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On the use of the fluorescence, ultraviolet–visible and near infrared spectroscopy with chemometrics for the discrimination between plum brandies of different varietal origins

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ABSTRACT

This paper investigates the use of synchronous fluorescence, UV–Vis and near infrared (NIR) spectroscopy coupled with chemometric methods to discriminate samples of high-quality plum brandies (*Slivovica*) of different varietal origins (*Prunus domestica* L.). Synchronous fluorescence spectra (SFS) for wavelength differences in the range of 70–100 nm, NIR spectra in the wavenumber range of 4000–7500 cm^{-1} and UV–Vis spectra in the wavelength interval of 220–320 nm were compared. The best discrimination models were created by linear discriminant analysis based on principal component analysis applied to SFS recorded with wavelength difference either 80 nm or 100 nm, allowing the classification of plum brandy according to harvest time as early (summer) and late (autumn) plum varieties; the total correct classifications were 96% and 100% for the calibration and prediction steps, respectively.

1. Introduction

Plum brandy, called also *'Slivovica'* or *'Slivovice'*, is mainly made in the Central and East Europe (the Czech Republic, Hungary, Poland, Slovakia, Romania and Balkan Peninsula), with long tradition and, to a lesser extent in a West Europe (France, Italia and Germany) (Regulation (EC) No. 110/2008; European Union (EC) 2008).

Plum brandy has an intense fruit aroma and delicious taste, its physicochemical and organoleptic characteristics are influenced by four main production steps, namely: (I) selection of raw material (species and varieties, fruit quality), (II) fermentation (selected conditions), (III) the type of distillation, and (IV) aging and finishing of the product.

In the production of authentic plum brandy with minimum alcoholic strength of 37.5%, European plum species (*Prunus domestica* L.) are the most commonly used (Regulation (EC) No. 110/2008; European Union (EC) 2008). Several different maturation parameters have been defined for plums, based on characteristics related to method of pollination (self-pollination/cross-pollination); harvest time (early/late; summer/autumn); colour of the skin and flesh fruit; and chemical profile (antioxidant properties and phenolic profiles) (Nunes, Rato, Barros, Saraiva, & Coimbra, 2009; Treutter et al., 2012).

Plum brandy is generally made from local cultivated *Prunus domestica* L. varieties, where good quality fruit of high sugar content produces the best spirit. Pecić et al. (2012) compared the composition and the sensory characteristics of plum spirits made of different plum varieties of the genus *Prunus*: the autochthonous cultivars (Crvena ranka and Metlaš) and flavourful variety Požegača, originating from Serbia. The results indicated that the brandy made of a plum cultivar Crvena ranka had the best taste characteristic, and that the types of wooden casks had no significant effect on the sensory properties of the brandies matured longer than 11 years.

In Bosnia and Herzegovina, the three most popular plum varieties used in plum brandy production are Bilska rana – Buhler (early plum variety), Stanley and Požegača (late plum variety). Their distillates were characterized by different content of the volatile compounds, esters and higher alcohols. According to the results of a sensory analysis, distillates from the early plum variety (Bilska rana), which matured in July and in the half of August, provided sensory more interesting brandy. The tail distillation fraction of Bilska rana contained a high concentration of isopentyl acetate and ethyl lactate, thus the two esters could be the main predictors of a sensory profile of brandy made of Bilska rana (Spaho, Dürr, Grba, Velagić-Habul, & Blesić, 2013).

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Polish sensory unique plum brandy *'Śliwowica Łącka'* is produced in a region with specific climatic and soil conditions, using a specific fermentation of variety Węgierka Zwykła plums. Its originality results from on a high sugar concentration and unique aroma profile of blue plum fruit, as well as diverse microbiota during spontaneous fermentation (Satora & Tuszyński, 2008). Recently, the chemical composition of plum spirits derived from four varieties of plums (Węgierka Zwykła, Węgierka Dąbrowicka, Stanley and Čačanska Lepotica) was evaluated and the highest concentration of volatiles was found in Węgierka Zwykła spirits. However, a sensory evaluation of plum spirits did not show statistically significant differences between four varieties (Satora, Kostrz, Sroka, & Tarko, 2017).

In the Czech Republic 16 plum cultivars were tested for their resistance against *Plum pox virus* during the harvests 2004–2007 as well as for their suitability for subsequent processing into prunes, damson cheese and distillates. Katinka, Anna Spath, and Veeblue were recommended for the production of distillates (Bohačenko, Pinkrová, Komárková, & Paprštein, 2010). Various plum cultivars (summer: Carpatin, Silvia, BN7-237-7, Tuleu gras, Superb, Dâmbovita, and autumn: D'agen, Stanley, Record, Blue free, Joris plum and BN68), grooving in Romania, showed statistically significant differences in antioxidant capacity. Autumn varieties showed higher antioxidant capacity than the summer ones (Mihalache Arion et al., 2014).

