

# Antioxidant Capacities and Phenolics Levels of French Wines from Different Varieties and Vintages

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Phenolics from grapes and wines can play a role against oxidation and development of atherosclerosis. Levels of phenolics, major catechins [(+)-catechin, (–)-epicatechin, procyanidin dimers B1, B2, B3, and B4], phenolic acids (gallic acid and caffeic acid), caftaric acid, malvidin-3-glucoside, peonidin-3-glucoside, and cyanidin-3-glucoside were quantified by HPLC with UV detection for 54 French varietal commercial wines taken from southern France to study the antioxidant capacity and the daily dietary intake of these compounds for the French population. The highest antioxidant capacity was obtained with red wines and ranged from 12.8 mmol/L (Grenache) to 25.2 mmol/L (Pinot Noir). For white wines, Chardonnay enriched in phenolics by special wine-making was found to have an antioxidant capacity of 13.8 mmol/L, comparable to red wine values. For red wines classified by vintages (1996–1999) antioxidant capacities were ~20 mmol/L and then decreased to 13.4 mmol/L for vintages 1995–1991. Sweet white wines have 1.7 times more antioxidant capacity (3.2 mmol/L) than dry white wines (1.91 mmol/L). On the basis of a still significant French wine consumption of 180 mL/day/person, the current daily intake of catechins (monomers and dimers B1, B2, B3, and B4) averaged 5 (dry white wine), 4.36 (sweet white wines), 7.70 (rosé wines), 31.98 (red wines), and 66.94 (dry white wine enriched in phenolic) mg/day/resident for the French population. Red wine, and particularly Pinot Noir, Egiodola, Syrah, Cabernet Sauvignon, and Merlot varieties, or Chardonnay enriched in phenolics during wine-making for white varieties contribute to a very significant catechin dietary intake.

**Keywords:** Wine; phenolics; antioxidant capacity; levels; varieties; vintages

## INTRODUCTION

The health effects of alcoholic beverages on health conducted in epidemiological studies have shown that coronary heart diseases are less prevalent in populations consuming moderate and regular amounts of wine (1–4). In one of the more famous studies, Renaud and De Lorgeril (5) suggest an explanation of the phenomenon particularly favorable to the French population with regard to cardiovascular disease, known as the “French paradox”. The results of the Monica program (3), a worldwide CAD (coronary artery diseases) surveillance system organized by the World Health Organization (WHO), confirm that mortality levels provoked by CAD are much lower in France than in other industrialized countries, even though the consumption of saturated fats in France is much the same and blood cholesterol levels are generally higher. Furthermore, other factors associated with the risk of coronary artery disease, such as arterial blood pressure, body weight, and smoking, are no lower in France than in the other countries. This is the French paradox. Recently, Renaud et al. (6) evaluated the health risks of wine and beer

drinking among >36000 middle-aged men in eastern France. Moderate intake of both wine and beer was associated with lower relative risk for cardiovascular diseases. The risk was more significant with the intake of wine. For all causes of mortality, only daily wine intake (22–32 g of alcohol) was associated with a lower risk due to lower incidence of cardiovascular diseases and cancers, and it was concluded that moderate consumption of only wine was associated with a lower all-cause mortality. Attention turned to the nonalcoholic fractions of wine, and particularly red wine, as an important source of polyphenols, which are capable of inhibiting the processes behind CAD. This hypothesis is supported by the results of recent epidemiological studies concerning foodstuff polyphenols, particularly flavonoids. A correlation was also noticed between increasing levels of flavonoid ingestion from fruit and vegetables and reduction in CAD. The studies carried out by Hertog et al. (7), Knekt et al. (8), and Rimm et al. (9) reveal the benefits of a diet rich in flavonoids.

The inhibition of human low-density lipoproteins (LDL) was demonstrated by the addition of the mixture of polyphenols from wine (10). Red wine diluted 1000-fold inhibited the *in vitro* oxidation of human LDL significantly more than  $\alpha$ -tocopherol. (+)-Catechin and (–)-epicatechin are the basic units of the catechin group. The procyanidins are formed from the association of several of these monomeric units: two to five units for catechin oligomers and over five units for catechin

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polymers. These molecules possess a structure that confers on them an antioxidant property which can inhibit the processes leading in the long term to atherosclerosis and arterial thrombosis.

The flavonoids are the most lipophilic of the natural antioxidants, but less so than  $\alpha$ -tocopherol.  $\alpha$ -Tocopherol seems to be located in the lipid membrane within the phospholipid bilayer, whereas the flavonoids are probably mainly located at the polar surface of the bilayer. The aqueous, that is, transported in the plasma, free radicals would therefore be captured more easily by the flavonoids than by the less accessible  $\alpha$ -tocopherol.

Thus, the flavonoids could be concentrated near the membranous surface of the LDL particles, ready to capture the oxygenated aqueous free radicals. They would in this way prevent the consumption of lipophilic  $\alpha$ -tocopherol and thus delay oxidation of the lipids contained in the LDL (11). Catechins and procyanidins have been shown in vitro to be powerful inhibitors of LDL oxidation, more so than  $\alpha$ -tocopherol (12), and of platelet aggregation (13). Moreover, it has been shown that the consumption of wine by humans leads to an increase in the antioxidant capacity of plasma (14). It was also demonstrated by Maffei Facino et al. (15) that a diet enriched with procyanidins enhances antioxidant activity and reduces myocardial postischemic damage in rats with an increase in plasma levels of ascorbic acid. More recently, it was shown in humans that wine supplementation to a high-fat or Mediterranean diet increases plasma antioxidant capacity, decreases DNA damage, and normalizes endothelial function (16).

Other studies have been carried out on the antioxidant activity—through inhibition of copper-catalyzed oxidation of human LDL—of a selection of California wines, made from Cabernet Sauvignon, Merlot, Zinfandel, Petite Syrah, Pinot Noir, Sauvignon Blanc, and Chardonnay. The relative inhibition of LDL oxidation (calculated with respect to the total phenol concentration of each sample) varied from 46 to 100% for red wines and from 3 to 6% for white wines (17). The antioxidant activity of wines made with long maceration times exclusively from Rhône Valley Syrah and Grenache varieties was 60% relative inhibition of LDL oxidation (18).

All of the properties and studies reported support the present hypotheses for explaining the reduced risk of mortality from CAD in moderate and regular consumers of wine (in particular red wine).

In the present study we evaluated antioxidant capacity, total phenol content, major catechins [(+)-catechin, (-)-epicatechin, and dimers B1, B2, B3, and B4], some phenolic acids, gallic acid, caffeic acid, a cinnamate (caftaric acid), and major anthocyanins mavidin-3-glucoside, peonidin-3-glucoside, and cyanidin-3-glucoside for 54 commercial varietal wines taken from southern France to provide antioxidant activities and concentration data of phenolics for varietal wines and to appreciate the daily dietary intake of catechins for the French population.

