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Management Prospects of Winery By-Products Based on Phenolic Compounds and Antioxidant Activity of Grape Skins: The Case of Greek Ionian Islands

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***Abstract*—**The aim of this work was to recover phenolic compounds from grape skins produced in Greek varieties of the Ionian Islands in order to form the basis of calculations for their further utilization in the context of the circular economy. Isolation and further utilization of phenolic compounds is an important issue in winery by-products. For this purpose, 37 samples were collected, extracted, and analyzed in an attempt to provide the appropriate basis for their sustainable exploitation. Extraction of the bioactive compounds was held using an eco-friendly, non-toxic, and highly effective water-glycerol solvent system. Then, extracts were analyzed using UV-Vis, liquid chromatography-mass spectrometry (LC-MS), FTIR, and Raman spectroscopy. Also, total phenolic content and antioxidant activity were measured. LC-MS chromatography showed qualitative differences between different varieties. Peaks were attributed to monomeric 3-flavanols as well as monomeric, dimeric, and trimeric proanthocyanidins. The FT-IR and Raman spectra agreed with the chromatographic data and contributed to identifying phenolic compounds. Grape skins exhibited high total phenolic content (TPC), and it was proved that during vinification, a large number of polyphenols remained in the pomace. This study confirmed that grape skins from Ionian Islands are a promising source of bioactive compounds, suggesting their utilization under a bio-economic and environmental strategic framework.

***Keywords*—**Antioxidant activity, grape skin, phenolic compounds, waste recovery.

I. Introduction

GRAPE is one of the world's largest fruit crops, with more than 75 million tons is cultivated mainly as *Vitis vinifera* L. for wine production [1]. According to the Ministry of Rural Development and Food, the Ionian Islands produced 1,179.25 tons of grapes for wine production in 2017 [2].

The wine industry is producing large volumes of solid wastes, which are mainly disposed of in the environment. Grape pomace has high organic matter, and they could cause soil and water pollution. Furthermore, they are typically characterized by high levels of chemical oxygen demand (COD) [3].

Grape skins have a large content of bioactive compounds like phenolic compounds. This content depends on the variety of grapes and on the vinification conditions. Anthocyanins, catechins, flavonol glycosides, phenolic acids, and stilbenes are some of them [4]. Grape phenolic compounds are responsible for some of the most important wine properties like color, astringency, and flavor [5]. In addition, they act against ultraviolet radiation, pathogens, and environmental stress [6]. The antioxidant activity of them reacts to free radicals and neutralize them, helping to prevent related diseases [7].

Extraction of phenolic compounds is the first step to their use in industry. In general, the most common is the solid-liquid extraction method combining different types of organic solvents such as methanol, ethanol, acetone, and ethyl acetate [5]. Valorization of winery waste biomass should include processes that generate far less or even zero further waste. Otherwise, no concept of "green" or "sustainable" could be substantiated. Thus, the development of green processes is necessary. However, one of the major ways to comply with the principles of green chemistry is to reduce the use of toxic, volatile organic solvents and to encourage their replacement by novel, environmentally friendly liquids. In this framework, the selection of an appropriate solvent is of paramount importance to the sustainable character of an extraction method.

Glycerol is a bio-liquid considered a by-product of the biodiesel industry [8], which can be included as a renewable and safe solvent with high efficiency of extract/product [9]. This solvent has not been used widely for extraction purposes, despite the fact that it possesses, lack of toxicity and flammability. Water/glycerol mixtures may be very effective in extracting polyphenols [10], [11].

The objective of this work was to examine the extraction of phenolic compounds from grape skin from the traditional Ionian Islands. For this purpose, they were using a non-toxic water/glycerol mixture solvent. Also, the extracts were studied qualitatively, and their antioxidant activity was measured. The study will contribute to the management of by-products of the Ionian wineries.

II. Materials and Methods

A. Materials

1. Chemicals

All the solvents used were extra purity (> 99.5%), including water, glycerol, and methanol. Phenolic standards with a purity of 98-99% (cinnamic acid, gallic acid, caftaric acid, catechin

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and epicatechin, epicatechin gallete, rutin, quercetin, kaempferol 3-glucoside, p-coumaric acid, and isoharmentin 3-glucoside) were purchased from Aldrich (Steinheim, Germany) used for identification in MS. Folin-Ciocalteu reagent was used for TPC measurement, as well as caffeic acid. 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2'-azino-bis- (3- ethylbenzothia-zoline-6-sulphonic acid) (ABTS) used for the free radical preparation tests, as well as Trolox.

