Antiradical Properties of Commercial Cognacs Assessed by the DPPH• Test

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Antiradical activities of some commercial cognacs were evaluated by the DPPH• test. Different mathematical models for the evaluation of the antiradical efficiency of the cognac samples were proposed and discussed. Nonflavonoid phenols were found to be the main substances responsible of the radical scavenging activity of cognacs. In particular the strongest correlations between antiradical activity measurements and cognac chemical characteristics was found for ellagitannins, high molecular weight polyphenols, which are extracted from the wood and solubilized in the spirit mainly during first year aging.

Keywords: *Chain-breaking activity; antioxidant activity; polyphenols; cognac*

INTRODUCTION

Natural antioxidants present in plant foods have recently attracted considerable attention for their presumed role in protecting human body against a wide number of degenerative diseases. A growing experimental evidence has recently suggested that these compounds can affect a wide range of cell biological functions by virtue of their radical scavenging activity (Southon, 1998). Recent papers have highlighted the role of phenolic compounds as the major source of natural antioxidants in foods of plant origin. There is a considerable amount of data on the antioxidant properties of single selected phenol compounds and raw and processed phenol-containing foods (Shahidi and Wanasundara, 1992; Heinonen et al., 1998; Lu and Foo, 2000). However, a clear relationship between food phenol composition and antioxidant activity has been scarcely elucidated. This is probably due to the fact that the antioxidant capacity of polyphenols can greatly vary depending on several variables such as the chemical structure of the molecule and its concentration and oxidation degree. These latter, on their own, can also depend on the technological history of the product and on the storage and/or aging conditions adopted. It has been recently pointed out that processing can have many effects not all of which result in a loss of content and activity of natural antioxidants (Nicoli et al., 1999). In particular, increase in the antioxidant efficiency of some phenol compounds has been observed as a consequence of slight oxidative stress during processing and storage (Kikugava et al., 1990, Cheigh et al., 1995, Manzocco et al., 1998).

From this point of view, technologies at the basis of alcoholic beverage and spirit production are interesting examples since the antioxidant capacity of the final product can be greatly reduced or increased depending on the technological procedures adopted.

Despite the extensive works carried out on the assessment of the antioxidant properties of several wines and beverages in relation to their phenolic content and technological history (Kinsella et al., 1993; Hertong et al., 1993; Kanner et al., 1994; Vinson et al., 1995; Nicoli et al., 1997; Wiseman et al., 1997; Manzocco et al., 1998), few data are still available about spirits (Duthie et al., 1998; Goldberg et al., 1999; Rayssiguier et al., 1999; Chaugier et al., 1998; Trevithick et al., 1999). For these kind of product, aging in wood cask represent one of the most important technological steps of the whole production process. During aging in wood, the flavor of the fresh spirit becomes smoothed and mellowed. The flavor is changed through the extraction of hydrolyzed or ethanolyzed wood compounds and evaporation of ethanol, water, and volatile compounds; slow oxidation reactions and other chemical and enzymatic changes can also contribute to the formation of new compounds (Cantagrel et al., 1995; Maga, 1989). This is the case for cognac, a wine spirit which can be produced only in France in the Charente region. Viriot et al. (1993) reported that polyphenols originating from wood are major solutes of cognacs aged in oak casks. It is likely that the final product could exhibit interesting antioxidant properties depending on the content, chemical properties, and oxidation degree of phenols extracted. Factors related to aging conditions such as alcohol content of the spirit, toast or char level of oak, cooperage techniques used, age and size of the barrel, and time and temperature of storage in the oak cask are expected to strongly affect the final antioxidant properties of cognacs. For instance, it has been observed that the intensity of charring during the making up of the barrels is very important because the wood pyrolysis yields substances having antioxidative properties (Shahidi et al., 1992).

The aim of this work was to evaluate the antiradical activity of some commercial cognacs by DPPH• test. Due to the complex kinetic behavior of the bleaching reaction

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of DPPH• in the presence of a mixture of polyphenols, different mathematical models have been considered. Correlation analysis between antioxidant activity measurements and cognac composition is then discussed.

