Food Chemistry 209 (2016) 162–170

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Evaluation of antioxidant capacity in coffees marketed in Colombia: Relationship with the extent of non-enzymatic browning

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ARTICLE INFO

Article history:
Received 12 December 2015
Received in revised form 13 March 2016
Accepted 13 April 2016
Available online 22 April 2016

Keywords:
Antioxidant
Coffee
Non-enzymatic browning
Color
Browning index
Total phenolics
HMF
Furfural

ABSTRACT

Fifty-eight samples of commercial Colombian coffee with different characteristics (soluble, ground, decaffeinated, etc) were evaluated for antioxidant capacity (AC) (ABTS and FRAP), total soluble phenolics (TP), browning index (BI), color parameters (L^*, a^*, b^*, c^* and h^*), HMF and furfural. The AC in Colombian coffees was very varied (164–1000, 100.8–885.9 μmol of Trolox equiv/g and 12.5–127 mg gallic acid equiv/g, respectively for ABTS, FRAP and TP). AC, TP, BI, color, HMF and furfural values were higher ($p < 0.05$) in soluble coffees than in ground ones, showing the lyophilized samples which showed the highest average values. Significant lineal correlations ($p < 0.05$) were found between AC and color parameters, BI, HMF. No significant ($p < 0.05$) differences in the AC between the different types of coffee were found. This work confirms the direct relationship between the rate of non-enzymatic browning and antioxidant capacity.

1. Introduction

The coffee bean is an important product all over the world and its trade is increasing year after year. In Colombia, coffee is the flagship product of the economy with a production of 7.2×10^4 tons per year, i.e. 11.4% of world market (Naranjo, Vélez, & Rojano, 2011). The coffee is widely consumed as a beverage all over the world and in Colombia can be found wide variety of coffees in trade, which can be classified according to the degree (light, medium, dark) and type of roasting (natural and torrefacto), soluble (lyophilized), ground, flavored, with designation of origin (DO), organics, decaffeinated and mixtures, among others (Colcafe, 2015; Juan Valdez, 2015).

Coffee is also known to be a rich source of compounds with potent antioxidant activity. The AC of coffee has been attributed to its content in polyphenols and melanoidins (Delgado-Andrade & Morales, 2005). During roasting process, the green coffee beans are subjected to temperatures between 200 and 250 °C depending on the degree of roasting. This process causes significant physicochemical changes which involve thermal degradation of natural phenolic antioxidants, generation of flavors and brown-colored compounds (melanoidins) products of the Maillard reaction (MR) (Liu & Kitts, 2011). Melanoidins are formed in the final stages of the MR, these compounds have been associated with important biological activities as antioxidants (Pastoriza & Rufián-Henares, 2014), chelating activity (Tagliazucchi, Verzelloni, & Conte, 2010) and antimicrobial (Rufián-Henares & Morales, 2008).

The AC of coffee can be influenced by several factors, such as the variety and origin of coffee (Parras, Martineztome, Jimenez, & Murcia, 2007), the roasting degree (Nicoli, Anese, Manzocco, & Lerici, 1997), the type of roasting (natural or torrefacto), their blends (López-Galilea, de Peña, & Cid, 2007), and the technological parameters applied for coffee brew extraction. Several methods that have been used to evaluate the AC of coffee include FRAP, ABTS and the determination of TP (Borrelli, Visconti, Mennella, Anese, & Fogliano, 2002; Sánchez-González, Jiménez-Escrig, & Saura-Calixto, 2005).

The color is an important characteristic in roasted coffee that can be evaluated by the color parameters L^*, a^* and b^* (Summa, de la Calle, Brohee, Stadler, & Anklam, 2007). During the roasting process of coffee beans, the lightness parameter L^* was negatively correlated to the roasting time at a given temperature, and a linear correlation between the reciprocal of lightness and roasting time was confirmed (Sacchetti, Di Mattia, Pittia, & Mastrocola, 2009). In fact, the radical scavenging capacity is a linear function of L^*

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http://dx.doi.org/10.1016/j.foodchem.2016.04.038
0308-8146/

(Summa et al., 2007). The extent of browning is measured by the absorbance at 420 nm and is a useful end-point measurement for quantifying the yield of high molecular weight melanoidins (Wijewickreme, Kitts, & Durance, 1997). Brown color property while is useful indicator for the development of MR, is not directly correlated to the antioxidant potential of crude or fractionated MR products (MRPs) (Liu & Kitts, 2011).

5-Hydroxymethylfurfural (HMF) and furfural, are formed during heat processing of foods by acid-catalyzed dehydration of reducing sugars and MR (Antal, Mok, & Richards, 1990) and have been used for years as quality indicators of thermally processed food.

Although many studies have been conducted using different methods of extraction and preparation of samples for measurement of color, MRPs and AC in order to relate coffee AC and the degree of roasting, few studies have evaluated the AC and its relation to the degree of browning in commercial coffees of different types. Since the Colombian coffee is exported to more than 90 countries (Federación Nacional de Cafeteros de Colombia, 2011), the aim of this study was to evaluate the relation between the antioxidant activity and non-enzymatic browning degree, in order to know if the type (degree and type of roasting, soluble, ground, flavored, with designation of origin (DO), organics, decaffeinated and mixtures, etc.) of coffee can influence the parameters studied.

