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Effect of different conching processes on procyanidin content and antioxidant properties of chocolate

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ABSTRACT

The effect of two conching processes, namely Long Time Conching (LTC) and Short Time Conching (STC), on the content of bioactive compounds and on their activity in chocolate was investigated. The dark chocolates so produced were extracted with both organic solvent and water to investigate the content and different contribution of procyanidins, water-soluble phenolic and melanoidin fractions to the overall antioxidant activity. The procyanidin content and pattern were deeply affected by the different processing conditions: after conching the STC-samples presented a higher amount of monomers compared to the LTC-ones which, in turn, resulted more polymerized as confirmed by the presence of P10 polymers.
Both STC- and LTC-products presented comparable phenolic content and FRAP values but products collected at the different conching steps, and in particular during LTC, showed a significant improvement of the radical scavenging properties ($TEAC_{PROC}$). The aqueous extract showed a lower antioxidant activity compared to $TEAC_{PROC}$. Based on the analysis of the melanoidin fraction, no further development of Maillard reaction occurred as a consequence of conching.

1. Introduction

Chocolate is a highly processed product of cocoa which is known to be rich in flavonoids, compounds which have long been associated to both the healthy and sensory properties of cocoa derived products. Flavan-3-ols, the most abundant flavonoids in cocoa, comprise the monomeric (−)-epicatechin and (+)-catechin and their oligomeric and polymeric forms, procyanidins. These compounds are being actively studied in several food matrices because of their relevant biological properties and beneficial effects on cardiovascular disease (Schroeter et al., 2006), blood pressure (Flammer et al., 2007; Murphy et al., 2003; Taubert, Roesen, Lehmann, Jung, & Schömig, 2007), platelet functions as well as diabetes, plasma LDL and HDL cholesterol (Baba et al., 2007). However, when present at high concentration, they can cause bitterness and astringency (Serra Bonvehì & Ventura Coll, 1997) which are well known for eliciting negative consumer reactions. In particular, flavan-3-ols monomers are considered to impart bitterness whilst astringency is more dependent on oligomers and polymer content.

Nowadays there is a growing awareness of consumers about the potential health benefits related to the consumption of flavan-3-ols-rich foods, and thus a balanced content of these compounds in the final product is desired along with the aroma and sensory properties which represent determinants for product quality and consumer choice.

Several studies have been devoted to the evaluation of polyphenol modification as a consequence of both oxidation and epimerization phenomena during cocoa processing (Andres-Lacueva et al., 2008; Arlorio et al., 2008; Caligiani, Cirlini, Palla, Ravaglia, & Arlorio, 2007; Cooper et al., 2007; Di Mattia et al., 2013; Mazor Jolic, Redovnikovic, Markovic, Sipusic, & Delonga, 2011, Payne, Hurst, Miller, Rank, & Stuart, 2010; Suazo, Davidov-Pardo, & Arozarena, 2014). As occurs in other plant-derived foods, the phenolic content of products made of cocoa is largely dependent upon several factors including both the raw material quality (cultivar, origin, agricultural and post-harvest practices) and formulation as well the technological parameters adopted during processing (Jalil & Ismail, 2008; Wollgast & Anklam, 2000).

Cocoa transformation consists of a multi-step process that, starting from cocoa beans fermentation, includes in sequence drying, roasting, nib-grinding and refining, conching and tempering. Conching is the unit operation based on the agitation of chocolate mass at high temperatures (above 50 °C) and it is an essential step for the development of the proper viscosity and the attainment of the final texture and flavour (Afoakwaa, Patersona, & Fowler, 2007; Beckett, 2008). It is usually a two-step process which takes place in the same equipment where the first step aims to decrease moisture content, drive out undesirable volatile residues from fermentation and coat all the solid particle surfaces with fat. In the second step, more fat and emulsifiers are added to obtain a liquid homogenized paste. Different time/temperature combinations

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are selected according to the final product to be manufactured: in dark chocolates temperatures ranging from 70 to 90 °C can be used; variation in conching time/temperature combinations obviously modifies viscosity, final texture and flavour of chocolate (Konar, 2013; Owusu, Petersen, & Heimdal, 2012, 2013). The choice of the time/temperature combination is one of the most important process parameters and can be often used in order to modulate and increase the functional properties of some foods, such as coffee and cooked must (Mrkić, Cocci, Dalla Rosa, & Sacchetti, 2006; Sacchetti, Di Mattia, Pittia, & Mastrocola, 2009).

Among the different steps of cocoa processing, little attention has been paid to conching and on its effect on polyphenol content and antioxidant properties. Robinson, Ranalli, and Phillips (1961) observed stereochemical changes in (−)-epicatechin as a consequence of conching but no effect on its concentration whilst Bordin Schumacher et al. (2009) observed a not significant reduction of total polyphenol content upon conching time. Sulistyowati and Misnawi (2008) reported that the antioxidant activity and the polyphenol concentration of chocolates were significantly reduced by the combined effect of high alkaline concentration and conching temperature. However, only combined treatments were considered and no data regarding the sole conching process were presented.

Another important class of antioxidant compounds in cocoa-derived products is represented by Maillard reaction products (MRPs), compounds which are formed in food matrices containing reducing sugars and proteins as a consequence of high temperatures processing. If in literature some works can be found on the development of Maillard reactions upon roasting of cocoa beans (Owusu et al., 2012; Payne et al., 2010; Summa et al., 2006, 2008), very limited are the studies on MRPs formation during chocolate conching, and they are mainly focussed on volatile compounds evolution (Counet, Callemien, Ouwerx, & Collin, 2002; Owusu et al., 2012) without taking into account other MRPs such as melanoidin and their contribution to the antioxidant properties.

