine powder.

2.3. Radical Scavenging Properties Evaluation, DPPH Assay

The evaluation of the radical scavenging properties is reported as the first step in determining the interactions among the compounds and can be defined as an index of food quality [25–27].

The free radical scavenging activities of defatted red grape seeds and red grape skins were evaluated for their ability to bleach the stable radical DPPH (2,2-diprenyl-1-picrylhydrazyl). Thus, monitoring the decrease in absorbance gives an assessment of the ability of the compound to scavenge free radicals [13,28,29].

Inhibition of the free radical DPPH• was expressed as TEAC (Trolox Equivalent Activity Capacity) [29,30]. Trolox was utilized as the standard, and the calibration curve (5 μM, 10 μM, 50 μM, 100 μM, 200 μM, and 400 μM) was prepared using methanol as the solvent.

Then, 100 mg of finely ground sample (DGS and RGSK) were extracted in 10 mL of methanol for 40 min in an ultrasonic bath. The solution was filtered with 0.45 μm PTFE syringe filter; then, 100 μL of the solution was mixed with 3 mL of DPPH 60 μM and placed in the dark for 30 min. The absorbance of each sample was measured at 515 nm. For the preparation of the blank sample, 100 μL of methanol was added to 3 mL of DPPH solution. All experiments were carried out in triplicate. The antiradical activity was recorded as the percentage of inhibition of the DPPH radical.

The radical scavenging activity was calculated by the following equation:

$$\text{Scavenging activity (\%)} = (A_0 - A_i/A_0) \times 100, \quad (1)$$

where A_0 is the absorbance of DPPH without the sample, and A_i is the absorbance of the sample and DPPH.

The results were reported as TEAC (μmol Trolox equivalents (TE)/g of sample) and as IC_{50} values (μM of the sample capable of determining a 50% decrease in absorbance) [29,30].

The equation for the calibration curve of Trolox was $y = 0.0037x + 0.1655$ and $R^2 = 0.987$.

2.4. Determination of Phenolic Compounds

2.4.1. Total Phenolic Content (TPC) Analysis

The total phenolic content (TPC) of the defatted red grape seeds and red grape skins was evaluated by the Folin-Ciocalteu colorimetric method [13,31,32]. First, 10 mL methanol/water (80:20 *v*/*v*) was added to 0.1 g of the finely ground flour sample (DGS and RGSK); then, the obtained mixture was filtered through a 0.45 μm PTFE syringe filter. Next, 125 μL of the solution was mixed with 625 μL of diluted (1:5) Folin-Ciocalteau reagent and 120 μL of 7% Na_2CO_3. The samples were left in the dark for 1h at room temperature. The mixture's absorbance was measured at 765 nm. The TPC was measured four times for each sample. Gallic acid was utilized as the standard, and a calibration curve was created by using solution at different concentrations (0.001, 0.01, 0.025, 0.05, 0.1, and 0.25 mg mL^{-1}). The total polyphenol content was expressed as mg of gallic acid equivalent (GAE) g^{-1} of the flour sample, by means of an equation from the standard gallic acid calibration curve ($y = 10.955x + 0.1405$ with $R^2 = 0.992$).

2.4.2. Extraction Procedure of Free and Bound Phenolics in Red Grape Skins and Defatted Red Grape Seeds

The importance of investigating extractable and non-extractable phenolic compounds is now recognized by the scientific community [33,34].

Free and bound phenolics were extracted using modified methods [35,36].

Free phenolics were extracted using 20 g of RGSK and DGS flours. In detail, the samples were homogenized for 10 min in 50 mL of cold acetone (+4 °C; 80%); then, (maintaining the refrigerated condition) they were continuously stirred for 30 min. The mixture was centrifuged at 2500× *g* for 10 min, and the supernatant was recovered. The pellet was re-extracted four times (repeating the protocol described above), and the supernatants were collected and evaporated under vacuum at 45 °C. The residue was stored at −80 °C until TPC analysis.

To obtain the bound phenolics, the residues left over from the previous extraction were digested in 50 mL of NaOH 4 M for 1 h at room temperature and acidified using hydrochloric acid to pH 2. Subsequently, the solution was extracted with ethyl acetate (25 mL) four times, and the collected supernatants were evaporated at a temperature of 45 °C and stored at −80 °C until analysis of TPC. Both extractions for free and bound phenolics were performed in triplicate.

