

Società Chimica Italiana - Divisione di Spettrometria di Massa



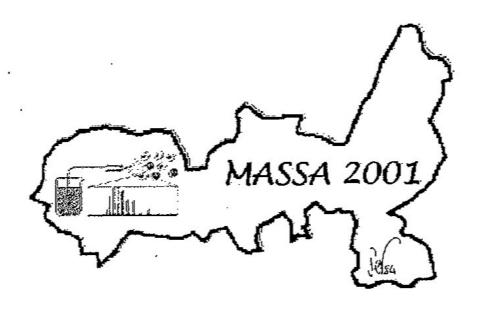
CNR - Centro di Studio per le Macromolecole Stereordinate ed Otticamente Attive



Università di Pisa - Dipartimento di Chimica e Chimica Industriale



Associazione Italiana di Scienza e Tecnologia delle Macromolecole



## MASSA 2001 "IONISSEA NELLO SPAZIO"

An International Symposium on Mass Spectrometry

Hotel Select - Marina di Campo (LI) 24-27 Giugno 2001

Programme and Abstracts

## STUDY OF FLAVOUR COMPOUNDS FROM TRADITIONAL BALSAMIC VINEGAR OF REGGIO EMILIA (ITALY)

Zeppa Giuseppe<sup>1</sup>, Giordano Manuela<sup>1</sup>, Gerbi Vincenzo<sup>1</sup>, Meglioli Giuseppe<sup>2</sup>

<sup>1</sup>-Dipartimento di Valorizzazione e Protezione delle Risorse agroforestali – Sezione Industrie agrarie – Università degli Studi di Torino – Via L. da Vinci 44 – 10095 – Grugliasco (TO - Italy

<sup>2</sup> - ITIS 'L. Nobili' - Via Makallè 10 - 42100 - Reggio Emilia - Italy

Traditional balsamic vinegar is a special vinegar whose origin dates back to the X-XI century. In difference to common vinegar, it is produced from acetic fermentation of cooked grape must. According to Italian legislation the traditional balsamic vinegar is aged at least 12 years in barrels of different sizes and woods but it is possible to find vinegar aged 40-50 years. During this aging time the used-up vinegar is replaced with new cooked must following the 'Solera' method with a production battery composed of a set of 5-7 barrels.

Many studies have been conducted on the traditional balsamic vinegar composition and its fermentation processes but its flavour was never analysed. The aim of this work is then to identify the main volatile compounds of traditional balsamic vinegar.

For this purpose five traditional balsamic vinegars from a produced battery of about 50 years old were examined. The volatile compound extraction was done by Solid Phase Extraction with C18 cartridge<sup>1</sup>. Identification of components was achieved by a Shimadzu model GC-17A gas chromatograph coupled with a Shimadzu QP-5000 quadrupole mass spectrometer.

The GC was equipped with a DB-WAX capillary column (30  $\,\text{m}$  x 0.25  $\,\text{mm}$  i.d.; film thickness 0.25  $\,\text{\mu m}$ ) and a split-splitless injector. Operating conditions were reported in a previous work<sup>2</sup>. Mass spectra were recorded at an ionization voltage of 70 eV in the 35-250 amu range.

Compound identification was made using known retention times and by mass spectra with the aid of a NIST 62 mass spectral data base. Quantitative measurements of each component were carried out by a Varian GC-3400 gas chromatograph equipped with a split-splitless injector, a flame ionization detector and a Spectra-Physics 4270 integrator with no consideration of extraction recoveries, i.e. calibration factors F=1.00 for all compounds. The column and the operating GC conditions were the same as described above. Triplicate analysis were performed for each sample.

The volatile substances isolated and identified were about a hundred. There were a large amounts of ketones, aldehydes, ethyl and acetic esters from alcoholic and acetic fermentation. Also the furan derivates from Maillard reaction such as the furfural from pentoses sugars, the 5-methyl-2-furaldehyde and the 5-hydroxymethylfurfural or HMF from hexoses sugars, the 5-acetoxymethylfurfural from HMF and the 2-furoic acid from ascorbic acid were highly abundant and quite significant<sup>3</sup>. From wood barrels used for vinegar aging the cyclotene, the maltol and the 5-hydroxymaltol result<sup>4</sup>.

The fragmentation of rearranged Amadori and Heyns intermediate compounds leads to  $\alpha$ -dicarbonyl compounds such as diacetyl and hydroxyacetone also present in the volatile fraction of this product. Other identified compounds are the nitrogen-containing heterocyclic products (eg. pyrroles and 2-pyrrolydinone) produced by Strecker oxidative degradation of amino acids in the presence of  $\alpha$ -dicarbonyl compounds.

Considerable quantities of lactones were determined such as the  $\gamma$ -butyrolactone, the dehydromevalonic lactone, the pantolactone and the solerone from oxidative degradation of hydroxylated fatty acids during alcoholic fermentation<sup>5</sup>.  $\alpha$ -Angelica lactone (from sugars degradation) and the whisky lactone (from wood barrels) were also present. Among the numerous unknown compounds there are the dioxanes, the dioxolanes and the glycol esters. Concentration of aroma compounds in the five vinegars are very different and are higher in the older samples on account of their greater oxidation.

<sup>2</sup> Gerbi, V.; Zeppa, G.; Carnacini, A. Ital. J. Food Sci. 1992, 4, 259.

11

2217.

Di Stefano, R. Bull. O.I.V. 1991, 64, 219.

<sup>&</sup>lt;sup>3</sup> Vernin, G.; Parkanyi, C.; In Mechanism of formation of heterocyclic compounds in Maillard and pyrolysis reactions. Vernin, G., Ed.; Ellis Horwood: Chichester, U.K., 1982.

<sup>4</sup> Cutzach, I.; Chatonnet, P.; Henry, R.; Dubourdieu, D. J. Agric. Food Chem. 1997, 45,

<sup>&</sup>lt;sup>5</sup> Cutzach, I.; Chatonnet, P.; Dubourdieu, D. J. Int.Sci.Vigne Vin 1988, 32, 99.