The aim of this work was thus to study the effect of two conching processes, carried out at two different time/temperature combinations, on the content of flavan-3-ols monomers and their oligomers, on the degree of polymerization and on the *in vitro* functional properties of the dark chocolates produced. Chocolates were also investigated for their water-soluble antioxidant properties, which can be considered more interesting from a nutritional viewpoint, and for the contribution of the water-soluble phenolic fractions and melanoidins to the overall antioxidant activity.

2. Materials & methods

Samples, from cocoa liquors up to the conched products, were kindly provided by Belcolade, Puratos (Groot-Bijgaarden, Belgium).

All reagents were of analytical grade (Sigma Aldrich, Steinheim, Germany).

2.1. Sample preparation and conching process

Cocoa liquor was stored in a solid state until the day before processing and then melted (45 °C, 12–15 h). Chocolate was processed in lots of 60 kg by using the following formulation: 64% cocoa mass, 33% sucrose, 2.6% cocoa butter, and 0.4% soy lecithin. Two processes, developed within the company and characterized by different time–temperature combinations, were used: a Short Time Conching (STC) and a Long Time Conching (LTC). STC consisted in a dry step at 90 °C for 6 h and then a wet step at 60 °C for 1 h. LTC was as following: a dry step at 60 °C for 6 h and a then wet step at the same conditions (60 °C, 6 h). All the other steps (refining and emulsifier addition) of the two conching processes were substantially carried out at the same conditions. The flow sheet of both STC and LTC processes is reported in Fig. 1.

Both the conching processes were carried out in a pilot plant by processing the mass (60 kg) through a—Frisse Double—Overthrow Conche, Laboratory version DUC006. Three batches were processed and aliquots

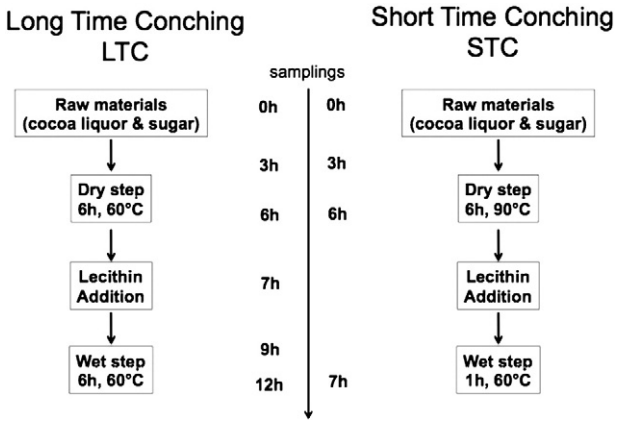

Fig. 1. Flow sheet and samplings of the two conching processes Long Time Conching (LTC) and Short Time Conching (STC) used for the production of dark chocolate.

of 200 g were sampled upon processing time: for the STC process, samplings were taken at 0 h, 3 h, 6 h and 7 h whilst for the LTC process samplings were 0 h, 3 h, 6 h, 7 h, 9 h, and 12 h.

The theoretical equivalent thermal effect (C-value) of the two chocolates was calculated as described by Sacchetti et al. (2009), considering a $T_{ref} = 100$ °C and a thermal dependence factor $z = 33$ °C as for a generic cooking process; the theoretical equivalent thermal factors resulted to be 183 min and 44 min for STC and LTC respectively.

Chocolate samples (Fig. 1) were stored at room temperature, away from light and heat, until analysis. Raw materials were processed on consecutive dates.

2.2. Sample defatting

8 g of grounded chocolate was defatted three times by extracting with 50 mL of hexane, as described by Adamson et al. (1999); each time the supernatant was discharged and the lipid-free solids were air dried.

2.3. Extraction of procyanidins

Sample extraction was carried out according to the procedure described by Gu, House, Wu, Ou, and Prior (2006) with slight modifications. 1 g of defatted material was extracted with 5 mL acetone, water and acetic acid in a ratio by volume of 70:29.5:0.5 respectively. The solids were pelletized by centrifuging for 10 min at 4000 *g* and the supernatant was filtered through cellulose filters.

This extract was used for the evaluation of the total polyphenol index, radical scavenging activities and ferric reducing properties of the procyanidin fraction. For procyanidin analysis, samples were extracted, kept at −32 °C and analysed on the same day of extraction; the extract was diluted (1:2) and submitted to a further filtration step by means of nylon filters (0.45 μm).

2.4. Extraction of water-soluble antioxidants

The extraction of the water-soluble antioxidants was carried out according to a procedure described by Summa et al. (2006) with some modifications. The defatted and powdered chocolate samples were extracted in hot water using an automatic shaker bath for 20 min at 70 °C. The ratio between cocoa powder and water was 1:8. Subsequently, the aqueous solutions were filtered through paper filters (Whatman paper no. 40 ashless filters, Maidstone, UK). The filtrate was split into three amounts, one for determination of the antiradical activity by means of the ABTS assay ($TEAC_{WSF}$) and the others for solid phase extraction and dialysis to obtain two fractions rich in water-soluble polyphenolic compounds and melanoidins, respectively. These fractions