2. Plant Material

Grape pomace was provided by Greek wineries. 37 samples were from Cephalonia, Zakynthos, Corfu, and Lefkada region. More details about the variety and the region are presented in Table I.

TABLE I
GRAPE POMACE VARIETIES FROM IONIAN ISLANDS

Ionian Island	Variety
Zakynthos	Pavlos
	Avgoustiatis
	Robola
	Goustolidi
	Savvatiano
Corfu	Robola
	Cabernet Sauvignon
	Kakotrygis
Cephalonia	Sauvignon Blanc
	Tsaousi
	Robola
	Goustolidi
	Mavrodaphne
Lefkada	Vardea
	Vertzami

B. Methods

1. Moisture Removal

Initial moisture of crude grape pomace was estimated at 73% (w/w). The drying process of samples was then carried by airflow and followed by the separation of grape seeds from the skins using a series of sieves. Grape skins of each variety were sealed in polypropylene bags and stored at -20 °C until their usage.

2. Preprocessing and Defatting

After refrigerating, grape skins were remained at 25 °C for six h. Then, they were powdered with a mixer (Philips HR 2074, N.V.) for 2 min. During grinding were 15 s rest periods to avoid overheating of the samples. The crushed grape skins powder was continuously defatting with n-hexane with a magnetic stirrer at 600 rpm for 30 min at 25 °C [5].

3. Phenolic Extraction of Grape Skins

Defatted samples extracted with water and glycerol (80:20 v/v) at 600 rpm for 60 min at room temperature. The ratio of skin powder and water/glycerol (80:20 v/v) followed was 1 to 20 (w/v), and the process was repeated three times. The three fractions were filtered through a 0.45 μm filter and stored (-20 °C) until further analysis.

4. Determination of TPC and Antioxidant Activity

TPC was estimated using the Folin-Ciocalteu reagent [12]. In addition, antioxidant activity was estimated using DPPH and ABTS assay, and antiradical activity (A_{AR}) was also calculated [13]-[15].

The TPC concentration (C_{TPC}) was calculated and expressed as mg caffeic acid equivalents per mL extract (mg CAE mL^{-1}). DPPH and ABTS were expressed as mg trolox equivalents g^{-1} dry weight. A_{AR} was calculated according to:

$$A_{AR}\ (\mu mol\ DPPH/g\ dw) = \frac{C_{DPPH}}{C_{TPC}} \times \left(1 - \frac{A_{515\ (f)}}{A_{515\ (i)}}\right) \times Y_{TPC} \quad (1)$$

where C_{DPPH} is the initial molar concentration of DPPH (μmol L^{-1}), $A_{515(f)}$: Sample's absorbance, and $A_{515(i)}$: absorbance of a blank sample.

5. LC-DAD/MS Analysis

The system was a Shimadzu liquid chromatography/mass spectrometer (LC/MS-2010A) equipped with an LC-10ADvp binary pump, a DGU-14A degasser, a SIL-10ADvp autosampler, an SPD-M10Avp Photo Diode Array Detector, and a quadrupole mass detector (MSD) with an electron spray ion source (MS-ESI, Electrospray Ionization). The detector was set in negative ion mode.

A reversed-phase column Supelco (Discovery HS C18), length 250 mm, internal diameter 4 mm with material porosity of 5 μm was used, and it eluted the analytes at a flow rate of 1 mL min^{-1}. Solvent A was acidified water with formic acid (pH = 2) and solvent B was acidified methanol with formic acid adjusted to (pH = 2). The program followed was from 0-1 min, 5% solvent (B), 2-5 min, 10% solvent (B), 6-15 min, 33% solvent (B) 16-25 min, 41% solvent (B), 26-35 min, 62% solvent (B), 36-42 min, 66% solvent (B), 43-55 min, 100% solvent (B), 56-65 min, 5% solvent (B). Chromatograms were recorded at four wavelengths (280, 320, 360, and 520) nm [16].

6. FTIR Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) spectra were obtained using a Thermo Nicolet 6700 FTIR (Thermo Electron Corporation, Madison, WI, USA) equipped with a deuterated triglycine sulfate (DTGS) detector. The spectra were obtained in diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique. The speed of the interferometer moving mirror was 0.6329 mm s^{-1}. Spectra were recorded with a resolution of 4 cm^{-1} and 100 scans. Before the analysis of each sample, the background was recorded. Triple FTIR spectra of each sample were obtained, using a different sub-sample each time. Spectrum processing was performed using the software (OMNIC ver.9.1, Thermo Fisher Scientific Inc., Waltham, MA, USA).