MATERIALS AND METHODS

Material. A total of 12 cognacs of 4 various commercial denominations (3-Star, VSOP, Napoleon, and XO) have been analyzed. The commercial denomination indicates the minimum age of cognac which it is used in the blend.

Chemical Analyses. Total phenols were determined using the procedure described by Blouin et al. (1972). Analysis was performed using 5% v/v Folin−Ciocalteau reagent and 15% w/v sodium carbonate. The solutions stayed for 30 min at 80 °C, and then the absorbance was determined at 760 nm. Gallic acid was used as the standard.

Determination of the ellagitannins in the foregoing samples was carried out by high-performance liquid chromatography, following the technique developed by Viriot et al. (1993). Results were expressed in milligrams of ellagic acid calculated by the difference between total ellagic acid (after acid hydrolysis) and the preexisting free ellagic acid.

Phenolic acids (ellagic acid, gallic acid, vanillic acid, syringic acid), aromatic aldehydes (vanillin, syringaldehyde, coniferaldehyde, sinapaldeyde), furanic aldehydes (5-(hydroxymethyl)furfural, furfural, 5-methylfurfural), and scopoletin were chromatographed by HPLC on a Merck Lichrospher RP18 (5 μm) column (25 cm × 4 mm i.d.). Samples were filtered through a Millipore membrane (0.45 μm). Cognac volume injected was 20 μL. Gradient elution was with 4% acetic acid and 0.5% 1-propanol in water (solvent A) and methanol (solvent B). A linear gradient from 0% to 40% B in 50 min, 0% solvent B, was then maintained for 40 min to purge the system. The flow rate was 1 mL/min. Phenolic acids were detected at 280 nm; aromatic aldehydes, furanic aldehydes, and scopoletin at 313 nm.

Antiradical Activity. Antiradical activity of the cognacs was determined using the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH•) (Brand-Williams et al., 1995). This method was chosen for its widespread use for the assessment of the antioxidant capacity of foods (Pilling and Seakins, 1996; Hopia et al., 1998; Saint Cricq de Gaulejac et al., 1999; Sanchez-Moreno et al., 1998; Von Gadow et al., 1997). In its radical form DPPH• absorbs at 515 nm, but upon reduction by an antioxidant or radical species its absorption decreases.

A volume of 3.0 mL of 6.1×10^{-5} M DPPH• methanol solution was used. The reaction was started by the addition of 10 μL of samples. The bleaching of DPPH• was followed at 515 nm (Uvikon 860, Kontron Instruments, Milano, Italy) at 0 min, 1 min, and every 1 min until the reaction reached a steady state. This plateau was reached within 10 min.

Mathematical Models. The following equations have been used in order to describe the kinetic behavior of the samples using DPPH• test:

fourth-order equation (T4)

$$A = a + bt^2 + ct^4$$

multiplicative model (Ln)

$$A = (t + 1)^b a$$

logistic model (Lg)

$$A_0 - A = c/[1 + \exp(a + bt)]$$

where A_0 is the initial optical density at zero time, A is the optical density at increasing time t, and a, b, and c are constants.

Antiradical Measurements. The antiradical activity was expressed in a different way in relation to the mathematical models applied: fourth order equation, the value of the slope "B" of the regression line $1/A^3 = a + Bt$ (Manzocco et al., 1998); multiplicative model, the absolute value of the slope "BLN" of the regression line obtained using ln transformation of the function $\ln(A) = \ln a + \mathrm{BLN} \ln(t + 1)$ (Sànchez-Moreno et al., 1998); logistic model, the characteristics of the function such as maximum, slope, and "lag time", maximum MLG = c, slope SLG = $-cb/4$, and lag time LLG = $(2 - a)/b$.

Statistical Analysis. Results were processed by Statistica/W ver. 4.5 program (Stat Soft Inc., 1993).

