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Direct HPLC Analysis of Quercetin and *trans*-Resveratrol in Red Wine, Grape, and Winemaking Byproducts

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A simple and fast reversed-phase HPLC method using diode array detection was developed and validated for the simultaneous determination of *trans*-resveratrol and quercetin in Sicilian red wine from the *Nero d'Avola* red grape variety. Investigation was also extended to the quantitative determination of resveratrol and quercetin in grape skins and winemaking byproducts obtained from the same cultivar. Samples were eluted using a C18 narrow-bore column under isocratic conditions in less than 20 min. Quantification of *trans*-resveratrol and quercetin in red wine was performed without any sample pretreatment, whereas the determination of these phenolic compounds in grape skins and wine pomage required a solvent extraction procedure. Linearity was demonstrated over the 0.39−12.5 and 0.45−57.6 μg/mL range for *trans*-resveratrol and quercetin, respectively. Detection limits in real samples were in the low ppm level (0.07 mg/L for *trans*-resveratrol and 0.12 mg/L for quercetin). The HPLC−UV/DAD method was applied for the routine analyses of red wine and grape skin and winemaking byproduct extracts to evaluate their *trans*-resveratrol and quercetin content. In particular, a very high content of quercetin was found in wine pomace, suggesting the use of this wine byproduct as a potential source of this health-promoting phenolic compound.

KEYWORDS: ***trans*-Resveratrol, quercetin, wine, winemaking byproducts, HPLC−UV/DAD**

INTRODUCTION

Phytoalexins are a group of low-molecular-mass compounds produced in grape vines and in a large number of plants as a defense response to situations of stress, such as microbial infections and UV irradiation (*1*).

trans-Resveratrol (3,5,4′-trihydroxystilbene), a phytoalexin that belongs to the group of compounds known as stilbenes, is known to occur in grapes and consequently in grape products and in wine. It is abundant in grape skin and present in higher concentration in red grape varieties compared with white varieties (*2*). *trans*-Resveratrol was originally identified as the active ingredient of an Oriental herb (Kojo-kon) used for treatment of a wide variety of diseases including dermatitis, gonorrhea, fever, hyperlipidemia, atherosclerosis, and inflammation. A number of studies have demonstrated the antioxidant effects of resveratrol and its ability to inhibit platelet aggregation and low-density lipoprotein (LDL) oxidation (*3*, *4*). As a consequence, over the past decade resveratrol has gained great attention and a number of scientific papers have appeared relating to the moderate consumption of red wine and its beneficial effects on health (*5*, *6*).

Quercetin is a flavonol that occurs widely in plants and is significantly present in red wine. Several biological actions of quercetin including protection of LDL cholesterol against oxidation (*7*) and promotion of endothelial vasorelaxation (*8*) have been reported. A synergistic effect between ethanol and the grape polyphenols, quercetin and resveratrol, in inhibiting the inducible nitric oxide synthase pathway involved in the damage of vascular walls and DNA has been demonstrated (*9*). Further, resveratrol, quercetin, and other polyphenols have been associated with a reduced risk of cancer (*10*).

Resveratrol and quercetin in wine are usually analyzed by reversed-phase high-performance liquid chromatography (RP-HPLC) with standard-bore columns. Most LC methods perform separation by gradient elution with spectrophotometric UV diode array detection (DAD) (*5*, *11*−*15*). Fluorimetric (*15*, *16*), fluorimetric in series with UV-DAD (*17*), and electrochemical detector (*18*, *19*) have been also applied to enhance the sensitivity of detection in HPLC. Methods based on gas chromatography and gas chromatography−mass spectrometry (GC−MS) (*20*, *21*) have been proposed for resveratrol. However, derivatization is required prior to GC analysis of this substance to enhance volatility, and this time-consuming procedure may result in some *trans* to *cis* isomerization of resveratrol (22). In past years, much work has been published on the application of LC coupled with MS for the analysis of

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these compounds (*23*, *26*). However, this hyphenated technique is very expensive and consequently not widely used in routine laboratories of wine industry. More recently, some applications have involved the use of capillary electrophoresis for the determination of phenolic compounds in wine (*27*−*29*).

