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Assessment of the development of browning, antioxidant activity and volatile organic compounds in thermally processed sugar model wines

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ABSTRACT

The study evaluates the contribution of the fructose and glucose's degradation for the Madeira wine's features. The browning index, antioxidant activity and volatile organic compounds developed by the glucose and fructose model systems simulating thermally processed sweet Madeira wines were assessed. Sixteen different fructose/glucose model systems were prepared in synthetic wine and stored at 50 °C for 4 months. Then, three model wines were also submitted to 70 °C for 1 month. The browning index and the antioxidant activity ranged between 0.00 and 0.27 AU and 3.0–65.3 mg(GAE)/L, respectively. The development of several volatile organic compounds was demonstrated (up to 47). The identified compounds were mostly furans, with 5-hydroxymethylfurfural as the most abundant. For the first time, it was shown that the origin of sotolon in sweet wine can be associated with the acid-catalyzed fructose degradation mechanism. Other 2(5H)-furanones were also identified. It could be concluded that part of the browning, antioxidant activity and aroma compounds developed in sweet fortified wines is associated with the thermal degradation of fructose in acid medium.

1. Introduction

It is generally accepted that sugar in acidic media can be degraded into several low-molecular weight compounds, such as furans and pyrans (Belitz, Grosch, & Schieberle, 2009, pp. 248–339). Additionally, brown-colored compounds can also be formed. Parallel to the sugar degradation reaction in acidic medium, Maillard reaction can also occur, leading to similar products. This complex reaction is also known to develop browning due to a series of subsequent and parallel reactions between carbonyl compounds (such as sugars) and free amino groups (usually amino acids). Maillard reaction is very important in food quality, mainly in heat-processed foods, affecting not only color but also the flavor and nutritional value. It can produce high antioxidant activity products, namely melanoidins, although in contrast, can eventually have toxicological implications, such as acrylamide formation (Osada & Shibamoto, 2006; Yilmaz & Toledo, 2005). In general, the sugar type determines the flavor compounds formed and the amino acids affect the kinetics (van Boekel, 2006).

Considering that this kind of reactions develop complex intermediates and final reaction products, researchers commonly use model systems to perform their studies. These studies usually use water as solvent and only a limited number of reports have dealt with hydro alcoholic systems (Pripis-Nicolau, de Revel, Bertrand, & Maujean, 2000; Shen & Wu, 2004; Shen, Tseng, & Wu, 2007). Shen and Wu (2004) used ethanolic systems and proved that the browning extent and the 5-hydroxymethylfurfural (HMF) content rise with the ethanol increase. They also found different product profiles in aqueous and ethanolic model systems indicating some differences in the reaction mechanisms (Shen et al., 2007). Furthermore, there are some studies that highlight the formation of flavor components in model wine systems, at low pH and temperatures. Sanz and Martínez-Castro (2009) and Kroh (1994)

Abbreviations: ABTS, 2,2′-Azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid; Arg, L-arginine; Asp, L-aspartic acid; Cys, L-cysteine; Fru, D(−)-fructose; Glc, D(+)-Glucose; GAE, gallic acid equivalents; GABA, γ-aminobutyric acid; HMF, 5-hydroxymethylfurfural; TAA, total antioxidant activity; VOCs, volatile organic compounds.

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studied model wine systems containing glucose with alanine, arginine and proline. Pripis-Nicolau et al. (2000) reported the reaction of carbonyls (acetoin and acetol) and dicarbonyls (glyoxal, methylglyoxal, diacetyl and pentan-2,3-dione) with 14 amino acids. They found that this reaction leads to the formation of many products, including pyrazines, methylthiazoles, acetylthiazoles, acetylthiazolines, acetylthiazolidines, trimethyloxazole, and dimethylethyloxazoles, especially due to the presence of cysteine, through decarboxylation and participation in the Strecker degradation mechanism. Moreover, they also found that these compounds have a remarkable odor, with notes resembling sulfur, corn, pungent, nut, popcorn, roasted hazelnut, toasted, roasted, and ripe fruits. Later, Marchand, de Revel, Vercauteren, and Bertrand (2002) have proved the occurrence of a Maillard intermediate (*N*-(2-sulfanylethyl)-2-oxopropanamide) in the formation of 2-acetylthiazole from methylglyoxal and cysteine using a model wine system. Recently, Pons, Lavigne, Landais, Darriet, and Dubourdieu (2010), used model wine solutions at 40 °C during 6 months for testing the ability of several reported precursors to produce sotolon under very different experimental conditions.

Considering that Maillard reaction takes place as low as 50 °C, favored at pH 4–7 and that caramelization, even if it requires higher temperatures, is favored at pH 3–9 (Kroh, 1994; Morales & Jiménez-Pérez, 2001), it is reasonable to admit that both reactions can eventually occur during the heating process traditionally applied to the Madeira wines (up to 50 °C during at least 3 months) – *estufagem* – and contribute to their browning and flavor. Madeira wine processing is described elsewhere (A.C. Pereira et al., 2016; V. Pereira, Albuquerque, Ferreira, Cacho, & Marques, 2011). These wines hold an alcohol by volume between 17 and 22% (v/v: mL ethanol/100 mL wine) and are produced in different styles, namely dry (total sugars: 49.1–64.8 g/L), medium-dry (64.8–80.4 g/L), medium-sweet (80.4–96.1 g/L), and sweet wines (>96.1 g/L) (IVBAM). Previous reports indicate that the total amino acid content, which can vary between 644 and 178 mg/L, can decrease up to 30% after being submitted to *estufagem* (V. Pereira, Pereira, Pérez Trujillo, Cacho, & Marques, 2015).