2.4.3. Analysis of Phenolics in Grape Seeds and Skins by High Performance Liquid Chromatography Coupled with Quadrupole Time-of-Flight Mass Spectrometry

An HPLC/MS method was used to identify the biophenols. First, 10 mg of each extract of the free and bound phenolics of the red grape skins and defatted red grape seeds were dissolved/diluted in 1.0 mL of methanol in an autosampler vial; then, they were submitted to sonication for a period of 5 min. The equipment, utilized in this method, consisted of an Alliance 2695 (Waters) HPLC system equipped with autosampler, degasser, and column heater coupled with a quadrupole time-of-flight (Waters Q-TOF Premier) mass spectrometer. The compounds were separated using a Thermo Hypersil Gold column, 5 cm, 2.1 mm, 1.9 um particle size, under the following conditions: column temperature, 30 °C; injected volume 5 µL. All samples were injected in triplicate by means of a thermostatic autosampler maintained at 15 °C. The HPLC analyses were carried out by combining solvent A (water, with 0.1 v/v% formic acid) and solvent B (methanol, with 0.1 v/v% formic acid) under the following gradient program: from 0 to 1 min, 95% A (flow rate 0.25 mL/min); from 1 to 15 min, 100% B (flow rate 0.25 mL/min); from 15 to 20 min, the same percentage of solvent B was maintained at flow 0.25 mL/min; from 20 to 21 min 100% B (flow rate 0.25 mL/min); and from 21 to 26 min, 95% A (flow rate 0.25 mL/min), for column re-equilibration. The MS experiments were carried out using the Waters Q-TOF Premier adopting dynamic range enhancement (DRE) as the acquisition mode to avoid MCP saturation and maintain a good sensitivity. This guarantees correctly quantifying both compounds present in high concentration and in trace levels, providing more reliable results. Electrospray ionization (ESI) was utilized in negative ion mode under the following conditions: capillary voltage, 2.0 KV; desolvation temperature, 300.0 °C; sampling cone, 30.0 V; extraction cone, 2.0 V; ion guide, 2 V; source temperature, 80 °C; cone gas N2, flow 35.0 L/h; desolvation gas N2, flow 300.0 L/h; scan time, 1 s; and interscan delay, 0.1 s. The acquisition mass range was 100–1000 m/z; to acquire data with an accurate mass selection, an appropriate lock mass was selected.

2.5. Statistical Analysis

All analyses were carried out in triplicate. Data are reported as mean ± standard deviation (SD). An ANOVA one-way test was performed to ascertain significant differences among biophenolic content in the skin and seeds extracts. To ascertain differences among samples of the same nature (i.e., DSG and RGSK) undergoing a different treatment, a *t*-test for independent samples by group was performed.

3. Results

The characterization of defatted grape seed (DGS) and red grape skin (RGSK) flours was carried out as follows: (i) antioxidant properties' assessment by total phenolic content

(TPC) analysis and antiradical activity by DPPH assay (TEAC and IC_{50} values); (ii) qualitative and quantitative analysis of the phenolics in thegrape seeds and skins.

3.1. Radical Scavenging Properties of Defatted Grape Seed (DGS) and Red Grape Skin (RGSK) Flours

The TPC of grape seed and skin flours are reported in Table 1 as mg of gallic acid equivalent (GAE)g^{-1} of each sample. The TPC value of red grape skins was higher than defatted red grape seeds (24.16 ± 0.18 and 20.69 ± 0.13 mg GAE g^{-1}, respectively).

The radical scavenging properties of the defatted grape seeds and red grape skins were evaluated by DPPH assays as TEAC (Trolox Equivalent Activity Capacity) and IC_{50} values (μM of the sample capable of determining a 50% decrease in absorbance) (Table 1). Defatted grape seeds showed the highest TEAC value (134.23 ± 2.22 μM Trolox Equivalent TE g^{-1}); the TEAC value for red grape skins was 101.35 ± 1.32 μM TE g^{-1}. The lowest IC_{50} values were observed in red grape skin flour (20.27 μM), while defatted grape seed flour showed a higher value (26.85 μM). The results covering the measurements of total phenolic content (TPC), TEAC, and IC_{50} values are shown in Table 1.

Table 1. Total phenolic content (TPC) (mean ± SD), TEAC (mean ± SD), and IC_{50} values (DPPH assay) of defatted grape seeds (DGS) and red grape skins (RGSK).