The aim of this work was the development and the validation of a rapid and reliable reversed-phase liquid chromatography method with UV−visible diode array detector for the identification and determination of the red wine phenolic components *trans*-resveratrol and quercetin. It involves direct injections of wine samples without cleanup steps and the use of narrow-bore C_{18} column under isocratic conditions. Furthermore, our investigation was focused on the quantitative determination of *trans*-resveratrol and quercetin in grape pomace, a winemaking byproduct obtained from a pressing step in wine production. This product was analyzed as a potential source of these health-promoting phenolics in order to find possible industrial uses to add value to this material.

EXPERIMENTAL PROCEDURES

Materials. Quercetin and *trans*-resveratrol were purchased from Sigma (St. Louis, MO). Acetonitrile, methanol, and 2-propanol were HPLC grade and were obtained from Carlo Erba (Milan, Italy). Analytical-reagent-grade formic acid and HPLC-grade water were supplied by Carlo Erba (Milan, Italy).

RP-HPLC Analysis. The HPLC equipment consisted of a Shimadzu LC-10A$_{VP}$ system including two LC-10AD$_{VP}$ solvent delivery units, an SPD-M10A$_{VP}$ UV−vis photodiode array detector, an SCL-10A$_{VP}$ system controller, a CTO-10AS$_{VP}$ column oven, a DGU-14A degaser, and a model 8125 Rheodyne injection valve with a 5-μL loop. Data were processed using the Shimadzu Class VP 5.3 HPLC data system on a Pentium II 400 PC compatible computer. The column was a Luna 18 (2) (250 mm × 2.0 mm, 5 μm, Phenomenex, Torrance, CA) in conjunction with a Luna C18 (2) (30 mm × 2.0 mm, 5 μm) guard cartridge column. The column temperature was 30 °C. Elution was performed using a mobile phase made up of 1% (v/v) formic acid aqueous solution−acetonitrile−2-propanol (70:22:8) at a flow rate of 0.2 mL/min. Chromatograms were recorded at 306 and 370 nm for *trans*-resveratrol and quercetin, respectively. Analytes in each sample were identified by comparing their retention times and UV−vis spectra, in the 220−450 nm range, with those of authentic compounds. Peak purity was checked to exclude any contribution from interfering peaks.

Liquid Chromatography-Electrospray Mass Spectrometry (LC-ESI-MS). Identification of *trans*-resveratrol and quercetin was also confirmed by HPLC on-line coupled with electrospray ionization mass spectrometry (HPLC-ESI-MS) under the same chromatographic conditions as for UV detection. A postcolumn flow splitter was used to introduce 1/10 of the HPLC eluate into the mass spectrometer. The mobile phase was delivered by Waters 2690 series Alliance quaternary pump (Waters, Milford, MA) equipped with a 120-vial capacity sample management system. The injection volume was 5 μL.

A Quattro LC triple quadrupole instrument (Micromass, Manchester, UK) equipped with a electrospray interface and Masslynx v.3.4 software (Micromass) was used for data acquisition and processing.The nebulizing gas (nitrogen, 99.999% purity) and the desolvation gas (nitrogen, 99.998% purity) were delivered at flow rates of 55 and 500 L/h, respectively. Optimal operating parameters of the ESI interface and quadrupole were found by infusing standard solutions of *trans*-resveratrol and quercetin in the mobile phase (0.1 μg/mL) at 5 μL/min using a Harvard syringe pump. The mass spectrometer was operated in negative ion (NI) mode and was scanned over the m/z 200−500 range with a step size of 0.1 Da and a dwell time of 2 ms per step. Quadrupoles were tuned to unit mass resolution. The optimum conditions of the interface were as follows: electrospray voltage −2.5 kV, cone voltage −40 V, rf lens 0.5 V, source temperature 130 °C, desolvation temperature 150 °C. All calculations concerning the quantitative analysis were performed by external calibration.