## MATERIALS AND METHODS

**Materials.** (+)-Catechin, (-)-epicatechin, gallic acid, and caffeic acid were obtained from Aldrich, and malvidin-3-glucoside, peonidin-3-glucoside, and cyanidin-3-glucoside were from Extrasynthèse. Caftaric acid was provided by Ursa Vorschek. Procyanidin dimers B1, B2, B3, and B4 were obtained from grape seeds as detailed below. The structures of the catechin compounds analyzed are given in Figure 1.

**Wine Samples.** We analyzed 54 samples of different French varietal wines: 34 red (Merlot, Cabernet Sauvignon, Pinot Noir, Grenache, Syrah, Egiodola, Mourvedre, Carignan, Trempanillo, and Aramon); 18 white [7 sweet (Semillon) and 11 dry (Chardonnay, Viognier, Sauvignon, Terret Sauvignon, Marsanne, and Roussane)], and 2 rosés from the Syrah variety in commercial bottles from France. The wine samples analyzed were from all viticultural areas of southern France and of vintage years from 1986 to 1999. All wines analyzed are frequently consumed in France.

**Total Phenols Content.** Total phenols were analyzed according to the Folin-Ciocalteu method (19), calibrating against gallic acid standards and expressing the results as gallic acid equivalents (GAE).

**Antioxidant Capacity of Wines.** Antioxidant capacity was determined by the total antioxidant status method of Randox. A kit Randox catalog no. NX2332 (Randox Laboratories Ltd., Crumlin, U.K.) was used. The assay is based on the 2,2'-azino-di(3-ethylbenzthiazoline sulfonate) (ATBS) incubated with a peroxidase (metmyoglobin) and  $H_2O_2$  to produce the radical cation  $ABTS^{+\cdot}$ . This has a relatively stable blue-green color, which is measured at 600 nm. Antioxidants in the added sample cause suppression of this color production to a degree proportional to their concentration. This analytical procedure has been applied to physiological antioxidant compounds and radical-scavenging drugs, and an antioxidant ranking based on their reactivity relative to a 1.0 mmol/L Trolox standard has been established. The Trolox equivalent antioxidant capacity of plasma from an adult reference population has been measured and the method optimized and validated (20). We used this automated method to investigate the total plasma antioxidant capacity of wines.

**Extraction and Isolation of Crude Procyanidins.** Grape seeds (*Vitis vinifera*), 150 g, were extracted with methanol as described by Bourzeix et al. (21) and by Weinges et al. (22). The extract (3 mL, 300 mg) was chromatographed on Fractogel TSK HW-40(s) (25–40  $\mu$ m) (450  $\times$  25 mm i.d.) with methanol as eluant, using an ISCO (Lincoln, NE) model UA-5 absorbance monitor set at 280 nm, a peristaltic Miniplus2 pump (Gilson Inc., Middleton, WI), and an ISCO 328 fraction collector. Ten fractions containing procyanidins were collected.

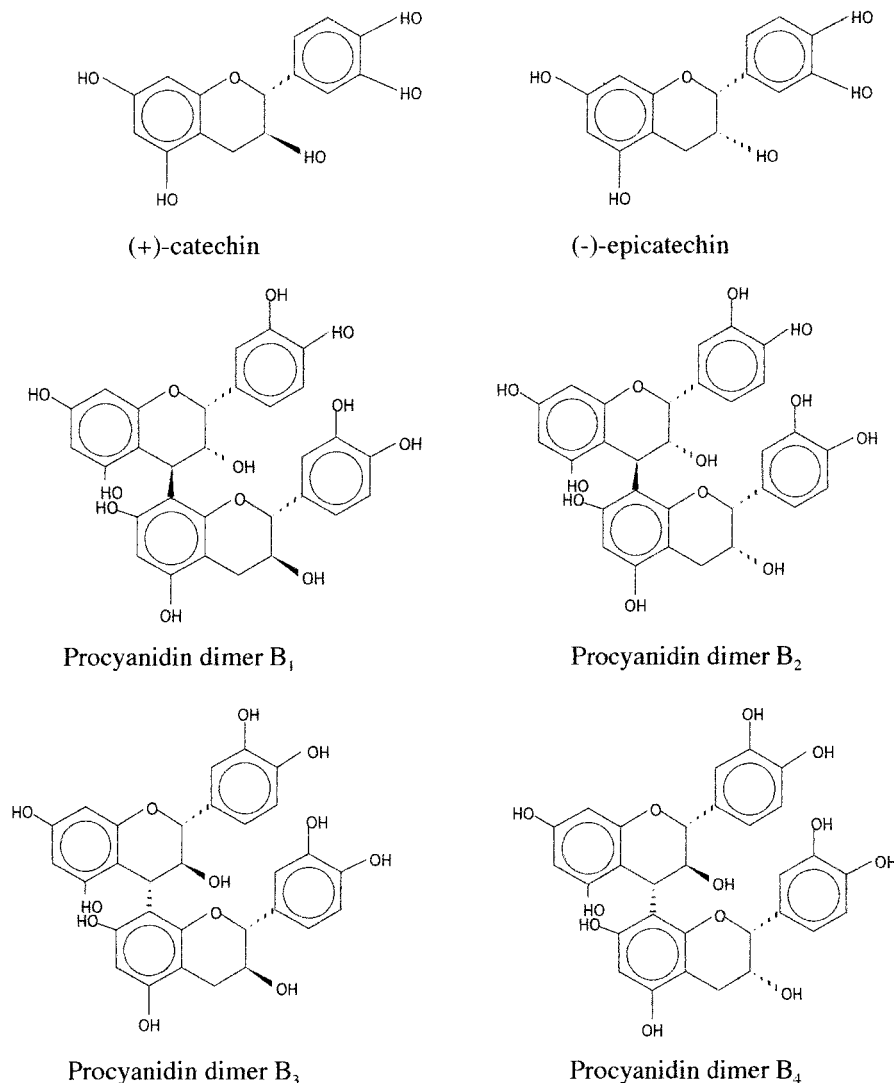
**Isolation of Purified Procyanidins.** Semipreparative HPLC was performed with a Waters 510 pump (Waters, Milford, MA) a U6K injector, and a Hewlett-Packard (Palo Alto, CA) model 1050 UV-vis detector set at 280 nm. The column was a Waters RCM Novapak C18 (25  $\times$  100 mm, 4  $\mu$ m particle size). Elution was carried out by a linear gradient of 0–500 mL/L methanol with the solvent described below at 2 mL/min.

**TLC Analysis.** Silica plates (DC Alufolien-Kieselgel 60, 0.2 mm thick, Merck, EM Separation Technology, Gibbstown, NJ) were developed with toluene/acetone/formic acid (3:3:1 v/v/v) as described by Lea et al. (23). The plates were visualized by spraying with a solution of vanillin (100 g/L) in concentrated HCl.