Table 1. Polyphenols, Furanic Aldehydes, and Scopoletin Contents in 12 Analyzed Samples of Cognacs[a]

chemical	mean	SD	min	max
tot. polyphenols	432	161.34	163	648
ellagitannins	22.18	15.26	0.00	45.30
ellagic acid	16.34	5.89	3.90	23.90
gallic acid	9.79	3.82	3.40	17.60
vanillic acid	1.03	0.56	0.40	2.20
syringic acid	1.71	0.63	0.80	2.90
vanillin	1.50	0.47	0.71	2.09
syringaldehyde	3.39	1.07	1.85	5.00
coniferaldehyde	1.06	0.28	0.82	1.74
sinapaldehyde	1.62	0.58	0.65	2.93
5-(hydroxymethyl)furfural	37.78	14.79	22.70	66.50
furfural	12.38	1.35	10.00	14.20
5-methylfurfural	0.57	0.13	0.42	0.84
scopoletin	0.06	0.03	0.03	0.11

[a] Results are expressed as mg/L.

RESULTS AND DISCUSSION

There was a wide range of phenol concentrations in the cognacs analyzed as shown in Table 1. The values varied from 163 to 648 mg/L (average 432 mg/L) as measured by the Folin−Ciocalteau reagent. Usually the phenol content of cognac increases with the duration of aging although other factors such as the wood type, the state and use of the barrel, and the alcohol content of the spirit during the course of aging can affect it (Cantagrel et al., 1993; Puech, 1984; Sarni et al., 1990; Puech and Moutounet, 1992). The contents of ellagitannins, high molecular weight phenols, were found to vary from 0 to 45.3 mg/L. The maximum value observed can be attributed to a young cognac whereas the minimum value zero to an old cognac. In fact, as reported by Viriot et al. (1993), the kinetic of extraction of ellagitannins from wood in cognacs of various ages shows a pattern characterized by a maximum concentration after about 5 years of aging and a following decrease to zero value after 30 years. The content of ellagic acid was observed to be between 3.9 and 23.9 mg/L. A similar range of ellagic acid content was found by Viriot et al. (1993) in young cognacs (1−10 years old). Ellagic acid arises especially from the degradation of ellagitannins. Unlike ellagitannins, ellagic acid is slowly released in the spirit during the entire aging period. The average content of vanillin in cognacs was 1.5 mg/L. This compound and its relatives such as syringaldehyde, coniferaldehyde, and sinapaldehyde are important to aroma of matured distilled spirits. Threshold of vanillin in 40% ethanol is 0.1 mg/L (Maga, 1989). Vanillin clearly exceeded the threshold concentration in cognac samples. This is in agreement with the quantitative data of about 2 mg/L reported for some brandies aged in charred oak barrels (Salagoity-Auguste et al., 1992). The furanic aldehydes content (furfural, 5-methylfurfural, and 5-(hydroxymethyl)furfural) varied widely in cognac samples. Different conditions such as the presence of caramel, the state and use of the barrel, and the length of maturation affected the concentrations of these compounds (Onishi et al., 1977; Quesada Granados et al., 1996). From an aromatic point of view, furfurals are

Table 2. Determination Coefficients (r^2) Obtained by Applying the Various Mathematical Models to the Cognac Samples

cognac sample no.	Ln[a]	T4[b]	Lg[c]
1	0.966	0.995	0.999
2	0.949	0.972	0.996
3	0.994	0.996	0.982
4	0.999	0.988	0.983
5	0.999	0.988	0.983
6	0.996	0.999	0.998
7	0.945	0.961	0.992
8	0.955	0.987	0.995
9	0.996	0.994	0.978
10	0.943	0.974	0.997
11	0.995	0.988	0.992
12	0.979	0.990	0.985

[a] Multiplicative model. [b] Fourth-order equation. [c] Logistic model.

Table 3. Correlation Coefficients between the Determination Coefficients of the Various Mathematical Models

	correlations		
model	1	2	3
Ln[a] (1)	1.00	0.82[d]	−0.61[d]
T4[b] (2)	0.82[d]	1.00	−0.39
Lg[c] (3)	−0.61[d]	−0.39	1.00

[a] Multiplicative model. [b] Fourth-order equation. [c] Logistic model. [d] Significant at 5%.

