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Evolution of some physicochemical and antioxidant properties of black garlic whole bulbs and peeled cloves

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ABSTRACT

Black garlic was produced at three different temperatures of heat treatment (72°, 75° and 78 °C) and close to 90% of relative humidity. Two types of material source were used: whole bulbs and peeled cloves. Total soluble solids content (°Brix), pH, water activity (a_w), browning intensive (L value), total polyphenol content, antioxidant capacity and total polyphenol index of the raw and heated garlic were determined. This study showed the changes occurring in the physicochemical and antioxidant properties of the garlic during the heat-treatment evolution. The soluble solids content (°Brix) in garlic increased gradually and the pH decreased in whole bulbs and peeled garlics. The polyphenol content measured by the Folin–Ciocalteu method showed a significant increase during the heat-treatment in all the cases. Also, the antioxidant capacity measured by the ABTS radical increased significantly during the heat-treatment.

1. Introduction

Garlic has been considered in many cultures to be a food with exceptional therapeutic qualities. The properties beneficial to health of garlic have been described in many research works describing its preventive and even curative effects in many diseases (Bayan, Koulivand, & Gorji, 2014; Milner, 2010; Omar, 2013; Tsai, Chen, Sheen, & Lii, 2012). However, raw garlic consumption is not very widespread mainly due to its characteristic pungent taste. Therefore, many new industrial processes are being investigated in order to obtain garlic products with improved organoleptic properties retaining and even enhancing its beneficial properties. This is the case of black garlic, a product traditionally manufactured in southeast Asia and recently extended to other garlic producing areas like California (U.S.A.), Argentina, Canada and Europe.

Black garlic is manufactured by keeping raw garlic in a temperature and humidity controlled room for several days. The changes in the processing length depend mainly on the temperature. If the processing temperature is high then the processing duration is shorter. Previous reports have described processing temperatures of between 40–90 °C and heating times of between 5–45 days (Bae, Cho, Won, Lee, & Park, 2014; Sasaki, Lu, Machiya, Tanahashi, & Hamada, 2007; Wang, Feng, Liu, & Yan, 2010). At the end of the heat-treatment, black garlic is partly dehydrated. Finally whole bulbs or peeled cloves of black garlic are packaged in plastic or glass containers without adding any preservatives.

The physicochemical characteristics of black garlic and raw garlic are very different (Choi et al., 2008). During heating, raw garlic undergoes intensive Maillard browning. In early days of heating, caramel and brown tones appear and a few days later the garlic changes its color to black. Black garlic has a rubbery texture and its taste is bittersweet without the characteristic pungent flavor of raw garlic.

There are many reports of bioassays on the beneficial effects on health of black garlic (Lee et al., 2009; Sato, Kohno, Hamano, & Niwano, 2006; Seo et al., 2009; Wang et al., 2010). However, few reports describe black garlic processing. The aim of this study was to evaluate, through different analytical techniques, some physicochemical and antioxidants properties of black garlic produced at three different temperatures, comparing two different products as raw material source, whole bulbs and peeled cloves.

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2. Materials and methods

2.1. Samples

Black garlic was manufactured at three different heating temperatures (72 °C, 75 °C and 78 °C) with relative humidity of nearly 90%. Raw garlic samples and samples taken (whole bulbs and peeled cloves) during the aging of garlic were analyzed. Sampling was made at different times depending on the heating temperature. Thus, when the heat treatment was at 78 °C, samples were taken after 5, 10 and 14 days of heat treatment; at 75 °C, samples were taken after 7, 14 and 21 days of heat treatment, and at 72 °C, samples were taken after 11, 24 and 33 days of heat treatment.

All samples were crushed and divided into three sub-samples. A previous peeling before crushing was needed in whole garlic bulbs.

2.2. Measurement of soluble solids content, pH, a_w, and browning intensity

Total soluble solids content (°Brix), pH, water activity (a_w), and browning intensity (L value) were determined in all samples during heat treatment. Determinations in duplicate were carried out. Garlic soluble solids (°Brix) were measured by an *Abbe Refractometer*. Garlic pH was measured with a pH meter *Crison Basic 20*. Garlic water activity (a_w) was measured with an *Aqualab Series 3/3TE* meter with a temperature stabilizer. Garlic browning intensity was determined by a *Konica Minolta CR-410 Croma Meter colorimeter*. L value was taken because this reading corresponds to product luminescence (L-100 = white; L-0 = black).

2.3. Total polyphenol content, antioxidant capacity and total polyphenol index

A *Perkin Elmer Lambda 20 UV VIS spectrophotometer* was used to analyze raw and heated garlic, total polyphenol content, antioxidant capacity and total polyphenol index. A previous garlic extraction was prepared to analyze antioxidant properties. Before this, all samples were lyophilized and five extracts per sample were obtained. Garlic extract was prepared dissolving 0.3 g of the lyophilized sample in 10 ml of a mixture at 50% v/v of ethanol and distilled water. Next, samples were stirred during one hour and then filtered using a Buchner funnel with *Whatman paper* into a vacuum flask connected to a vacuum pump filter. The filtered extract was leveled at 25 ml with a hydroalcoholic solution of 50% v/v.