7. Raman Spectroscopy

A DeltaNu Advantage 785 visible–infrared Raman spectrometer (DeltaNu Inc., Laramie, WY, USA) equipped with a 785 nm diode laser for excitation with a maximum output power of 71.6 mW was used to record the spectra. Each spectrum was a 10 s acquisition over the spectral range of 2000-

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200 cm^{-1} using a resolution of 8 cm^{-1}. The spectrometer was accompanied by NuSpec software.

C. Statistical Analysis

All the experiments were done in triplicates, and the results were given as mean ± standard deviation (SD).

III. Results and Discussion

Characteristic quantitative analysis of phenolic compounds by LC-MS is shown in Table II. The phenolic compounds were identified by comparing the UV and MS spectrum with corresponding standard compounds and other studies. Quantification was made only for the main compounds. Main peaks were attributed to monomeric 3-flavanols as well as monomeric, dimeric, and trimeric proanthocyanidins.

UV-Vis spectra of flavonoids showed two absorption bands, I and II. Zone I had an absorbance range of 300-370 nm due to the structure of rings B and C, while band II had an absorbance range of 250-300 nm and due to the A-ring of flavonoids. In the absorbance range 260-280 nm we also confirmed the existence of phenolic compounds and particular phenolic acids [16]. Extracts from white grape skin varieties were more enriched in phenolic acids than red grape skins. Finally, absorptions at 520 nm were attributed to anthocyanins.

Generally from the MS spectra the [M-H]$^-$ = 289 m/z attributed to (epi)-catechin, [M-H]$^-$ = 441 m/z to monomeric (epi)-catechin of gallic acid, [M-H]$^-$ = 577 m/z to (epi)-catechin dimer, [M-H]$^-$ = 729 m/z to proanthocyanidin gallic acid dimer and [M-H]$^-$ = 865 m/z to proanthocyanidin trimer [17]-[19]. Specifically, the peak at 15.5 min was attributed to caftaric acid ([M-H]$^-$ = 310 m/z) [20]. Peaks at 17.3 min and 20.5 min were attributed to catechin and epicatechin respectively ([M-H]$^-$ = 289 m/z). Peaks at 25.0; 31.1; 34.2; 34.4 and 37.7 min were attributed to p-coumaric acid ([M-H]$^-$ = 163 m/z); rutin ([M-H]$^-$ = 609 m/z); kaempferol 3-O-galactoside ([M-H]$^-$ = 446 m/z); isorhamnentin 3-O-glycoside ([M-H]$^-$ = 477 m/z) and quercetin ([M-H]$^-$ = 301 m/z) respectively.

TABLE II
Tentative Identity of Major Polyphenols of the Robola Variety Extract from Cephalonia

Peak Rt (min)	UV-Vis (λmax)	[M-H]$^-$ (m/z)	Tentative Identity
7.4	274	146	cinnamic acid
9.5	215; 270	168	gallic acid
13.5	217	330	monogaloglucose
14.8	218; 278	576	procyanidin dimer
15.0	217; 277	576	procyanidin dimer
15.3	278	577	procyanidin dimer
15.5	286; 328	310	caftaric acid
15.9	218; 277	865	procyanidin trimer
16.4	220; 279	576	procyanidin dimer
16.8	220; 277	576	procyanidin dimer
17.3	278	288	catechin
17.8	278; 375	576	procyanidin dimer
18.3	223; 271	443	epicatechin gallate
19.1	219; 278	865	procyanidin trimer
19.2	222; 278	896	catechin trimer
19.3	222; 278	577	procyanidin dimer
20.5	278	289	epicatechin
25.0	226	163	p-coumaric acid
30.5	225; 354	476	quercetin 3-glucuronide
31.1	226; 355	609	rutin
33.5	264; 348	446	kaempferol 7-O-glucoside
34.2	265; 349	446	kaempferol 3-O-galactoside
34.4	226; 350	477	isorhamnentin 3-O-glycoside
37.7	373	301	quercetin

A representative FTIR spectrum from the grape skin sample is presented in Fig. 1. FTIR analysis was performed using the DRIFT technique. It was observed that the spectra showed significant similarities. The samples consist of water, protein, fat, organic acid, sugar, nitrogen compounds, and flavonoids.