Table 4. Antiradical Measurements of 12 Cognac Samples Expressed by the Various Mathematical Models Applied

cognac sample no.	B[a]	BLN[b]	MLG[c]	SLG[d]	LLG[e]
1	20.8	0.63	0.70	0.15	−2.09
2	17.2	0.54	0.66	0.11	−2.72
3	0.5	0.19	0.37	0.04	−3.94
4	114.2	0.74	0.73	0.26	−0.92
5	113.2	0.83	0.71	0.22	−0.54
6	6.1	0.50	0.60	0.10	−1.67
7	108.7	0.75	0.74	0.14	−2.29
8	110.7	0.69	0.73	0.21	−1.51
9	7.2	0.52	0.61	0.10	−1.75
10	90.6	0.64	0.72	0.20	−1.67
11	60.7	0.64	0.71	0.14	−2.48
12	10.5	0.61	0.63	0.11	−1.17

[a] Slope of the regression line $1/A^3 = a + Bt$ obtained from the fourth-order model. [b] Absolute value of the slope of the linear equation obtained from the multiplicative model. [c] Maximum. [d] Slope. [e] "Lag time" from the logistic model.

believed to participate in the odor of caramelization and may contribute to "hotness" of spirits (Singleton, 1995). The content of scopoletin ranged from 30 to 110 μg/L. The concentration of this coumarin varied in relation to the origin of the oak wood, the age of the barrels and the length of maturation (Puech and Moutounet, 1992).

The coefficients of determination (r^2) referred to the antioxidant measurements calculated from the different mathematical models applied to the cognac samples are shown in Table 2. Only the multiplicative model presented a strong correlation with the others (Table 3). In Table 4 the chain-breaking activity of the cognac samples, expressed in relation to the mathematical models considered, is reported. The results of correlation analysis of these data are shown in Table 5. It is interesting to note that with the only exception of "lag time" (LLG), which is one of the parameters describing the logistic model, all the other antiradical measurements are significantly correlated.

Table 5. Correlation Coefficients between the Antiradical Activity Measurements of the Various Mathematical Models

	correlations				
model	1	2	3	4	5
B[a] (1)	1.00	0.78[f]	0.70[f]	0.87[f]	0.50
BLN[b] (2)	0.78[f]	1.00	0.94[f]	0.82[f]	0.78[f]
MLG[c] (3)	0.70[f]	0.94[f]	1.00	0.76[f]	0.65[f]
SLG[d] (4)	0.87[f]	0.82[f]	0.76[f]	1.00	0.73[f]
LLG[e] (5)	0.50	0.78[f]	0.65[f]	0.73[f]	1.00

[a] Slope of the regression line $1/A^3 = a + Bt$ obtained from the fourth-order model. [b] Absolute value of the slope of the linear equation obtained from the multiplicative model. [c] Maximum. [d] Slope. [e] "lag time" from the logistic model. [f] Significant at 5%.

Table 6. Antiradical Activity (expressed as $-OD^{-3}$ min^{-1} from the Fourth-Order Model) for Total Phenols (Expressed as Gallic Acid Equivalents, GAE) Ratio of the Cognacs[a]

cognac sample no.	chain-breaking activity ($-OD^{-3}$ min^{-1} mg of GAE^{-1})
1	189.4 ± 11.7
2	202.3 ± 13.5
3	10.3 ± 0.4
4	608.2 ± 32.8
5	747.3 ± 35.8
6	78.7 ± 3.4
7	628 ± 39.5
8	612 ± 24.4
9	74.9 ± 3.5
10	466.2 ± 26.0
11	435.9 ± 23.6
12	88.5 ± 4.1

[a] Data are mean ± SD of results from four different preparations.

Table 6 shows the chain-breaking activity of cognac samples. In comparison to the data reported by Manzocco et al. (1999) about the chain-breaking activity of Montepulciano d'Abruzzo wines (3.86−9.93 $-OD^{-3}$ min^{-1} mg of GAE^{-1}), the cognac samples presented antiradical activity much higher. Large amounts of phenolic compounds, mostly flavonoids, were contained in these wines while in cognac samples nonflavonoid phenols extracted from oak barrel staves were present. Flavonoids have been reported to have multiple biological effects mostly attributed to their antioxidant activity (Kanner et al., 1994). Vivas and Glories (1996) reported that ellagitannins, the major nonflavonoids in oak-aged wines and matured spirits, have a greater oxygen-scavenging capacity than wine polyphenols.

