

## Dealcoholized Wines by Spinning Cone Column Distillation: Phenolic Compounds and Antioxidant Activity Measured by the 1,1-Diphenyl-2-picrylhydrazyl Method

YULISSA Y. BELISARIO-SÁNCHEZ,<sup>†</sup> AMAURY TABOADA-RODRÍGUEZ,<sup>‡</sup>  
FULGENCIO MARÍN-INIESTA,<sup>‡</sup> AND ANTONIO LÓPEZ-GÓMEZ<sup>\*,†</sup>

<sup>†</sup>Department of Food Engineering and Agricultural Equipment, Technical University of Cartagena, Paseo Alfonso XIII 48, 30203 Cartagena, Spain, and <sup>‡</sup>Department of Food Technology, Nutrition and Bromatology, University of Murcia, Campus de Espinardo, 30071 Murcia, Spain

Spinning cone column (SCC) distillation has been shown to be a commercially suitable technique for dealcoholized wine (DW) manufacturing, but there are not enough studies about its influence on the DW quality. So, the effect of this technique on the antioxidant activity (% of remaining 1,1-diphenyl-2-picrylhydrazyl radical) and the phenolic compound composition of red, rose, and white DW, obtained at pilot plant scale, has been analyzed. Nineteen raw wines (RWs) from different grape varieties and five different Spanish viticultural regions have been studied before and after dealcoholization. The total phenolic content, flavonols, tartaric esters, and anthocyanins, was determined by spectrophotometry, while the content of phenolic compounds such as stilbenes (*trans*- and *cis*-resveratrol), flavonols (rutin, quercetin, and myricetin), flavan-3-ols [(+)-catechin and (–)-epicatechin], anthocyanins (malvidin 3-glucoside), and non-flavonoids (gallic, caffeic, and *p*-coumaric acids) was determined by high-performance liquid chromatography (HPLC). The resveratrol contents in red wines were between 1.81 and 34.01 mg/L in RWs and between 2.12 and 39.57 mg/L in DWs, Merlot being the grape producing the RWs and DWs with higher resveratrol content. In general, the percent of remaining DPPH\* was similar or slightly higher (until 5 units of % of remaining DPPH\*) in DWs versus RWs. This small difference may be due to removal of SO<sub>2</sub> (that is an antioxidant) from RWs during distillation. DWs and RWs show similar contents of the studied phenolic compounds, with a tendency, in some cases, to exhibit increases after dealcoholization, caused by the concentration effect via removal of the ethanol. From this work, we can deduce that SCC distillation is a dealcoholization technique minimally destructive with the wine phenolic compounds.

**KEYWORDS:** Dealcoholized wines; SCC distillation; resveratrol; phenolic compounds; antioxidant activity; DPPH

### INTRODUCTION

Although the question of whether the potential health benefits of wine intake are due to alcohol or the nonalcoholic fraction of wine remains unclear, according to research carried out by Greenrod et al. (1) consumption of dealcoholized red wine significantly decreased the level of  $\gamma$ -radiation-induced DNA damage 1 and 2 h postconsumption by 20%, while in contrast, alcohol tended to increase the level of radiation-induced genome damage. In fact, DNA damage, mediated by reactive oxygen species, is implicated in the aging process and associated diseases such as atherosclerosis, cancer, and Alzheimer's disease (2).

Most of the beneficial effects associated with the moderate consumption of red wine are related to polyphenols. López et al. (3) demonstrated that the administration of dealcoholized red wine and dealcoholized white wine rich diets to rats modulates

the oxidative stress and the inflammatory response in the carrageenan-induced granuloma pouch, used as a model of acute inflammation. It has been assumed that red wine shows more protective effects than white wine in vitro because of its high content of polyphenolic antioxidants (3). Moreover, wine also contains nonpolyphenolic compounds with antioxidant activity, such as sulfites (4).

These phenolic compounds can be classified into two groups: the flavonoids and non-flavonoids. The major flavonoids in wine include conjugates of the flavonols rutin, quercetin, and myricetin, flavan-3-ols (+)-catechin and (–)-epicatechin, and anthocyanins such as malvidin 3-glucoside. The non-flavonoids include hydroxybenzoates *p*-hydroxybenzoic acid and gallic acid, hydroxycinnamates caffeic, caftaric, and *p*-coumaric acids, and stilbenes *trans* (*t*)-resveratrol and *cis* (*c*)-resveratrol (5, 6). These compounds have antioxidant properties, and they are effective radical scavengers with respect to oxygen free radicals and lipid peroxidation (7, 8). Since flavonoids mainly act by scavenging free

\*To whom correspondence should be addressed. E-mail: antonio.lopez@upct.es. Telephone: +34-968325516. Fax: +34-968325433.

radicals whereas resveratrol is a better chelator of copper, it seems possible that the presence of two types of antioxidants in wine may be advantageous. In fact, the possibility that numerous compounds unequally distributed in wines may interact to reinforce their specific antioxidant properties has to be considered (9). Hence, Frankel et al. (10, 11), Frémont et al. (9), and Soleas et al. (12) considered that the health significance of resveratrol in relation to the other antioxidants is an open question.

Low-alcohol and alcohol-free wines can be produced by different techniques: (i) distillation under vacuum or atmospheric pressure, (ii) evaporation, (iii) freeze concentration, (iv) membrane processes [dialysis, reverse osmosis, and membrane contactors (18)], (v) adsorption (on resins or on silica gels), and (vi) extraction using organic solvents or supercritical carbon dioxide (13). However, the spinning cone column (SCC), vacuum distillation equipment (14, 15), and a reverse osmosis (RO) system (16, 17) are among the systems more utilized in the industry (18).

The SCC is a distillation device with established commercial applications, such as alcohol adjustment of wines and recovery of flavors from fruit juices, tea, and coffee (14). An SCC consists of a vertical pack of alternate rotating and stationary cones and, as compared to the traditional plate and packed distillation columns, has particular characteristics for the low-temperature distillation of thermally sensitive foodstuffs (15).

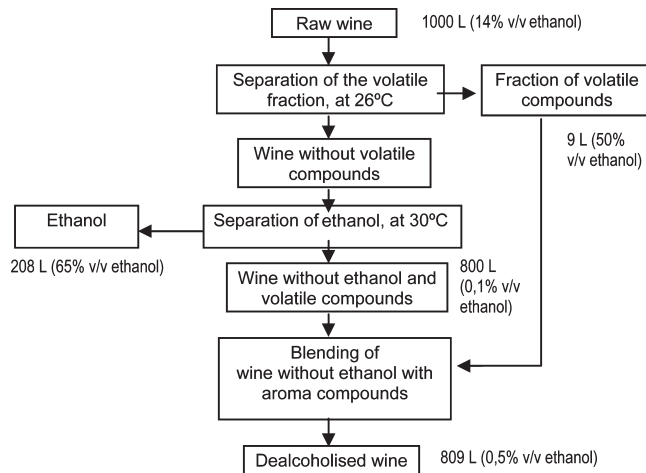
The physical behavior of the SCC has been studied using different modeling techniques (14, 15, 19, 20). However, the quality of low-alcohol wines obtained from different technologies has been not studied much, and the work has focused mainly on sensory quality and aroma fraction (18, 21–23), not on phenolic compounds.

For the reasons given above, and because the dealcoholized wine begins to break with effort in the beverage market, it is important to determine the extent to which the SCC distillation dealcoholization process changes the composition of phenolic compounds and antioxidant activity in wine. This paper makes a comparative analysis of the phenolic composition of wines before and after they have been dealcoholized, using the SCC distillation technique at pilot plant level.

## MATERIALS AND METHODS

**SCC Distillation.** It is performed in a SCC distillation pilot plant (the manufacturer is Conetech; the production capacity is 1000 L/8 h, including dead times for preparing each step; and the column is 0.33 m in diameter and 2 m in height), at mild operation temperatures (26–30 °C), and at a vacuum of < 32 mmHg. It is not a standard model, but an adaptation of the SCC's normal system, because it does not use external steam as the stripping agent. In this column, a very small amount of the same wine is converted into a form of low-temperature vapor (the stripping agent) created when it “flashes off” in the high-vacuum environment in the column. The wine dealcoholization takes place in two steps: a first stage of aroma recovery (working at 26 °C, with a capacity of 700 L/h) and a second stage of ethanol removal (at 30 °C, and a capacity of 230 L/h). After ethanol separation, the complete aromatic fraction is added back to the wine (41). The process flow-sheet used, with volatiles and ethanol separation by SCC distillation, is shown in Figure 1.

**Wine Samples.** The phenolic composition and the antioxidant activity were determined for 38 samples from 19 raw wines (RWs) (before SCC distillation) and the 19 corresponding dealcoholized wines (DWs) (after SCC distillation). These samples were 13 red, 2 rose, and 4 white DWs with less than 0.3% (v/v) ethanol. The origin of RW was from five different Spanish appellations (“Denominaciones de Origen”), Vinos de Madrid, Jumilla, Málaga, Alicante, and La Mancha. The Spanish wine samples were monovarietal from the grapevine varieties (vintage 2006, if other year is not indicated): Petit Verdot, Garnacha, Syrah (vintage 2006 and 2007),



**Figure 1.** Dealcoholized wine making process flow-sheet, with volatiles and ethanol separation by the SCC distillation technique. The figures are given in volume (liters) on a basis time of 8 h, for the SCC distillation pilot plant used.