2. Materials and methods

2.1. Samples and reagents

Fifty-eight samples of commercial Colombian coffee with different characteristics (soluble, ground, flavored, with DO, decaffeinated and roasting degree (dark, medium, light) and type (natural or torrefacto)) were obtained in triplicate from three different local markets (Table 1).

2.2′-Azino-bis (3-ethylbenzenothiazoline6- sulfonic acid) (ABTS), gallic acid and 2.4.6-Tri (2-pyridyl)-s-triazine (TPTZ) were purchased from Sigma-Aldrich Chemical (Oakville-Ontario, Canada). Trolox (6-hydroxy-2.5.7.8-tetramethylchroman-2-carboxylic acid) was obtained from MP Biomedicals (Illkirch-Graffenstaden, France), Folin–Ciocalteau reagent (2.0 N) and 2-furaldehyde from Merck (Darmstadt, Germany) and HMF from Alfa Aesar (MA, USA).

2.2. Antioxidant and total phenolics determination

2.2.1. Sample preparation

Coffee extracts were used in this study. Extraction of antioxidant compounds was performed following the method described by Contreras-Calderón, Calderón-Jaimes, Guerra-Hernández, and García-Villanova (2011). 0.5 g of the sample were used to extraction. The extracts were stored at −18 °C in amber flasks. The extraction and measurements were made in triplicate.

2.2.2. Measurement of ABTS

The ABTS assay was performed following Re et al. (1999). 100 μL of test sample, diluted appropriately (1/100) with water were used for determination, and absorbance was measured at 730 nm (Varian Cary® 50 UV–vis Spectrophotometer). Aqueous solutions of Trolox (concentrations between 0 and 200 μM) were used for calibration. Results were expressed as micromoles of Trolox equivalents (TEs) per gram (μmol of TEs/g).

2.2.3. FRAP assay

The FRAP assay was performed as previously described by Pulido, Bravo, and Saura-Calixto (2000). 30 μL of test sample, diluted appropriately (1/50) with water were used for determination, and absorbance was measured at 595 nm (Varian Cary® 50 UV–vis Spectrophotometer). Aqueous solutions of Trolox (concentrations between 0 and 500 μM) were used for calibration. Results were expressed as μmol of TEs/g.

2.2.4. Total phenolics (TP)

The TP content was determined using the Folin–Ciocalteu assay (Rover & Brown, 2013). 100 μL of test sample, diluted appropriately (1/10) with water were used for determination, and absorbance was measured at 725 nm against the blank (Varian Cary® 50 UV–vis Spectrophotometer). Aqueous solutions of gallic acid (concentration between 0 and 100 ppm) were used for calibration. Results were expressed as mg of gallic acid equivalents (GAEs) per g (mg of GAEs/g).

2.3. Color determination

Color was determined using an X-Rite 939 spectrodensitometer and calibrated with a white and black standard. 8 g of sample were placed in Petri dishes (9 cm diameter × 1.5 cm height) and color was recorded using the CIELab uniform color space at room temperature. Color determined by CIE (Commission Internationale l'Eclairage) classifies color in three dimensions; L^*, brightness, a^*, red to green color and b^*, yellow to blue color. Chroma (c^*) and hue (h^*) were also measured with spectrodensitometer. The results were expressed in accordance with the CIELAB system with reference to illuminant D65 and with a visual angle of 0° (Cortés, Esteve, & Frígola, 2008). The measurements were made in triplicate.

2.4. Browning index (BI)

Non-enzymatic browning index was determined with an absorbance measure at 420 nm (Meydav, Saguy, & Kopelman, 1977) with some modifications. Approximately 1.5 g of sample was added to 7 ml of deionized water and centrifuged at 4500 rpm during 10 min at room temperature, this process is repeated twice. The supernatants were clarified with 1500 μL of Carrez I [15% potassium ferrocyanide (w/v)] and 1500 μL of Carrez II [30% zinc acetate (w/v)] and water was added to make the final volume 25 ml. After filtering the mixture, the absorbance is measured at 420 nm. The extracts were made in triplicate.

2.5. Hydroxymethylfurfural (HMF) and furfural determination

Furanic compounds were determined in the obtained extracts for browning index, following a method described by Contreras-Calderón, Guerra-Hernández, and García-Villanova (2009) with some modifications. The supernatants were filtered through a 0.45 μm filter and the samples were then analyzed with a Shimadzu HPLC system equipped with a LC-20 AD pump, a SIL-20A HT autosampler, and a SPD-M20A diode-array detector. 20 μL of filtered solution were separated in a reversed-phase C_{18} column (LiChroCART 250-4 LiChrospher 100, 250 × 4.0 mm, 5 μm, Merck). HMF (between 0.01 and 120 mg/L) and furfural (between 0.01 and 3 mg/L) were quantified using the external standard method.

2.6. Statistical analysis

Multivariate statistics (including principal component analyses (PCA) and cluster analyses (CA)) were employed to quantitatively investigate relationships among the 58 samples of coffee with respect to the 9 indicators (3 related to antioxidant capacity and 6 related to non-enzymatic browning), variables were standardized before the analysis and principal components with