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Analytical Methods

Coulometric titration with electrogenerated oxidants as a tool for evaluation of cognac and brandy antioxidant properties

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ABSTRACT

Stoichiometric coefficients for reactions of cognac antioxidants with coulometric titrants (electrogenerated bromine and hexacyanoferrate(III) ions) have been found. Ellagic and gallic acids react with both titrants while aldehydes (vanillin, syringic and coniferaldehyde) – with electrogenerated bromine only. Furfurals do not show significant reactivity toward both oxidants. Cognac and brandy total antioxidant capacity (TAC) and ferric reducing power (FRP) based on reactions with electrogenerated bromine and hexacyanoferrate(III) ions, respectively, have been evaluated. Both parameters for cognacs are statistically significant higher than for brandies and grow with the age increase. Beverages under investigation has shown relatively high antiradical activity toward 2,2-diphenyl-1-picrylhydrazyl (7–92% and 5–93% for cognacs and brandies, respectively). Total phenolics content has been evaluated by Folin–Ciocalteu method. Older beverages represent the higher phenolics content caused by more time of extraction from oak barrels. Positive correlations ($r = 0.8077–0.9617$) have been observed for TAC and FRP with antiradical activity and total phenolics content.

1. Introduction

Cognac is an alcoholic beverage rich in polyphenols and its moderate consumption has shown potential beneficial effects on health. Cognac has been described to possess antioxidant properties due to its phenolic constituents and has been established to decrease the risk of cardiovascular diseases (da Porto, Calligaris, Celotti, & Nicoli, 2000; Goldberg, Hoffman, Yang, & Soleas, 1999). Mechanisms that have been proposed to explain the prevention of cardiovascular diseases by polyphenols include reduced oxidation of low-density lipoprotein, inhibition of platelet aggregation and neutrophil adhesion (Carusio, Wangensteen, Filipelli, & Andriantsitohaina, 2008). Polyphenols have also been reported to affect the activity of enzymes critically involved in pathways regulating cell proliferation and activation (Perez-Vizcaino, Duarte, & Andriantsitohaina, 2006).

Despite the extensive works devoted to the assessment of the antioxidant properties of several wines and other alcoholic beverages in relation to their phenolic content (de Quirós, Lage-Yusty, & López-Hernández, 2009; Figueiredo-González, Cancho-Grande, and Simal-Gándara, 2013; García, Grande, & Gándara, 2004; Puértolas, Saldaña, Condón, Álvarez, & Raso, 2010; Pérez-Lamela, García-Falcón, Simal-Gándara, and Orriols-Fernández, 2007), only few data have been presented on the antioxidant properties of cognac (da Porto et al., 2000; Goldberg et al., 1999). This is why, there is a constant quest to determine cognac antioxidant properties and associated methods of evaluation.

The most common approaches used for evaluation of antioxidant properties of alcoholic beverages are spectrophotometric determination of antiradical activity by reaction with 2,2-diphenyl-1-picrylhydrazyl (DPPH) (Aoshima, Tsunoue, Koda, & Kiso, 2004; da Porto et al., 2000) and total phenolics content by Folin–Ciocalteu method (Alonso, Castro, Rodriguez, Guillen, & Barroso, 2004; Vicente, de Abreu, Goulart, & de Vasconcelos, 2011).

Antioxidants being easily oxidizable compounds are widely investigated using electrochemical methods. A lot of articles have been focused on electrochemical evaluation of foodstuff antioxidant properties including alcoholic beverages, namely wines (Arribas et al., 2013; Šeruga, Novak, & Jakobek, 2011). Polarographic assay based on hydrogen peroxide scavenging has been developed for the determination of antioxidant activity of strong alcoholic beverages (Gorjanovic et al., 2010).

Special attention is paid to cognac and brandy recognition and classification based on their responses to the voltammetric electronic tongue analysis (Cetó, Llobet, Marco, & del Valle, 2013), mid infrared spectroscopy (Picque et al., 2006), front face fluorescence spectroscopy (Sádecká, Tóthová, & Májek, 2009) and further chemometric signals processing.