**HPLC Analysis.** A Hewlett-Packard model 1090 with three low-pressure pumps and a diode array UV detector coupled to a Hewlett-Packard Chemstation was used for solvent delivery system and detection. A Hewlett-Packard Nucleosil 100 C18 column (250  $\times$  4 mm, 5  $\mu$ m particle size) was used for the stationary phase with a flow of 0.7 mL/min. The solvents used for separation were as follows: solvent A, 50 mM dihydrogen ammonium phosphate adjusted to pH 2.6 with orthophosphoric acid; solvent B, 20% A with 80% acetonitrile; and solvent C, 0.2 M orthophosphoric acid adjusted with ammonia to pH 1.5 and solvent gradient conditions as described by Lamuela-Raventos et al. (24). Temperature was thermostated at 25  $^{\circ}$ C.

## RESULTS AND DISCUSSION

The different wine-making techniques are important factors influencing phenolics levels in wine (21). The aim of this study was to analyze antioxidant capacity and



**Figure 1.** Structures of catechin compounds analyzed.

phenolics and catechins contents of wines from diverse varieties and vintages from France. The results obtained were used to evaluate the phenolics levels and catechins intake from regular, moderate wine consumption.

The concentrations of total phenols as determined by the Folin–Ciocalteu method varied from 1018 to 3545 mg/L GAE for the red wines and from 262 to 1425 mg/L GAE for the white wines (Table 1). The maximal total phenol levels of French varietal wines are highest in comparison with total phenol levels of wines from California (25).

Thus, the red wines studied had high overall levels of catechins (sum of monomers and procyanidin dimers analyzed) (average = 177.72 mg/L), but there were considerable differences among the red wines (minimum of 61.7 mg/L to maximum of 825.4 mg/L) (Table 1). Levels of catechins in the white wines were lower: average = 26.36 mg/L (minimum = 13.6 mg/L to maximum = 38.35 mg/L) with the exception of the Chardonnay enriched in phenolics by the special wine-making technique (371.9 mg/L). A statistical treatment of the data from Table 1 is given in Table 2 by wine type. In Figure 2, we present the antioxidant capacity levels classified by vintages. The levels are very closed to 20 mmol/L for red vintages from 1996–1999. A decrease of 33% of antioxidant activity is effective for vintages (1995–1991). White dry wine from 1999 vin-

tage are 10-fold less powerful in antioxidant activity than the red wine 1999 vintage.

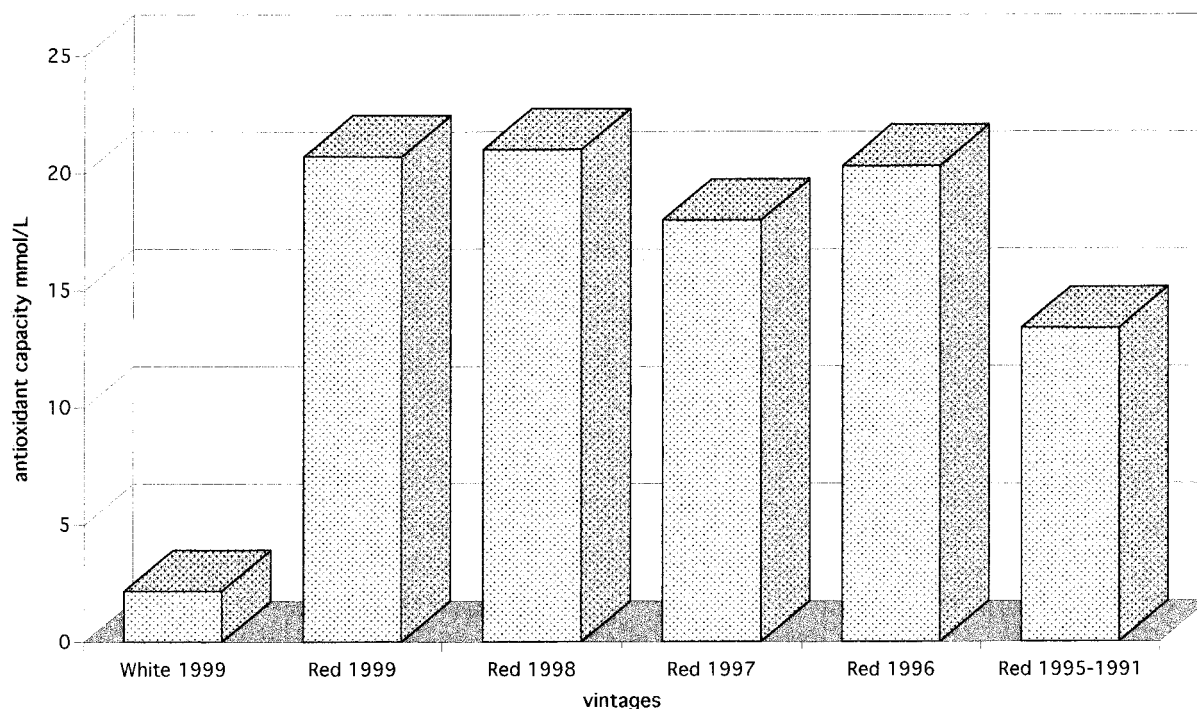
The most interesting varieties for high levels of antioxidant capacities are Pinot Noir, Egiodola, Mourvedre, Syrah, Cabernet Sauvignon, and Merlot for red wines and Semillon for white wine (Figure 3). The classification by wine types for antioxidant activity (Figure 4) shows that the lowest activity is obtained with dry white wines; sweet white wines have 1.7-fold more activity than dry white wines. The antioxidant capacity levels are the same (3.2 mmol/L) for sweet white wines and rosé wines, but the best antioxidant activity for white wine is obtained with a white dry Chardonnay made by a special wine-making technique with a natural enrichment in phenolics. This wine was obtained by crushing the grapes with must, seeds, and skins fermentation: the wine-making was the same as for a red wine, including a maceration step (6 days) with an increase of temperature to 28 °C. The antioxidant capacity level of this wine (13.8 mmol/L) is within the range of some red wines. The average antioxidant capacity of red wines gave the highest value (18.96 mmol/L).