	Defatted Red Grape Seeds (DGS)	**Red Grape Skins (RGSK)**
Total phenolic content (TPC) (mg GAE g^{-1})	20.69 ± 0.13	24.16 ± 0.18
TEAC (μM Trolox Equivalent g^{-1})	134.2 ± 2.22	101.3 ± 1.32
IC_{50} (μM)	26.85	20.27

3.2. Qualitative and Quantitative Analysis of Phenolics in Grape Seeds and Skins

For the chemical analysis of bioactive substances, free and bound phenolics were extracted from RGSK and DGS using the modified methods of Gong et al. [35,36]. Phenolics were identified by comparison with the retention time, MS spectra, and accurate mass measurement obtained from the literature data [11,37,38]. A total of 20 biophenols were identified by HPLC–HRMS (Table 2).

Table 2. Brute formulas and accurate masses (calculated and experimental) of quasi molecular ions of phenolic compounds detected in red grape seeds and red skin extracts in negative ion mode LC/MS data.

Biophenols	**Formula**	**m/z [M − H]$^-$**		**Δ ppm**	**RT (min)**
		Calculated	Experimental		
Delphinidin-3-glucoside	$C_{15}H_{11}ClO_6$	463.067	463.075	17	10.1
Isorhamnetin	$C_{16}H_{12}O_7$	315.050	315.0504	1.2	12.7
Kaempferol	$C_{15}H_{10}O_6$	285.041	285.039	−7.0	12.8
Quercetin 3-O-hexuronide	$C_{21}H_{18}O_{13}$	477.067	477.0742	15	10.0
Quercetin 3-O-hexoside	$C_{21}H_{20}O_{12}$	463.088	463.0863	−3.7	10.1
Myricetin	$C_{21}H_{19}O_{12}$	317.031	317.032	3.2	7.8
Epicatechin	$C_{15}H_{14}O_6$	289.072	289.0697	−8.0	7.9
Procyanidin dimer isomer 1	$C_{15}H_{10}O_8$	577.135	577.1375	4.3	7.9
Ellagic acid	$C_{15}H_{14}O_6$	300.999	301.002	10	11.6
Procyanidin dimer isomer 2	$C_{30}H_{26}O_{12}$	577.135	577.1375	4.3	7.4
Quercetin	$C_{14}H_6O_8$	301.035	301.039	13	11.7
Resveratrol tetramer	$C_{30}H_{26}O_{12}$	905.260	905.269	9.9	10.0
Resveratrol hexoside	$C_{15}H_{10}O_7$	389.124	389.128	10	9.5

Ferulic acid	$C_{10}H_{10}O_4$	193.051	193.052	5.2	7.1
Vanillic acid	$C_8H_8O_4$	167.034	167.036	12	2.0
Caffeic acid	$C_9H_8O_4$	179.035	179.0341	−5.0	7.1
p-Hydroxybenzoic acid	$C_7H_6O_3$	137.024	137.024	0	4.4
Gallic acid	$C_7H_6O_5$	169.014	169.0128	−7.1	1.2
p-Coumaric Acid	$C_9H_8O_3$	163.039	163.04	6.1	8.7
Syringic acid	$C_9H_{10}O_5$	197.045	197.044	−5.1	8.6

In total, 17 biophenols were found in the defatted seeds as the free fraction and as the bound ones. In red grape skins, 8 and 14 biophenols were found as the free fraction and as the bound fraction, respectively (Scheme S1 in Supplementary Materials).

4. Discussion

The total phenolic content and free-radical scavenging activity toward the DPPH radical of DGS and RGSK are shown in Table 1. Higher TPC values were recorded in red grape skins compared to defatted red grape seeds (respectively 24.16 ± 0.18 and 20.69 ± 0.13 mg GAE g^{-1}), in accordance with the data reported in the literature [39–43].

As shown in Table 3, the TPC values found in defatted grape seed and red grape skin flours closely match the data reported by several other authors. Chamorro et al. evaluated the total content of phenols as 23.6 ± 0.8 mg GAE g^{-1} in the pomace from Spanish grapes [39]. Values between 17.91 and 35.10 mg GAE g^{-1} were found by Casagrande et al. [40]. TPC values higher than those found in the analyzed samples were reported by Beres et al. in red grape pomace [41]. A previous work recorded a value of 4.7 mg GAE g^{-1} for the pomace of red grapes from Brazil [42]. However, the growing region is not the unique element that impacts the TPC in grape pomace. The TPC values are influenced by the winemaking techniques, weather, and genotype. Sung and Lee documented values of total polyphenol content in the range of 7.92 mg GAE g^{-1} to 43.69 mg GAE g^{-1} in grape seeds from different cultivars. [43].