The correlations between antiradical activity measurements and cognacs chemical characteristics are presented in Table 7. Significant correlations were found between antiradical activity measurements and total polyphenols. It is interesting to note that the phenols present in cognac are lignin-derived phenols contrary to wines where large amounts of polyphenols originate from grape. The strong correlations observed between antiradical activity measurements and ellagitannins indicated that high weight molecular polyphenols are the major contributors of the overall antioxidant capacity of the cognacs. This can be attributed to the structures of ellagitannins characterized by the presence of several hydroxy functions in *ortho* which exhibit a higher ability to donate a hydrogen atom and to support the unpaired electron as compared to the low molecular weight ones, as also stated by Cheigh et al. (1995) and

Table 7. Correlation Coefficients between 14 Chemical Characteristics and the Antiradical Activity Measurements on 12 Cognac Samples

chemical	BLN[b]	B[a]	MLG[c]	SLG[d]	LLG[e]
tot. polyphenols	0.81[f]	0.91[f]	0.80[f]	0.86[f]	0.58[f]
ellagitannins	0.74[f]	0.89[f]	0.66[f]	0.86[f]	0.45
ellagic acid	0.54	0.62[f]	0.66[f]	0.65[f]	0.41
gallic acid	0.52	0.56	0.61[f]	0.52	0.45
vanillic acid	0.30	0.39	0.46	0.35	0.16
syringic acid	0.43	0.29	0.43	0.27	0.48
vanillin	0.48	0.36	0.47	0.34	0.55
syringaldehyde	0.48	0.38	0.43	0.34	0.54
coniferaldehyde	0.37	0.56	0.28	0.52	0.30
sinapaldehyde	0.09	0.35	0.08	0.48	0.04
5-(hydroxymethyl)-furfural	0.33	0.32	0.26	0.25	0.26
furfural	−0.26	−0.11	−0.47	−0.12	0.10
5-methylfurfural	0.10	0.47	0.03	0.21	−0.03
scopoletin	0.49	0.44	0.50	0.39	0.44

[a] Slope of the regression line $1/A^3 = a + Bt$ obtained from the fourth-order model. [b] Absolute value of the slope of the linear equation obtained from the multiplicative model. [c] Maximum. [d] Slope. [e] "Lag time" from the logistic model. [f] Significant at 5%.

Nicoli et al. (1999). In fact, as stated from Ariga and Hamano (1990) and Hagerman et al. (1998), the antiradical efficiency of polyphenols tends to increase in the order of progressive polymerization. For example the C−C dimers of catechin have been shown to be ca. three times more active than catechin in scavenging radicals (Saint-Cricq de Gaulejac et al., 1999).

No significant correlations were observed between antiradical activity measurements and furfural and 5-(hydroxymethyl)furfural. This suggests that the procedure of the addition of caramel as well as some aging conditions (i.e., heat treatment of the wood cask, type of wood, and state and use of the barrel) which can influence the extent of the extraction of nonenzymatic browning reaction products do not seem to affect the antioxidant capacity of the samples

CONCLUSIONS

Results indicated that cognac exhibits interesting antiradical properties related to nonflavonoid phenols. In particular, ellagitannins, as well as ellagic acid, which are extracted from the wood during aging, seem to be the most important contributors to the overall antioxidant properties of the product. On the contrary, compounds present in caramel as well as those formed as a consequence of the heat treatment of the barrel do not seem to have significant antioxidant properties. The strongest correlation observed between antiradical activity measurements and cognac phenol compounds permit one to confirm that the mathematical models applied were good.

These findings confirmed that aging in wood casks is a key technological step not only for the formation of the color and the flavor of the spirit but also for the development of antioxidant properties. Further research is needed to elucidate the role of the different single aging variables such as ethanol concentration of spirit, barrel size, and intensity of charring in determining the final antioxidant properties of the product.

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