A correlation coefficient of  $r = 0.959$  ( $p < 10^{-7}$ ) was found between antioxidant capacity and total phenol content in GAE (Figure 5). Concentrations of individual phenolic constituents were correlated with the antioxi-

Table 1. Levels of Phenolics and Antioxidant Capacity (AC) for French Varietal Wines

wine	vintage	color	AC, mmol/L	total phenol content, mg/L	catechin	epicat-echin	B1	B2	B3	B4	gallic acid	caffeic acid	caftaric acid	malvidin-3-glucoside	peonidin-3-glucoside	cyanidin-3-glucoside	catechins sum <sup>a</sup>
1 Cabernet Sauvignon	1999	red	19.2	2081	40.1	25.5	16.5	17	68	5	39.85	7.1	59.2	37.4	3.65	0.85	172.1
2 Egirodola	1999	red	21.6	2300	69.5	70	9.8	55.9	90.4	7.6	38.4	4.4	29.7	100	13	1.8	303.2
3 Syrah	1999	red	20.2	2338	36	24.5	27.3	29.4	67.3	7.3	35.4	9.3	63.7	36.1	4.7	0.8	191.8
4 Merlot	1999	red	19.9	2239	36	28	10	19	71.7	2.8	33.9	4.4	60.9	34.3	5.4	1	167.5
5 Cabernet Sauvignon	1999	red	21.2	2532	48.8	29.3	40.2	36	65.2	5.9	40.1	8.1	54.8	35.7	3.6	0.45	225.4
6 Merlot	1997	red	21.7	2200	38.1	19.9	6.5	19.1	40.6	4.6	30.4	5.2	75.3	26.2	0.2	0.3	128.8
7 Syrah	1998	red	20.1	2063	42	18.3	12.6	28.7	68.9	0.5	33.1	11	67.3	29.8	3.1	0.3	170.95
8 Cabernet Sauvignon	1998	red	17.5	2486	38.8	39.8	8.5	32.8	49.4	4.8	35.6	4.7	77.8	44.3	NF <sup>b</sup>	0.5	174.1
9 Pinot Noir	1996	red	21.2	2329	74	32.4	26.2	37.1	102	0.5	39.8	12.8	40.4	7.7	1	0.1	272.15
10 Syrah	1998	red	19.7	2293	28.7	17.6	9.3	27.8	61	4.7	31.3	14.7	51.2	34.6	3.9	0.5	149.1
11 Merlot	1993	red	17.7	2365	35.8	24.4	10.4	16.7	71.1	2.1	41.6	3.7	59.6	16.1	2.2	0.6	160.7
12 Grenache	1997	red	15.9	1991	1689	32.8	31.2	9.1	21.5	38.7	5.3	23.9	5.8	63.4	25.3	0.5	0
13 Cote de la Maleperre	1997	red	17.4	2157	51	46.6	8.6	34.7	49.1	2.7	37	4.6	73.3	15	0	0.2	192.7
14 Cabernet Sauvignon	1997	red	17.4	2157	33.1	18	6.5	21	34.2	2.2	25.8	6.3	66.1	20.1	0	0.3	115
15 Merlot	1996	red	15.3	1783	41.8	39	7.7	22.7	37.4	2.8	35	3.4	73.3	15	0	0.3	151.4
16 Merlot	1998	red	19.3	2324	54.3	41	10.7	54.6	55.3	2.9	33.4	4.1	69.2	38.5	0.5	0.1	218.8
17 Cabernet Sauvignon	1996	red	29.9	1842	41.8	39	7.7	22.7	37.4	2.8	35	3.4	73.3	15	0	0.3	151.4
18 Cabernet Sauvignon	1996	red	16.5	1987	39.5	26.11	15.2	27.8	46	2.9	33.47	6.3	58	7.1	1.3	0	157.4
19 Cabernet Sauvignon	1993	red	20.5	2338	34.5	20	28.5	26.8	63.5	4.4	35.6	7	60.85	21	1.87	0.23	177.7
20 Syrah	1999	red	22.1	2590	48.8	21.6	39.8	51.8	85.5	7.3	11.3	5.2	66.1	26.9	2.9	0.5	254.8
21 Pinot	1998	red	29.2	3345	212	103	50.8	163	261	36	61.6	11.1	28.6	10.5	2.3	0	825.4
22 Egirodola	1998	red	23.3	2734	45.1	43.8	10	50	89	0.7	66	2.9	28.6	10.8	1.1	0.15	238.6
23 Mourvedre	1997	red	22.4	2275	37	17.5	8.5	10	71.3	7.45	32.6	14.7	104.2	3.3	0.1	0	151.75
24 Grenache	1991	red	9.6	1018	15.1	10	6.2	12.9	13.1	4.4	8.9	5.5	1	3.8	1.1	0	61.7
25 Grenache	1996	red	17.5	2014	28.3	21.5	10	19.9	26.3	8.8	25.1	9.6	28.7	15.8	1.2	0	86.5
26 Mourvedre	1996	red	21.8	2257	30.3	30.8	12.8	4.2	59.2	3.15	15.3	22.9	27.4	3.2	0.75	0	140.45
27 Mourvedre	1998	red	22.8	2550	20.38	17	10.9	18.5	41.2	2.3	39.1	9.3	57.65	1.5	0.2	0	113.18
28 Carignan	1994	red	14.3	1644	18.4	12.2	11.9	18.8	38.6	1.5	27.6	10.2	46.8	3.8	0.3	0	101.4
29 Carignan	1995	red	16.3	1734	23.4	10	10.4	14.7	49.3	5.2	28.6	20.7	28.6	2.75	0.25	0	113
30 Carignan	1992	red	11.7	1360	4.4	11.6	6.6	13.2	5	3.3	2.2	24.9	19.1	0.9	0.1	0	44.1
31 Merlot	1998	red	22.2	2698	37.2	50.4	24.8	8	62	13.2	4.2	26.2	24.7	15.9	3.55	1.6	195.8
32 Aramon	1993	red	12.2	1397	22.9	16	13.7	11.2	12.7	4.4	8	40.6	0	1.9	0.6	0	80.9
33 Merlot	1994	red	16.2	2144	25.5	27.5	24	15.3	30	6.3	15.3	19.5	29.3	2.3	0.1	0	128.6
34 Tempranillo	1998	red	15.4	1982	20.2	16.5	4.6	9.5	35.2	1.6	141.3	23.3	0	9.4	0.5	0.1	87.6
35 Semillon sweet	1986	white	3.5	710	4	1	5.7	5.55	5.04	1.05	9.7	0.41	6.7	NF	NF	NF	22.34
36 Semillon sweet	1991	white	3.45	597	3.8	1	2.8	2.6	4.3	8.7	1.1	0.82	20.25	NF	NF	NF	23.2
37 Semillon sweet	1994	white	3.65	773	2.9	1	3.1	1.75	14.4	0.75	6	1.58	17.11	NF	NF	NF	23.9
38 Semillon sweet	1995	white	3.55	724	4.7	2.3	1.9	2.8	11	0.8	9.25	2.15	9.15	NF	NF	NF	23.5
39 Semillon sweet	1997	white	3.7	688	6.1	2.6	2.5	3.7	14.6	0.6	6.3	2.15	22.4	NF	NF	NF	30.1
40 Semillon sweet	1998	white	2.1	557	6.4	1	4.2	3.5	6.95	0.8	4.5	1.93	5.74	NF	NF	NF	22.85
41 Semillon sweet	1999	white	2.5	552	1.35	1	3.8	1.2	15.4	1.3	3.85	2.15	16.6	NF	NF	NF	24.05
42 Terret Sauvignon	1997	white	2.11	289	6.2	1.5	5.8	3	14.8	1.3	1.1	3.1	26.2	NF	NF	NF	32.6
43 Terret Sauvignon	1998	white	2.21	308	6.2	2.7	3.7	3.1	7.3	1.9	1.3	4.1	36.1	NF	NF	NF	24.9
44 Sauvignon	1998	white	1.69	262	4.1	3.3	1	1.1	3.6	0.5	2.4	1.7	23.5	NF	NF	NF	13.6
45 Chardonnay	1999	white	2.31	379	7.5	7	0.8	4.7	7.6	1.1	2.6	4.9	24.7	NF	NF	NF	28.7
46 Chardonnay <sup>c</sup>	1999	white	13.8	1425	98	100	27.2	58.2	59.2	29.3	25.3	3.2	83.4	NF	NF	NF	371.9
47 Vignier	1999	white	1.79	288	5.3	3.45	0.45	3.8	7.4	0.2	2	2.2	22	NF	NF	NF	27.9
48 Sauvignon	1999	white	1.98	330	7.8	4.2	4.9	2.7	7.6	0.7	1.6	3.8	22.1	NF	NF	NF	27.9
49 Chardonnay	1999	white	2.27	323	6.9	3.1	4.75	6.8	10.9	1.6	1.7	7.6	36.9	NF	NF	NF	34.05
50 Marsanne	1999	white	2.28	301	6.2	1.9	0.8	4.7	6.6	0.95	1.6	2.3	44.8	NF	NF	NF	21.15
51 Roussanne	1999	white	2.49	374	9.1	3.8	1.9	4.5	8.9	0.95	2.8	4.5	34.4	NF	NF	NF	29.15
52 Vignier	1997	white	1.69	279	6.8	2.65	4.65	5.55	12.7	6	12	1	13.9	0	0	0	38.35
53 Rose de Syrah	1999	rose	2.9	482	2.5	2.3	4.5	6.6	10.6	3.6	5.1	0.8	16.1	6.6	0.6	0.1	30.1
54 Rose de Syrah	1998	rose	3.5	673	1416	5.4	5.4	5.2	20.5	4.4	2.5	5	18.4	14.8	0.9	0	55.5
av			13.11	1548	29.9	21.3	11	20	42	4.5	20.5	7.9	41.5	18.9	1.7	0.3	114

