

Spanish Sparkling Wines (Cavas) As Inhibitors of in Vitro Human Low-Density Lipoprotein Oxidation

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Forty-seven dealcoholized sparkling wines (cava) from the Penedès area in Spain were tested for their antioxidant activity in a low-density lipoprotein system. The effect of different quality-related parameters, such as harvest year or grape variety, was investigated. Twenty-two phenolic compounds were separated by high-performance liquid chromatography and identified by comparing their retention time and their ultraviolet spectra with those of pure standards. When tested at the same total phenol concentration, the antioxidant activity of these white sparkling wines was found to be similar to that reported for red wines. This activity was positively correlated with the total phenolic content, *trans*-caffeic acid, coumaric acid, protocatechuic acid, and quercetin 3-glucuronide. The wines made of the classic cava wine coupage had superior antioxidant activity compared to those of other cultivars.

Keywords: *Sparkling wine; cava; phenolics; antioxidant; LDL oxidation*

INTRODUCTION

Among the different processes of wine-making, sparkling wine production is a very distinctive one. Grapes are harvested at lower sugar contents (°Brix), and the must obtained by pressure is first fermented in temperature-controlled tanks, followed by a second fermentation for a minimum of 9 months (for Spanish sparkling wine) in the bottle. Sparkling wine produced in Spain according to the Méthode Traditionnelle Champenoise is known as cava. Cava production is very important for the economy of the Penedès area in Spain. This region produces most of the sparkling wine consumed in Spain and exported to other countries of the European Union, Japan, and the United States. Traditionally, three different varieties of autochthonous grapes (Macabeo, Xarel.lo, and Parellada) are used for making cava. However, after 1986, the use of Chardonnay grapes was allowed, and since then they have been used extensively. Many factors affect the quality of the final product; among these are the pressure applied to the grapes to obtain the must, the must (first, second pressings), the grape varieties used, and the aging period during the second fermentation in contact with lees.

Phenolic compounds are known to contribute to sensory properties (Robichaud and Noble, 1990), but in recent years their antioxidant properties have attracted much interest. Since the so-called "French Paradox" was established on the basis of epidemiological studies, several other works have been carried out to prove the relationship between wine consumption and low rates of cardiovascular heart disease (CHD). Frankel et al.

(1993) first suggested the inhibition of low-density lipoprotein (LDL) oxidation by wine phenolics as a mechanism to explain the beneficial effects of red wine. The phenolic composition of wine varies not only with the variety of grape used but also with the wine-making procedures (Singleton and Trousdale, 1983). Red wines contain more phenolics and have been reported to be more active than white wines in preventing LDL oxidation (Frankel et al., 1995). Other authors have reported that the phenols present in white wines have antioxidant capacities comparable to or higher than those of red wines (Hurtado et al., 1997; Caldú et al., 1996; Vinson and Hontz, 1995). On the other hand, another study reported prooxidant activity for white wines (Fuhrman et al., 1995). To our knowledge, the effect of sparkling wines on LDL oxidation has not been previously reported.

This paper presents a study of the antioxidant activity of dealcoholized cava samples using an assay based on the inhibition of in vitro oxidation of human LDL particles. The aim of this work was to study the antioxidant activity of this type of wine toward LDL oxidation and the influence on antioxidant activity of conditions affecting the sensory quality of the final product.

MATERIALS AND METHODS

Samples. A total of 47 sparkling wines (cavas) were tested. Twenty-one sparkling wines were collected during two consecutive harvests [1990 ($n = 10$) and 1991 ($n = 11$)] from three different wineries [winery A ($n = 5$), winery B ($n = 8$), and winery C ($n = 8$)]. All of these wines were a coupage (CP) of the autochthonous varieties Macabeo, Xarel.lo, and Parellada. Twelve other sparkling wines were obtained from a winery for two consecutive harvests [1993 ($n = 6$) and 1994 ($n = 6$)]. These samples were made from three varietal autochthonous grapes from the Penedès region [Macabeo (M), Xarel.lo (X),