The chemical composition and/or varietal origin of fruit spirits mentioned above were determined using traditional chromatographic methods, which are relatively expensive, time-consuming and require highly skilled operators (Ledauphin, Guichard, Saint-Clair, Picoche, & Barillier, 2003; Nikićević, 2005; Nikićević et al., 2011; Pecić et al., 2012; Satora, & Tuszyński, 2008; Satora et al., 2017; Spaho et al., 2013). For these reasons, there is an ongoing demand for rapid, inexpensive and efficient techniques for the discrimination of fruit spirits according to fruit variety. As a consequence, there is a growing interest in the development of innovative spectroscopic procedures, which meet all the aforementioned requirements. Therefore, fluorescence (Airado-Rodríguez, Galeano-Díaz, Durán-Merás, & Wold, 2009; Azcarate et al., 2015; Dufour, Letort, Laguet, Lebecque, & Serra, 2006) and NIR spectroscopy (Cozzolino, Smyth, & Gishen, 2003) were developed mainly for the classification of wines according to grape variety; and UV−Vis spectroscopy for the classification of aged Brazilian cachaças according to the wood species used (da Silva, De Keukeleire, Cardoso, & Franco, 2012). Presently, there is no study described in literature dealing with the classification of fruit spirit drinks according to fruit varieties using molecular spectrometric methods. However, there are investigations focused on characterization and discrimination of fruit spirits according to fruit species, using synchronous fluorescence spectra (SFS) (Tomková, Sádecká, & Hroboňová, 2015) and NIR spectra (Jakubíková, Sádecká, Kleinová, & Májek, 2016) in combination with chemometric methods, or determination of methanol and ethanol in fruit brandies, using Fourier Transform Infrared spectra and chemometrics (Coldea et al., 2013). Moreover, it was demonstrated that excitation-emission matrix fluorescence spectroscopy combined with parallel factor analysis is a valuable tool for characterization of white (Coelho et al., 2015) and red wines (Airado-Rodríguez et al., 2009), as well as for determination of authenticity or counterfeiting of grape distillates (Markechová, Májek, & Sádecká, 2014).

The aim of this work was to evaluate the potential of spectral techniques, such as synchronous fluorescence, UV−Vis and NIR spectroscopy, in combination with statistic methods for the charac terization/classification of plum brandy samples according to harvest time as early (summer) and late (autumn) plum varieties.

2. Material and methods

2.1. Samples

Thirty-one plum brandies of different varieties of the genus Prunus (*Prunus domestica* L.), were included in this study. The samples were divided into two groups: early (summer, S) plum varieties and late (autumn, A) plum varieties (Table 1); these are based on harvest time of plums. Plums were harvested in different Slovak and Czech regions such as Veselé pri Piešťanoch, Prague, Zlín, Slup, etc., between July and October 2012. Aliquots of 20 kg per variety were stored no longer than one week at 4 °C in darkness prior to processing. All brandies were made in one distillery by the same procedure as follows: 10 kg of plums with addition of 0.05 kg sugar were used to obtain 1 L of distillate with the alcohol content around 50–52% (v/v), which has not been modified in any way. Two samples of each variety were prepared. All samples were stored in colorless bottles at room temperature in the dark for 3 years. The samples were randomly split into a calibration set (consisting of two thirds of the samples selected from each group) and a prediction set (consisting of the remaining one third of the samples) using a leave-one-out method as described by He et al. (2012). The calibration and prediction set thus, contained twenty-one (S, n = 9; A, n = 12) and ten (S, n = 4; A, n = 6) samples, respectively.

2.2. Synchronous fluorescence spectroscopy

SFS were recorded using a Perkin-Elmer LS 50 luminescence spectrofluorometer equipped with a Xenon lamp. Excitation/emission slits were both set at 5.0/5.0 nm, and scan speed was 200 nm/min. The right-angle (90°) geometry was used for the spectra acquisition and bulk samples were placed in 1 cm × 1 cm × 4.5 cm quartz cuvette. SFS were obtained by simultaneous scanning of excitation and emission monochromators in the excitation wavelength (λ_{ex}) ranged from 200 to 500 nm (with a step of 0.5 nm) and maintaining the constant value of the $\Delta\lambda = \lambda_{em} - \lambda_{ex}$ in the range from 10 to 100 nm with a step of 10 nm. The spectra were recorded in triplicate for each sample at temperature 25 °C. The spectrometer was connected to a computer supplied with FL Data Manager Software (Perkin-Elmer) for spectral acquisition and data processing. Contour plots of spectra were plotting the fluorescence intensity (z-axis) as a combined function of the excitation wavelength (x-axis) and the wavelength interval $\Delta\lambda$ (y-axis).

2.3. NIR spectroscopy

NIR absorption measurements were carried out using a IR spectrophotometer NICOLET 8700™ (Thermo Scientific, USA) equipped with a quartz cuvette with an optical path of 2 mm. NIR spectra were obtained between 4000 and 10,000 cm^{-1} (2500–1000 nm) with a 6 cm^{-1} resolution at room temperature. The spectrum of each bulk sample was the average of 50 successive scans. NIR spectra were collected by data acquisition software OMNIC 8.1 (Thermo Electron Corp., USA) and saved in absorbance format.

2.4. UV−Vis spectroscopy

The UV absorption spectra were obtained using an UV–Vis spectrophotometer Evolution 201 (Thermo Scientific, USA) and quartz cuvette (1 cm × 1 cm × 4.5 cm). The spectra were recorded from 200 to 500 nm with a step of 0.5 nm at room temperature in triplicate for each sample diluted with water (1:10). UV−Vis spectra were collected by data acquisition software INSIGHT (Thermo Scientific, USA).