Monastrell, Monastrell condolina, Tempranillo (vintage 2006 and 2007), Cabernet Sauvignon (red and rose), Merlot (2007), Macabeo, Bobal, Airén, Malvar, Moscatel romano, and two coupages: aged (“crianza”, vintage 2004) from Monastrell, Tempranillo, Cabernet Sauvignon, and Petit verdot and young (“joven”, vintage 2006) from Monastrell, Merlot, Tempranillo, Syrah, and Cabernet Sauvignon. In our preliminary studies of this technique, the same wine has been dealcoholized in three different batches (for three different wines) and the quality differences (phenolic content and other quality parameters) have been not significant between the different batches of the same wine (Table 1). This is essential for the industrial acceptance of this technique, to yield a product with a uniform quality, so because of the cost of experimentation, the SCC distillation took place only once for each different wine.

**Chemicals.** The stilbene *trans* (*t*)-resveratrol (CAS registry no. 501-36-0), the hydroxybenzoate gallic acid (CAS registry no. 149-91-7), the hydroxycinnamates caffeic acid (CAS registry no. 331-39-5) and *p*-coumaric acid (CAS registry no. 501-98-4), the flavan-3-ols (–)-epicatechin (CAS registry no. 490-46-0) and (+)-catechin (CAS registry no. 7295-85-4), the flavonols rutin (CAS registry no. 207671-50-9), myricetin (CAS registry no. 529-44-2), and quercetin (CAS registry no. 117-39-5), and the anthocyanin malvidin 3-glucoside (CAS registry no. 7228-78-6) were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO). The methanol, ethanol, and solvents were liquid chromatography grade and were purchased from Sigma Aldrich Chemical Co. Milli Q water was obtained from Milli-Q water purification equipment (Millipore, Bedford, MA). The 1,1-diphenyl-2-picrylhydrazyl (DPPH, CAS registry no. 1898-66-4) was from Sigma Aldrich Chemical Co.

**Sample Extraction for Resveratrol High-Performance Liquid Chromatography (HPLC) Analysis.** The method followed for sample extraction has been the proposed by Malovaná et al. (24), with some modifications. Sep-Pak Plus C-18 cartridges have been used for the solid phase extraction using methanol as the eluent. The Sep-Pak Plus C-18 cartridge was first conditioned with 4 mL of methanol, followed by 4 mL of water, and then 5 mL of wine was introduced into the cartridge; this cartridge was dried with a nitrogen gas stream, and compounds were eluted with 1.5 mL of methanol. The solution obtained was injected into the HPLC system after being filtered through a 0.45 mm cellulose filter (Millipore). The separation was conducted in Agilent HPLC equipment (series 1100) with a PDA detector. A Luna 5  $\mu$  C 18(2) [250 mm  $\times$  4.6 mm (inside diameter)] column from Phenomenex was used. The eluent was monitored at two different wavelengths, 284 and 305 nm, where *cis* and *trans* isomers have maximum absorbance, respectively. The volume injected was 20  $\mu$ L, with a methanol/acetic acid/water (10:2:88, v/v) mixture as solvent A and a methanol/acetic acid/water (90:2:8, v/v) mixture as solvent B. The following gradient was used for solvent A: 100, 50, 0, and 100% (corresponding times of 0, 60, 100, and 110 min, respectively). The following gradient was used for solvent B: 0, 50, 100, and

**Table 1.** Results<sup>a</sup> of the Preliminary SCC Trials with Three Different Red Wines

	DW from red wine 1 (Crianza 2004)			DW from red wine 2 (Tempranillo 2006)			DW from red wine 3 (Garnacha Tintorera 06) <sup>g</sup>		
	batch 1	batch 2	batch 3	batch 1	batch 2	batch 3	batch 1	batch 2	batch 3
% DPPH <sup>*</sup> <sub>rem</sub>	13.92 ± 0.62	14.05 ± 0.12	13.60 ± 0.25	20.60 ± 0.60	21.11 ± 0.40	20.93 ± 0.25	19.49 ± 0.93	20.23 ± 0.35	20.11 ± 0.28
total phenolics <sup>b</sup>	1731.4 ± 5.2	1717.2 ± 9.8	1723.9 ± 10.6	1249.8 ± 21.8	1255.9 ± 38.2	1250.1 ± 23.8	1940.3 ± 80.0	1903.5 ± 75.2	1972.4 ± 65.0
tartaric esters <sup>c</sup>	42.21 ± 0.37	41.99 ± 0.99	41.60 ± 0.60	45.13 ± 0.39	45.22 ± 0.55	44.99 ± 0.35	42.41 ± 0.22	41.22 ± 0.89	42.01 ± 0.35
flavonols <sup>d</sup>	25.74 ± 2.01	27.55 ± 0.67	27.06 ± 0.42	22.93 ± 1.59	20.88 ± 1.50	21.10 ± 0.99	37.19 ± 0.41	37.01 ± 0.25	36.88 ± 0.56
anthocyanins <sup>e</sup>	113.23 ± 0.69	112.68 ± 0.76	111.72 ± 0.47	78.36 ± 1.25	77.51 ± 1.69	77.99 ± 0.94	169.23 ± 1.10	172.33 ± 1.99	171.11 ± 1.66
<i>trans</i> -resveratrol <sup>f</sup>	3.43 ± 0.14	3.37 ± 0.12	3.33 ± 0.11	ND <sup>h</sup>	ND <sup>h</sup>	ND <sup>h</sup>	ND <sup>h</sup>	ND <sup>h</sup>	ND <sup>h</sup>
<i>cis</i> -resveratrol <sup>f</sup>	7.73 ± 0.15	7.87 ± 0.09	7.80 ± 0.08	2.12 ± 0.23	2.14 ± 0.13	2.28 ± 0.37	23.19 ± 0.30	22.90 ± 0.22	23.40 ± 0.38
gallic acid <sup>f</sup>	27.35 ± 0.66	26.43 ± 0.52	27.19 ± 0.44	11.78 ± 0.42	11.64 ± 0.50	11.33 ± 0.41	181.56 ± 9.91	173.11 ± 10.12	175.82 ± 8.22
epicatechin <sup>f</sup>	47.32 ± 0.81	49.05 ± 1.10	47.60 ± 0.92	14.94 ± 0.56	14.60 ± 0.78	14.52 ± 0.61	55.76 ± 1.99	54.66 ± 1.53	55.92 ± 1.45
catechin <sup>f</sup>	82.07 ± 0.45	83.09 ± 0.73	82.77 ± 0.56	24.60 ± 0.56	24.54 ± 0.77	24.31 ± 0.43	37.94 ± 2.20	37.72 ± 2.11	36.71 ± 1.98
caffeic acid <sup>f</sup>	4.61 ± 1.01	4.78 ± 1.06	3.92 ± 1.68	ND <sup>h</sup>	ND <sup>h</sup>	ND <sup>h</sup>	10.58 ± 0.71	9.92 ± 0.83	10.02 ± 0.64
<i>p</i> -coumaric acid <sup>f</sup>	1.64 ± 0.06	1.72 ± 0.08	1.75 ± 0.10	1.42 ± 0.08	1.47 ± 0.10	1.58 ± 0.07	3.18 ± 0.02	3.11 ± 0.08	3.22 ± 0.06
rutin <sup>f</sup>	22.05 ± 0.09	22.12 ± 0.50	21.60 ± 0.08	25.60 ± 0.13	25.39 ± 0.19	25.44 ± 0.22	15.75 ± 0.13	16.21 ± 0.11	16.02 ± 0.15
myricetin <sup>f</sup>	10.58 ± 0.16	10.73 ± 0.13	10.90 ± 0.11	4.75 ± 0.17	4.66 ± 0.18	4.47 ± 0.15	6.88 ± 0.60	7.73 ± 0.55	7.44 ± 0.39
quercetin <sup>f</sup>	4.37 ± 0.02	4.16 ± 0.17	4.23 ± 0.08	4.34 ± 0.04	4.21 ± 0.09	4.30 ± 0.08	14.38 ± 1.47	14.99 ± 1.52	15.76 ± 1.13
malvidin <sup>f</sup>	12.17 ± 0.09	12.06 ± 0.08	11.99 ± 0.12	20.73 ± 1.59	22.01 ± 1.28	20.97 ± 1.19	24.76 ± 4.66	21.85 ± 3.18	22.67 ± 3.47

<sup>a</sup> Average of three replicates ± the standard deviation. <sup>b</sup> Milligrams of gallic acid per liter. <sup>c</sup> Milligrams of caffeic acid per liter. <sup>d</sup> Milligrams of quercetin per liter. <sup>e</sup> Milligrams of malvidin 3-glucoside per liter. <sup>f</sup> Values given as milligrams per liter. No statistical difference between the batches has been found. <sup>g</sup> Garnacha Tintorera 06 is a red wine from the Spanish grape variety Garnacha Tintorera (vintage 2006 and DO Jumilla), used only in the preliminary SCC trials, but not included in the rest of the study shown in this paper. <sup>h</sup> Not detected.

0% (corresponding times of 0, 60, 100, and 110 min, respectively). The flow rate was 0.2 mL/min.

**Percentage of Remaining DPPH\* (% DPPH\*<sub>rem</sub>).** The free radical scavenging activity in the wines, and dealcoholized wines, was determined using the 1,1-diphenyl-2-picrylhydrazyl (DPPH\*) method, and it was expressed as the percentage of remaining DPPH\* (% DPPH\*<sub>rem</sub>). This method measures the ability of a wine to scavenge free radicals in the oxidation process. The higher the free radical scavenging activity of a wine, the lower the percentage of remaining DPPH\* (25, 26).