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Table 1. Characteristics of the Samples Included in This Study

sample	<i>n</i>	coupage ^a	winery ^b	harvest year ^b
1-2	2	CP	A	1990
3-6	4	CP	B	1990
7-10	4	CP	C	1990
11-13	3	CP	A	1991
14-17	4	CP	B	1991
18-21	4	CP	C	1991
22	1	X	D	1993
23	1	P	D	1993
24	1	M	D	1993
25	1	C	D	1993
26	1	CP	D	1993
27	1	CPC	D	1993
28	1	X	D	1994
29	1	P	D	1994
30	1	M	D	1994
31	1	C	D	1994
32	1	CP	D	1994
33	1	CPC	D	1994
34-35	2	X	u	u
36	1	P	u	u
37	1	M	u	u
38-40	3	C	u	u
41-42	2	PC	u	u
43-44	2	CP	u	u
45-47	3	CPC	u	u

^a X, Xarel.lo; P, Parellada; M, Macabeo; C, Chardonnay; CP = M, X, and P (1:1:1); CPC, M, X, P, and C (3:3:3:1); PC, Pinot noir and C. ^b u, unknown.

and Parellada (P)] and another one from Chardonnay grapes (C) and two coupages, one with the three autochthonous varieties (1:1:1, CP) and the other plus Chardonnay (3:3:3:1, CPC). All samples were fermented in the bottle for 23 months. The 14 remaining samples were commercial sparkling wines. Seven of them were made from monovarietal wines [Xarel.lo (X, *n* = 2), Parellada (P, *n* = 1), Macabeo (M, *n* = 1), Chardonnay (C, *n* = 3)], and seven were coupages: Pinot noir and Chardonnay (PC, *n* = 2); Macabeo, Xarel.lo, and Parellada (CP, *n* = 2); and Macabeo, Xarel.lo, Parellada, and Chardonnay (CPC, *n* = 3). The different cavas used in this experiment are listed in Table 1.

Chemicals. Phenolic reference compounds included gallic acid, (+)-catechin, syringic acid, *trans*-caffeic acid, (-)-epicatechin, protocatechuic acid, tyrosol, *trans*-*p*-coumaric acid, *trans*-ferulic acid, *trans*-resveratrol, and quercetin were all obtained from commercial sources. *trans*-Caftaric and *trans*-coutaric acids were provided by V. L. Singleton and A. L. Waterhouse, and procyanidin B3 was from H. Peleg and A. C. Noble of the Department of Viticulture and Enology, University of California, Davis, CA. 2-*S*-Glutathionylcaftaric acid and fertaric acid were provided by U. Vrhosek at the University of Ljubljana, Biotechnical Faculty, Department of Wine Technology. *trans*-Piceid was extracted from *Polygonum cuspidatum*, as previously described (Waterhouse and Lamuela-Raventós, 1994). The *cis* isomers were obtained by exposure of the *trans* isomers to UV light (Engelsma, 1974; Singleton et al., 1978). Hexanal, bovine serum albumin standard, Lowry modified reagent, and Folin-Ciocalteu phenol reagent were purchased from Sigma Chemical Co. (St. Louis, MO). Copper sulfate was obtained from Fisher Scientific (Fair Lawn, NJ).

Wine Analytical Methods. The following parameters were determined in the sparkling wines. All analyses were done in duplicate.

Total Phenols. Total phenols were analyzed by measuring the absorbance at 280 nm in a 1 mm cell and according to the Folin-Ciocalteu method described by Singleton and Rossi (1965), using a Shimadzu UV-1201 UV-vis spectrophotometer. The results were expressed as milligrams of gallic acid equivalents (GAE) per liter.

Phenolic Compounds. Phenolic composition was determined by using an HPLC method as previously described by Betés-Saura et al. (1996).

