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Analytical Methods

Multivariate statistical analysis of botrytised wines of different origin

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Abstract

The study examined several types of compounds can be suitable to characterise wines made from botrytised grapes and to determine their origin and authenticity. Amines, acids, macro- and microelements of botrytised sweet wine specialities, coming from Hungary and different countries, were analysed. Measured values of twenty-one Tokaji aszú wines and twenty-three foreign botrytised wines were compared by multivariate statistical methods. Characterising the effect of *Botrytis cinerea* and the winemaking technology, amines were the most suitable components for determination of authenticity and origin of wines from the three types of compounds studied. However, in acids and elemental composition, differentiation of wine samples by principal component analysis was not complete but a tendency can be observed for separation according to origin. The knowledge on composition of acids and elements can support the results of amine analysis in reaching the goal to determine the origin of wines.

Keywords: *Botrytis cinerea*; Tokaji aszú wines; Botrytised wines; Amines; Acids; Micro-, Macro-elements; Origin; Authenticity; HPLC; Atomic absorption

1. Introduction

Botrytis cinerea can cause a destructive grey mould rot or a so-called noble rot in certain conditions on grape berries. In the latter instance, the rotting process is slowed down by the effect of dry weather and sunshine. Piercing and weakening the grape skin, *B. cinerea* as noble mould alters the composition of grapes by converting it to a raisin-like form with an unusually pleasant, special taste and delicious flavour. These berries are called as aszú grapes. During this natural process of noble rot, water content decreases and the compounds are concentrated (sugar, acids, aroma compounds, etc.). Using aszú grapes in wine making process, it yields wines of special quality that are highly prized, sweet, smooth and full-bodied with a pleasant bouquet (Haraszti, 2002; Ribéreau-Gayon, Ribéreau-Gayon, & Seguin, 1980).

Tokaj wines are made from white grape varieties such as Furmint, Yellow Muscat and Linden Leaf. To produce aszú wines, the shrivelled, raisin-like aszú grapes are harvested in October and November into wooden butts with a capacity of 20–25 kg. Three, four, five or six butts of aszú-paste is added to newly fermented dry wine of the same year in a 'Gönci' oak barrel (136 l) mixed and soaked for one or two days in order to extract the natural sugar content and flavours. The wine is then drawn off to ferment. The quantity of aszú grapes above is specified on the label of the bottles of aszú wine. *Eszencia* is the first run juice of the aszú grapes, which seeps from the press under the own weight of grapes (Haraszti, 2002).

Wine is a widely consumed beverage in the world with thousands of years of tradition. Determination of its authenticity is one of the most important aspects in food quality and safety. Many successful studies have shown that it is possible to distinguish grape variety, vintage years or geographical zones on the basis of chemical parameters. Several papers have been published about classification of wines (Arvanitoyannis, Katsota, Psarra, Soufleros, & Kallithroka, 1999; Csomós, Héberger, & Simon-Sarkadi, 2002; Day, Zhang, & Martin, 1995; Etiévant, Schlich, Cantagrel, Bertrand, & Bouvier, 1989; Héberger, Csomós, & Simon-Sarkadi, 2003; Kiss & Sass-Kiss, 2005; Latorre, García-Jares, Médina, & Herrero, 1994; Murányi & Kovács, 2000; Vasconcelos & Dasneves, 1989) but only few studies

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are available about classification of botrytised wines (Havadi, Kiss, Sass-Kiss, Adányi, & Váradi, 2006; Kiss & Sass-Kiss, 2005). Recently, pattern recognition has become a useful and often applied method in food analysis. (Berrueta, Alonso-Salces, & Héberger, 2007).

Putrescine, spermidine, spermine from biogenic amines are the major cellular polyamines in living organisms. These biogenic amines are involved in cellular growth, regulation of nucleic acids and protein synthesis, stabilisation of lipids, brain development, nerve growth and regeneration (Hernandez, Sanchez, & de Tarlovsky, 2006; Igarashi, 2006; Igarashi & Kashiwagi, 2000; Schreiber, Boeshore, Laube, Veh, & Zigmond, 2004). Other biogenic amines such as histamine, tyramine, and phenylethylamine etc. are formed primarily by decarboxylation of amino acids by the action of microorganisms. Numerous research works have appeared in the literature dealing with formation of biogenic amines by the effect of yeast fermentation in foods and beverages, including wine (Hyötyläinen, Savola, Lehtonen, & Riekkola, 2001; Kállay & Nyitrainé, 2003; Lehtonen, 1996; Leitao, Marques, & San Romao, 2005; Vidal-Carou, Lahoz-Portolés, Bover-Cid, & Mariné-Font, 2003). Only a few publications appeared about aliphatic primer amines, which are formed by the action of bacteria (Bast, 1971, 1972) or could be found in wines produced from grapes infected by moulds (*B. cinerea, Penicillium expansum*) (Eder, Brandes, & Paar, 2002; Hajós, Sass-Kiss, Szerdahelyi, & Bardócz, 2000; Kiss, Korbász, & Sass-Kiss, 2006; Sass-Kiss, Szerdahelyi, & Hajós, 2000). It was established that the content of primer aliphatic amines in grape berries increased mostly as a result of *B. cinerea* infection. During wine-making process, amine content continued to increase in wines, e.g. primer aliphatic amines and tyramine. As a consequence, the amine composition of botrytised wines obtains a specific character that makes possible to distinguish them from normal wines (Sass-Kiss & Hajós, 2005; Sass-Kiss et al., 2000).