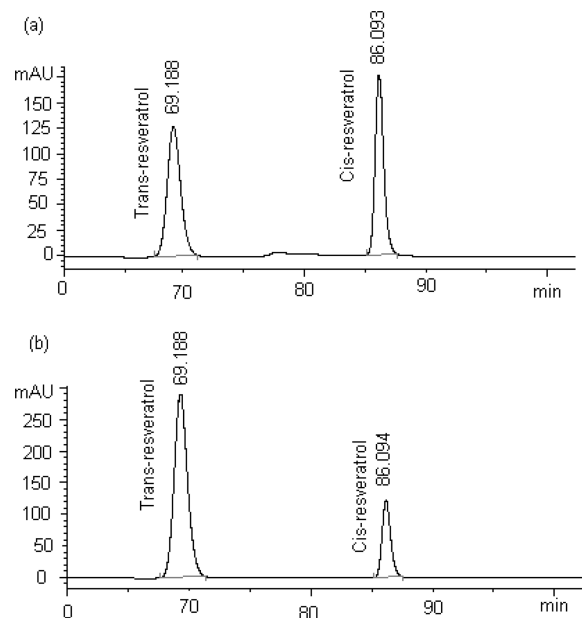
The wine sample (0.1 mL) was added to 3.9 mL of DPPH\* (25 mg/L in methanol). The absorbance at 515 nm was measured at different time intervals until equilibrium was reached. All measurements were performed in triplicate. The determination of the percentage of remaining DPPH\* was conducted by spectrophotometry at 515 nm in an Evolution 300 spectrophotometer, with optical glass cuvettes of 1 cm and a bandwidth of 1.5 nm (25). The equation for calculating % DPPH\*<sub>rem</sub> was

$$\% \text{ DPPH}^*_{\text{rem}} = [A_f / (A_o + A_v)] \times 100$$

where  $A_o$  is the absorbance of a methanol solution of 25 mg/L DPPH,  $A_v$  is the absorbance of 3.9 mL of methanol and 0.1 mL of a wine sample, and  $A_f$  is the absorbance at the end of the reaction of 3.9 mL of the methanol solution of DPPH and 0.1 mL of a wine sample.

**Total Phenolic, Flavonol, Tartaric Ester, and Anthocyanin Content Analysis.** The total phenolic, flavonol, tartaric ester, and anthocyanin content was determined according to the method used by Cliff et al. (27). A sample of 0.5 mL in volume was taken from each wine (dealcoholized or not) and diluted to a volume of 5 mL with 10% ethanol. A 0.25 mL aliquot of each diluted sample was subsequently added to 0.25 mL of 0.1% HCl in 95% ethanol, and 4.55 mL of 2% HCl. Each sample was vortexed and allowed to stand for 15 min. The absorbance of each sample was measured in a 1 cm quartz cuvette at 280, 320, 360, and 520 nm using a Beckmann DU 640 spectrophotometer. Absorbance readings at each wavelength corresponded to total phenolic ( $A_{280}$ ), tartaric ester ( $A_{320}$ ), flavonol ( $A_{360}$ ), and anthocyanin ( $A_{520}$ ) content, which was determined from standard curves constructed using dilutions of gallic acid (in 10% ethanol), caffeic acid (in 10% ethanol), quercetin (in 95% ethanol), and malvidin 3-glucoside (in 10% ethanol) at 280, 320, 360, and 520 nm, respectively.

**Identification and Quantification of Phenolic Compounds.** Gallic acid, caffeic acid, *p*-coumaric acid, (–)-epicatechin, (+)-catechin, rutin, myricetin, quercetin, and malvidin 3-glucoside were identified and quantified by HPLC according to the method used by Cantos et al. (28). The analyses were performed on an HPLC Waters Alliance 2695 system, with a Waters 2487 separations module equipped with a dual absorbance



**Figure 2.** Chromatograms of *trans*-resveratrol and *cis*-resveratrol in standard solutions: (a) at 284 nm and (b) at 305 nm.

detector and a Microchart RP-18 column (Merck, Darmstadt, Germany) (250  $\mu\text{m} \times 4 \mu\text{m}$ , 5  $\mu\text{m}$  particle size), using as solvents water with 5% formic acid (solvent A) and methanol (solvent B) at a flow rate of 1 mL/min. Elution was performed with a gradient from 2 to 32% B for 30 min, to 40% B at 40 min, and to 95% B at 50 min, and then the gradient became isocratic for 5 min. Chromatograms were recorded at 510, 370, 320, and 280 nm.

**Calibration Curves. Phenolic Compounds.** Calibration curves have been determined for all compounds determined by HPLC, and the  $r^2$  values were as follows:  $r^2 = 0.998$  for gallic acid,  $r^2 = 0.995$  for (–)-epicatechin,  $r^2 = 0.996$  for (+)-catechin,  $r^2 = 0.989$  for caffeic acid,  $r^2 = 0.985$  for *p*-coumaric acid,  $r^2 = 0.999$  for rutin,  $r^2 = 0.999$  for myricetin,  $r^2 = 0.977$  for quercetin, and  $r^2 = 0.999$  for malvidin.

**Resveratrol.** To build the calibration curve of *trans*-resveratrol, solutions of *trans*-resveratrol from 0.2 to 25 mg/L were prepared by dilution of a standard solution of 500 mg/L in methanol; all dissolutions were stored at 4 °C and protected from light. For the calibration of

the *cis*-resveratrol, since its commercial standard is not available, diluted solutions of *trans*-resveratrol were exposed to UV irradiation as described elsewhere (30). The exposure to UV light causes *trans*-resveratrol to be transformed to *cis*-resveratrol. The three provided concentrations were measured by graphics, and curves were obtained with  $r^2$  values of 0.998 and 0.995. **Figure 2** shows the chromatogram with the two peaks corresponding to *trans*-resveratrol and *cis*-resveratrol. For each standard, the limit of detection (LoD) and the limit of quantification (LoQ) were fixed at 3 and 10 times, respectively, the signal-to-noise ratio (S/N) (42). The values obtained for LoD and LoQ in *trans*-resveratrol are 0.03 and 0.11 mg/L and in *cis*-resveratrol 0.12 and 0.40 mg/L, respectively.

**Quantification of Ethanol.** The ethanol content was quantified in the RWs and DWs directly, without any previous treatment of the filtered sample (in a 0.45  $\mu$ m nylon filter, from Millipore), in a Thermo Finnigan Trace As 2000 gas chromatograph, equipped with a flame ionization detector (FID), and a 30 m J&W Scientific DB-5 capillary column (0.25 mm inside diameter, 0.25  $\mu$ m film thickness), and an AS2000 autosampler. The oven temperature was controlled with a temperature elevation program during analysis, which was initially set at 62 °C for 2.5 min, then increased at a rate of 25 °C/min to 120 °C, and maintained at this temperature for 4 min. The detector temperature was 300 °C (250 °C at the injector port). The flow rate of the carrier gas, helium, was set at

1 mL/min and the split vent at 25 mL/min. The volume of injection was 1  $\mu$ L in splitless mode. The ethanol standard curve was determined for concentrations between 0.05 and 15% (v/v).

**Statistical Analysis.** Data were analyzed using the STAT-GRAPHICS Plus statistical package. Analysis of variance was conducted on the analytical variables to determine the main effects of the dealcoholization process and kind of wine (red, rose, and white). Duncan's multiple-range tests were used to separate the means ( $p \leq 0.05$ ) for the analytical data.

## RESULTS AND DISCUSSION

The ethanol content obtained for the 19 RWs studied was between 11.95 and 14.00% (v/v), while for the corresponding DWs, it was 0.05–0.15% (v/v). For the aroma fraction stream, the ethanol content was between 46.00 and 50.00% (v/v). On the basis of 8 h, from 1000.00 L of RW [with the maximum ethanol content of 14.00% (v/v) ethanol] the following values were obtained: 208.00 L for the ethanol stream [65.00% (v/v) ethanol], 9.00 L of aroma fraction [50% (v/v) ethanol], 800.00 L of DW without aroma fraction [0.10% (v/v) ethanol], and 809.00 L of