LDL Oxidation in Vitro. LDL was prepared from the blood of five normolipidemic, nonsmoking, healthy volunteers (Frankel et al., 1992); the antioxidant activity of cava wine samples to inhibit copper-catalyzed oxidation of human LDL was assessed as described previously (Frankel et al., 1992). Antioxidant activity of cava was calculated as percent inhibition of hexanal production and expressed as

$$\% \text{ inhibition} = [(C - S)/C] \times 100 \quad (1)$$

where *C* is the amount of hexanal formed in the control sample and *S* is the amount of hexanal formed in the sample containing cava. The percentage of inhibition was calculated at the propagation phase of oxidation. Relative percent inhibition of LDL oxidation was calculated by multiplying the inhibition at 20 μM GAE by the dilution factor used for the extract in the LDL oxidation assay and by setting the highest inhibition value as 100% (Frankel et al., 1995).

Statistics. The Minitab Computer program (release 9, Minitab Inc., Addison-Wesley Publishing Co., Reading, MA) was used for statistical treatment of the data. Significant differences within sets of data were determined by one-way analysis of variance (Wagner, 1992). Significance level was in all cases *p* < 0.05. Significant correlations were calculated by regression analysis.

RESULTS

The amount of total phenolic compounds in the cava wine samples ranged from 109 to 202 mg of GAE/L, as analyzed by absorbance at 280 nm, and from 133 to 216 mg of GAE/L as analyzed according to the Folin-Ciocalteu method. In a preliminary study with 21 samples harvested in 1990 and 1991, the samples of winery A contained more total phenolics (*p* < 0.001) (139–173 mg of GAE/L, averaging 156 mg of GAE/L) than samples from winery B (125–136 mg of GAE/L, averaging 130 mg of GAE/L) or winery C (109–147 mg of GAE/L, averaging 132 mg of GAE/L). The harvest, quality, or aging time had no significant effect (*p* > 0.05) on total phenolic compounds. There were no significant differences (*p* > 0.05) in total phenol content when samples harvested in years 1990, 1991, 1993, and 1994 were compared. A significantly higher content (*p* < 0.05) of total phenols was found in samples made of Chardonnay grapes (170 mg/L), compared to samples made of the Macabeo, Xarel.lo, and Parellada coupage (138 mg/L) (Table 2).

The concentration of phenolic compounds in cava wines was normalized to the same molarity (GAE) as measured by using the Folin-Ciocalteu method and their antioxidant activity tested with the *in vitro* LDL assay. The inhibition of hexanal formation in LDL varied from 16.7 to 58.6% and from 35.7 to 85.9% at 10 and 20 μM phenolics, respectively. The antioxidant activity at the same total phenol concentrations of 10 and 20 μM GAE was significantly (*p* < 0.05) related to the variety of grape employed and to the harvest year (Table 2).

The major phenolic compounds were analyzed by HPLC. Twenty-two compounds were separated and quantified (Table 3). Tyrosol was the most abundant compound determined by HPLC, with levels ranging from 3.7 to 20.5 mg/L, averaging 13.0 mg/L. The second most abundant compound was *trans*-caftaric acid (2.3–38.9 mg/L, averaging 12.4 mg/L), followed by *cis*-coutaric acid (3.3–13.3 mg/L, averaging 8.3 mg/L) and *trans*-coutaric acid (1.1–10.3 mg/L, averaging 6.1 mg/L). The remaining compounds identified were present in smaller amounts and averaged, in decreasing order, epicatechin

Table 2. Total Phenols As Analyzed by Absorbance at 280 nm and by the Folin–Ciocalteu Method and Percentage of LDL Oxidation Inhibition for the Cava Wines Grouped by Coupage and by Harvest Year