The most important acids always present in wines are tartaric acid, malic acid, citric acid, succinic acid and lactic acids. Tartaric, malic and citric acids come from the grape, the others form during the fermentation. Tartaric acid is the most important and most acidic component. Its high quantity gives for wine sharp and unpleasant hard taste therefore the excellent quality wines contain usually less tartaric acid. Among organic acids of biological origin, the most relevant one is lactic acid, which originates from alcoholic or malolactic fermentation. Quantitative determination of organic acids can corroborate sensorial, microbiological quality assessment (Kordis-Krapez, Abram, Kac, & Ferjancic, 2001) and authentication (Etiévant, Schlich, Cantagrel, Bertrand, & Bouvier, 1989) of wines. During infection of grapes with *B. cinerea* under ideal conditions, water is lost from the berry and the acid constituents are concentrated. However, at the same time, the *Botrytis* fungus metabolizes these organic acids for use as an energy source (Eperjesi, Kállay, & Magyar, 1998).

Daily consumption of wine in low quantities contributes significantly to the needs of the human organism for essential elements such as K, Ca, Mg, Cr, Co, Fe, F, I, Cu, Mn, Mo, Ni, Se, Zn (Day et al., 1995). At the same time, the analysis of certain elements in wines is of special interest due to their toxicity in case of excessive intake, and they also seem to have an effect on organoleptic properties of wine (Lara, Cerutti, Salonia, Olsina, & Martinez, 2005). In other aspects, the analysis of elements has an important role in characterisation and classification of wines for determination of authenticity and geographical origin (Baxter, Crews, Dennis, Godall, & Anderson, 1997; Marengo & Aceto, 2003; Martin et al., 1999).

The goal of our work was to study several types of compounds such as amines, acids and elemental composition of wines with regard to their suitability to characterise botrytised wines and to determine their origin and authenticity made from botrytised grapes. Using multivariate statistical methods, we analysed Tokaji aszú and foreign botrytised wines to determine differences between them and to establish which class of compounds is the best in determining the authenticity and origin of wines.

2. Materials and methods

2.1. Reagents and chemicals

All reagents and authentic compounds were of analytical reagent grade or HPLC grade as required. Acids used for sample digestion were hyper pure grade. Acetonitrile and methanol (HPLC grade) were obtained from Merck, standard solutions for elemental analysis were purchased from Carlo Erba, Merck and Pancreac. Ultra pure water generated by the Milli-Q System (Millipore) was used. Anhydrous sodium acetate, boric acid, potassium hydroxide, acetic acid, Brij 35 and 2-mercaptoethanol were from Reanal (Budapest, Hungary); *o*-phthaldialdehyde was from Fluka and sodium octane sulfonate was obtained from Romil (Cambridge, UK). Authentic amines – putrescine (Put), *i*-butyl amine (iBa), cadaverine (Cad), tyramine (Tyr), histamine (His), 2-methyl-butyl amine (2MeBa), agmatine (Agm), 3-methyl-butyl amine (3MeBa), *n*-pentyl-amine (Pa), spermidine (Spd), phenylethylamine (Phe), and hexyl amine (internal standard, Istd) – were purchased from Sigma.

2.2. Wine samples

Studied wines took part in the VIth International Wine Competition VinAgora organised 2004 in Budapest. After opening the bottles, wine samples were taken and frozen at −20 °C until analysis.

Twenty-six Tokaji aszú wines and twenty-four foreign wines produced from botrytised grapes were analysed. The foreign wines came from nine countries (Portugal: P/1, P/2; Italy: I/1, I/2; Spain: E/1–E/4; Austria: A/1–A/7; Slovakia: SK/1, SK/2; Switzerland: CH/1, CH/2; France: F/1–F/3; Germany: G; United States of America: USA).