<sup>a</sup> Sum of catechins: monomers (catechin + epicatechin) and dimers (B1, B2, B3, B4). <sup>b</sup> NF, not found. <sup>c</sup> Natural phenolic enriched by special wine-making.



**Figure 2.** Antioxidant capacity of dry wines (red and white) as a function of vintage.

**Table 2.** Statistical Treatment of Data from Table 1 by Wine Type

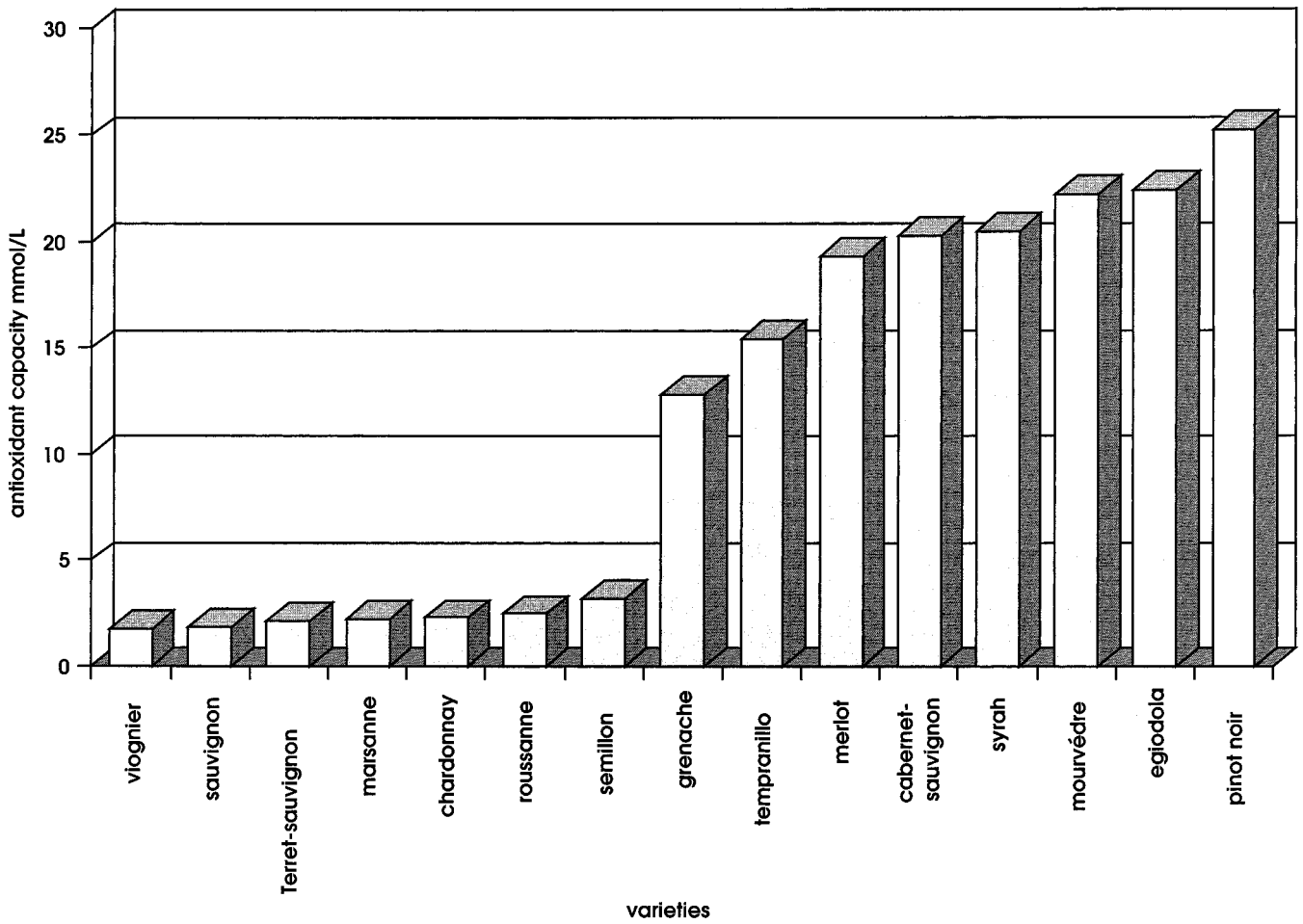
	red wine		dry white wine		sweet white wine	
	av	standard error	av	standard error	av	standard error
AC, mmol/L	18.9559	0.753792	3.14727	1.06831	3.20714	0.240394
total phenol content, mg/L	2155.26	78.4953	414.364	101.673	657.286	33.2163
catechin, mg/L	41.3406	5.70637	14.89182	8.3175	4.17857	0.667427
epicatechin, mg/L	29.4121	3.16402	12.1455	8.79619	1.41429	0.269416
B1, mg/L	15.1794	1.90469	5.08636	2.29005	3.42857	0.477949
B2, mg/L	28.6721	4.65436	8.92273	4.94929	3.01429	0.53992
B3, mg/L	58.7176	7.26025	13.3273	4.68004	10.2414	1.80387
B4, mg/L	5.21765	1.03834	4.04545	2.56926	2.0000	1.12000
catechin sum, mg/L	177.723	22.0447	59.1091	31.3416	24.2771	0.99586
gallic acid, mg/L	29.9624	2.42684	3.96364	2.14049	5.81429	1.14417
caffeic acid, mg/L	10.9676	1.47975	3.49091	0.54846	1.59857	0.26094
caftaric acid, mg/L	51.1765	4.28015	33.4545	5.65196	13.9929	2.5406
malvidin-3-glucoside, mg/L	20.0123	19.2402				
peonidin-3-glucoside, mg/L	1.8167	2.5303				
cyanidin-3-glucoside, mg/L	0.3234	0.4431				