	total phenols ^{a,e} (mg/L)	total phenols ^{b,e} (mg/L)	% inhibition ^{c,e} (at 10 μM)	% inhibition ^{c,e} (at 20 μM)
coupage ^d				
CP	138.1 ± 15.4 b	166.2 ± 18.4 a	40.5 ± 10.5 a	74.3 ± 8.5 a
X	146.7 ± 36.7 ab	152.9 ± 21.5 a	23.5 ± 5.2 b	58.6 ± 17.1 bc
P	149.7 ± 29.7 ab	164.8 ± 11.0 a	35.1 ± 9.3 ab	57.2 ± 5.7 bc
M	154.6 ± 22.4 ab	152.8 ± 19.5 a	27.9 ± 7.6 ab	51.4 ± 12.1 c
C	170.0 ± 20.5 a	186.1 ± 26.5 a	31.6 ± 9.1 ab	73.7 ± 4.3 ab
PC	156.7 ± 18.9 ab	176.2 ± 15.4 a	25.2 ± 4.9 b	64.2 ± 7.2 ab
CPC	146.3 ± 15.4 ab	177.6 ± 19.9 a	29.8 ± 8.1 ab	65.0 ± 2.5 ab
year				
1990	134.3 ± 17.6 a	163.7 ± 20.1 a	38.3 ± 10.2 ab	78.7 ± 3.8 a
1991	139.3 ± 12.1 a	168.8 ± 14.9 a	47.0 ± 7.4 a	72.6 ± 10.7 ab
1993	136.4 ± 14.6 a	148.9 ± 11.3 a	25.6 ± 2.9 c	63.5 ± 6.9 bc
1994	151.6 ± 23.0 a	165.6 ± 17.1 a	31.4 ± 11.2 bc	60.8 ± 7.9 c

^a Total phenols as analyzed by absorbance at 280 nm and expressed as mg/L gallic acid equivalents (GAE). ^b Total phenols as analyzed by the Folin–Ciocalteu method and expressed as mg/L GAE. ^c % inhibition = percentage of LDL oxidation inhibition. ^d See Table 1 for abbreviations. ^e Values within the same column followed by the same letter are not significantly different ($p > 0.05$).

Table 3. Phenolic Composition of the Cava Wines As Analyzed by HPLC (Individual Phenolics Have Been Grouped by Classes)

sample	tyrosol (mg/L)	cinnamate ^a (mg/L)	flavan-3- ol ^b (mg/L)	benzoate ^c (mg/L)	flavonol ^d (mg/L)	other ^e (mg/L)	sample	tyrosol (mg/L)	cinnamate ^a (mg/L)	flavan-3- ol ^b (mg/L)	benzoate ^c (mg/L)	flavonol ^d (mg/L)	other ^e (mg/L)
1	9.9	31.2	12.2	16.4	1.2		25	11.3	28.9	2.7	3.1		1.1
2	10.7	27.8	6.8	14.8	1.0		26	16.2	40.4	3.2	2.2		0.8
3	16.6	32.5	4.7	3.1	0.4		27	15.9	36.3	2.7	2.1		0.6
4	18.5	34.3	7.0	3.3	0.4		28	9.5	24.1	1.6	2.2	0.1	0.8
5	17.0	34.9	4.4	3.2	0.5		29	9.6	37.6	2.4	2.9	0.2	1.2
6	18.0	34.4	12.0	3.6	0.5		30	15.6	42.7	3.4	3.0	0.2	0.7
7	17.3	31.6	8.0	4.7	0.7		31	20.5	37.8	5.0	4.0	0.3	0.9
8	15.2	39.0	6.7	4.1	0.6		32	16.6	37.7	4.4	3.5	0.2	1.0
9	14.7	28.9	6.5	5.3	1.2		33	12.9	33.1	2.4	2.8	0.2	0.9
10	14.5	31.0	8.2	5.3	1.2		34	10.1	23.4	2.8	2.8	0.1	0.8
11	10.7	29.1	8.3	3.4	0.9		35	16.9	32.9	2.7	1.9	0.1	0.6
12	14.7	28.6	7.6	3.5	0.4		36	10.2	28.2	2.3	3.2	0.2	0.9
13	14.3	32.7	7.4	3.8	0.4		37	7.5	19.5	1.7	2.1	0.1	0.5
14	15.0	35.3	7.9	3.6	0.5		38	6.5	19.9	3.8	2.8	0.1	0.3
15	15.8	31.6	5.8	3.4	0.6		39	10.9	34.1	4.1	4.7	0.1	1.1
16	14.1	33.4	6.9	3.4	0.4		40	12.0	52.8	4.1	4.3	0.4	0.4
17	12.0	34.0	4.1	2.6	0.4		41	9.1	22.0	2.3	1.9	0.0	0.3
18	11.1	29.1	6.1	3.0	0.2		42	6.8	15.1	2.7	2.5	0.0	0.2
19	13.7	31.5	5.5	3.6	0.2		43	13.4	37.7	5.4	3.7	0.4	0.8
20	16.2	34.8	7.6	4.6	0.2		44	3.8	35.6	4.0	2.6	0.1	0.8
21	14.0	35.7	7.9	3.4	0.2		45	6.1	18.3	2.3	2.3	0.1	0.2
22	15.6	33.0	3.1	2.0		0.9	46	3.7	36.4	4.2	2.7	0.1	0.5
23	20.2	35.6	2.4	2.0		0.9	47	14.5	65.2	5.8	3.3	0.2	1.3
24	12.7	43.4	3.3	2.4		0.3							