Table 3. Phenolic compound concentrations (μg g^{-1}) in DGS and RGSK extracts and ANOVA one-way test results.

Biophenol	Free Phenolics in DGS Extract	Free Phenolics in RGSK Extract	Bound Phenolics in DGS Extract	Bound Phenolics in RGSK Extract	df	MS	*p*
			μg g^{-1}				
Delphinidin-3-glucoside	4.52	0.00	39.52	0.00	3	1097	4.9×10^{-9}
Isorhamnetin	6.09	2.70	0.00	0.00	3	25.03	3.5×10^{-6}
Kaempferol	3.60	3.17	0.00	0.00	3	11.56	1.4×10^{-3}
Quercetin 3-O-hexuronide	20.08	18.13	70.55	1.19	3	2689	8.1×10^{-7}
Quercetin 3-O-hexoside	4.85	0.00	37.63	0.00	3	988.23	4.8×10^{-9}
Myricetin	0.00	0.00	142.69	20.07	3	14,140	1.0×10^{-9}
Epicatechin	244.79	0.00	118.21	358.43	3	72,252	1.0×10^{-7}
Procyanidin dimer isom. 1	0.00	0.00	7.50	3.98	3	39.11	4.6×10^{-4}
Ellagic acid	25.21	1.84	21.36	0.00	3	509.05	8.5×10^{-7}
Procyanidin dimer isom. 2	33.32	0.00	5.38	85.74	3	4619	7.6×10^{-8}
Quercetin	110.92	91.03	90.63	15.85	3	5272	2.1×10^{-7}
Resveratrol tetramer	71.08	0.00	0.00	0.00	3	3789	6.1×10^{-15}
Resveratrol hexoside	73.38	0.00	72.71	96.20	3	5250	9.9×10^{-11}
Ferulic acid	0.00	0.00	70.51	73.13	3	5162	8.9×10^{-10}
Vanillic acid	69.30	0.00	96.31	130.28	3	9164	3.8×10^{-10}
Caffeic acid	86.88	67.62	1474.13	244.74	3	1,367,708	3.2×10^{-12}
p-Hydroxybenzoic acid	190.73	0.00	404.35	403.79	3	113,489	6.4×10^{-10}

Gallic acid	647.88	181.30	2649.23	3646.40	3	8,076,547	2.0×10^{-12}
p-Coumaric Acid	134.33	0.00	4641.65	856.33	3	14,365,546	1.4×10^{-8}
Syringic acid	506.70	185.21	66.78	153.61	3	111,031	3.0×10^{-13}

Defatted grape seed and red grape skin flours showed high TEAC and DPPH values that correlated with the total phenolic content. Other authors have reported results equivalent to those found in the samples studied; in particular, similar TEAC values were obtained from Cabernet Sauvignon grape marc (150–73 μM TE g^{-1}) [44]. Grape seeds from different cultivars showed antioxidant activity in a range from 28.2 to 121.2 μM TEAC g^{-1} [41,43]. In another work, the mean value of TEAC in defatted grape seeds was approximately 105.5 ± 2.0 μM TE g^{-1} [42].

Comparing the results, it was clear that both byproduct fractions revealed a reducing power; however, the radical scavenging activity was higher in RGSK as shown by the IC_{50} and TEAC values (DPPH assay). The compound with a lower IC_{50} value has higher antioxidant activity. This characteristic (discoloration) is proportional to the antioxidant charge present in the sample.

Regarding the HPLC-HRMS analysis of the acetonic extract of DGS and RGSK, 17 biophenols were found in the defatted seeds and 8 in red grape skins as the free fraction (Figure S1 in Supplementary Materials).

