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Analysis of lignin-derived phenolic compounds and their transformations in aged wine distillates

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ABSTRACT

Aromatic aldehydes and acids derived from lignin were studied by capillary zone electrophoresis in barrel matured wine distillates used in brandy production. Different conditions of analysis were applied to set up the best separation and reproducibility. The optimal separation was performed using 25 mM borate buffer containing 8% v/v ethanol as modifier. Total amount of guaiacol-type compounds (coniferaldehyde, vanillin, and vanillic acid) and syringol-type compounds (sinapaldehyde, syringaldehyde, and syringic acid) increased with increasing ageing time for distillates aged from 1 to 25 years. Sum of concentrations of syringic and vanillic acids can be also used for characterizing aged distillates according to their ageing level. The developed analysis method is simple, precise and cost efficient. It provides good separation efficiency, and it is ideally suited for the analysis of aged wine distillates for determination of their overall quality, approximate ageing time and signs of counterfeiting.

1. Introduction

Wood maturation has been done for hundreds of years to improve taste and flavour of spirits and has become an integral part of the production process of high quality alcoholic beverages, such as brandy, whisky, cognac, armagnac, rum. Ageing is one of the most important factors determining quality of wine distillates which are the main raw material in the production of brandy and other aged spirits.

Identification and differentiation of aged distillates is complicated by a rich chemical composition, resulted from the interaction between the components of the wine distillate and the oak barrel. Composition of aged distillates influencing their quality characteristics, especially taste and aroma, are caused by decomposition of wood macromolecules and subsequent extraction, reactions between wood components and constituents of the raw distillate, reactions involving wood extractables, reactions involving distillate components, evaporation of volatile compounds (van Jaarsveld & Hattingh, 2012). Transformations of lignin during ageing of the distillates are one of the most important factors influencing their quality. Lignin degradation process is very complex and is influenced by many factors. From these, the main are oak species and its age, barrels toasting intensity and their size, alcohol and other substances concentration in wine distillate, ageing conditions, such as temperature and air humidity (Baldwin, Black, Andreasen, & Adams, 1967; Jackson, 2008; Marche & Joseph, 1975; Няту, 1978). The science behind alcohol maturation in wood barrels is often considered “the last bastion” of scientific advancement of distilled spirits research.

Last decades, HPLC was considered the most suitable technique for analysing the low-volatility compounds produced during ageing. Canas, Belchior, Spranger, and Bruno-de-Sousa (2003) developed HPLC methods for determination of lignin-derived aromatic substances. This method has been applied to quantify low molecular weight phenolic compounds, such as phenolic aldehydes and acids in aged wine brandies (Bortoletto & Alcarde, 2015; Canas, Silva, & Belchior, 2008). It should be noted that a standardized HPLC method for determination of principal compounds extracted from wood during ageing of spirit drinks also exists (OIV-MA-BS-16, 2015). Common disadvantage of these methods is considerable duration of analysis. During express testing of several HPLC methods to analyze old distillates have been also observed worsening of the separation and short life of precolumns, probably due to the irreversible adsorption of the extracted polymeric

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substances, such as lignin oligomers and polysaccharides. After 90s, capillary zone electrophoresis (CZE) began increasingly used to analyze phenolic substances from different foods, such as olive oil (Carrasco-Pancorbo et al., 2004), berries (Ehala, Vaher, & Kaljurand, 2005), wine (Cartoni, Coccioli, & Jasionowska, 1995), and other products (Bjergegaard, Michaelsen, & Sørensen, 1992). The developing CZE has made it possible to analyze these compounds quicker and cost effective. However, CZE was rarely applied for analysis of aromatic substances of aged spirits. Thus, CZE was applied for analysis of aged brandy by Bronze et al. (1997) and Panossian, Mamikonyan, Torosyan, Gabrielyan, and Mkhitaryan (2001). The last ones concluded that the CZE is useful for the identification of counterfeit brandy, which is easy to recognize by the absence of sinapaldehyde, syringaldehyde, and coniferaldehyde, which are not detectable in false brandy. Delgado, Gómez-Cordovés, and Villarroya (1990), and Canas, Quaresma, Belchior, Spranger, and Bruno-de-Sousa (2004), studied relationships between phenolic aldehydes in brandies to evaluate their authenticity, ageing conditions and general quality.

Gas chromatography mass spectrometry (GC-MS) and liquid chromatography mass spectrometry (LC-MS) also have been applied to identify both volatile and non-volatile compounds produced during spirit maturation (Barnaba et al., 2015; MacNamara, Dabrowska, Baden, & Helle, 2011; De Rosso, Cancian, Panighel, Dalla Vedova, & Flamini, 2009).