^a Hydroxycinnamates: *trans*-caffeic acid, *cis*-caffeic acid, coumaric acid, *trans*-couteric acid, *cis*-couteric acid, *trans*-caftaric acid, *cis*-caftaric acid, *S*-glutathionylcaftaric and fertaric acid. ^b Flavan-3-ols: catechin, epicatechin, and procyanidin B3. ^c Benzoates: gallic acid, protocatechuic acid, and syringic acid. ^d Flavonols: quercetin 3-glucuronide. ^e Other: *trans*-resveratrol, *cis*-resveratrol, *trans*-piceid, and *cis*-piceid.

(2.3 mg/L), 2-*S*-glutathionylcaftaric acid (2.3 mg/L), catechin (2.2 mg/L), protocatechuic acid (2.0 mg/L), gallic acid (1.5 mg/L), *trans*-caffeic acid (1.4 mg/L), procyanidin B3 (1.2 mg/L), fertaric acid (0.7 mg/L), *cis*-caffeic acid (0.6 mg/L), syringic acid (0.6 mg/L), *cis*-caftaric acid (0.6 mg/L), *trans-p*-coumaric acid (0.5 mg/L), quercetin 3-glucuronide (quantified as quercetin, 0.4 mg/L), *cis*-piceid (0.4 mg/L), *cis*-resveratrol (0.2 mg/L), *trans*-piceid (0.2 mg/L), ferulic acid (0.2 mg/L), and *trans*-resveratrol (0.1 mg/L). Gallic acid was present in most of the samples in amounts not exceeding 2.6 mg/L.

Regression analyses of the relative LDL antioxidant activity at 20 μM GAE with the concentration of total phenolics and individual components gave a significant correlation for total phenolics, *trans*-caffeic acid, coumaric acid, protocatechuic acid, and quercetin 3-glucuronide (Table 4). Total phenolic content measured according to the Folin–Ciocalteu method showed a significant correlation ($r = 0.70$, $p < 0.001$) with the relative inhibition of LDL oxidation (Figure 1). Other

Table 4. Regression Analysis of Relative Inhibition of LDL Oxidation (Tested at 20 μM) and Total or Individual Phenolic Content

compound	r value	p value	% inh ^a
total phenolics (Folin)	0.70	<0.001	na
<i>trans</i> -caffeic acid	0.39	0.006	97
<i>p</i> -coumaric acid	0.35	0.02	25
protocatechuic acid	0.31	0.03	98
quercetin 3-glucuronide	0.31	0.04	na

^a Percent inhibition of LDL oxidation at 5 μM. na, data not available.

authors found a positive correlation between total phenolics and antioxidant activity with an LDL oxidation system (Caldú et al., 1996; Frankel et al., 1995).

Tyrosol, the main individual phenolic in the samples, did not correlate with antioxidant activity. This alcohol, with a single hydroxyl group in the aromatic ring, showed low antioxidant activity (44% at 20 μM) compared to caffeic acid or catechin.