**Table 2.** Contents of Resveratrol in Spanish RWs and DWs Obtained by the SCC Distillation Technique

wine <sup>a</sup>	<i>trans</i> -resveratrol <sup>b</sup>	<i>cis</i> -resveratrol <sup>b</sup>	total resveratrol <sup>b</sup>
red wines			
RW Petit Verdot, J, 2006	1.43 ± 0.24 a	8.98 ± 0.40 a	10.41 ± 0.16 a
DW Petit Verdot, J, 2006	3.32 ± 0.11	8.40 ± 0.60	11.72 ± 0.49
RW Garnacha, J, 2006	0.79 ± 0.01 a	3.79 ± 0.59 a	4.58 ± 0.59 a
DW Garnacha, J, 2006	1.01 ± 0.04	5.09 ± 0.59	6.10 ± 0.63
RW Syrah, J, 2006	3.30 ± 0.42	4.31 ± 0.07	7.62 ± 0.35
DW Syrah, J, 2006	2.04 ± 0.15	4.39 ± 0.05	6.43 ± 0.09
RW Monastrell, J, 2006	7.59 ± 0.44 a	9.97 ± 0.08	17.56 ± 0.52 a
DW Monastrell, J, 2006	9.42 ± 0.22	10.09 ± 0.06	19.51 ± 0.16
RW Monastrell Condomina, J, 2006	4.82 ± 0.99	9.48 ± 0.39	14.30 ± 1.38
DW Monastrell Condomina, J, 2006	4.48 ± 0.05	8.12 ± 0.14	12.60 ± 0.18
RW Tempranillo, J, 2006	ND	1.81 ± 0.44	1.81 ± 0.44
DW Tempranillo, J, 2006	ND	2.12 ± 0.23	2.12 ± 0.23
RW Crianza, J, 2004	3.78 ± 0.01	7.46 ± 0.01	11.24 ± 0.01
DW Crianza, J, 2004	3.43 ± 0.14	7.73 ± 0.15	11.16 ± 0.01
RW Joven, J, 2006	2.05 ± 0.02	3.87 ± 0.12	5.92 ± 0.13
DW Joven, J, 2006	2.05 ± 0.03	3.87 ± 0.42	5.33 ± 0.44
RW Tempranillo, J, 2007	2.12 ± 0.66	10.27 ± 0.05	12.39 ± 0.61
DW Tempranillo, J, 2007	2.27 ± 0.08	11.31 ± 0.64	13.58 ± 0.72
RW Syrah, J, 2007	2.39 ± 0.21 a	10.75 ± 0.66 a	13.14 ± 0.87 a
DW Syrah, J, 2007	4.12 ± 0.76	12.83 ± 0.66	16.95 ± 1.42
RW Merlot, J, 2007	4.68 ± 0.65	28.63 ± 0.17 a	34.01 ± 0.84 a
DW Merlot, J, 2007	5.38 ± 0.95	34.19 ± 1.10	39.57 ± 0.15
RW Cabernet Sauvignon, Man, 2006	2.07 ± 0.09 a	3.20 ± 0.05 a	5.27 ± 0.03 a
DW Cabernet Sauvignon, Man, 2006	3.58 ± 0.06	5.86 ± 0.42	9.44 ± 0.48
RW Garnacha, Mad, 2006	3.87 ± 0.11 a	7.18 ± 0.01 a	11.04 ± 0.12 a
DW Garnacha, Mad, 2006	5.56 ± 0.16	10.59 ± 0.09	16.16 ± 0.07
rose wines			
RW Cabernet Sauvignon, J, 2006	2.32 ± 0.08	ND	2.32 ± 0.08
DW Cabernet Sauvignon, J, 2006	2.52 ± 0.17	ND	2.52 ± 0.17
RW Bobal, Al, 2006	ND	5.56 ± 0.04 a	5.56 ± 0.04 a
DW Bobal, Al, 2006	ND	7.97 ± 0.13	7.97 ± 0.13
white wines			
RW Macabeo, J, 2006	ND	ND	ND
DW Macabeo, J, 2006	ND	ND	ND
RW Malvar, Mad, 2006	ND	ND	ND
DW Malvar, Mad, 2006	ND	ND	ND
RW Moscatel romano, Mal, 2006	ND	ND	ND
DW Moscatel romano, Mal, 2006	ND	ND	ND
RW Macabeo and Airén, Man, 2006	ND	ND	ND
DW Macabeo and Airén, Man, 2006	ND	ND	ND

<sup>a</sup> Abbreviations: J, Jumilla; Man, La Mancha; Mad, Vinos de Madrid; Mal, Málaga; Al, Alicante. The year is the vintage. <sup>b</sup> Values given in units of milligrams per liter. Average of three replicates ± the standard deviation. ND means not detected. The lowercase letter a indicates a significant ( $p \leq 0.05$ ) difference between the values of the RW and the corresponding DW.

DW with aroma fraction [0.50% (v/v) ethanol]. Therefore, the maximum concentration factor of DW due to the elimination of ethanol is around 1.24.

The contents of *trans*-resveratrol and *cis*-resveratrol, and the sum of both isomers, are listed in **Table 2** for raw wines (RWs) and the corresponding DWs obtained by SCC distillation. According to Cheynier et al. (29), the concentration of resveratrol in wines is generally lower than 10 mg/L (that of *trans*-resveratrol is between 0.6 and 10 mg/L and that of *cis*-resveratrol between 0.2 and 3 mg/L), although Moreno-Labanda et al. (30) and Lamikanra and Grimm (31) have found greater values (up to 30 mg/L in Monastrell wines made using macerative fermentations). From **Table 2**, we can deduce that the resveratrol contents of RWs and DWs are consistent with other data published previously (29–31). Nevertheless, the Jumilla red wines (dealcoholized or not) exhibit greater resveratrol contents (up to 39.57 mg/L in Merlot DW) than the rest of the wines studied here, from other Spanish viticultural regions, mainly for the 2007 vintage. These high resveratrol values can be explained by different factors affecting the RW resveratrol content, as this substance is one of a group of compounds (called phytoalexins) that are produced in plants during times of environmental stress such as adverse weather or insect, animal, or pathogenic attack. Therefore, vintage (and the environmental stress associated with it) should be considered as an important factor influencing the final resveratrol concentration (32).

On the other hand, it seems that this SCC distillation technology used for dealcoholization of wine does not decrease the resveratrol content in DW. This content is similar or higher in DW versus RW, probably because of the concentration effect of removal of ethanol from RW mainly in monovarietal wines, not from blending (or coupage) wines, such as Crianza and Joven wines. From **Table 2**, and in most cases, the total resveratrol content in each DW can be approximately obtained by multiplying the corresponding content in the RW by the aforementioned concentration factor of 1.24, or a slightly lower value, depending on the original ethanol content of the RW.

**Table 3** shows the results found for the percentage of remaining DPPH\* from the analyzed samples. We observe that free radical scavenging activity is similar or lower in DW than in the corresponding RW, with alcoholic content around 12% (v/v). It seems that antioxidant activity slightly decreases during the dealcoholization process, because in addition to phenolic compounds, the raw wine also contains nonpolyphenolic compounds with antioxidant activity, such as sulfites (4). In fact, it is known that the wine distilled via SCC releases all of its SO<sub>2</sub>, and in this way, the corresponding antioxidant activity due to this compound is subtracted (between 1 and 5 units of the percentage of remaining DPPH\*, after our data, not shown in this paper). From the results, and the mass balance of the SCC distillation, it seems that ethanol and free SO<sub>2</sub> have a similar relative volatility with respect to water, because the free SO<sub>2</sub> of the RW (~30 mg/L) exists mainly in the ethanol fraction (having more than 95% of the ethanol from the RW and more than 92% of the free SO<sub>2</sub> from the RW), because the level of the remaining free SO<sub>2</sub> in the DW (with the aroma fraction) is only 1–2 mg/L. Therefore, the DW needs the addition of preservatives (SO<sub>2</sub> or others) to achieve the necessary shelf life in the market. This is a problem we have studied, and the results will be published elsewhere.

In general, in white wines we note that there is not a significant increase ( $p \leq 0.05$ ) in the free radical scavenging activity, probably because of the lower SO<sub>2</sub> content in the white RW and the fact that the percentage of remaining DPPH\* measure interference decreases because there is no concentration of colored compounds in the white DW compared to the red DW (26, 33).

**Table 3.** Percentage of the Remaining DPPH\* in Spanish RWs and DWs Obtained by the SCC Distillation Technique

wine <sup>a</sup>	Spanish appellation	% DPPH* <sub>rem</sub> <sup>b</sup>
red wines		
RW Petit Verdot, 2006	Jumilla	17.02 ± 0.73 a
DW Petit Verdot, 2006	Jumilla	13.67 ± 1.20
RW Garnacha, 2006	Jumilla	3.19 ± 0.14 a
DW Garnacha, 2006	Jumilla	9.89 ± 0.83
RW Syrah, 2006	Jumilla	7.25 ± 0.15 a
DW Syrah, 2006	Jumilla	12.43 ± 1.71
RW Monastrell, 2006	Jumilla	4.14 ± 0.45 a
DW Monastrell, 2006	Jumilla	2.30 ± 0.12
RW Monastrell Condolina, 2006	Jumilla	14.69 ± 0.63 a
DW Monastrell Condolina, 2006	Jumilla	18.25 ± 0.67
RW Tempranillo, 2006	Jumilla	16.55 ± 0.57 a
DW Tempranillo, 2006	Jumilla	20.60 ± 0.60
RW Crianza, 2004	Jumilla	9.00 ± 0.79 a
DW Crianza, 2004	Jumilla	13.92 ± 0.62
RW Joven, 2006	Jumilla	5.87 ± 0.20 a
DW Joven, 2006	Jumilla	8.97 ± 0.05
RW Tempranillo, 2007	Jumilla	11.92 ± 0.80 a
DW Tempranillo, 2007	Jumilla	14.58 ± 0.60
RW Syrah, 2007	Jumilla	11.88 ± 0.53 a
DW Syrah, 2007	Jumilla	13.46 ± 0.59
RW Merlot, 2007	Jumilla	13.55 ± 0.49
DW Merlot, 2007	Jumilla	14.92 ± 0.84
RW Cabernet Sauvignon, 2006	La Mancha	15.08 ± 1.85 a
DW Cabernet Sauvignon, 2006	La Mancha	18.61 ± 0.69
RW Garnacha, 2006	Vinos de Madrid	13.11 ± 0.50
DW Garnacha, 2006	Vinos de Madrid	14.08 ± 0.74
rose wines		
RW Cabernet Sauvignon, 2006	Jumilla	38.32 ± 1.09
DW Cabernet Sauvignon, 2006	Jumilla	37.50 ± 0.86
RW Bobal, 2006	Alicante	12.81 ± 0.61
DW Bobal, 2006	Alicante	15.27 ± 2.75
white wines		
RW Macabeo, 2006	Jumilla	82.82 ± 0.77
DW Macabeo, 2006	Jumilla	82.19 ± 2.04
RW Malvar, 2006	Vinos de Madrid	68.83 ± 2.88
DW Malvar, 2006	Vinos de Madrid	73.07 ± 1.97
RW Moscatel romano, 2006	Málaga	94.10 ± 1.37
DW Moscatel romano, 2006	Málaga	91.50 ± 1.58
RW Macabeo and Airén, 2006	La Mancha	34.69 ± 2.78
DW Macabeo and Airén, 2006	La Mancha	32.50 ± 1.84

<sup>a</sup> The year is the vintage. <sup>b</sup> Values given as the percentage of remaining DPPH\*. Average of three replicates ± the standard deviation. The lowercase letter a indicates a significant ( $p \leq 0.05$ ) difference between the values of the RW and the corresponding DW.

