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Original Research Article

Beyond traditional balsamic vinegar: Compositional and sensorial characteristics of industrial balsamic vinegars and regulatory requirements

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ABSTRACT

Recently, new products with the name of balsamic vinegar (BV) have emerged worldwide and are rapidly gaining popularity along with the well-known Italian BVs. For the first time, the major physicochemical and sensorial characteristics of BVs produced in Greece were analyzed using recommended protocols, high throughput techniques (nuclear magnetic resonance (NMR), HPLC) and sensory descriptive analysis carried out by trained panelists. Data are discussed in comparison to those for Italian balsamic vinegars of Modena (BVMs) (Protected Geographical Indication, PGI). Greek BVs, although in line with existing official requirements, exhibited great variability in the content of individual sugars, organic acids and titratable acidity, which were reflected in both quality parameters and sensorial scores. Their heterogeneous sensorial profile was mainly characterized by high scores in *Pungency*, *Acidity* and low ones in *Sweetness*. From the chemical safety point of view, 5-hydroxymethyl-furfural (HMF) content was found to vary significantly, and future regulatory revision should consider this parameter. Our findings can assist the efforts of manufacturers of new BVs beyond minimum regulatory requirements.

1. Introduction

The Italian traditional balsamic vinegar of Modena and Reggio Emilia (TBVM and TBVRE) and the industrial balsamic vinegar of Modena (BVM), registered as "Protected Designation of Origin" (PDO) (Regulation (EC) No 813/2000) and "Protected Geographical Indication" (PGI) (Regulation (EC) No 583/2009), respectively, are unequivocally high-quality products, widely appreciated in modern gastronomy. Over the last decade, the literature was enriched with scientific publications on TBVM, TBVRE and BVM processing conditions, composition and sensory evaluation, using several analytical (Caligiani et al., 2007; Consonni et al., 2008; Falcone et al., 2007; Falcone, 2010; Masino et al., 2008) and sensorial approaches (Greco et al., 2013; Hillmann et al., 2012; Versari et al., 2013; Zeppa et al., 2013). Differences in the production process between and within PDO and PGI categories are reflected in their commercial price (Mattia, 2004).

In addition to these products, new ones regulated by the EU Reg. 583/2009 and traded under the name "balsamic vinegar" (BV) have emerged worldwide in recent years. These industrial products have gained consumer preference and market shares in a short time. Manufactured using different starting materials, processes and permitted additives, the new products are expected to differ from the established ones – as well as among them – in compositional and sensorial attributes.

As no literature data are available to support this statement, the aim of the present work was to analyze the main physicochemical and sensorial characteristics of BVs produced in Greece and discuss them in comparison to those of established Italian industrial BVs (PGI) of similar commercial value. Attention was focused on the parallel examination of the characteristics that are directly or indirectly related to the attributes appreciated for this type of

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vinegar, e.g. the sweet and sour taste. Our effort was focused on the potentially most important positive and negative characteristics of the new products contributing to the improvement of their production and supplying information to the authorities for regulatory purposes. Additional experiments for 5-hydroxymethyl-furfural (HMF) formation were also conducted to clarify some findings.

2. Materials and methods

2.1. Samples

A total of 11 representative samples of balsamic vinegar were subjected to physicochemical and sensory analysis. Based on a market search, samples of the five most popular products in the Greek market were bought from a supermarket in Thessaloniki (Greece) in March–May 2013. Five BVMs of similar commercial value to BVs and one TBVM sample were purchased randomly from a delicatessen and a supermarket in Milan in July 2013 (Table 1). All of the products were stored in a dark dry place at 20 ± 3 °C until the first opening. Then, aliquots of each sample were transferred in 10 mL vials that were kept in a freezer (−18 °C) for chemical analysis. Sensory analysis was conducted just after the first opening.

2.2. Reagents and chemicals

Sodium hydroxide and sulfuric acid (98%) were provided by Riedel-de Haën (Seelze, Germany). α-D-glucose was from Duchefa Biochemie (Haarlem, The Netherlands), D-fructose and glycerol were purchased from Panreac Quimica S.A. (Barcelona, Spain). Potassium hydrogen phthalate (99.5% purity) used as reference for alkalimetry, was supplied by Merck (Darmstadt, Germany), 5-hydroxymethyl-furfural (>99%) was purchased from Sigma Aldrich (Milan, Italy). Methanol (Chem-Lab., Zedelgen, Belgium) was HPLC grade and ultrahigh purity water was produced using a SG 2002 v.1.01 system (Barsbuttel, Germany). D_2O (99.98%) was purchased from Deutero (Kastellaun. Germany). 3-Trimethylsilyl-3,3,2,2-tetradeuteriopropionic acid sodium salt (TSP-d_4) was obtained from Cambridge Isotope Laboratories Inc. (Cambridge, MA, USA).