The aim of the current study was to evaluate the contribution of fructose and glucose thermal degradation for the Madeira wine features, assessing the browning index, antioxidant activity and volatile organic compounds (VOCs) of 16 different glucose and fructose model systems, prepared under the same conditions of baked sweet Madeira wines. The role of four amino acids, namely arginine (Arg), cysteine (Cys), γ-aminobutyric acid (GABA) and aspartic acid (Asp), was also studied, taking into consideration either their abundance in Madeira wine or their relevance in terms of reactivity (V. Pereira et al., 2015; V. Pereira, Pontes, Câmara, & Marques, 2008). Additionally, 3 model systems, prepared with fructose (Fru), fructose + cysteine (FruCys) and glucose (Glc), under overheating conditions (70 °C for 1 month) were also studied in order to accelerate the development of volatiles, which might be formed from eventual hot points of the heating coil fitted in the stainless steel tank, in which the wine thermal processing is performed. As far as we know, this is the first study that seeks to find the contribution of sweet fortified wine main sugars for the browning, antioxidant activity and aromas development.

2. Material and methods

2.1. Chemicals

Glc, Fru and *L-(+)*-tartaric acid were obtained from Merck Co. (Darmstadt, Germany), the amino acids Arg, Cys, Asp were purchased from Sigma Chemical Co. (St. Louis, MO, USA) and γ-aminobutyric acid (GABA) was supplied by Fluka BioChemika AG (Buchs, Switzerland). Ethanol was obtained from Panreac (Barcelona, Spain). Ethyl acetate was supplied by Lab-Scan (Dublin, Ireland). All chemicals had a purity grade higher than 98%.

2,2′-Azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) in the crystallized diammonium salt form (≈98.0%), gallic acid monohydrate (≥98.0%) and potassium persulfate were obtained from Fluka BioChemika AG (Buchs, Switzerland).

2.2. Preparation of model systems

For the preparation of the model systems, four amino acids were chosen: Arg, Cys, GABA and Asp, since they are important amino acids present in Madeira wines, shown in previous studies (V. Pereira et al., 2015; V. Pereira et al., 2008). The selected sugars were Fru and Glc, as they are the main sugars present in sweet Madeira wines. The model systems were prepared as described in Table 1. All model systems were prepared in synthetic wine (sweet Madeira wine typical conditions) containing 6 g/L of tartaric acid, 180 mL/L of ethanol and pH adjusted to 3.5, with a 1 mol/L NaOH solution. The first nine model systems intended to induce the Maillard reaction, the following three to induce the acidic degradation of sugar and the last four intended to ascertain the influence of the amino acid concentration. About 100 mL of each model system were placed into 100 mL Schott Duran® wide mouth bottles, remaining a small head space volume similar to the *estufagem* process procedure. The model systems were stored at 50 ± 0.5 °C in a Memmert UFE 400 oven (Schwabach, Germany) for 4 months to simulate the *estufagem* process (regulated conditions).

Other Fru, FruCys and Glc model systems were then submitted to overheating conditions (70 °C during 1 month) in order to identify the VOCs that clearly result or enhance from the rise of the heating temperature. Duplicates of all model systems were prepared.

2.3. Browning index

The browning index was evaluated by spectrophotometry, reading the absorbance at 420 nm ($A_{420\ nm}$) of each model systems against distilled water, after 4 months of heating. The readings were recorded on a Perkin Elmer Lambda 2 (Waltham, MA, USA) spectrophotometer using a 1 cm path length quartz cell. All samples were analyzed in triplicate.

2.4. Total antioxidant activity

Total antioxidant activity (TAA) determination, was based on the method reported by Re et al. (1999), according to the reaction of each model system with a stable ABTS radical cation ($ABTS^{\cdot+}$). Briefly, $ABTS^{\cdot+}$ was obtained by the reaction of 2 mmol/L ABTS diammonium salt with 70 mmol/L potassium persulfate in 50 mL of phosphate buffered saline (PBS). The mixture was left to stand in the dark at room temperature for about 16 h before use. For the antioxidant activity evaluation, the $ABTS^{\cdot+}$ solution was diluted with PBS to obtain the absorbance of 0.800 ± 0.030 at 734 nm. Then 12 μL of each model system were mixed with 3 mL of $ABTS^{\cdot+}$ solution. The absorbance was recorded at room temperature during 20 min. PBS solution was used as blank. The percentage of decrease of the absorbance at 734 nm was calculated by the formula $I = [(A_{blank} - A_{model\ system})/A_{blank}] \times 100$, where I = $ABTS^{\cdot+}$ inhibition (%), A_{blank} = absorbance of the blank sample (t = 0 min), $A_{model\ system}$ = absorbance of the tested model system at the end of the reaction (t = 20 min). The results were expressed as mg/L of gallic acid equivalents (GAE), by means of the following calibration curve: $I = 1.243\ GAE^{0.801}$ ($R^2 = 0.994$, between 1 and 150 mg/L).