Monovarietal wines from Tempranillo grapes showed significant differences in the percentage of remaining DPPH\* between different vintages (2006 and 2007), and these differences were more important than those found between the RW and the corresponding DW. That is according to the study of Di Majo et al. (34) in which the antioxidant properties of red wines appear to be more influenced by the vintages than for cultivars grown under the same conditions.

The red DW from Tempranillo grapes (vintage 2006) presented the highest percentage of remaining DPPH\* (20.6%) and at the same time the lowest concentration of total resveratrol. The red DW with the lowest percentage of remaining DPPH\* was from variety Monastrell (2.3%). This DW is second with regard to the highest concentration of total resveratrol (see **Table 2**). The rose DW from Cabernet Sauvignon presented a percentage of remaining DPPH\* of 37.5%, which is almost 3 times the level obtained for the rose DW from variety Bobal (12.81%). Also, the relation of resveratrol contents between both rose DW samples was similar to that found for antioxidant activity, according to Alen-Ruiz et al. (35).

**Table 4.** Total Phenolics, Flavonols, Tartaric Esters, and Anthocyanins in Spanish RWs and DWs Obtained by the SCC Distillation Technique

wine <sup>a</sup>	total phenolics <sup>b</sup> (mg of gallic acid/L)	flavonols <sup>b</sup> (mg of quercetin/L)	tartaric esters <sup>b</sup> (mg of caffeic acid/L)	anthocyanins <sup>b</sup> (mg of malvidin 3-glucoside/L)
red wines				
RW Petit Verdot, J, 2006	1129.9 ± 3.9 a	27.22 ± 1.41 a	31.50 ± 0.60 a	115.32 ± 0.43 a
DW Petit Verdot, J, 2006	1251.3 ± 30.0	31.41 ± 0.51	35.69 ± 0.12	121.14 ± 1.22
RW Garnacha, J, 2006	877.7 ± 13.2 a	20.89 ± 0.58 a	27.56 ± 0.58 a	59.74 ± 0.57 a
DW Garnacha, J, 2006	1078.6 ± 4.8	27.15 ± 1.29	36.72 ± 0.52	45.68 ± 1.98
RW Syrah, J, 2006	913.2 ± 3.7 a	21.07 ± 0.55 a	31.50 ± 0.53 a	71.23 ± 0.73 a
DW Syrah, J, 2006	714.0 ± 4.4	18.48 ± 0.78	26.89 ± 0.55	63.72 ± 0.52
RW Monastrell, J, 2006	1379.9 ± 9.2 a	28.00 ± 0.85 a	35.24 ± 0.40 a	76.23 ± 0.56 a
DW Monastrell, J, 2006	1625.7 ± 23.9	42.11 ± 0.82	51.32 ± 0.67	94.74 ± 0.45
RW Monastrell Condovina, J, 2006	801.6 ± 10.4 a	12.00 ± 1.35 a	44.05 ± 0.19 a	66.57 ± 0.38 a
DW Monastrell Condovina, J, 2006	877.8 ± 14.6	17.30 ± 0.77	47.12 ± 0.95	77.22 ± 0.64
RW Tempranillo, J, 2006	1020.9 ± 16.2 a	18.19 ± 0.57 a	41.86 ± 0.20 a	65.86 ± 0.57 a
DW Tempranillo, J, 2006	1249.8 ± 21.8	22.93 ± 1.59	45.13 ± 0.39	78.36 ± 1.25
RW Crianza, J, 2004	1394.5 ± 6.7 a	22.37 ± 1.07	36.58 ± 0.95 a	108.37 ± 0.94 a
DW Crianza, J, 2004	1731.4 ± 5.2	25.74 ± 2.01	42.21 ± 0.37	113.23 ± 0.69
RW Joven, J, 2006	1039.8 ± 20.6 a	17.00 ± 0.69 a	27.30 ± 0.87 a	65.82 ± 0.47 a
DW Joven, J, 2006	1267.2 ± 11.0	21.85 ± 0.62	32.84 ± 0.26	72.14 ± 0.89
RW Tempranillo, J, 2007	1065.4 ± 8.4 a	21.07 ± 0.69	42.24 ± 0.24 a	76.30 ± 0.47 a
DW Tempranillo, J, 2007	1617.1 ± 9.4	21.52 ± 0.78	44.30 ± 0.24	78.18 ± 0.95
RW Syrah, J, 2007	882.2 ± 13.7 a	22.59 ± 1.09	37.94 ± 0.30 a	63.80 ± 1.10 a
DW Syrah, J, 2007	977.6 ± 17.6	24.96 ± 0.50	42.56 ± 0.28	68.01 ± 0.65
RW Merlot, J, 2007	914.9 ± 10.2 a	19.63 ± 1.16	34.83 ± 0.37	64.53 ± 0.59 a
DW Merlot, J, 2007	838.7 ± 15.6	21.96 ± 0.64	36.75 ± 1.10	67.37 ± 0.78
RW Cabernet Sauvignon, Man, 2006	1239.8 ± 29.9 a	18.52 ± 0.83 a	9.13 ± 0.21 a	70.85 ± 0.99
DW Cabernet Sauvignon, Man, 2006	1322.5 ± 10.9	22.74 ± 0.61	29.02 ± 0.38	72.16 ± 0.66
RW Garnacha, Mad, 2006	502.1 ± 6.5 a	13.78 ± 0.50 a	21.62 ± 0.33 a	52.70 ± 0.84
DW Garnacha, Mad, 2006	565.41 ± 11.3	16.93 ± 0.78	24.85 ± 0.33	54.89 ± 1.20
rose wines				
RW Cabernet Sauvignon, J, 2006	415.7 ± 14.2 a	20.52 ± 0.90	36.22 ± 0.49	55.95 ± 0.67 a
DW Cabernet Sauvignon, J, 2006	549.6 ± 9.1	22.41 ± 0.98	37.74 ± 0.18	58.79 ± 0.85
RW Bobal, Al, 2006	271.3 ± 8.5 a	4.70 ± 0.85	16.88 ± 0.35	9.01 ± 0.63 a
DW Bobal, Al, 2006	300.9 ± 8.7	6.56 ± 0.38	17.85 ± 0.48	13.55 ± 1.18
white wines				
RW Macabeo, J, 2006	121.4 ± 6.8 a	1.59 ± 0.24	2.12 ± 0.17 a	ND
DW Macabeo, J, 2006	177.6 ± 7.5	2.70 ± 0.58	4.10 ± 0.12	ND
RW Malvar, Mad, 2006	84.8 ± 9.9 a	ND	3.72 ± 0.29	ND
DW Malvar, Mad, 2006	117.3 ± 12.7	ND	3.71 ± 0.29	ND
RW Moscatel romano, Mal, 2006	44.4 ± 11.7 a	ND	4.17 ± 0.19	ND
DW Moscatel romano, Mal, 2006	97.5 ± 7.2	ND	4.85 ± 0.73	ND
RW Macabeo and Airén, Man, 2006	84.0 ± 11.0 a	2.19 ± 0.30	9.98 ± 0.65 a	ND
DW Macabeo and Airén, Man, 2006	141.2 ± 16.9	1.59 ± 0.34	14.59 ± 0.28	ND

<sup>a</sup> Abbreviations: J, Jumilla; Man, La Mancha; Mad, Vinos de Madrid; Mal, Málaga; Al, Alicante. The year is the vintage. <sup>b</sup> Values are the average of three replicates ± the standard deviation. The lowercase letter a indicates a significant ( $p \leq 0.05$ ) difference between the values of the RW and the corresponding DW.

**Table 4** shows the results obtained for total phenolic, flavonol, tartaric ester, and anthocyanin content, in wines before and after SCC dealcoholization. These results are consistent with those obtained by Cliff et al. (27), López et al. (36), and Bautista-Ortín et al. (37). In **Table 4**, one can observe that there is a significant ( $p \leq 0.05$ ) trend in increasing phenolic compound content in red and rose DW except for the Syrah DW wines (vintage 2006), which have shown a significant diminution, including the anthocyanin values. Also, in all white and rose DWs, there was a significant increase ( $p \leq 0.05$ ) for the total phenolics, the flavonols, and the anthocyanins, because of the concentration effect produced for removal of ethanol from the corresponding RW. As before, from **Table 4**, and for many cases, the total phenolic, flavonol, tartaric ester, and anthocyanin contents of each DW can be approximately obtained by multiplying the corresponding content in RWs by the concentration factor of 1.24, or a slightly lower value, depending on the original ethanol content of the RW.