Standard Preparation. Stock solutions containing 3.90 mg/mL of *trans*-resveratrol and 5.76 mg/mL of quercetin in methanol were prepared. Solutions were stored at −4 °C in the darkness after elimination of oxygen with a nitrogen stream to avoid decomposition of phenolic compounds. For calibration purposes working solutions covering the range 0.39−12.50 μg/mL for *trans*-resveratrol and 0.45−57.60 μg/mL for quercetin were prepared by diluting stock solutions with the mobile phase.

Wine Sample Preparation. Five Sicilian red wines produced by the *Nero d'Avola* grape cultivar were analyzed. Three of them were purchased from a local market and were from the 2000 vintage. Wine samples A and B, as well as grape fruit and grape pomace, were kindly provided by Eno Agricola "Pachino" (Pachino, Siracusa, Italy) and were from the 2001 vintage. For each wine, triplicate *trans*-resveratrol and quercetin analyses were carried out immediately after bottle opening. All samples were filtered through a 0.45-μm membrane filter (Millipore, Milford, MA) and directly injected into the HPLC.

Grape Product Sample Preparation. Extraction of *trans*-resveratrol and quercetin from grape skins and wine pomace, which is the residue consisting predominantly of skins, seeds, and stems that remains after the juice has been pressed from grapes, was carried out by the following procedure. A 0.2−1 g portion of sample, which was previously lyophilized, was weighed into screw-capped glass tubes. The sample was extracted with 25 mL of a methanol/ethanol (8:2, v/v) mixture by ultrasonication for 15 min and shaking for 12 h at room temperature. After centrifugation at 10,000*g*, the remaining pellet was re-extracted for 1 h using 5 mL of fresh extraction solvent. The combined extracts were evaporated under reduced pressure at 30 °C, and the residue was dissolved in 1 mL of methanol and submitted to chromatographic analysis. During sample preparation, extracts were constantly protected from light using light-proof containers to avoid photochemical isomerization of *trans*-resveratrol to the *cis* form. Recovery was determined for the overall assay by adding known amounts of *trans*-resveratrol and quercetin standards on the range of 10−40% of the original concentration of the analyzed samples. Samples were extracted twice, and three HPLC replicate injection were performed for each extract.

RESULTS AND DISCUSSION

A preliminary study was devoted to the optimization of chromatographic conditions to obtain good separation of *trans*-resveratrol and quercetin within a short analysis time.

Using the developed HPLC method, *trans*-resveratrol and quercetin peaks were well-resolved under isocratic elution with retention times of 12.39 ± 0.29 and 19.80 ± 0.35 (n = 24) min, respectively. No interference from other phenolic compounds present in the analyzed samples was observed. Furthermore, as illustrated in **Figure 1**, the proposed method was able to separate quercetin and both *trans*- and *cis*-resveratrol in a single run, but we focused attention on determining the more interesting and abundant *trans* form.

Method Validation. Good linearity was established over about 2 orders of magnitude for both analytes. Calibration curves yielded the following equations: $y = 139506(\pm 800)x$ (r = 0.9998) for *trans*-resveratrol and $y = 86279(\pm 288)x$ (r = 0.9999) for quercetin. The limits of detections (LODs) were found to be 0.07 and 0.12 mg/L for *trans*-resveratrol and quercetin, respectively (S/N = 3). Correspondingly, quantification limits (LOQs) were 0.30 mg/L for *trans*-resveratrol and 0.35 mg/L for quercetin (S/N = 10).

The precision of the method was studied as intra- and interday assay at three concentration levels for each compound (0.78, 1.56, and 3.12 μg/mL for *trans*-resveratrol and 0.90, 7.20, and 57.60 μg/mL for quercetin). Day-to-day variation was assessed by analyzing replicates of standards with the same concentration on three separate days. The method was found to be precise with RSD values within 0.85–2.13% for *trans*-resveratrol and 1.15−.95% for quercetin (intraday assay). Interday RSDs were below 3% for both analytes (**Tables 1** and **2**). The accuracy of the method was established by determining the recovery of