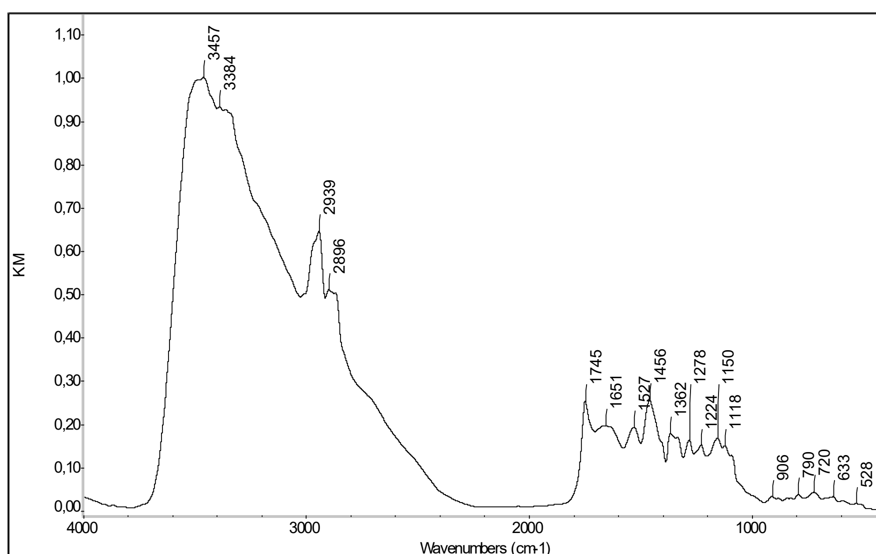

Fig. 1 Mean FT-IR spectrum derived from Robola sample

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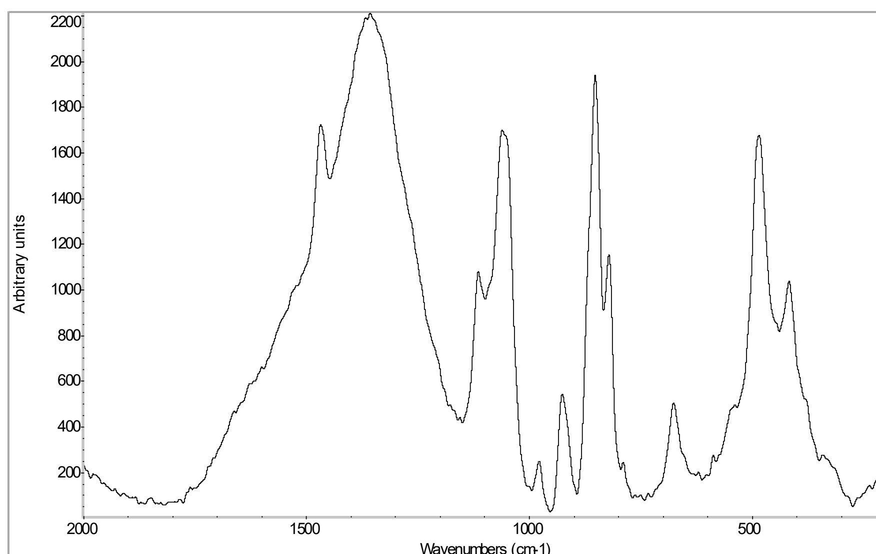

Fig. 2 Mean Raman spectrum derived from Robola sample

TABLE III
TPC AND ANTIOXIDANT ACTIVITY OF GRAPE SKIN EXTRACTS

Variety	$^aC_{TPC}$	^{b}DPPH	^{c}DPPH	^{d}ABTS
Sauvignon Blanc	0.12	0.60	29.55	42.16
Tsaousi	0.18	0.78	33.11	55.68
Robola	0.20	0.70	21.42	95.88
Robola	0.28	1.14	40.72	104.39
Goustolidi	0.47	0.90	42.73	133.55
Robola	0.21	0.65	19.94	110.33
Robola	0.35	1.05	31.16	169.49
Robola	0.27	0.86	25.93	150.28
Robola	0.21	0.53	16.75	101.45
Mavrodaphne	0.45	1.20	35.20	167.79
Robola	0.18	0.46	14.87	74.82
Robola	0.29	0.79	23.89	123.32
Avgoustiatis	0.34	0.88	26.39	122.11
Paul	0.36	1.04	30.72	147.46
Avgoustiatis, Skiadopoulos	0.37	1.43	36.57	155.69
Avgoustiatis, Katsali	0.33	1.15	33.99	150.04
Kakotrygis	0.32	1.14	33.70	130.51
Cabernet Sauvignon	0.56	1.47	42.73	157.46
Syrah	0.16	0.40	15.89	80.05
Matzavi	0.19	0.53	18.87	93.86
Robola	0.34	0.88	27.69	149.15
Moschato white	0.19	0.44	19.43	116.81
Mavrodaphne	0.42	1.43	22.17	107.75
Avgoustiatis, Pyrarnis	0.43	1.22	38.10	170.50
Vertzami	0.33	1.79	29.79	156.61
Vardea	0.23	0.48	19.23	123.27
Pavlos, Cardinal, Zambella	0.24	0.57	24.83	112.80

