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Non enzymatic browning during cocoa roasting as affected by processing time and temperature

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ABSTRACT

Non enzymatic browning (NEB) kinetics were studied at 125, 135 and 145 °C during a cocoa beans roasting process aimed to reach a final moisture content of 2 g 100 g^{-1}.

Colour lightness and hue angle decreased with roasting time following a first and a zero order kinetic, respectively. Moisture content being equal, high temperature-short time (HTST) roasting processes minimized the extent of browning reaction.

Melanoidins increased with roasting time following an asymptotic kinetic. Moisture content being equal, HTST processes maximized the melanoidins formation. The energy of activation of melanoidin formation (132 kJ mol^{-1}) was higher than those of colour changes and polyphenol oxidation (between 60 and 80 kJ mol^{-1}), thus NEB during roasting is not solely dependent on Maillard reaction occurrence. Hydroxymethylfurfural (HMF) increased exponentially with roasting time but its final content was low (0.1–0.8 g kg^{-1}). HTST processes minimized the HMF formation, which was not temperature dependent and was influenced by concentration.

1. Introduction

Cocoa, which is derived from the bean of *Theobroma cacao*, is the basic raw material for the production of chocolate. Cocoa and chocolate have recently gained much attention due to their potential beneficial in human health (Corti et al., 2009; Andújar et al., 2012).

To obtain cocoa powders, the cocoa bean must be subjected to a multiphasic post-harvest process during which it can be traded into industrial products having different colour and content of bioactive compounds depending on the fermentation, alkalinization and roasting process (Misnawi Jinap et al., 2003; Di Mattia et al., 2011; Krysiak et al., 2013).

Roasting is the most important technological operation in processing of cocoa beans (Krysiak, 2006, 2011) since it brings about formation of characteristic brown colour, mild aroma and texture of roasted beans. The literature reviews suggest that these features should be studied taking into account the general impact of process parameters such as time and temperature (Jinap et al., 1998; Krysiak et al., 2013). In fact, the degree of cocoa roasting is time-temperature dependent, with roasting times which can vary from 5 to 120 min and temperature of whole beans can typically vary from 120 to 150 °C (Krysiak, 2006, Krysiak et al., 2013).

During heat treatment, non-enzymatic browning (NEB) is retained to develop through the Maillard reaction (MR) pathways (Jinap et al., 1998) but NEB reaction involves not only reducing sugar and amino acids but also carbonyl compounds of organic acids or resulting from lipid oxidation (Hidalgo and Zamora, 2000; Piva et al., 2008). Moreover, brown coloured polymeric proanthocyanidins resulting from oxidation reactions are formed during cocoa processing (Misnawi Jinap et al., 2003) and also during roasting (Ioannone et al., 2015) and could take part to browning.

The final products of the MR, which include high molecular weight melanoidins, are responsible for colour formation and involved in sensory properties (i.e. taste, flavour and texture) of foods (Morales et al., 2012). Melanoidins show remarkable antioxidant activity (Manzocco et al., 2001; Yilmaz and Toledo, 2005) and recent studies showed that the reducing and radical scavenging

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Nomenclature

t	time (min)
M_0	initial moisture content (g g_{dw}^{-1})
M_t	moisture at time *t* (g g_{dw}^{-1})
M_E	moisture at equilibrium (g g_{dw}^{-1})
D_{eff}	effective diffusivity (m^2 s^{-1})
r	average radius (m)
α	shape factor of the Weibull equation (dimensionless)
β	rate factor of the Weibull equation (min)
L_0	initial lightness (adimensional)
k_L	rate constant of lightness loss (min^{-1})
$h°_0$	initial hue angle (180 rad π^{-1})
k_h	rate constant of hue angle decrease (180 rad π^{-1} min^{-1})
C_0	initial concentration (mol g_{dw}^{-1})
C_t	concentration at time *t* (mol g_{dw}^{-1})
C_E	concentration at equilibrium (mol g_{dw}^{-1})
k_{im}	initial rate of melanoidin formation (mol g_{dw}^{-1} min^{-1})
k_{0HMF}	pre-exponential factor of HMF formation kinetic (mol g_{dw}^{-1})
k_{HMF}	rate constant of HMF formation (min^{-1})
K_0	pre-exponential factor of Arrhenius equation (min^{-1})
Ea	activation energy (J mol^{-1})
R	universal gas constant (J mol^{-1} K^{-1})
T	inner temperature of the roasting chamber (K)
t_{50}	time to reach the 50% of final increase/decrease of a process (min)

activity of cocoa increased upon roasting due to the formation of Maillard reaction products (Summa et al., 2008; Ioannone et al., 2015) and that melanoidins contribute to the antioxidant activity of cocoa products (Di Mattia et al., 2014).