Identification of compounds that are relevant in differentiating spirits of different ages is still one of the major unsolved problems. Watts and Butzke (2003) partially solved the problem, studying cognac and brandy samples using headspace solid-phase microextraction coupled to GC-MS. They have found that four methylketones (2-heptanone, 2-nonanone, 2-undecanone, and 2-tridecanone) could be used to predict cognac age with a high degree of accuracy. Their concentrations increased with age. Computer-aided statistical analysis was used to determine which components play the most important role in discriminating samples.

Opportunity to determine quick and precise non- or low-volatile phenolic substances is extremely important to identify aged wine distillates and other spirits. The presence of atypical levels or unusual ratios of non-volatile congeners can indicate that maturation has been carried out unconventionally or reflect some form of adulteration (Buxton & Hughes, 2014, chap. 4). After reviewing past work on lignin-derived aromatic substances in brandy, it has become clear that most of the research conducted in this area has been limited to simply identifying low-volatile phenolic substances, without a deep analysis of the chain of reactions relating to the process of ageing. In addition, a simple and low-cost method to analyze a brandy or other distilled matured beverages is needed.

The main objectives of this study are to improve our understanding of the ageing process analyzing a mechanism of lignin degradation during maturation of wine distillates, to develop and apply a precise, simple, and cost-efficient analytical method for determination of lignin-derived aromatic substances, to clarify the relationship between the age of wine distillates as the main indicator of their quality and the accumulation of lignin degradation products, to find specific quality markers or components ratios differentiating old distillates from younger ones.

2. Materials and methods

2.1. Instrumentation

Electrophoresis was carried out using a Capel®-105 M capillary electrophoresis system (LLC « Lumex-marketing», St. Petersburg, Russian Federation) with variable wavelength UV-detector. A fused-silica capillary with internal diameter of 75 μm and total length 60 cm was used. For data processing, Elforun® software (St. Petersburg, Russian Federation) was used.

The ethanol content was determined using a DMA 4500 density meter (Anton Paar® GmbH, Graz, Austria) checked against internal laboratory reference solution.

pH values of electrolyte solution were measured using a HANNA 211 pH meter (Hanna Instruments, Milan, Italy).

2.2. Chemicals

Phenolic aldehydes (coniferaldehyde, vanillin, sinapaldehyde, syringaldehyde), acids (vanillic, p-coumaric, p-hydroxybenzoic, syringic, ferulic), sodium tetraborate, sodium hydroxide and ethyl alcohol (molecular biology grade) were obtained from Sigma-Aldrich (Steinheim, Germany). The purity of phenolic compounds was at least 97.0%, sodium tetraborate 99.0%, sodium hydroxide ≥99.5%, ethyl alcohol ≥99.5%. In all experiments, bidistilled water was used.

2.3. Samples and sample preparation

The studies were performed on 24 wine distillates with ageing time from 1 to 50 years and containing from 69.1 to 43.4% v/v alcohol provided directly by 3 manufacturers (JSC „Barza Albă", Bălți; JSC „Vinăria Bardar", Bardar; LLC „Călărași Divin", Călărași). Each manufacturer provided 8 samples. Before analyses, the distillates were diluted so that each contained the concentration of alcohol of 15 ± 1% v/v, filtered through a 0.45 μm Millipore membrane, and then centrifuged at 5000 rpm for 5 min.

2.4. Lignin-derived phenolic compounds determination and method optimization

Aromatic aldehydes and acids were studied by a modified CZE method developed by Bronze, Boas, and Belchior (1997). Different wavelengths have been tested to improve the precision and the reliability. In order to optimize the separation efficiency, concentration of sodium tetraborate and ethanol have been varied. Different voltages have been also tested. The detection and quantification limits of the developed method were calculated for the studied analytes using official OIV method – OIV-MA-AS1-10 (2015). The peaks in the electropherograms of real samples were identified by comparing migration time and UV spectra with those of standard solution, and by spiking the samples with standard compounds at several concentration levels.

2.5. Statistical analysis

Statistica 13.0, Excel 2007 and Advanced Grapher 2.2 were used to apply univariate and multivariate analysis of variance to establish whether significant differences ($p < 0.05$) existed between selected ageing markers in the analyzed age groups of distillates.

3. Spirit maturation: theoretical considerations

Maturation converts the sharp roughness of a young wine distillate into a soft mellow beverage and typically lasts from 3 to 20 years, but may continue for 50 years and even more. Wine distillates are aged in oak barrels or with oak chips. During this process the spirits preferentially extract certain components of the oak wood. A small fraction of lignin (3–5%) containing in oak wood is dissolved in the distillate (Puech, Robert, & Mouttet, 1989). Lignin degradation and oxidation products such as aromatic aldehydes and acids appear during maturation under the effect of the oxygen