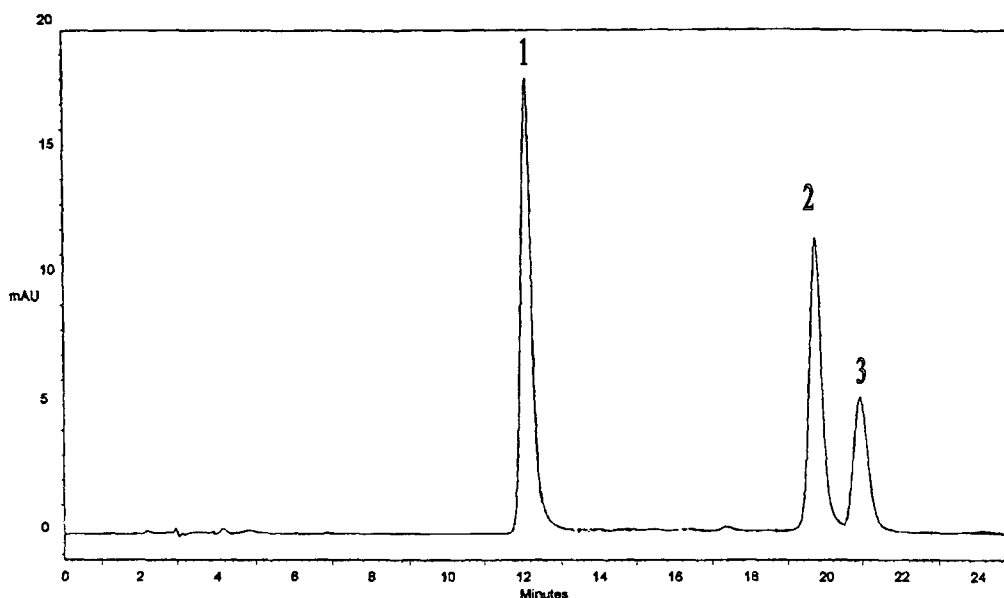

Figure 1. LC-UV/DAD chromatographic separation of (1) *trans*-resveratrol, (2) *cis*-resveratrol, and (3) quercetin. For chromatographic conditions see Experimental Procedures.

Table 1. HPLC-DAD Intraday Repeatability of *trans*-Resveratrol and Quercetin ($n = 6$)

analyte	concentration (μg/mL)[a]	RSD (%)
trans-resveratrol	0.39	2.13
	3.12	1.76
	12.5	0.85
quercetin	0.45	1.95
	7.20	1.37
	57.6	1.15

[a] Injection volume = 5 μL.

Table 2. HPLC-DAD Interday Precision of *trans*-Resveratrol and Quercetin ($n = 6$)

analyte/day	concn (μg/mL)[a]	RSD (%)	concn (μg/mL)[a]	RSD (%)	concn (μg/mL)[a]	RSD (%)
trans-resveratrol						
1	0.39	2.81	3.12	2.45	12.5	1.34
2		2.76		2.51		1.42
3		2.78		2.39		1.39
quercetin						
1	0.45	2.36	7.20	1.87	57.60	1.13
2		2.45		1.65		1.09
3		2.31		1.58		1.17

[a] Injection volume = 5 μL.

Table 3. Recovery of *trans*-Resveratrol and Quercetin in Wine Obtained in Accuracy Analysis

compound	amount in sample[a]	added[a]	found[a]	recovery (%)	RSD (%)
trans-resveratroll	2.63	0.23	2.82	98.60	1.03
	2.63	0.46	3.04	98.38	0.28
	2.63	0.69	3.22	96.98	0.70
Quercetin	7.72	0.93	8.64	99.88	2.94
	7.72	1.86	9.47	98.85	1.97
	7.72	3.72	11.06	96.69	2.45

[a] Values in μg/mL.