Almost all the red and rose DWs exhibited a significant increase ( $p \leq 0.05$ ) in the content of anthocyanins (see **Table 4**), resulting in more stable colors as well as lively and bright colors;

color measurements (data not shown in this paper) confirming these results were taken. In the DW from Garnacha and Syrah (from Jumilla, 2006 vintage), this content declined slightly, though without significant color changes (data not shown).

Gallic acid is one of the most abundant monomer phenolic compounds in red wine; this compound comes from the hydrolysis of flavonoid esters present in the skin and seeds of grapes (29). Frankel et al. (11) correlated the concentration of gallic acid in Californian wines with the relative antioxidant capacity. Our study on Spanish DW shows gallic acid contents between 10.07 and 63.92 mg/L for red DW, between 0.45 and 7.75 mg/L for rose DW, and between 2.80 and 4.20 mg/L for white DW (see **Table 5**). These results are consistent with the values published by Cheynier et al. (29) and Bautista-Ortín et al. (37). From **Table 5**, one can deduce that contents of gallic acid in most DWs presented a significant increase ( $p \leq 0.05$ ) compared to those in RWs.

The caffeic acid is a product of tartaric acid hydrolysis, which is induced in the grape by exposure to the sun (38). This acid is found in the wine at low concentrations: 5–13 mg/L for red wines and 1–4 mg/L for white wines (11). Nevertheless, levels between

**Table 5.** Flavonoid and Nonflavonoid Contents <sup>b</sup> in Spanish RWs and DWs Obtained by the SCC Distillation Technique

wine <sup>a</sup>	gallic acid <sup>b</sup>	epicatechin <sup>b</sup>	catechin <sup>b</sup>	caffeic acid <sup>b</sup>	<i>p</i> -coumaric acid <sup>b</sup>	rutin <sup>b</sup>	myricetin <sup>b</sup>	quercetin <sup>b</sup>	malvidin <sup>b</sup>
<b>red wines</b>									
RW Petit Verdot, J, 2006	9.12 ± 0.43 a	32.50 ± 0.34 a	54.92 ± 0.57 a	19.09 ± 0.24 a	12.09 ± 0.12 a	7.46 ± 0.10 a	4.67 ± 0.08 a	3.24 ± 0.06 a	10.89 ± 0.11 a
DW Petit Verdot, J, 2006	11.73 ± 0.33	35.17 ± 0.45	62.40 ± 0.70	23.85 ± 0.99	13.13 ± 0.11	9.91 ± 0.19	6.06 ± 0.03	3.96 ± 0.08	12.24 ± 0.17
RW Garnacha, J, 2006	11.40 ± 0.29 a	12.85 ± 0.55	19.86 ± 0.89	5.45 ± 0.22 a	8.67 ± 0.17 a	23.18 ± 0.22 a	2.15 ± 0.06 a	4.39 ± 0.03 a	9.31 ± 0.15 a
DW Garnacha, J, 2006	10.52 ± 0.27	13.00 ± 0.69	20.60 ± 0.71	8.10 ± 0.17	7.63 ± 0.14	29.21 ± 0.12	5.59 ± 0.09	5.58 ± 0.09	12.13 ± 0.13
RW Syrah, J, 2006	51.78 ± 0.40 a	25.38 ± 0.78 a	ND	3.19 ± 0.13	ND	8.32 ± 0.23 a	4.14 ± 0.17 a	1.25 ± 0.01 a	11.55 ± 0.09
DW Syrah, J, 2006	62.62 ± 0.75	29.62 ± 0.55	ND	3.58 ± 0.15	ND	9.29 ± 0.19	5.23 ± 0.20	0.91 ± 0.01	11.51 ± 0.19
RW Monastrell, J, 2006	37.61 ± 0.60 a	14.83 ± 0.71	ND	1.85 ± 0.12	ND	19.46 ± 0.15 a	3.15 ± 0.09 a	1.99 ± 0.03 a	12.06 ± 0.12 a
DW Monastrell, J, 2006	34.58 ± 0.56	16.17 ± 0.15	ND	1.70 ± 0.11	ND	23.46 ± 0.10	4.13 ± 0.06	2.70 ± 0.05	6.22 ± 0.08
RW Monastrell Condovina, J, 2006	62.40 ± 0.44	26.03 ± 0.89	76.34 ± 1.09 a	2.45 ± 0.10	1.79 ± 0.09	4.50 ± 0.11 a	3.54 ± 0.11 a	5.43 ± 0.10 a	9.96 ± 0.07 a
DW Monastrell Condovina, J, 2006	63.92 ± 0.98	26.25 ± 0.99	67.79 ± 0.98	2.29 ± 0.14	1.95 ± 0.08	5.13 ± 0.08	2.93 ± 0.07	4.89 ± 0.14	10.26 ± 0.05
RW Tempranillo, J, 2006	8.55 ± 0.48 a	10.69 ± 0.19 a	27.40 ± 0.72 a	ND	1.11 ± 0.05 a	16.90 ± 0.14 a	4.32 ± 0.13	4.01 ± 0.07 a	17.73 ± 2.69 a
DW Tempranillo, J, 2006	11.78 ± 0.42	14.94 ± 0.56	24.60 ± 0.56	ND	1.42 ± 0.08	25.60 ± 0.13	4.75 ± 0.17	4.34 ± 0.04	20.73 ± 1.59
RW Crianza, J, 2004	20.66 ± 0.45 a	35.67 ± 0.77 a	55.62 ± 0.73 a	2.92 ± 0.91 a	0.63 ± 0.07 a	13.76 ± 0.17 a	5.57 ± 0.10 a	3.17 ± 0.08 a	11.07 ± 0.02 a
DW Crianza, J, 2004	27.35 ± 0.66	47.32 ± 0.81	82.07 ± 0.45	4.61 ± 1.01	1.64 ± 0.06	22.05 ± 0.09	10.58 ± 0.16	4.37 ± 0.02	12.17 ± 0.09
RW Joven, J, 2006	15.86 ± 0.43 a	24.98 ± 0.94 a	43.48 ± 0.84 a	21.42 ± 0.88 a	12.35 ± 0.09 a	18.82 ± 0.19 a	7.59 ± 0.20 a	2.94 ± 0.01 a	14.86 ± 0.17 a
DW Joven, J, 2006	10.07 ± 0.12	16.55 ± 0.55	19.34 ± 0.92	12.68 ± 0.71	8.58 ± 0.08	9.06 ± 0.20	5.52 ± 0.18	2.65 ± 0.03	9.31 ± 0.11
RW Tempranillo, J, 2007	23.75 ± 0.23	8.67 ± 0.17 a	20.26 ± 0.42 a	ND	2.56 ± 0.03 a	7.37 ± 0.14	1.56 ± 0.09	4.10 ± 0.09 a	15.82 ± 2.34 a
DW Tempranillo, J, 2007	23.87 ± 0.34	10.50 ± 0.23	34.40 ± 0.55	ND	2.74 ± 0.07	8.85 ± 0.19	1.75 ± 0.07	8.56 ± 0.12	20.39 ± 1.08
RW Syrah, J, 2007	28.63 ± 0.29 a	17.35 ± 0.39 a	32.00 ± 0.37 a	ND a	2.52 ± 0.10	1.94 ± 0.08 a	4.10 ± 0.04 a	5.85 ± 0.06 a	12.89 ± 1.90 a
DW Syrah, J, 2007	35.77 ± 0.45	22.39 ± 0.19	45.10 ± 0.22	2.11 ± 0.12	2.54 ± 0.10	7.86 ± 0.06	5.43 ± 0.09	4.88 ± 0.03	21.43 ± 1.25
RW Merlot, J, 2007	43.50 ± 0.87	15.96 ± 0.67 a	45.73 ± 0.96 a	3.58 ± 0.17 a	3.78 ± 0.12 a	5.12 ± 0.10 a	2.12 ± 0.01 a	9.04 ± 0.10 a	16.93 ± 1.99 a
DW Merlot, J, 2007	41.09 ± 0.76	22.24 ± 0.88	53.01 ± 0.33	2.80 ± 0.20	4.47 ± 0.17	10.45 ± 0.22	3.07 ± 0.06	7.72 ± 0.19	17.64 ± 2.04
RW Cabernet Sauvignon, Man, 2006	15.18 ± 0.15 a	6.28 ± 0.66 a	11.26 ± 0.80 a	1.99 ± 0.11	2.32 ± 0.11 a	0.34 ± 0.06 a	1.42 ± 0.02 a	4.88 ± 0.09 a	7.56 ± 1.67 a
DW Cabernet Sauvignon, Man, 2006	20.75 ± 0.25	6.79 ± 0.43	14.06 ± 0.91	2.14 ± 0.21	3.08 ± 0.13	2.16 ± 0.05	1.10 ± 0.07	3.16 ± 0.06	9.820 ± 1.88
RW Garnacha, Mad, 2006	10.04 ± 0.09 a	12.45 ± 0.58 a	10.65 ± 0.17	3.06 ± 0.12	ND	1.39 ± 0.08 a	ND a	ND a	ND
DW Garnacha, Mad, 2006	11.63 ± 0.11	8.73 ± 0.71	10.13 ± 0.33	3.44 ± 0.17	ND	3.44 ± 0.02	0.83 ± 0.01	2.13 ± 0.01	ND
<b>rose wines</b>									
RW Cabernet Sauvignon, J, 2006	ND a	3.71 ± 0.51 a	18.25 ± 0.44 a	1.74 ± 0.11 a	2.64 ± 0.09 a	ND	ND	4.27 ± 0.08	4.91 ± 1.03
DW Cabernet Sauvignon, J, 2006	0.45 ± 0.01	5.27 ± 0.53	24.48 ± 0.99	2.19 ± 0.19	1.55 ± 0.08	ND	ND	4.16 ± 0.05	5.16 ± 1.29
RW Bobal, Al, 2006	3.32 ± 0.07 a	4.09 ± 0.34 a	ND	1.79 ± 0.20	ND	ND	ND	ND	7.76 ± 0.99
DW Bobal, Al, 2006	7.75 ± 0.17	6.36 ± 0.65	ND	2.03 ± 0.21	ND	ND	ND	ND	8.46 ± 0.38
<b>white wines</b>									
RW Macabeo, J, 2006	3.87 ± 0.10	0.54 ± 0.09	0.74 ± 0.05 a	0.10 ± 0.01 a	ND	ND	ND	ND	ND
DW Macabeo, J, 2006	3.98 ± 0.13	0.54 ± 0.08	1.15 ± 0.22	0.15 ± 0.02	ND	ND	ND	ND	ND
RW Malvar, Mad, 2006	6.47 ± 0.21 a	ND	ND	0.71 ± 0.01 a	ND	ND	ND	ND	ND
DW Malvar, Mad, 2006	4.20 ± 0.19	ND	ND	1.31 ± 0.09	ND	ND	ND	ND	ND
RW Moscatel romano, Mal, 2006	3.34 ± 0.17	4.98 ± 0.19	4.81 ± 0.30 a	10.17 ± 0.18 a	6.93 ± 0.11	1.30 ± 0.01	ND	ND	ND
DW Moscatel romano, Mal, 2006	3.35 ± 0.22	4.83 ± 0.18	7.45 ± 0.74	7.53 ± 0.15	6.76 ± 0.18	1.60 ± 0.17	ND	ND	ND
RW Macabeo and Airén, Man, 2006	2.80 ± 0.11	ND	ND	ND	ND	ND	ND	ND	ND
DW Macabeo and Airén, Man, 2006	2.80 ± 0.23	ND	ND	ND	ND	ND	ND	ND	ND

