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Design cocoa processing towards healthy cocoa products: The role of phenolics and melanoidins

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ABSTRACT

Roasting and fermentation are key steps in cocoa processing that can be modulated to optimize the presence of health-promoting compounds in the final product. Roasting promote melanoidins formation and polyphenols depolymerization. Results of Forastero and Criollo cocoa beans were processed in different conditions showed that higher fat content and high phenolic content could promote melanoidins formation. Forastero variety had the highest melanoidins and phenols concentration under severe roasting conditions. More severe thermal treatment decreased the concentration of total phenolic compounds and proanthocyanidins in both varieties and also influenced the flavan-3-ols profile. The antioxidant activity determined using DPPH Quencher assay was the highest in Forastero fractions above 20 kDa obtained under severe roasting condition; thus supporting the idea that melanoidins play a major role in roasted cocoa antioxidant activity. It can be concluded that a proper design of roasting process and the adequate selection of cocoa variety can optimize the cocoa health potential; especially melanoidins and phenolic compounds.

1. Introduction

Many products can be made with cocoa beans (*Theobroma cacao* L.) from a chocolate bar to soaps, which explains why this crop has acquired great economic importance worldwide. There are approximately 50 million people in the world population who depend economically on cocoa (seeds) harvest and derived products production as consumption (Foundation, 2010) (Kongor, et al., 2016). Nowadays, the global demand of cocoa beans is covered mostly by three varieties. Forastero variety trees which are resistant to diseases and pest attacks and provide cocoa beans classified as precursors of ordinary and "basic" notes; it is the primary raw material used in 80% of world chocolate production. Criollo cocoa variety from which only 5–10% of chocolate is made produces more aromatic and floral notes than other varieties. Its seeds are less bitter and smoother than Forastero beans and so highly prized (Aprotosoaie, Luca & Miron, 2016) and finally, Trinitario cocoa variety a hybrid resulting from cross-pollination between Criollo and Forastero varieties is used in about 10–15% of chocolate production and it produces some wine flavor notes (Kongor et al., 2016; Rusconi & Conti, 2010). However, the importance of cocoa beans is growing in modern culture because of its economic value and the new research of the potential health benefits found in its chemical compounds (De Araujo et al., 2016). Epidemiological studies indicate that cocoa has a cardioprotective effect and immune-modulatory power. *In vitro* studies have shown that cocoa exert anti-tumor and anti-inflammatory effects and clinical evidence suggests cocoa consumption can affect gut microbiota as a prebiotic and regulates mood, brain responses and improves cognitive function in elderly people (Castell, Pérez-Cano, & Bisson, 2013; De Araujo, et al., 2016). The basis of these health-promoting effects relies on polyphenols (flavanols, procyanidins and anthocyanins), which are potent antioxidant molecules that can attenuate some inflammatory processes (Castell et al., 2013). Nevertheless, the chemical phenolic composition is affected by the cocoa variety as well as climatic conditions and bean-growing region (Oracz, Zyzelewicz, & Nebesny, 2015). It has been reported that Criollo cocoa beans possesses only two-third of the total phenolic concentration that Forastero beans contains mainly that fact is attributed to anthocyani(di)ns absence (Afoakwa, 2014).

Although the cocoa variety determines the initial phenolic content on the beans, the post-harvest process (fermentation and roasting) and its parameters; which are aimed to guarantee high quality flavor and taste modify the phenolic profile in the processed products; affecting its functional properties (Kongor et al., 2016). Fermentation is the critical point in cocoa processing, which properly applied and controlled

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generates aroma precursors or substrates (peptides and amino acids) required to produce the characteristic flavour and taste of chocolate (Aprotosoaie et al., 2016; Oracz et al., 2015). On the other hand, its application can decrease up to 50% of total phenolic content principally by the degradation of flavan-3-ols, procyanidins and anthocyanins compounds because of enzymatic oxidation (Oracz et al., 2015).

However, polyphenols are not the only compounds from cocoa beans that could have a beneficial effect on the human health. Many bioactive compounds are present in the bean and many others are formed during cocoa roasting. In the roasting process several compounds in the raw cocoa and the precursors formed during fermentation interact each other producing the non-enzymatic browning which develops through the Maillard reaction (MR) important products that contribute to the mild aroma and intense brown color of the bean (Aprotosoaie et al., 2016). The main MR brown products (MRPs) formed during cocoa roasting are the heterogeneous high molecular weight polymer named “melanoidins” (Oliviero, Capuano, Cämmerer, & Fogliano, 2009; Summa et al., 2008). Water-soluble melanoidins have been mostly characterized and studied, due to recent findings on their functional properties using *in vitro and in vivo* models (antimicrobial, prebiotic, antihypertensive activity, anti-adhesive, metal-chelating and antioxidant capacity) (Mesías & Delgado-Andrade, 2017; Morales, Somoza & Fogliano, 2012; Moreira, Nunes, Domingues, & Coimbra, 2012). The knowledge about its chemical and functional properties has been mainly achieved studying those formed in coffee and still a field not very explored in cocoa; where it is unknown if cocoa variety plays an important role in its synthesis (Bellesia & Tagliazucchi, 2014; Pastoriza & Rufián-Henares, 2014; Sacchetti et al., 2016; Summa et al., 2008).