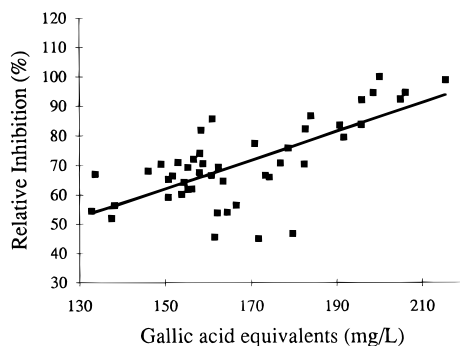


Figure 1. Regression plot for relative percent inhibition of LDL oxidation by wines at 20 μ M GAE versus total phenol content as analyzed according to the Folin–Ciocalteu method. Correlation coefficient: $r = 0.70$. Calculated regression equation, $Y = 0.49X - 10.81$. Relative percent inhibition was calculated by multiplying the inhibition at 20 μ M GAE by the corresponding dilution factor used for the extract. The highest inhibition was set as 100%.

Total hydroxycinnamates present in the samples did not show correlation with the relative inhibition of LDL oxidation. This is in accordance with the results of a study on grape extracts (Meyer et al., 1997). However, some individual hydroxycinnamates, *trans*-caffeic acid and coumaric acid, showed low but significant correlations with the relative percentage of LDL oxidation inhibition by the wines at 20 μ M GAE ($r = 0.39$, $p = 0.006$; and $r = 0.35$, $p = 0.02$, respectively). In experiments with standard compounds, caffeic acid and cftaric acid showed high antioxidant activity (97 and 98% at 5 μ M, respectively) using the same model system (Meyer et al., 1998).

In the benzoic acids group, protocatechuic acid showed a low but significant correlation ($r = 0.31$, $p = 0.03$) with the relative percentage of LDL oxidation inhibition (Table 4). Protocatechuic acid, with two *o*-hydroxyl groups, is expected to be a good antioxidant (Heimann and Reiff, 1953) and showed high antioxidant activity in the LDL system (98% at 5 μ M). Other authors found correlations between hydroxybenzoates and antioxidant activity of grape extracts (Meyer et al., 1997) and between gallic acid and antioxidant activity of wines (Frankel et al., 1995). In our study, gallic acid did not correlate with antioxidant activity, but in contrast to the previous studies, the concentration of protocatechuic acid in our samples was higher than that of gallic acid. Therefore, interaction effects may influence the relative antioxidant activity of these wine samples.

In the flavan-3-ol group, catechin and epicatechin did not correlate with relative inhibition of LDL oxidation. In contrast, flavan-3-ols were found to be strongly correlated with the antioxidant activity of wines (Soleas et al., 1997; Frankel et al., 1995) and grape juices (Meyer et al., 1997). However, these experiments included red wines or red grape juice, in which flavan-3-ols together with anthocyanins are the main phenolic compounds.

In the flavonols group, quercetin 3-glucuronide showed low but significant correlation ($r = 0.31$, $p = 0.04$) with the relative inhibition of LDL oxidation (Table 4). Other studies showed relations between quercetin (Soleas et al., 1997) and quercetin and rutin (Frankel et al., 1995) with the antioxidant activity of wines.

DISCUSSION

The amount of total phenolic compounds found in cavas (109–202 mg/L) measured by absorbance at 280

nm was lower than those reported in white wines by other authors, on the basis of the Folin–Ciocalteu method (Frankel et al., 1995; Simonetti et al., 1996). The difference may be due to the analytical method used. When we analyzed our samples by using the Folin method, total phenols were between 1 and 36% higher than the values obtained by measuring absorbance at 280 nm. Both absorbance at 280 nm and Folin–Ciocalteu are nonspecific methods. Any compound containing an aromatic ring absorbs at 280 nm, and any compound with reducing capacity reacts with the Folin–Ciocalteu reagent. The proportionality of the molar response of the Folin to the number and relative position of hydroxyl groups may account, at least in part, for the higher values of total phenolics obtained with the Folin method.

The amount of total phenolics is influenced by the variety of grape used. The varietal wines made of Chardonnay grapes had a significantly ($p < 0.05$) higher content of phenolics (170 mg/L) compared to wines made from Xarel.lo, Macabeo, and Parelada blends. Winery was also a factor that affected the total phenolic content. Samples processed in winery A also contained more total phenolics (156 mg/L, $p < 0.05$) than samples from winery B or C (130 and 132 mg/L, respectively).

