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ScienceDirect
Food Chemistry 106 (2008) 1057–1065
Food Chemistry
www.elsevier.com/locate/foodchem

Heat-induced chemical, physical and functional changes during grape must cooking

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Received 10 January 2007; received in revised form 30 April 2007; accepted 12 July 2007

Abstract

Cooked must is a product that could be used in food formulations, directly or after fermentation, to obtain many traditional foods. Must cooking was conducted in boilers of different materials (copper and stainless steel) for different times in order to obtain differently concentrated products.

The concentration of many constituents (sugars, organic acids, nitrogen compounds, metal ions and polyphenols) was observed upon cooking, together with the increase of neo-formation compounds, such as hydroxymethylfurfural and melanoidins, which give, to the musts, the typical brown colour and caramel-like odour. The concentration of metal ions, in particular, determined high levels of lead and copper (in the case of use of copper boilers) in the final products.

Polyphenol heat concentration determined the degradation of simple phenolics, such as catechins, and the formation of condensed tannins, which determined a loss of the antioxidant activity of the phenolic fraction, whereas the formation of melanoidins improved the total antioxidant activity of the product.

Keywords: Grape must; Heat concentration; Browning; Hydroxymethylfurfural; Melanoidins; Polyphenols; Antioxidant activity

1. Introduction

Grape must cooking is an ancestral practice in Mediterranean countries and it is required for the production of many traditional Italian foods and beverages, such as traditional balsamic vinegars of Modena and Reggio Emilia, "vino cotto" (namely cooked wine), a liquor wine from the Marche and Abruzzo regions, Marsala wines from Sicily and mosto cotto (cooked must), from the Apulia region, which is used as a filling in bakery formulations (Repubblica Italiana, 2006). Apart from Italy, cooked must is also used for Spanish sweet wines (Rivero-Pérez, Peréz Magariño, & Gonzàles-San José, 2002).

Cooked must is mainly produced from white grapes (e.g. Trebbiano cultivar) and is obtained by direct heating of must over an open fire in uncovered boilers or pans which are traditionally made of copper. The must is cooked until its volume is reduced by 10–60% according to the production technology and, once cooled down, it could either be fermented in barrels or used as is, depending on the product to be obtained.

Must cooking is traditionally carried out below boiling temperatures (80–95 °C) and could require quite long processing times (up to 48 h), depending on the capacity of the cooking pan. During cooking the must becomes dark and dense and many chemical changes occur due to the prolonged thermal treatment.

Product cooking determines the concentration of naturally occurring chemicals in must, among which are sugars and acids. Under acidic conditions, as occurring in fresh

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doi:10.1016/j.foodchem.2007.07.026

and cooked musts, sugars undergo thermal degradation with the formation of furan derivatives (Belitz & Grosch, 1999). Some authors (Antonelli, Chinnici, & Masino, 2004) investigated furans in cooked musts and attributed their formation to thermal degradation of sugars under acid conditions, even though furans such as 5-hydroxymethylfurfural (HMF) could be formed also in the Maillard reaction. Moreover, alpha-amino acids are present in grape musts and these compounds could undergo thermal condensation with sugars to form Maillard reaction products (MRPs) (Belitz & Grosch, 1999; Martins, Jongen, & van Boekel, 2001).

MRPs, such as HMF and melanoidins, were determined in sweet wines obtained from cooked musts (Mastrocola, Sacchetti, Di Mattia, Seghetti, & Piva, 2006; Rivero-Pérez et al., 2002) and the most concentrated and browned the product, the higher was the concentration of these compounds. If furanic compounds, and HMF in particular, are supposed to have negative effects on human health, compounds formed in the last phases of the Maillard reaction, such as melanoidins, are gaining attention due to their antioxidant potential (Lee & Shibamoto, 2002; Manzocco, Calligaris, Mastrocola, Nicoli, & Lerici, 2001). MRPs were shown to contribute to the antioxidant activity of products from cooked musts (Mastrocola, Di Mattia, Seghetti, & Sacchetti, 2005; Mastrocola et al., 2006) but the relative contribution of these compounds to the total antioxidant activity of cooked musts is still unknown.

