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Stable isotope ratio analysis for verifying the authenticity of balsamic and wine vinegar

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Abstract: Wine vinegar is defined by EC Regulation 479/2008 (Annex IV, sections 1 and 17) as a product obtained from the acetous fermentation of wine, which is in turn defined as a product obtained exclusively from the alcoholic fermentation of fresh grapes, whether crushed or not, or from grape must. According to this definition, wine vinegar cannot contain acetic acids obtained from either petroleum derivatives or pyrolysis of wood (synthetic acetic acid) or from the fermentation of non-grape sugars (e.g. from beet or cane). Moreover, wine and wine vinegar cannot be produced from dried grapes diluted with water, therefore the so-called 'raisin vinegar', commonly produced in some Mediterranean countries by fermenting dried grapes and rehydrating with tap water, cannot be considered wine vinegar. This also applies to 'Aceto Balsamico di Modena' (ABM), an Italian PGI (Protected Geographical Indication) a salad dressing today renowned all over the world, obtained by mixing wine vinegar and grape must [1].

In the case of must and wine, since 1991 the addition of water and exogenous sugars has been detected by analyzing the isotopic ratios of hydrogen (D/H) and carbon ($^{13}\text{C}/^{12}\text{C}$) in ethanol and of oxygen ($^{18}\text{O}/^{16}\text{O}$) in water [2]. Addition is detected by comparing the results against an appropriate databank, such as the official databank set up in 1991 [3] by the European Union for all wine-producing countries within its territory. In 2013 isotopic methods have been recognized by the European Committee for Standardization (CEN) and in part by OIV (International Organization of Vine and Wine) as a means of detecting the presence of exogenous acetic acid and tap water in wine vinegar [4]. On the other hand, application of these techniques to the ingredients of ABM (wine vinegar and must) or the possibility of using the wine databank as reference for vinegar and balsamic vinegar had been not yet investigated.

To fill these gaps, we considered several different production chains (wine, wine vinegar, must and balsamic vinegar). We found that impurities are extracted together with acetic acid during the preparation of the sample, but they do not affect the $^{13}\text{C}/^{12}\text{C}$ of acetic acid, nor are the D/H values of acetic acid affected under a composite NMR experiment. Repeatability and reproducibility are comparable in wine vinegar and ABM and generally lower than those quoted in the official methods. In addition, we found no changes in the isotopic values from wine to vinegar and to ABM, and from the original must to the ABM must, providing experimental evidence that reference data from wine databanks can also be used to evaluate the authenticity of vinegar and ABM [5, 6].

References:

- [1] EU Regulation 583/2009
- [2] OIV-MA-AS311-05; OIV-MA-AS312-07; OIV-MA-AS2-12
- [3] EU Regulations 2347 and 2348/91
- [4] EN 16466-1, 2, 3; OIV 510/2013; OIV 511/2013
- [5] Camin, F.; Bontempo, L.; Perini, M.; Tonon, A.; Breas, O.; Guillou, C.; Moreno-Rojas, J.M.; Gagliano, G. Control of wine vinegar authenticity through $\delta^{18}\text{O}$ analysis. *Food Control* 2013, 29, 107-111
- [6] Perini, M.; Paolini, M.; Simoni, M.; Bontempo, L.; Vrhovsek, U.; Sacco, M.; Thomas, F.; Jamin, E.; Hermann, E.; Camin F. Stable isotope ratio analysis for verifying the authenticity of balsamic and wine vinegar. *Journal of Agriculture and Food Chemistry* 2014, 62, 8197-8203.