dant activity. The best  $r$  value was found for gallic acid, 0.83 ( $p < 10^{-7}$ ), followed by procyanidin B3,  $r = 0.73$  ( $p < 10^{-7}$ ), catechin sum,  $r = 0.705$  ( $p < 10^{-7}$ ), epicatechin,  $r = 0.67$  ( $p < 10^{-7}$ ), catechin,  $r = 0.66$  ( $p < 10^{-7}$ ), caftaric acid,  $r = 0.64$  ( $p < 10^{-7}$ ), and procyanidins B1 and B2,  $r = 0.63-0.61$  ( $p < 10^{-7}$ ). A third group, procyanidin B4 and caffeic acid, showed a lower correlation of 0.36-0.35 ( $p < 0.005$ ). A fourth group constituted of anthocyanins (malvidin-3-glucoside, peonidin-3-glucoside, and cyanidin-3-glucoside) gave the lowest correlations,  $r < 0.3$  ( $p < 0.099$ ). These results indicate that the phenolic compounds found in wines at different levels are active in potentially protecting antioxidant activity.

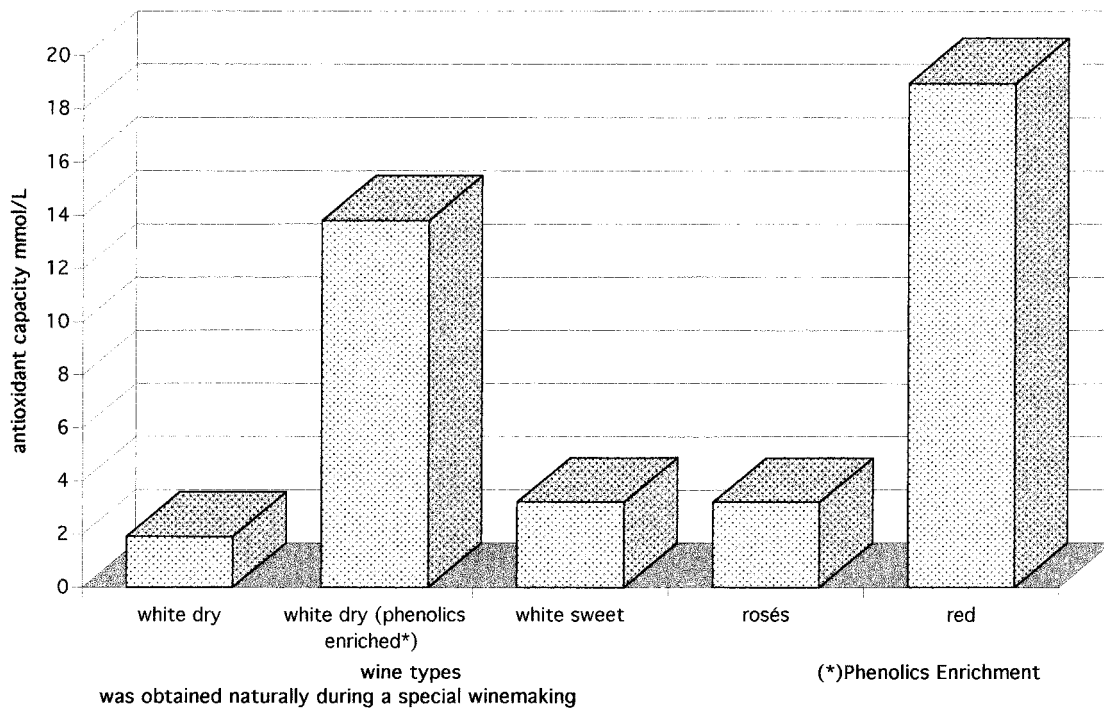
All of the compounds studied were present in each of the 34 red wines analyzed. For the catechin monomers, the mean concentration [sum of (+)-catechin and (-)-epicatechin] was 70.7 mg/L. The quantity of procyanidin dimers (sum of B1, B2, B3, and B4) was 107.7 mg/L, and that of malvidin-3-glucoside was 20 mg/L. The white wines showed very low concentrations of monomers (5 mg/L) and the absence of malvidin-3-glucoside. Highest concentrations of catechins in red varietal wines were found in Pinot Noir (548.7 mg/L), Cabernet Sauvignon

(172.7 mg/L), and Merlot (159.3 mg/L). Egidola was found to be richest in malvidin-3-glucoside (100 mg/L), 4 times higher than the other red varieties. The mean contents of each phenolic are given in Table 1.

Over the past few years, the consumption of wine in France has fallen considerably. In 1986, the mean consumption was 305 mL/person/day (26). This level fell sharply to 180 mL/person/day in 1995 (27). An estimation of the intake of catechins was calculated from these latest consumption figures and our results on the catechin (monomers and dimers) content of the 54 varietal wines. Our estimation can only be considered for regular consumption of the same variety wine over a sufficiently long period of time. Daily intake of each phenolic compound by variety of wine is indicated in Table 3. The consumption of 180 mL of Pinot Noir or Egidola wine for which the mean catechin concentrations are, respectively, 548.77 and 270.9 mg/L, gives a mean daily intake of 98.77 and 48.76 mg of catechins (monomers and dimers). This reasoning applied to dry white wine for regular (daily), moderate (180 mL) consumption gives estimations of catechins intake of only 5 mg for white sweet wine but 66.94 mg for a



**Figure 3.** Antioxidant capacity of white and red wines as a function of variety.



**Figure 4.** Antioxidant capacity as a function of wine type.

special white dry Chardonnay wine enriched by special wine-making. This is surprising and interesting because the total red wines average catechin daily intake is only

31.98 mg; this is the half the result obtained with the Chardonnay white dry wine enriched in phenolics. If traditional wine-making for white wine can increase