$^aC_{TPC}$ (mg mL^{-1}) ± SD: Concentration of TPC expressed as mg CAE mL^{-1} of extract

^{b}DPPH (A_{AR}): A_{AR} expressed as μmol of DPPH g^{-1} of dry weight.

^{c}DPPH (mg trolox g^{-1}): The inhibition of free radical DPPH expressed as mg trolox equivalents g^{-1} dry weight.

^{d}ABTS (mg trolox g^{-1}): The inhibition of free radical ABTS expressed as mg trolox equivalents g^{-1} dry weight.

Grape skins spectra showed absorption bands at different wavenumbers, as follows: 3457 cm^{-1} (stretching vibration of O-H of sugars) [21]; 3384 cm^{-1} (stretching vibration of C-N of proteins) [21]; 2939 cm^{-1} (symmetrical stretching vibration of C-H (-CH_2) of lipids) [21], [22]; 2896 cm^{-1} (asymmetric stretching vibration of C-H (-CH_2) of lipids) [21], [22]; 1745 cm^{-1} (stretching vibration of C=O and -COOR of pectin, triglyceride ester linkages and amide I) [21]; 1651 cm^{-1} (asymmetric stretching of C=O and -COO^- of triglyceride ester linkages) [23]; 1527 cm^{-1} (stretching and bending vibration of C-N and N-H of proteins and amide II) [21]; 1456 cm^{-1} (stretching and bending vibration of C-N and -CH_2 of amide III and lipids) [21]; 1362 cm^{-1} (symmetrical bending vibration of -CH_3 of lipids) [21]; 1278 cm^{-1} (asymmetric stretching vibration of C-O-C of lipids) [21]; 1150 cm^{-1} (stretching vibration of C-O and C-O-C of polysaccharides and coutin) [26]; 1118 cm^{-1} (stretching vibration of C-O-C of sugars) [22]; 790 cm^{-1} (stretching vibration of C-C of lipids) [24]; 720 cm^{-1} (swing vibration of -CH_2- of sugars) [24] and 633 cm^{-1} (bending vibration of C-H of aromatic ring) [25], [26].

Raman spectrum from grape skin extract is presented in Fig. 2; the samples consisted of phenolic compounds. In more detail were contained phenolic acids, flavonols, flavanones, tannins, and anthocyanins.

Respectively, grape skins spectra showed absorption bands at different wavenumbers, as follows: 1849 cm^{-1} (bending vibration of C=O) [22]; 1628 cm^{-1} (bending vibration of C=C) [22]; 1466 cm^{-1} (stretching vibration of C-H; -CH_3 and C=C) [22]; 1364 cm^{-1} (stretching vibration of C-H; -CH_3 and -OH) [22]; 1112 cm^{-1} (bending vibration of C-C and C-O) [27]; 1058 cm^{-1} (bending vibration of benzene) [27], [28]; 975 cm^{-1} (bending vibration of C-CH_3) [28], [29]; 924 cm^{-1} (bending vibration of C-CH_3) [27], [28]; 850 cm^{-1} (bending vibration of C-C) [25]; 819 cm^{-1} (bending vibration of -CH_2) [26]; 786 cm^{-1} (bending vibration of C-C and -CH_2) [26] and 673 cm^{-1} (deformation of C=O) [25], [26].

TPC and antioxidant activity were estimated by Folin-Ciocalteu method, DPPH, and ABTS assays. The results are displayed in Table III.

Grape skins exhibited high TPC, and it was proved that

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during vinification a large amount of polyphenols remained in the pomace. Also, the results were related to the various characteristics. DPPH and ABTS result showed that the antioxidant activity is influenced by assay. DPPH assay had greater sensitivity to hydrophilic extracts as of grape skins, and ABTS assay had greater sensitivity to lipophilic extracts.

The above results, combined with production data by variety and per island on an annual basis, allowed for a first mass balance estimation that could form the basis of any management plan after a feasibility study.

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