Table 4. Concentration of *trans*-Resveratrol and Quercetin in *Nero d'Avola* Red Wine Samples

sample	*trans*-resveratrol (mg/L)[a]	quercetin (mg/L)[a]
A	0.56 ± 0.06	0.89 ± 0.04
B	1.25 ± 0.05	1.55 ± 0.03
C	0.82 ± 0.05	4.20 ± 0.05
D	2.86 ± 0.03	8.84 ± 0.08
E	2.63 ± 0.07	7.72 ± 0.06

[a] Mean value ± SD ($n = 3$).

trans-resveratrol and quercetin spiked to the sample in the range of 10−50% of the original concentration in wines, grape skins, and wine pomace and analyzing them in triplicate according to the proposed method. For all samples analyzed results were of the same order as those reported in **Table 3** for a wine sample. In all analyzed wine samples mean recovery for each concentration ranged from 96.69% to 99.88% ($n = 3$) and the relative standard deviation of the results for each concentration was less than 3% (**Table 3**).

Analysis of Wine. The optimized procedure was applied to the determination of *trans*-resveratrol and quercetin in the five red wines under investigation. **Figure 2** shows the chromatograms registered at 306 and 370 nm for a wine sample, and the insets A and B depict the UV−vis spectra relevant to the peak of *trans*-resveratrol and quercetin. The identification of both compounds was confirmed by ESI-MS data. As reported in **Figure 3**, ESI-MS mass spectra of *trans*-resveratrol and quercetin were characterized by the deprotonated molecules $[M - H]^-$ at m/z 227 and 301, respectively.

Table 4 summarizes the values of *trans*-resveratrol and quercetin found in the red wine samples analyzed. In agreement with other authors (*14*), there was a considerable variability in *trans*-resveratrol concentration in wines produced by the same grape variety. Remarkable differences were observed also for quercetin content in the same samples. However, it has to be noticed that wine samples A, B, and C were aged for at least 12 months in the bottle, whereas wines D and E were young red wines that were sampled before they were bottled. On the basis of these observations, our findings were not unexpected since a number of factors such as growing conditions, wine-making techniques, aging, and storage conditions are known to affect phenolic composition in wines. In addition, the wide range