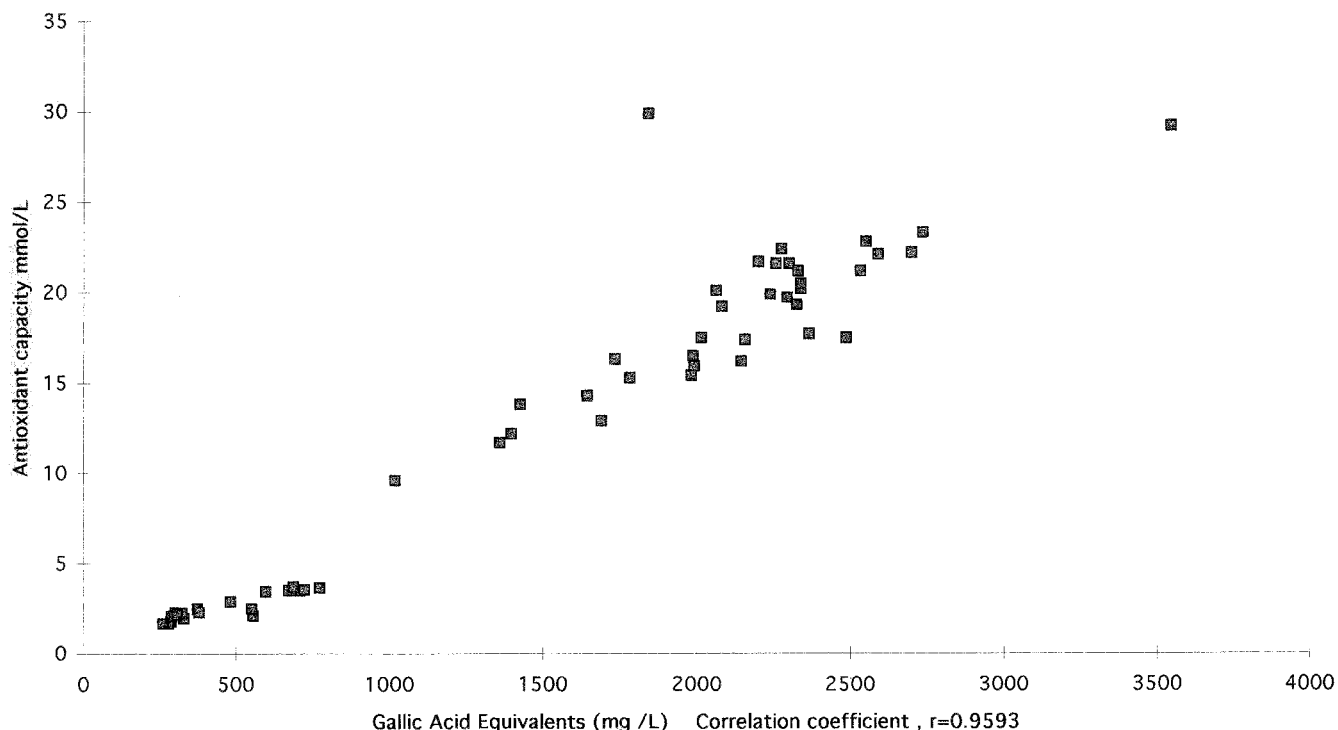


Figure 5. Antioxidant capacity of wines versus total phenol content as gallic acid equivalents.

Table 3. Catechin Levels and Daily Catechin Intake Averages as a Function of Vintage, Variety, and Type of Wine

Cabernet										
red varieties	Pinot Noir	Egiodola	Syrah	Sauvignon	Merlot	Mourvedre	Grenache	Tempranillo	Carignan	Aramon
catechin level, mg/L	548.77	270.9	191.66	172.78	149.40	135.12	95.6	87.6	86.16	80.9
catechin daily intake, <sup>a</sup> mg	98.77	48.76	34.49	31.10	26.89	24.32	17.20	15.76	15.50	14.56
Terret										
white varieties	Chardonnay <sup>b</sup>	Viognier	Chardonnay	Roussanne	Sauvignon	Semillon	Marsanne	Sauvignon		
catechin level, mg/L	371.9	33.125	31.375	29.15	28.75	24.27	21.15	20.75		
catechin daily intake, <sup>a</sup> mg	66.94	5.96	5.64	5.247	5.175	4.36	3.807	3.73		
wine vintages	white 1999	red 1999	red 1998	red 1997	red 1996	red 1995–1991				
catechin level, mg/L	27.55	219.13	215.54	153.99	153.81	88.28				
catechin daily intake, <sup>a</sup> mg	4.96	39.44	38.79	27.71	27.68	15.89				
wine types	white Chardonnay <sup>b</sup>	white dry	white sweet	rosé	red					
catechin levels, mg/L	371.9	27.83	24.27	42.8	177.72					
catechin daily intake, <sup>a</sup> mg	66.94	5.00	4.36	7.70	31.98					

<sup>a</sup> Based on French consumption of 180 mL of wine/day/person. <sup>b</sup> White wine enriched in polyphenols with a special wine-making.

catechin daily intake to 6 times less than for the red, special wine-making for white wine would permit 2-fold greater daily catechin intake than for red wines.

Daily intake of catechins from wines (Figure 2) ranged from 3.73 to 98.2 mg/person for total catechins (including monomers and dimers). The best results were obtained with Pinot Noir, Chardonnay with special wine-making, Egiodola, Syrah, Cabernet Sauvignon, and Merlot varieties. Amounts of total catechin daily intake of Pinot Noir were 1.5 times more than for Chardonnay with special wine-making, 2 times more than for Egiodola, 3 times more than for Syrah and Cabernet Sauvignon, 3.6 times more than for Merlot, and almost 18 times more than for Chardonnay with traditional wine-making. Rosé wine from Syrah gave daily intake results for total catechins close to 7.7 mg/person (1.5-fold than for traditional white wines). These results confirmed data obtained on Egiodola, Cabernet Sauvignon, and Merlot by Teissedre and Landrault (28).

Recently, in an epidemiological study on 180 subjects, concentrations of (+)-catechin in plasma were found to be 3-fold higher in a diet with fruits and vegetables but without wine and 4-fold higher in a diet with wine but without vegetable and fruits in comparison to a diet without fruits, vegetables, and wine. When the consumption of vegetables, fruits, and wine was combined, the plasmatic catechin concentration was the highest and antioxidant and antiaggregant activities of catechins could partly explain the relative protection against coronary heart disease (29).

CONCLUSION

The highest antioxidant capacity was obtained with red wines for Pinot Noir 25.2 mmol/L. For white wines, Chardonnay enriched in phenolics by special wine-making was found to have an antioxidant capacity of 13.8 mmol/L, comparable to red wine level values. Sweet

white wines from Semillon have 1.7 time more antioxidant capacity (3.2 mmol/L) than traditional dry white wines (1.91 mmol/L). Catechin intake is 6 times higher from red wines (31.98 mg/person/day) than from traditional white wines (5 mg/person/day). Catechin intake can be highest with Pinot Noir (98.77 mg/day/person) and white Chardonnay made by a special wine-making process (66.94 mg/person/day), Egiodola, Syrah, and Cabernet Sauvignon varieties. It would be important in the future to investigate other phenolic compounds to refine this estimation. However, it will also be very important in the future to obtain data on the bioavailability of catechin compound monomers and dimers in the plasma after absorption of different wine types.