The Folin–Ciocalteu method was a better predictor of antioxidant activity of cava wines than absorption at 280 nm. The relative antioxidant activity of cava correlates better with total phenols measured by Folin ($r = 0.70$, Figure 1) than with total phenols measured by absorbance at 280 ($r = 0.447$). Because the Folin–Ciocalteu method measures reducing capacity, the results may support a similar mechanism by which phenolic compounds prevent LDL oxidation.

The antioxidant activity of the wines tested in the present study is comparable to that of previous studies with California wines (Frankel et al., 1995) and with California-grown grapes (Meyer et al., 1997). Inhibition of oxidation is comparable to that produced by red wines at the same molar concentration. Evidently, both red and white wines have phenolic compounds of similar antioxidant activity.

Although the total phenolic content of wines is affected by many factors, these differences do not always translate into differences in antioxidant activity. In our study, the variety of grapes used significantly ($p < 0.05$) influenced the antioxidant activity of the resulting wines. Differences in antioxidant activity due to grape variety were previously reported in an LDL system (Meyer et al., 1997) and in a liposome system (Yi et al., 1997). In the present study, wines made of the classic cava coupage (CP) had the highest antioxidant activity at 10 and 20 μ M GAE. At 10 μ M GAE, the differences in antioxidant activity were less significant than at 20 μ M GAE (Table 2). Monovarietal wines made of Xarel.lo, Macabeo, or Parelada (included in the CP coupage) were significantly less active than CP wines. On the other hand, wines that included Chardonnay grapes in the mixes of wines tended to have decreased antioxidant activity compared with Chardonnay alone (C 74%, PC 64%, and CPC 65% inhibition of LDL oxidation at 20 μ M GAE), but the differences were not significant. Apparently, some of these blends can either reinforce or antagonize antioxidant activity. The harvest year also affected the antioxidant activity of the cava wines. Surprisingly, the oldest wines were more active than the younger wines, when tested at the same molar

concentration (Table 2). The wine appears to be a good medium for the preservation of phenolic antioxidants.

HPLC analyses of the samples showed that the major individual phenolics in the cavas are tyrosol and the hydroxycinnamates *trans*-caftaric acid, *cis*-coutaric acid, and *trans*-coutaric acid. The hydroxycinnamates were the most abundant class of phenolics, followed by tyrosol, flavan-3-ols, benzoic acids, procyanidins, stilbenes, and flavonols (Table 3). Similar results were obtained in another study with wines from the same area and varieties (Betés-Saura et al., 1996) and with California white wines (Singleton and Trousdale, 1983). Hydroxycinnamic acids were the major phenolics in white monovarietal wines, made from different cultivars grown in the Ontario region (Soleas et al., 1997). These results are in contrast with the data from six samples of California white wines (Frankel et al., 1995). However, many of the hydroxycinnamates identified in this work were not reported in that publication. In contrast, the amounts of the flavan-3-ols, catechin and epicatechin, reported in that work are much higher than what we found in our wines. These differences may be due not only to the cultivars but also to the processing and analytical methods. The vinification process produces an important change in the contents of phenolics in the initial grape juice (Betés-Saura et al., 1996).

The results of this study with white sparkling wines show that their antioxidant activity toward LDL oxidation can be related to several phenolic compounds. The low correlation values can be explained by the low concentration, measured by HPLC, of phenolic compounds in white wines (0.1–10 mg/L), the small differences among samples for contents of a given phenol, and the small differences in antioxidant activity. However, these correlations are statistically significant. As reported previously (Soleas et al., 1997; Meyer et al., 1997; Frankel et al., 1995), the antioxidant activity of wines results from the action of a combination of phenolic compounds. The compounds mainly responsible for antioxidant activity can vary depending on the type and composition of the sample. As catechin is one of the main antioxidants in red wine, caffeic acid may be considered one of the main antioxidants in white wine.

ABBREVIATIONS USED

LDL, low-density lipoprotein; UV, ultraviolet; CHD, cardiovascular heart disease; CP, coupage; M, Macabeo; X, Xarel.lo; P, Parellada; C, Chardonnay; GAE, gallic acid equivalents; HPLC, high-performance liquid chromatography.

LITERATURE CITED

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