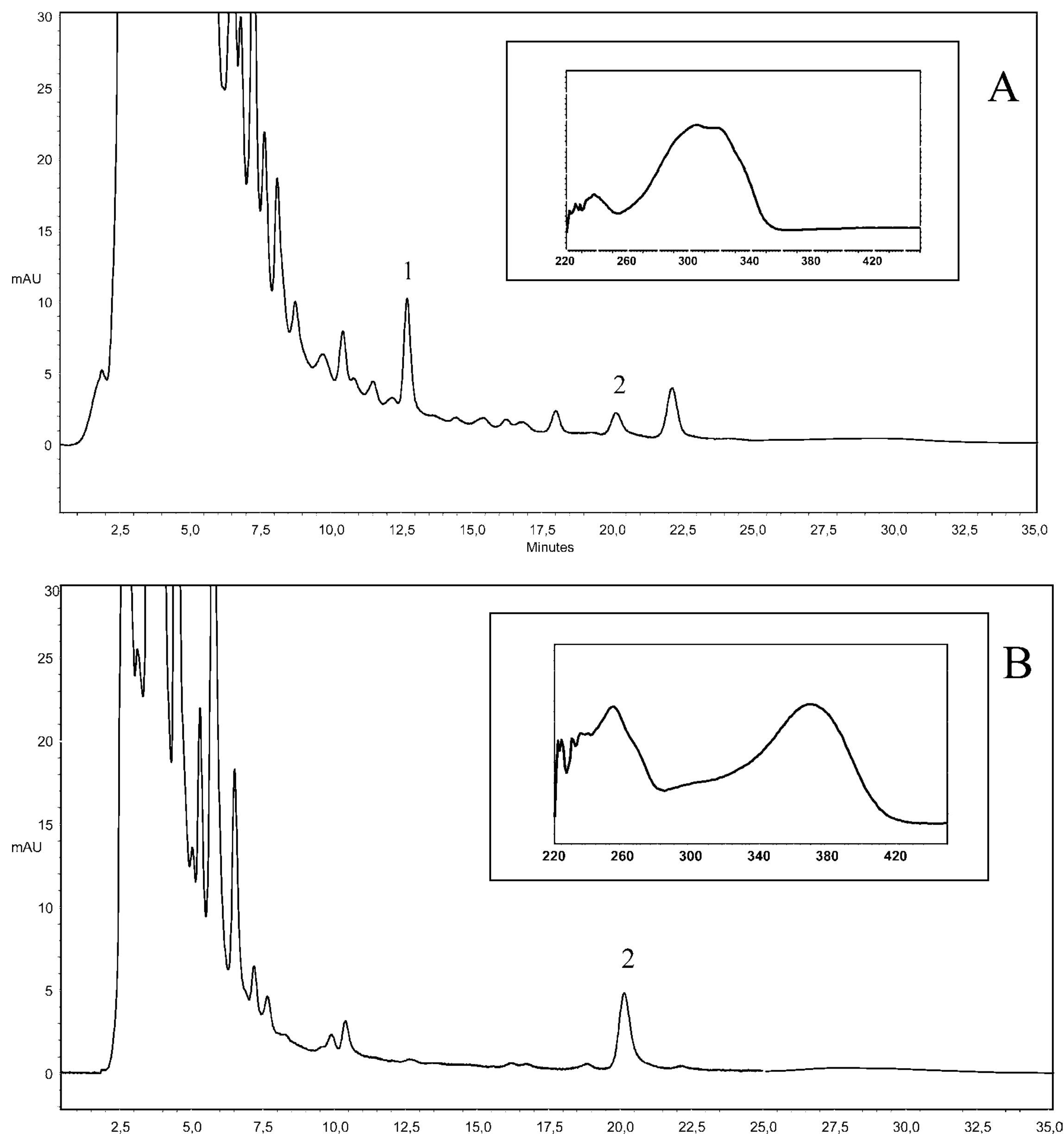

Figure 2. Separation of *trans*-resveratrol (peak 1) and quercetin (peak 2) in a red wine sample. Panel A: HPLC-UV/DAD chromatogram detected at 306 nm. Inset: UV spectrum of *trans*-resveratrol. Panel B: HPLC-UV/DAD chromatogram detected at 370 nm. Inset: UV spectrum of quercetin. Chromatographic conditions as in the text.

which the concentration of *trans*-resveratrol spans can be explained considering that this phytoalexin and other stilbenes are produced by grapes in response to mold infections and physiological stresses and their levels in grapes and wines may be low if those phenomena were less marked. Furthermore, in all of the tested samples quercetin level was always higher than that of *trans*-resveratrol, and for aged bottled wine it was in agreement with data regarding Italian wines (*30*).

Analysis of Grape Products. Preliminary tests were carried out to determine the most appropriate extraction solvents to extract *trans*-resveratrol and quercetin from grape skins and wine pomace samples. In a first step samples were lyophilized to eliminate all water contained, and the weight losses were 51% for grape skin and 62% for grape pomace, respectively. In a further step three different solvent systems such as acetone, acetone/water (7:3, v/v), and methanol/ethanol (8:2, v/v) were tested. Significant differences were observed in the amounts of *trans*-resveratrol, depending on the extraction system. Using acetone as extraction solvent, very complex chromatograms were obtained that did not allow the easy identification and accurate quantitation of *trans*-resveratrol in the extracted samples. In contrast, *trans*-resveratrol was eluted in a cleaner zone when acetone/water or methanol/ethanol was used as solvent mixtures. Furthermore, as reported in **Table 5**, quantitative analysis of the analytes in the extracts proved that both acetone/water and methanol/ethanol solvent mixtures exhibited similar extraction yields. Since the variation between replicate extractions was lowest when methanol/ethanol was used (**Table 5**) and the presence of water increased the time required for drying the samples, methanol/ethanol (8:2, v/v) was selected as the extraction solvent for routine analysis of *trans*-resveratrol and quercetin from dried grape skin and pomace.