<sup>a</sup> Abbreviations: J, Jumilla; Man, La Mancha; Mad, Vinos de Madrid; Mal, Málaga; Al, Alicante. The year is the vintage. <sup>b</sup> Values given in units of milligrams per liter. Average of three replicates ± the standard deviation. ND means not detected. The lowercase letter a indicates a significant ( $p \leq 0.05$ ) difference between the values of the RW and the corresponding DW.

15 and 17 mg/L have been reported (39, 40), and Cheyner et al. (29) showed a wider range for this compound (0.4–8 mg/L for white wines and 0.3–26 mg/L for red wines). According to these previously published data, in our study similar levels of caffeic acid are found, between ND and 23.85 mg/L for red DWs and between 2.03 and 2.19 mg/L for rose DWs. White DWs exhibited caffeic acid contents of ND to 7.53 mg/L. The highest caffeic acid values were found in red DW from Petit Verdot grapes grown in Jumilla appellation (see Table 5). Generally, from Table 5, it can be deduced that the SCC distillation technique produces an increase (approximately equivalent to multiplying by the concentration factor of 1.24) in caffeic acid content in corresponding DWs.

The *p*-coumaric acid content in red wines is between 0.4 and 15 mg/L (29), but in ref 37, Monastrell red wines present values of 0.3–4.6 mg/L. The DWs obtained by SCC distillation exhibit *p*-coumaric acid contents (see Table 5) between ND and 13.13 mg/L for red DWs and between ND and 1.55 mg/L for rose DWs, and for white DW, only the DW from Moscatel Romano grapes presented a detectable amount of 6.93 mg/L while in the rest it was not detected. These results are consistent with those obtained by the aforementioned authors. Normally, the concentration effect of ethanol removal is also observed for this compound (generally with the same intensity as observed above), as the dealcoholization process leads to an increase in *p*-coumaric acid content in DWs.

The (+)-catechin content in DWs is between ND and 82.07 mg/L for red DWs and between ND and 24.48 mg/L for rose DWs; the white DW shows values between ND and 7.45 mg/L for this compound (see Table 5). The (–)-epicatechin concentrations are between 6.79 and 47.32 mg/L for red DWs, between 5.27 and 6.35 mg/L for rose DWs, and between ND and 4.83 mg/L for white DWs. These values are consistent with the data from refs 29 and 37. The red DW with the highest content of (+)-catechin and (–)-epicatechin is DW Crianza (2004 vintage), with values of 82.07 and 47.32 mg/L, respectively. Once more, the concentration effect (normally the same as that observed above for the rest of the phenolic compounds) is observed for these compounds, which are present at higher concentrations in the corresponding DW.

Malvidin 3-glucoside is one of the anthocyanins most abundant in red wine and is primarily responsible for its color (29). In our study (see Table 5), the red DWs have contents of 6.22–21.43 mg/L, while the rose DWs present values of 5.16–8.46 mg/L. These results are consistent with those obtained by other authors (29, 37). The highest malvidin 3-glucoside content is exhibited by the red DW from Syrah grapes grown in Jumilla appellation, with a value of 21.43 mg/L. Also, as with malvidin 3-glucoside (see Table 5), the content of flavonols rutin, quercetin, and myricetin slightly increases in the red DW because of the same concentration effect of ethanol removal. The flavonol content (see Table 5) of red DW is 2.16–29.21 mg/L for rutin, 0.83–10.58 mg/L for myricetin, and 0.91–8.56 mg/L for quercetin. These results are consistent with the range described by other authors (29, 37).

From the results obtained for phenolic compounds (gallic acid, epicatechin, catechin, caffeic acid, *p*-coumaric acid, rutin, myricetin, quercetin, and malvidin 3-glucoside) and total phenolic, flavonol, tartaric ester, and anthocyanin contents, in Spanish RW and the corresponding DW, we can observe that, normally, there is a concentration effect, and a trend in increasing (~24%) phenolic compound content in red, rose, and white DW, produced by the SCC distillation technique. Also, the red and rose DWs obtained with SCC distillation have a higher content of resveratrol than the corresponding RWs. These results show that the technique of SCC distillation used to separate the ethanol

from raw wine is not aggressive, keeping or increasing the amount of beneficial compounds in the DW as resveratrol and other phenolic compounds with antioxidant activity.

These findings are consistent with two fundamental principals: (i) the thermodynamic property of phenolic compounds as nonvolatile compounds, thus not eliminated by a volatility-based process such as SCC distillation, and (ii) the low temperature of this process (under vacuum) which allows preservation of the molecular integrity of the phenolic compounds. This last conclusion is consistent with the findings of other authors (43, 44), which have shown that use of low temperatures may preserve the stability and antioxidant activity of phenolic compounds in the processing of wine and other sources of phenolic compounds.

Nevertheless, the antioxidant activity measured by the DPPH\* method is normally lower in DWs (~5 units of % DPPH\*<sub>rem</sub>) than in the corresponding RWs but should take into account the fact that the SO<sub>2</sub> present in the RW, with antioxidant activity, is removed during SCC distillation to yield the DW. In our laboratory, the loss in SO<sub>2</sub> in the DW has been correlated with the alteration of antioxidant activity measured by the DPPH\* method (results not shown), but a deeper study concerning this observation must be conducted, considering the DPPH method and other techniques that measure antioxidant activity. In any case, to preserve this difference in antioxidant activity, the SO<sub>2</sub> can again be added to the DW, which was done in the commercial DWs actually in the market, to achieve a more stable bottled product.

#### ACKNOWLEDGMENT

We are grateful to Wineries and Vineyards Casa de la Ermita, S.L. (from Jumilla, Spain), and CDTI (Spanish Center for the Development of Industrial Technology), which have financed this work through the Projects IDI-20070268 and IDI-20070330.

#### LITERATURE CITED

- (1) Greenrod, W.; Stockley, C. S.; Burcham, P.; Abbey, M.; Fenech, M. Moderate acute intake of dealcoholised red wine, but not alcohol, is protective against radiation-induced DNA damage ex vivo: Results of a comparative in vivo intervention study in younger men. *Mutat. Res.* **2005**, *591*, 290–301.
- (2) Lu, T.; Pan, Y.; Kao, S. Y.; Li, C.; Kohane, I.; Chan, J.; Yankner, B. A. Gene regulation and DNA damage in the ageing human brain. *Nature* **2004**, *429*, 883–891.
- (3) López, D.; Pavelkova, M.; Gallova, L.; Simonetti, P.; Gardana, C.; Lojek, A.; Loaliza, R.; Mitjavila, M. T. Dealcoholised red and white wines decrease oxidative stress associated with inflammation in rats. *Br. J. Nutr.* **2007**, *98*, 611–619.
- (4) Mitsuhashi, H.; Ikeuchi, H.; Nojima, Y. Is sulphite an antiatherogenic compound in wine?. *Clin. Chem.* **2001**, *47*, 1872–1873.
- (5) Woraratphoka, J.; Intarapichet, K.; Indrapichate, K. Phenolic compounds and antioxidative properties of selected wines from the Northeast of Thailand. *Food Chem.* **2007**, *104*, 1485–1490.
- (6) Gil-Muñoz, R.; Gómez-Plaza, E.; Martínez, A.; López-Roca, J. M. Evolution of phenolic compounds during wine fermentation and post-fermentation: Influence of grape temperature. *J. Food Compos. Anal.* **1999**, *12*, 259–272.
- (7) Nardini, M.; D'Aquino, M.; Tomassi, G.; Gentili, V.; Di felice, M.; Scaccini, C. Inhibition of human low density lipoprotein oxidation by caffeic acid and other hydroxycinnamic acid derivatives. *Free Radical Biol. Med.* **1995**, *19*, 541–552.
- (8) Gambelli, L.; Santaroni, G. P. Polyphenols content in some Italian red wines of different geographical origins. *J. Food Compos. Anal.* **2004**, *17*, 613–618.
- (9) Frémon, L.; Belguendouz, L.; Delpal, S. Antioxidant activity of resveratrol and alcohol-free wine polyphenols related to LDL oxidation and polyunsaturated fatty acids. *Life Sci.* **1999**, *64*, 2511–2521.