#### LITERATURE CITED

- (1) St-Leger, A. S.; Cochrane, A. L.; Moore, F. Factors associated with cardiac mortality in developed countries with particular reference to the consumption of wine. *Lancet* **1979**, *1*, 1017–1020.
- (2) Friedman, L. A.; Kimball, A. W. Coronary heart disease mortality and alcohol consumption in Framingham. *Am. J. Epidemiol.* **1986**, *124*, 481–489.
- (3) World Health Organisation. *World Health Statistics Annual*; WHO: Geneva, Switzerland, 1989.
- (4) Klatsky, A. L.; Armstrong, M. A. Alcoholic beverage choice and risk of coronary artery disease mortality: do red wine drinkers fare best? *Am. J. Epidemiol.* **1993**, *71*, 467–469.
- (5) Renaud, S.; de Lorgeril, M. Wine, alcohol, platelets, and the French paradox for coronary heart disease. *Lancet* **1992**, *339*, 1523–1526.
- (6) Renaud, S.; Guéguen, R.; Siest Gérard, Salamon R. Wine, beer, and mortality in middle-aged men from eastern France. *Arch. Intern. Med.* **1999**, *159*, 1865–1870.
- (7) Hertog, M. G. L.; Feskens, E. J. M.; Hollman, P. C. H.; Katan, M. B.; Kromhout, D. Dietary antioxidant flavonoids and risk of coronary heart disease. The Zutphen elderly study. *Lancet* **1993**, *342*, 1007–1011.
- (8) Knekt, P.; Jarvinen, R.; Reunanen, A. J.; Maatela, J. Flavonoid intake and coronary mortality in Finland: a cohort study. *Br. Med. J.* **1996**, *312*, 478–481.
- (9) Rimm, E. B.; Katan, M. B.; Ascherio, A.; Stampfer, M. J.; Willett, W. C. Relation between intake of flavonoids and risk for coronary heart disease in male health professionals. *Ann. Intern. Med.* **1996**, *155*, 391–396.
- (10) Frankel, E. N.; Kanner, J. B.; German, E.; Kinsella, J. E. Inhibition of human low density lipoprotein by phenolic substances in red wine. *Lancet* **1993**, *341*, 454–457.
- (11) Carando, S.; Teissedre, P. L. Catechin and procyanidin levels in French wines contribution to dietary intake. In *Plant Polyphenols 2: Chemistry, Biology, Pharmacology, Ecology*; Gross et al., Eds.; Kluwer Academic/Plenum Publishers: New York, 1999; pp 725–737.
- (12) Teissedre, P. L.; Frankel, E. N.; Waterhouse, A. L.; Peleg, H.; German, J. B. Inhibition of in vitro human LDL oxidation by phenolic antioxidants from grapes and wines. *J. Sci. Food Agric.* **1996**, *122*, 157–168.
- (13) Ruf, J. C.; Berger, J. L.; Renaud, S. Platelet rebound effect of alcohol withdrawal and wine drinking in rats. *Atheroscler., Thromb. Vascular Biol.* **1995**, *15*, 140–144.
- (14) Fuhrman, B.; Lavy, A.; Aviram, M. Consumption of red wine with meals reduces the susceptibility to human plasma and low-density lipoprotein to lipid peroxidation. *Am. J. Clin. Nutr.* **1995**, *61*, 549–554.
- (15) Maffei Facino, R.; Carini, M.; Aldini, G.; Berti, F.; Rossoni, G.; Bombardelli, E. Diet enriched with procyanidins enhances antioxidant activity and reduces myocardial post-ischaemic damage in rats. *Life Sci.* **1999**, *64*, 627–642.
- (16) Leighton, F.; Cuevas, A.; Guash, V.; Perez, D. D.; Strobel, P.; San Martin, A. 1999. Plasma Polyphenols and antioxidants, oxidative DNA damage and endothelial function in a diet and wine intervention study in humans. *Drugs Exp. Clin. Res.* **1999**, *25*, 133–141.
- (17) 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 lipoprotein. *J. Agric. Food Chem.* **1995**, *43*, 890–894.
- (18) Teissedre, P. L.; Waterhouse, A. L.; Frankel, E. N. Principal phytochemicals in French syrah and grenache rhône wines and their antioxidant activity in inhibiting oxidation of human low-density lipoproteins. *J. Int. Sci. Vigne Vin* **1995**, *29* (4), 205–212.
- (19) Singleton, V. L.; Rossi, J. A. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *Am. J. Enol. Vitic.* **1965**, *16*, 144–158.
- (20) Miller, N. J.; Rice-Evans, C.; Davies, M. J.; Gopinathan, V.; Milner, A. A novel method for measuring antioxidant capacity and its application to monitoring the antioxidant status in premature neonates. *Clin. Sci.* **1993**, *84*, 407–412.
- (21) Bourzeix, M.; Weyland, D.; Heredia, N. A study of catechins and procyanidins of grape custers, the wine and other by-products of the wine. *Bull. O.I.V.* **1986**, *59*, 1171–1254.
- (22) Weinges, K.; Piretti, M. V. Isolierung des procyanidins B1 aus weintrauben. *Liebigs Ann. Chem. Dtsch.* **1971**, *748*, 218–220.
- (23) Lea, A. G. H.; Bridle, P.; Timberlake, C. F.; Singleton, V. L. The procyanidins of white grapes and wine. *Am. J. Enol. Vitic.* **1979**, *30*, 289–300.
- (24) Lamuela-Raventos, R. M.; Waterhouse, A. L. A direct hplc separation of wine phenolics. *Am. J. Enol. Vitic.* **1994**, *45*, 1–5.
- (25) Waterhouse, A. L.; Teissedre, P. L. Levels of phenolics in California varietal wines. In *Wine Nutritional and Therapeutic Benefits*; Watkins, T. C., Ed.; ACS Symposium Series 661; American Chemical Society: Washington, DC, 1997; pp 12–23.
- (26) Darret, G.; Couzy, F.; Antoine, J. M.; Magliola, C.; Mareschi, J. P. Estimation of minerals and trace elements provided by beverages for the adult in France. *Ann. Nutr. Metab.* **1986**, *30*, 335–344.
- (27) Boulet, D.; Laporte, J. P.; Aigrin, P.; Lalanne, J. B. The development of behaviour of wine consumption in France. *ONIVINS Inf.* **1995**, *26*, 72–112.
- (28) Teissedre, P. L.; Landraut, N. Wine phenolics: contribution to dietary intake and bioavailability. *Food Res. Int.* **2000**, *33*, 461–467.
- (29) Ruidavets, J. B.; Teissedre, P. L.; Ferrières, J.; Carando, S.; Bougard, S.; Cabanis, J. C. Catechin in the mediterranean diet: vegetable, fruit or wine? *Atherosclerosis* **2000**, *153*, 107–117.

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