Using the selected extraction procedure, recovery was determined by adding varying amounts of *trans*-resveratrol and quercetin standard at three levels in the range of 10−40% into the grape skin and wine pomace extracts. Recovery was between

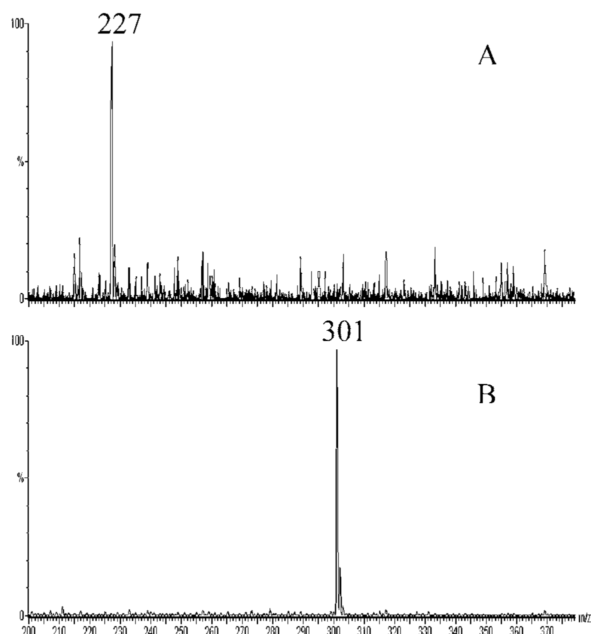

Figure 3. ESI mass spectra of (A) all-*trans* resveratrol and (B) quercetin in a red wine extract sample.

Table 5. Mean Concentrations (μg/g) and Standard Deviation ($n = 3$) of *trans*-Resveratrol and Quercetin in Grape Skin and Grape Pomace Extracted with Different Solvents

sample	extraction solvent	*trans*-resveratrol (μg/g)[a]	quercetin (μg/g)[a]
grape skin	acetone	32.5 ± 4.1	0.15 ± 0.07
	acetone/water (7:3, v/v)	26.2 ± 1.8	0.15 ± 0.05
	methanol/ethanol (8:2, v/v)	27.5 ± 1.3	0.16 ± 0.04
grape pomace	acetone	8.9 ± 2.1	104.7 ± 2.5
	acetone/water (7:3, v/v)	5.89 ± 0.08	103.2 ± 2.3
	methanol/ethanol (8:2, v/v)	6.00 ± 0.05	103.9 ± 1.6

[a] Mean value ± SD ($n = 6$).

Table 6. Concentration of *trans*-Resveratrol and Quercetin in Grape Skin and Grape Pomace Extract

sample	*trans*-resveratrol (μg/g)[a]	quercetin (μg/g)[a]
grape skin	27.5 ± 1.3	0.16 ± 0.04
grape pomace	6.00 ± 0.05	103.9 ± 1.6

[a] Mean value ± SD ($n = 6$).

97.2 ± 1.3% and 102.5 ± 1.0% for *trans*-resveratrol and between 96.9 ± 0.9% to 103.1 ± 1.1% for quercetin in both samples.

As can be seen from results summarized in **Table 6**, quercetin and *trans*-resveratrol were found in the analyzed extracts, the levels of the former being considerably higher. A significant result of our analyses is that the quercetin content of wine pomace is very high, so that this wine byproduct could be a potential source of this health-promoting phenolic compound, considering that quercetin exhibits antioxidant and antiplatelet aggregation activity similar to, if not greater than, that of resveratrol (*4*, *7*, *8*).

CONCLUSIONS

A simple, rapid, and reliable RP-HPLC method was developed for routine analysis of *trans*-resveratrol and quercetin in red wine, grape skin, and wine pomace samples. Good separation was demonstrated under isocratic conditions. The method was characterized by good precision, linearity, and accuracy. The proposed method allowed us the determination of *trans*-resveratrol and quercetin in wine by direct injection without sample pretreatmen and in grape skin and pomace after lyophilization and solvent extraction. The results obtained in this investigation are in agreement with previous research for resveratrol and quercetin composition in red wine. On the other hand, findings of this study provide a deeper knowledge regarding the content of these antioxidants in grape products.

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