- (10) Frankel, E. N.; Waterhouse, A. L.; Kinsella, J. E. Inhibition of human LDL oxidation by resveratrol. *Lancet* **1993**, *341*, 1103–1104.
- (11) Frankel, E. N.; Waterhouse, A. L.; Teissedre, P. L. Principal phenolic phytochemicals in selected California wines and their antioxidant activity in inhibiting oxidation of human low density lipoproteins. *J. Agric. Food Chem.* **1995**, *43*, 890–894.
- (12) Soleas, G. P.; Diamendis, E. P.; Goldberg, D. M. Wine as a biological fluid: History, production and role in disease prevention. *J. Clin. Lab. Anal.* **1997**, *11*, 287–313.
- (13) Pickering, G. J. Low- and reduced-alcohol wine (a review). *J. Wine Res.* **2000**, *2*, 129–144.
- (14) Prince, R. G. H.; Desho, S. Y.; Langrish, T. A. G. Spinning cone column capacity and mass-transfer performance. I. *Chem. Eng. Symp. Ser.* **1997**, *142*, 769–781.
- (15) Makarytchev, S. V.; Langrish, T. A. G.; Prince, R. G. H. Structure and regimes of liquid film flow in spinning cone columns. *Chem. Eng. Sci.* **1998**, *53*, 1541–1550.
- (16) Bui, K.; Moulin, D. R.; Galzy, P. A reverse osmosis for production of low ethanol content wine. *Am. J. Enol. Vitic.* **1986**, *37*, 297.
- (17) Chinaud, N.; Broussous, P.; Ferrari, G. Application de l'osmose inverse à la désalcoolisation des vins. *J. Int. Sci. Vigne Vin* **1991**, *25*, 245.
- (18) Diban, N.; Athes, V.; Bes, M.; Souchon, I. Ethanol and aroma compounds transfer study for partial dealcoholization of wine using membrane contactor. *J. Membr. Sci.* **2008**, *311*, 136–146.
- (19) Makarytchev, S. V.; Langrish, T. A. G.; Fletcher, D. F. Mass transfer analysis of spinning cone columns using CFD. *Chem. Eng. Res. Des.* **2004**, *82*, 752.
- (20) Makarytchev, S. V.; Langrish, T. A. G.; Fletcher, D. F. Exploration of spinning cone column capacity and mass transfer performance using CFD. *Chem. Eng. Res. Des.* **2005**, *83*, 1372–1380.
- (21) Gómez-Plaza, E.; López-Nicolás, J. M.; López-Roca, J. M.; Martínez-Cutillas, A. Dealcoholization of wine. Behaviour of the aroma components during the process. *Lebensm.-Wiss. -Technol.* **1999**, *32*, 384–386.
- (22) Pickering, G. J.; Heatherbell, D. A.; Barnes, M. F. The production of reduced-alcohol wine using glucose oxidase treated juice. Part I. Composition. *Am. J. Enol. Vitic.* **1999**, *50*, 291–298.
- (23) Pickering, G. J.; Heatherbell, D. A.; Barnes, M. F. GC-MS Analysis of reduced-alcohol Muller-Thurgau wine produced using glucose oxidase-treated juice. *Lebensm.-Wiss. -Technol.* **2001**, *34*, 89–94.
- (24) Malovaná, S.; García Montelongo, F. J.; Pérez, J. P.; Rodríguez-Delgado, M. A. Optimisation of simple preparation for the determination of trans-resveratrol and other polyphenolic compounds in wines by high performance liquid chromatography. *Anal. Chim. Acta* **2001**, *428*, 245–253.
- (25) Sánchez-Moreno, C.; Larrauri, J. A.; Saura-Calixto, F. Free radical scavenging capacity and inhibition of lipid oxidation of wines, grape juices and related polyphenolic constituents. *Food Res. Int.* **1999**, *32*, 407–412.
- (26) Prior, R. L.; Wu, X. L.; Schaich, K. Standardized methods for the determination of antioxidant capacity and phenolics in foods and dietary supplements. *J. Agric. Food Chem.* **2005**, *53*, 4290–4302.
- (27) Cliff, M. A.; King, M. C.; Schlosser, J. Anthocyanins, phenolic composition, colour measurement and sensory analysis of BC commercial red wines. *Food Res. Int.* **2007**, *40*, 92–100.
- (28) Cantos, E.; Garcia-Viguera, C.; Pascual-Teresa, S.; Tomás-Barberán, F. Effect of postharvest ultraviolet irradiation on resveratrol and other phenolics of Cv. Napoleon table grapes. *J. Agric. Food Chem.* **2000**, *48*, 4606–4612.
- (29) Cheynier, V.; Moutounet, M.; Sarni-Manchado, P. Los compuestos fenólicos. In *Enología: Fundamentos científicos y tecnológicos*; Flaney, C., Ed.; AMV Ediciones: Madrid, 2000; pp 114–136.
- (30) Moreno-Labanda, J. F.; Mallavia, R.; Perez-Fons, L.; Lizama, V.; Saura, D.; Micol, V. Determination of piceid and resveratrol in Spanish wines deriving from Monastrell (*Vitis vinifera* L.) grape variety. *J. Agric. Food Chem.* **2004**, *52*, 5396–5403.
- (31) Lamikanra, O.; Grimm, C. C. Hydroxylated stilbenes in selected American wines. *J. Agric. Food Chem.* **1996**, *44*, 1111–1115.
- (32) Langcake, P.; Pryce, R. J. The production of resveratrol and the viniferins by grapevines in response to ultraviolet irradiation. *Phytochemistry* **1977**, *16*, 1193–1196.
- (33) Arnao, B. M. Some methodological problems in the determination of antioxidant activity using chromogen radicals: A practical case. *Trends Food Sci. Technol.* **2000**, *11*, 419–421.
- (34) Di Majo, D.; Guardia, M. L.; Giammanco, S.; Neve, L. L.; Giammanco, M. The antioxidant capacity of red wine in relationship with its polyphenolic constituents. *Food Chem.* **2008**, *111*, 45–49.
- (35) Alén-Ruiz, F.; García-Falcón, M. S.; Pérez-Lamela, M. C.; Martínez-Carballo, E.; Simal-Gándara, J. Influence of major polyphenols on antioxidant activity in Mencía and Brancellao red wines. *Food Chem.* **2009**, *113*, 53–60.
- (36) López, M.; Martínez, F.; Del Valle, C.; Ortea, C.; Miro, M. Analysis of phenolic constituents of biological interest in red wines by high-performance liquid chromatography. *J. Chromatogr., A* **2001**, *922*, 359–363.
- (37) Bautista-Ortín, A. B.; Romero-Cascales, I.; Fernández-Fernández, J. I.; López-Roca, J. M.; Gómez-Plaza, E. Influence of the yeast strain on Monastrell wine colour. *Innovative Food Sci. Emerging Technol.* **2007**, *8*, 322–328.
- (38) Price, S. F.; Breen, P. J.; Vallado, M.; Watson, B. T. Cluster sun exposure and quercetin in Pinot noir grapes and wine. *Am. J. Enol. Vitic.* **1995**, *46*, 187–194.
- (39) García-Falcón, M. S.; Pérez-Lamela, C.; Martínez-Carballo, E.; Simal-Gándara, J. Determination of phenolic compounds in wines: Influence of bottle storage of young red wines on their evolution. *Food Chem.* **2007**, *105*, 248–259.
- (40) Ghiselli, A.; Nardini, M.; Baldi, A.; Scaccini, C. Antioxidant activity of different phenolic fractions separated from an Italian red wine. *J. Agric. Food Chem.* **1998**, *46*, 361–367.
- (41) Harders, T.; Sykes, S. Comparison of a Spinning Cone Column and other distillation columns. *Food Aust.* **1999**, *51*, 469.
- (42) Vian, M. A.; Tomao, V.; Gallet, S.; Coulomb, P. O.; Lacombe, J. M. Simple and rapid method for *cis*- and *trans*-resveratrol and piceid isomers determination in wine by high-performance liquid chromatography using Chromolith columns. *J. Chromatogr., A* **2005**, *1085*, 224–229.
- (43) Mansfield, A. K.; Zoecklein, B. W. Effect of Fermentation, Postfermentation, and Postbottling Heat Treatment on Cabernet Sauvignon Glycoconjugates. *Am. J. Enol. Vitic.* **2003**, *54* (2), 99–104.
- (44) Klopotek, Y.; Otto, K.; Bohm, V. Processing Strawberries to Different Products Alters Contents of Vitamin C, Total Phenolics, Total Anthocyanins, and Antioxidant Capacity. *J. Agric. Food Chem.* **2005**, *53*, 5640–5646.

---

Received October 3, 2008. Revised manuscript received June 20, 2009.  
Accepted June 23, 2009.