The polyphenol concentration of garlic samples was determined by *Folin–Ciocalteu method* (Singleton, Orthofer, & Lamuela-Raventos, 1999). To a volumetric 25 ml flask, 0.5 ml of extract, 10 ml of distilled water, 1 ml of *Folin–Ciocalteu* reagent and 3 ml of carbonate sodium 20% w/v were added, and diluted to volume (25 ml) with distilled water. The mixture was heated at 50 °C during 5 min to accelerate the coloration reaction. Subsequently, it was cooled with water and the reading was performed in the *spec troPHOTO"meter* at 765 nm. The reading was compared to a calibration curve prepared with different gallic acid solutions: 75, 100, 200, 250, 300 ppm. Polyphenol content results were expressed considering the dilution of the sample (0.3 g in 25 ml) in grams of gallic acid equivalent per kilogram of lyophilized sample.

Raw and heated garlic antioxidant capacity was determined by *ABTS radical method* (Re et al., 1999). A mix of 2.557 ml of a solution of 7 mM *ABTS reagent* and 0.333 ml of a solution of 2.25 mM potassium persulfate in distilled water was made. The prepared solution was stored in darkness during 16 h, enough time for the radical formation ($ABTS^+$). Then, 0.15 ml of the $ABTS^+$ solution was diluted in 15 ml of ethanol. The absorbance value at 734 nm was adjusted near 0.7 (A_0). Next, 0.980 ml of $ABTS^+$ solution and 0.02 ml of garlic extract sample were added. After stirring it, the absorbance was read at 734 nm after 7 min (A_1). The inhibition percentage was calculated by the following expression:

$$\% \text{ inhibition} = (A_0 - A_1) * 100/A_0$$

A calibration curve was built with the following Trolox concentrations: 0.1; 0.5; 1 and 1.5 mM. Considering the sample dilution, results were expressed in mmol Trolox-equivalent per kilogram of lyophilized sample.

Total polyphenol index was calculated multiplying the garlic extract absorbance reading at 280 nm per the sample dilution.

2.4. Statistical analysis

All results obtained in this study were analyzed by an analysis of variance. Average values at different processing times were compared according to the Tukey test.

3. Results and discussion

3.1. °Brix, pH, a_w y browning intensity

Soluble solids content, pH, water activity and browning intensity are shown in Table 1. It is noted that the evolution of the physicochemical characteristics in whole garlic bulbs was very similar to that of peeled garlic cloves. During heat-treatment, in the garlic, its soluble solid content (°Brix) and browning intensity increased, and its pH and a_w decreased. However, it was observed that in whole garlic bulbs and peeled cloves the soluble solid content, pH and browning intensity changed faster if the temperature was higher. Similar °Brix readings were obtained in whole garlic bulbs and peeled garlic cloves even from different initial °Brix readings. The increase in garlic soluble solid content could be the reason for the characteristic black garlic sweetness (Sasaki et al., 2007) (see Fig. 1).

At the end of the heat-treatment, homogeneous Tukey tests showed °Brix readings always higher than raw garlic ones. Significant differences in °Brix readings at three temperatures and in the two types of products manufactured/made (Table 1) were observed. At the end of the heat-treatment, whole garlic bulbs °Brix readings with heat-treatment at 78 °C and 75 °C (44.00 and 45.25, respectively) were lower than those of peeled garlic cloves °Brix readings (45.33 and 47.5, respectively.).

In Fig. 2 it is shown how the pH decreased during the manufacturing process. Raw garlic pH was nearly 6 (5.93 and 6.31 in whole garlic bulbs and peeled garlic cloves, respectively) whereas black garlic pH at the end of heat-treatment reached values below 3.8 in all the cases. Changes in pH whole bulbs and peeled cloves samples were very similar. It was demonstrated how if the heat-treatment of the garlic was at a higher/high temperature then the pH decreased more rapidly (Fig. 2).

At higher temperatures (78 °C) lower pH values were reached. The same observation has recently been described Bae et al., 2014). A heating temperature of over 60 °C and a decrease in pH below 4.2 are two important factors for preventing the possibility of anaerobic bacteria proliferation.

Water activity (a_w) decreased less than other parameters because black garlic was manufactured maintaining high relative humidity. However, raw and black garlic a_w at the end of heat-treatment showed significant differences (Table 1).

At 78 °C, whole garlic bulbs a_w showed significant differences in all the samples. However, at this temperature, peeled garlic cloves a_w showed significant differences between samples taken after 5 and after 10 days of heat-treatment. At 75 °C, significant differences were observed in whole garlic bulbs and peeled garlic cloves between the 7th and 14th days of heat-treatment.