The complexity of chemical processes in melanoidins transformation implies very variable and rarely comparable and reproducible results from one research to another, limiting their understanding. So, some research groups have focused on creating models under controlled factors that allow melanoidins to be obtained in a less complex way than those that are extracted directly from food products (Mesías & Delgado-Andrade, 2017). Nevertheless, the central idea that could benefit in a better way the quality of life of the world population is that these bioactive compounds could be consumed in the daily diet.

There are no studies investigating the possibility of preserve a higher phenolics amount as well as obtain melanoidins induced by roasting of different cocoa beans varieties. Additionally, studies on unfermented cocoa processing to obtain polyphenol-rich cocoa products are scarce (Schinella et al., 2010; Hühn, 2017). Thus, most of the cocoa derived products on the actual market offer a high expectation of sensory attributes (color and flavor) but poor quality as a functional food.

Therefore, the objective of this research was to compare the cocoa variety effect (Criollo and Forastero) of unfermented beans on bioactive compounds (phenolics and melanoidins) profile after undergoing different roasting parameters (temperature and water-weight loss), evaluating their antioxidant capacity by implementing a 2^2 factorial design.

2. Materials and methods

2.1. Materials

One kilogram per variety of unfermented, dried cocoa (*Theobroma cacao* L.) beans (Criollo and Forastero) were provided by the Mexican company “CACEP” from Villahermosa, Tabasco (Mexico). Reagents of analytical grade were purchased from Sigma–Aldrich (Germany) and Merck (Germany). (+)-Catechin, (−)-epicatechin, procyanidin B1, procyanidin B2 and 5-Hydroxymethylfurfural as standards and acetonitrile and methanol, as solvents for HPLC analysis were obtained from Sigma-Aldrich (USA).

Table 1
Complete 2^2 factorial design. Experimental values and coded levels employed for the roasting process of Forastero and Criollo cocoa beans.

Run	Coded variables		Decoded variables	
	x_1	x_2	Roasting temperature (°C), x_1	Weight loss (%), x_2
1	−1	−1	130.0	7.5
2	−1	+1	130.0	12.5
3	+1	−1	150.0	7.5
4	+1	+1	150.0	12.5

Temperature levels: (−1) 130 °C, (+1) 150 °C; Weight Loss levels: (−1) 7.5%, (+1) 150 °C.

2.2. Experimental roasting design

The dried cocoa beans were hand-peeled and placed in trays in amounts of 200 g per roasting treatment. A convection oven (HBG76S651E, Bosch, Munich, Germany) was used on a specific temperature (130 °C/150 °C) for different times in order to reach the weight loss percentage set by the experimental design reported in Table 1. During roasting the beans were removed from the oven every 30 min to measure their weight loss and their final moisture content was between 2 and 5%.

2.3. Defatting of cocoa

Unroasted and roasted cocoa beans were crushed with a pestle and mortar to obtain small pieces known as nibs. The nibs were ground at room temperature for 3 min at 17,000 rpm (MC300, Moulinex, China). The fine powder was defatted by maceration at 30–40 °C with petroleum ether (1:2 ratio p/v) for 2 h and centrifuged at 3000 rpm for 15 min at 4 °C (Heraeus Multifuge X3R, ThermoScientific, Germany). The supernatant was discarded after placed it at 5 °C overnight, the process was repeated two times. The resulting defatted cocoa powders were air dried at room temperature overnight and fat content were calculated by subtracting final net weight from non-defatted cocoa.

2.4. Sugar determination

According to the method of Matsuura-Endo (2004) with minor modifications, defatted cocoa samples (500 mg) were sieved (0.2 mm Kitchen sieve) to ensure the homogeneity and extracted in a 50 mL Greiner capped centrifuge tube by 25 mL of deionised water. Extraction of sugars was achieved by heating the tubes at 60 °C for 15 min, tubes being hand shacked every 5 min. Colloidal material present in the aqueous extract was precipitated by adding 0.5 mL of Carrez I solution plus 0.5 mL of Carrez II solution. The solution was then centrifuged to separate the pellet and filtered (0.25 μm). All the filtered supernatant was transferred into a 50 mL volumetric flask and filled up with water till the mark. Carbohydrates were determined by HPLC (Thermo Surveyor LC, San José California, USA) using a Grace prevail carbohydrate ES column (5 μm, 250 mm × ID 4.6 mm) and a ELSD polymerlabs detector (Evaporation temperature 90 °C, Nebulizer temp. 50 °C, N_2 gas flow 1.6 slm). Elution was achieved isocratically by a mobile phase made up 75% deionized water and 25% ACN. Standard calibration curves of sucrose, glucose and fructose were prepared (0.25, 0.50, 0.75, 1.0, 1.5 and 2.0 mM; $r^2 = 0.998$; $r^2 = 0.998$; $r^2 = 0.998$) and used for quantitative analysis. Results were expressed in g/Kg of cocoa beans (w/w).

2.5. pH measurements

The pH was determined according to Sacchetti et al. (2016). with some modifications. One gram of ground defatted cocoa were