During roasting process, furans, small cyclic ethers conferring flavour to chocolate, can be formed (Crews and Castle, 2007). Furans and, in particular, 5-(hydroxymethyl)furan-2-carbaldehyde or 5-hydroxymethylfurfural (HMF) have widely been used as marker compounds in foods and beverages to monitor heat-treatment processes (Murkovic and Bornik, 2007). HMF, which is formed in the Maillard reaction (Nursten, 2005; Agila and Barringer, 2012), has been used as a marker of Maillard reaction in roasted products (Murkovic and Bornik, 2007; Oliviero et al., 2009). However, HMF is not solely formed through the MR pathways but the thermal degradation of sugars is also responsible for its formation (Kroh, 1994; Cämmerer et al., 1999; Shinoda et al., 2005; Piva et al., 2008; Murkovic and Bornik, 2007). The International Agency for Research on Cancer classifies furans as "possibly carcinogenic to humans" (IARC, 1995), and, eventhough HMF is cytotoxic only at high concentrations, experimental results on the metabolic activation of HMF show a genotoxic potential of this compound (Glatt and Sommer, 2006; Capuano and Fogliano, 2011).

If furanic compounds, and HMF especially, are supposed to have negative effects on human health, the compounds formed in the last phases of MR, such as melanoidins, are gaining attention due to their health beneficial properties (Somoza, 2005; Morales et al., 2012; Moreira et al., 2012). Thus, aim of this work was to study the thermal dependence of the most important physical and chemical changes induced by NEB during the cocoa roasting process and, in particular, the formation of bioactive compounds, such as melanoidins and furans. This, in order to identify the processing conditions that permit to maximize the formation of melanoidins and to minimize that of HMF.

2. Materials and methods

2.1. Materials

Fermented and dried cocoa (*Theobroma cacao* L.) beans (cv. Criollo) were purchased from the Peruvian company "Cacaotera" in Rome (Italy). The initial batch consisted of 10 kg of cocoa from the same lot. Two aliquots of 35 g (replicates) were taken and maintained for both control samples and samples to be further processed at each time-temperature combination. The beans of each aliquot were intact, healthy and of homogeneous size.

2.2. Roasting process

Cocoa beans were subjected to roasting at three selected temperatures (125, 135 and 145 °C) for increasing times until they reached about 1.8 g 100 $g_{f.w.}^{-1}$ moisture content.

The roasting process was carried out in a ventilated electric oven model Air-o-steam COMBI 6 GN 1/1, (Electrolux, Stockholm, Sweden) by keeping air flow rate (1 m s^{-1}) and relative humidity (1, 0.8 and 0.6% at 125, 135 and 145 °C respectively) constant. Approximately 35 g of cocoa beans with uniform size were placed in single layer on an aluminium plate and inserted in the pre-heated oven. Due to the heat capacity of the oven, the set temperature decreased only 4 °C upon product loading and was re-stabilized after 40 s, thus the roasting temperature could be considered constant over processing. The whole portion of roasted cocoa were taken off the oven after determined time limits and brought to ambient temperature (20 ± 2 °C) before analysis. The roasting process was carried out at least in duplicate.

2.3. Physical analyses

2.3.1. Weight and radius determination

The weight of all cocoa samples was determined using a technical balance (±0.01 g).

The principal axes of cocoa beans were measured by means of a digital caliper (Mytutoyo, Aurora, IL) on 50 randomly sampled cocoa beans and the equivalent radius of a sphere (mm) was determined according to Ndukwu et al. (2012).

2.3.2. Moisture and water activity determination

Samples were ground in a coffee mill (Super Junior "S", Moulinex, Paris, F) to obtain a mean particle size lower than 500 μm prior to analysis.

Moisture content of cocoa samples was determined gravimetrically by a moisture analyser (Sartorius MA150, Goettingen, Germany) according to Di Mattia et al. (2013).

Water activity was measured by an Aqualab (Decagon Devices, Pullman,WA) dew point hygrometer.

2.3.3. Colour analysis

Reflectance analyses were carried out by a Minolta (Tokyo, Japan) CM-500 spectrophotometer using the CIE D_{65} illuminant and 10° standard observer conditions (CIE, 1986). Before analysis, the instrument was calibrated on a white standard. Measurements were carried out in the SCI (specular component included)