Hydroxybenzoic acids (p-hydroxybenzoic, gallic, syringic, and vanillic acids) were detected in significant amounts in the DGS extracts, accounting for 10% of the free phenol total. Hydroxycinnamic acids (caffeic, ferulic acids, and p-coumaric) were present in the content at about 10% of the total. Epicatechin and quercetin were the most abundant flavonoids in the DGS (244.79 and 110.92 μg g^{-1}, respectively). The free phenolic compound content in RGSK was much lower than in the DGS where appreciable concentrations of syringic and gallic acid were found (185.21 and 181.30 μg g^{-1}, respectively).

Digestion with 4M NaOH for 1 h of the solid matrix remaining after the extraction to obtain the free phenols yielded a further extract that contained bound phenols. Hydrolysis allowed the release of biophenols from the matrix. The basic digestion of the DGS-showed p-coumaric acid at 4641.65 μg g^{-1}, gallic acid at 2649.23 μg g^{-1} and caffeic acid at 1474.13 μg g^{-1}. Myricetin, epicatechin, and quercetin were the most abundant bound flavonoids in the DGS (142.69, 118.21 and 90.63 μg g^{-1}, respectively).

The highest bound phenolic compounds contained in the RGSK extract were gallic acid at 3646.40 μg g^{-1}, followed by p-coumaric and benzoic acids. A single cyanidin derivative (delphinidin-3-glucoside) was detected in the free and the bound fraction of the defatted seed extracts.

The results of the statistical analyses on the free and bound levels of the biophenols (ANOVA, Table 3, and *t*-test, not shown) ascertained that the measurements among samples were significantly different. The comparison (by means of a *t*-test) of their levels in the DSG undergoing differing extraction procedures showed that only the quercetin level was unaffected by the sample treatment. Whereas the *t*-test for the RGSK showed insignificantly differing levels of isorhamnetin, ellagic acid, epicatechin, and procyanidin dimer B.

The evaluation of the free and bound extracts results showed a significant increase in the levels of gallic acid after the basic hydrolytic step, hinting at the decomposition of larger molecules.

Among these, the compounds that are most closely related to the increase in gallic acid are proanthocyanidins. Proanthocyanidins are powerful free radical scavengers and contribute to the beneficial effects of consuming foods rich in them [33,45,46].

The high content of different bioactive compounds and non-extractable polyphenols in the main byproducts of the wine industry, such as seeds and skins, makes these matrices interesting from the point of view of their possible use as flour. Grape byproduct incorporation in bakery and pastry products may lead to many health benefits. Food such as bread and pasta can be enriched with the partial replacement of flour with the flour of

the byproducts of grape processing, because it is a gluten-free ingredient, and represents a rich source of bioactive compounds to obtain healthy formulations.

In addition, byproducts of the wine industry, due to the presence of antioxidant compounds, if added to some perishable foods, together with the increase in nutritional value, could slow the oxidation process of lipids, thus extending the shelf life of the products.

5. Conclusions

The recovery of value-added compounds from food byproducts and waste represents a major challenge, although commercial implementation depends on several parameters that should be considered. Their enhancement allows giving a second life to wine processing's byproducts and contributing to the reduction in both production costs and the residual amount. According to national and international directives related to waste management, the main strategies for the effective management system and sustainability of the food industry emphasize the importance of the prevention/minimization of waste as well as the valorization and promotion of byproducts. This study showed that defatted seeds and grape skins (low-cost byproducts of the wine and grape juice industry) hold promise as additives in functional foods [12].

The phenolic profile of the byproducts as well as the scavenging radical activity were studied. The free phenolic fraction extracted from DGS flours with acetone showed an interesting profile. Appreciable quantities of phenolic acids (including gallic and syringic acid), epicatechin, and quercetin were quantified. The main constituents identified and quantified in the extracts from red grape skins were quercetin and gallic and syringic acids. Digestion with NaOH of the solid matrix left over after extraction with acetone produced bound phenols. Both DGS and RGSK extracts showed ample amounts of bound phenolic acids (p-coumaric acid, gallic, and caffeic), along with myricetin, epicatechin, and quercetin among the most abundant bound flavonoids.

The high variety of biophenols in the grape byproducts confirms their possible use to enhance the nutritional and functional values of food products.

Additionally, defatted seeds and grape skins are gluten-free ingredients and are a rich source of dietary fibre.

The introduction into the most common foods (bakery products, pasta, and yogurt) of grape byproducts as a bioactive food ingredient, without preliminary processing, can increase the profits of producers, considering them as value-added products. Ongoing studies in this direction are being carried out.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su14116702/s1.

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