This study is aimed to understand the most important chemical and physical changes undergone by musts during cooking and to evaluate the effect of these changes on product quality and potential health properties. To this end, cooking was conducted for different times to give products of different concentrations and in boilers of different materials: copper and stainless steel.

2. Materials and methods

2.1. Materials

White grapes of Trebbiano d'Abruzzo were removed from stalks and pressed. The obtained must was divided into aliquots of 100 l and concentrated in copper and stainless steel boilers of 120 l capacity to about 65, 40 and 30 l. The masses were rapidly heated to boiling point; then the temperature was set at 95 °C for the whole process (up to 18 h). Each concentration process was duplicated. Samples for organic acid and physical analyses were taken at the end of the processes and treated with sodium azide to avoid further fermentation. Samples to be analyzed for sugar, amino acids, metal ions, polyphenols content, MRPs content and antioxidant activity were frozen and stored at −40 °C to reduce the rate of both chemical oxidation and Maillard reaction. Three different subsamples were taken and submitted to analysis.

2.2. Physical determinations

2.2.1. Density

This was measured at 20 °C using the official EU community methods for the analysis of musts and wines (EEC, 1990).

2.2.2. Viscosity

Viscosity was measured at 25 °C by a Stress Tech Rheometer (Reologica Instruments AB, Sweden) equipped with a coaxial cylinder measuring system (CC25). Analyses were carried out by varying the flow rate in a range between 0.33 and 87.67 s^{-1}. Data were fitted by the power law equation ($X = K\gamma^n$) for the calculation of K and n.

2.2.3. Colour

Reflectance analyses were carried out by a Minolta (Tokyo, Japan) CM-500 spectrophotometer using the CIE illuminant D65 and 10° standard observer conditions (CIE, 1986). Before analysis, the instrument was calibrated on a white standard (L^*: 96.58; a^*: −0.09; b^*: −0.05 on SCE modality). Samples were poured into white beakers (L^*: 68.08; a^*: −0.54; b^*: −0.52 on SCE modality) of 1 cm height and were covered with a transparent glass in order to set the optical path constant. Transparent glass showed no significant influence on colour determinations (data not reported). Colour measurements were carried out in the SCE (specular component excluded) modality as the glass determines a high specular reflection.

2.3. Chemical determinations

2.3.1. General measures

Total dry extract, density, refractometric index, titable acidity, pH, total nitrogen and hydroxymethylfurfural (HMF) content were determined using the official EU community methods for the analysis of wines (EEC, 1990). For HMF determination, samples were diluted 1:10 with 10% ethanol solution to enter the linear range. 5-(Hydroxymethyl)-furfural (Sigma, Steinheim, Germany) was used for calibration curves. Spectrophotometric determinations were carried out with a Perkin–Elmer (Boston, MA) Lamba Bio 20 spectrophotometer.

2.3.2. Sugar determination

Musts were purified using C18 SPE cartridges (500 mg, 6 ml) (International Sorbent Technology, UK); 500 μl of sample were loaded into the column previously conditioned with 2.5 ml of methanol and 5 ml of water. Sugars were eluted with 5 ml of 0.1 N sulphuric acid, made up to 5 ml final volume and analysed by HPLC. Isocratic separation of analytes was carried out at 35 °C using an Aminex HPX-87C (Bio-Rad, Watford, UK) carbohydrate column (300 × 7.8 mm) equipped with a Bio-Rad Carbo-C precolumn (30 mm × 4.6 mm). The system consisted of a Spectra System (ThermoFinnigan, Rodano, Italy) P4000 pump, Spectra System AS3000 autosampler, a degasser and a