2.3. Cooking must procedure

Grape must from the red variety, Xinomavro (Naoussa, Northern Greece, 40°42′ N, 21°47′ E, 300 m altitude), was used in the study of HMF kinetics at semi-pilot and laboratory-scale experiments. For the former, 80 L of must were concentrated in a 100 L stainless steel flat-bottomed container in an open flame with the use of a proper burner device. The concentration process was exhaustive and lasted 5 h. Laboratory-scale experiments were performed in three similar set-ups consisting of an aluminum pot (12 L) with slightly round bottom and a burner connected to its gas tank. °Brix and HMF content were determined periodically in triplicate (the kinetics are shown in Tables S1 and S2 in Appendix A, Supplementary Material).

2.4. Analysis of sugars and derivatives

Total soluble solids were expressed as °Brix, and determined using a handheld refractometer (Schmidt & Haensch, GmbH & Co., Berlin, Germany). Total sugars were estimated using the phenol sulfuric acid method (DuBois et al., 1956). Density at 20 °C was determined with a pycnometer according to the method OIV-MA-AS2-01A (OIV, 2012).

2.4.1. Glucose, fructose, glycerol and HMF analysis

Glucose, fructose and glycerol were separated on a hydrogen form cation exchange resin-based column Agilent HI-plex H (Agilent Technologies, Santa Clara, CA, USA) by isocratic elution after adequate adjustment of the elution conditions used by Sanarico et al. (2003). The isocratic system was a 5 mM sulfuric acid solution at a flow rate of 0.5 mL/min. The column was equilibrated in an oven at 65 °C. The injection volume was 10 μL. The samples were properly diluted in the mobile phase and filtered through 0.45 μm pore size regenerated cellulose membrane filters (Schleicher & Schuell, Dassel, Germany) before injection. The HPLC system was composed of an LC-10Advp pump (Shimadzu, Kyoto, Japan), and a refractive index detector (RID-6A, Shimadzu). Clarity Software (DataApex, Prague, Czech Republic) was used for data processing. Quantification was made using calibration curves for standard glucose, fructose and glycerol in the range 2.5–60 mg/kg ($y = 569x + 162.5$, $R^2 = 0.999$; $y = 634.6x + 201.5$, $R^2 = 0.999$, and $y = 552.6x - 11.42$, $R^2 = 0.999$, respectively). Total reducing sugar content was then calculated as the sum of glucose and fructose contents.

The determination of 5-hydroxymethyl-furfural (HMF) was carried out according to an established method (Theobald et al., 1998) after adjustment of the mobile phase composition. Briefly, the samples were diluted in the mobile phase and filtered through 0.45 μm pore-size membrane filters. The separation was conducted on a Nucleosil 100 C18 (250 × 4.6 mm; 5 μm) chromatographic column MZ-Analysentechnik GmbH (Mainz, Germany) under isocratic elution with methanol/water (20:80, v/v) at 0.5 mL/min. The oven temperature was 40 °C and the injected volume 10 μL. The solvent delivery system consisted of a LC-20AD pump (Shimadzu, Kyoto, Japan) and a Rheodyne

Table 1
Labeling and commercial price of balsamic vinegar samples.

Sample no.	Country/product type	First material	Aging*	Acidity (% w/v)	Commercial price**
1	Greece/BV	Wine and concentrated grape must	+	7	0.9
2		Dry raisins	+	6	1.1
3		Wine and concentrated grape, caramel color	+	6	1.0
4		Wine and cooked grape must	++	6.2	1.7
5	Greece/BVM (PGI)	Wine and concentrated grape must	++	6	1.5
6	Italy/BVM (PGI)	Concentrated grape must and wine vinegar	+	6	3.5
7		Concentrated grape must and wine vinegar	+	6	6.0
8		Cooked grape must, wine vinegar, caramel color E150D	+	6	4.4
9		Concentrated grape must, cooked grape must, wine vinegar	+	6	7.0
10		Cooked grape must wine vinegar	+	6	4.5
11	Italy/TBVM (PDO)	Cooked grape must	+++	–	100

* + more than 2 months, ++ more than 6 months, +++ more than 12 years.
** Expressed as percentage of the value of 100 mL of sample 11.