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Coulometry with electrogenerated titrants is characterized by high sensitivity, simplicity, accuracy and reliability as well as possibility of miniaturization. Coulometric generation of the titrant species precludes the use of standard solutions. Besides, it is also a very attractive form of providing reagents for systems based on true titration where the sample volume and the amount of reagent added up to the end point are the only parameters necessary for analyte quantification. Constant-current coulometry is successfully applied for the organic analysis in particular to evaluation of tea and coffee ferric reducing power (Ziyatdinova, Nizamova, & Budnikov, 2011) and total antioxidant capacity of juices, balsams and tinctures (Abdullin, Turova, Budnikov, Ziyatdinova, & Gajsina, 2002).

It should be noted that there is no any information about application of coulometry for hot spirits antioxidant properties measurements. The aim of present work is evaluation of cognac antioxidants reactivity toward electrogenerated oxidants and development of coulometric methods for cognac and brandy antioxidant properties assay based on sample titration with electrogenerated bromine and hexacyanoferrate(III) ions.

2. Experimental

2.1. Chemicals and reagents

Ellagic (95% purity) and gallic acids (99%), vanillin (99%) were purchased from Sigma (Germany). Syringaldehyde (98%), coniferaldehyde (98%), 5-hydroxymethylfurfural (99%) and furfural of 99% purity were obtained from Aldrich (Germany). Their 0.4–5.0 mM stock solutions were prepared daily dissolving a definite amount of the substance in 10.0 mL of ethanol (rectificate).

2,2-Diphenyl-1-picrylhydrazyl (DPPH) and Folin–Ciocalteu reagent were purchased from Aldrich (Germany). DPPH stock solution (61 μM) were prepared by dissolving a definite amount in methanol (chemical grade purity).

All other chemicals were analytical reagent grade purity and used as received. Double distilled water was used for the measurements. The experiments were carried out at laboratory temperature (20–23 °C). All solutions of compounds under investigation were prepared exactly before measurements.

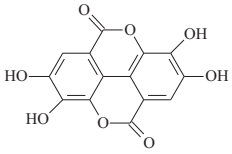
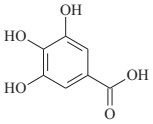
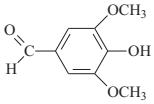
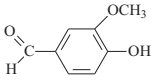
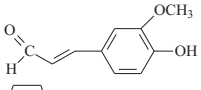
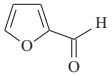
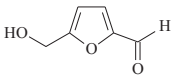
2.2. Materials

The cognacs and brandies analyzed were commercially available samples of different trademarks. A total 11 cognacs of 3 various commercial denominations (VS, VSOP and XO) as well as 18 ordinary and vintage brandies of Russian (Ru), Armenian (Am), Ukraine (Ua) and Azerbaijan (Az) origin have been analyzed. The commercial denomination indicates the minimum or average age of spirit which is used in the blend for cognac and brandy, respectively. Brandy denomination kV means average age of 6 years, KS – 10 years and OS – 20 years.

2.3. Instrumentation

Coulometric measurements were carried out using P-5827 M potentiostat (ZIP, Gomel, Belarus) with four-electrode two-compartment electrochemical cell. A bare platinum foil with 1 cm^2 surface area was used as the working electrode, and a platinum wire separated from the anodic compartment with a semipermeable diaphragm – as the auxiliary electrode. A pair of polarized platinum electrodes was used for detection of the titration end-point (ΔE = 200 mV). Surface of platinum electrodes was cleaned by HNO_3 and then rinsed thoroughly with double distilled water.

Table 1
Stoichiometric coefficients of the reactions between cognac antioxidants and electrogenerated oxidants.

Compound	Structure	ν(compound):ν(Br_2)	ν(compound):ν($FeCN_6^{3-}$)
Ellagic acid		1:2	1:4
Gallic acid		1:2	1:4
Syringaldehyde		1:1	–
Vanillin		1:1	–
Coniferaldehyde		1:2.5	–
Furfural		–	–
5-Hydroxymethyl-furfural		1:0.5	–