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The influence of the roasting process conditions on the polyphenol content in cocoa beans, nibs and chocolates

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ABSTRACT

The process of roasting is a significant step in cocoa bean processing. Heating results in the formation of many advantageous features of beans, such as taste, color, texture. However, these positive changes can also be accompanied by reactions reducing the content of bioactive compounds such as polyphenols. It is therefore important to select the appropriate roasting process conditions (time, temperature, humidity and flow rate of air), as well as fineness of the beans. The article describes the research on the influence of roasting parameters (temperature, roasting time, air flow rate and relative humidity) on the kinetics of changes in the content of phenolic compounds in whole beans and in cocoa nibs of different particle size. Additonally, chocolates were obtained from cocoa liquor prepared from cocoa beans roasted as whole beans as well as from fraction of cocoa nibs of middle particle size.

LC–MS/MS analysis of phenolic compounds in the roasted beans, nibs and chocolates showed that the degradation of these compounds in beans and nibs was lower when they were roasted in air with increased relative humidity. The greatest degradation of compounds both in whole beans and nibs was observed for epicatechin and procyanidin B2, regardless of the roasting conditions applied. There were no differences as the course of degradation of polyphenolic compounds in beans and nibs, roasted under constant and non-constant process parameters. The loss of flavanols in the process of chocolate preparation was not high.

1. Introduction

The cocoa beans constitute a basic raw material used in the production of chocolate and cocoa. Both beans and obtained from them products are still a subject of scientists' interest due to its unique properties.

To obtain chocolate from cocoa beans, the beans have to undergo a complicated technological process. One very important step in this process is roasting with its primary aim to convert dry fermented beans into microbiologically clean raw material with a characteristic aroma and taste and with a proper brittleness. The convection roasting method is most commonly applied. In this method, raw cocoa beans are subjected to a forced flow of hot air. The literature indicates the thermal processing of cocoa beans in the range of temperature between 130 and 150 °C and for time between 15 and 45 min (Belitz, Grosch, & Schieberle, 2009; Krysiak, 2002, 2006; Minifie, 1999; Nebesny & Rutkowski, 1998).

To roasting can also be subjected cocoa nibs or liquor (Beckett, 2000; Fadini, Gilabert, Pezoa, & Marsaioli, 1997; Finken, 1996). The benefits of such alternative allow to roast smaller particles at a lower temperature and a more homogenous temperature profile. Such process also requires less time due to easier heat transfer through the product. This enables obtaining a product with more physico-chemical properties, which is not without significance for further processing of this raw material.

The cocoa bean is a material comprising a variety of nutritional compounds such as carbohydrates, proteins. It is also rich in biologically active compounds, such as phenolic compounds (Hammerstone, Lazarus, Mitchell, Rucker, & Schmitz, 1999; Keen, Holt, Polagruto, Wang, & Schmitz, 2002; Misnawi, Jinap, Jamilah, & Nazamid, 2004; Sanbogi, Osakabe, Natsume, Takizawa, et al., 1998; Zhu et al., 2002).

The largest group of phenolic compounds found in raw cocoa beans are flavanols, represented primarily by flavan-3-ol — catechin and flavan-3,4-diols — leucoanthocyanins (Dreosti, 2000; Hannum, Schmitz, & Keen, 2002; Zhu et al., 2002; Di Mattia et al., 2013; Oracz, Nebesny, & Żyżelewicz, 2015). The cocoa beans contain also procyanidins (condensed tannins) (Hammerstone et al., 1999; Hannum et al., 2002; Kothe, Zimmermann, & Galensa, 2013). They constitute about 60% of the total polyphenol content (Dreosti, 2000). Other phenolic compounds present in the beans include mainly flavonol — quercetin and its glycosides, flavon-isovitexin, phenols — clovamide and deoxyclovamide (Dreosti, 2000; Wollgast & Anklam, 2000).

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Another phenolic compounds in fresh cocoa beans are anthocyanins (4%), which occur most frequently as glycoside derivatives of cyanidin: cyanidin 3-*O*-galactoside and cyanidin 3-*O*-arabinoside (Wollgast & Anklam, 2000; Niemenak, Rohsius, Elwers, Omokolo Ndoumou, & Lieberei, 2006; Andres-Lacueva et al., 2008). The type and amount of phenolic compounds plays a significant role in the development of such properties of the beans and products therefrom obtained as astringency or bitterness. They also play an important role of antioxidants.

The total content of phenolic compounds is about 6–8% based on the dry matter of the bean (Dreosti, 2000; Ferrazzano, Amato, Ingenito, De Natale, & Pollio, 2009; Othman, Ismail, Ghani, & Adenan, 2007; Tomas-Barberan et al., 2007). The reason for such large differences in the content of phenolic compounds is conditioned by: varieties of cocoa beans, region of cultivation and running processes on plantations (fermentation, drying). The literature (Clapperton et al., 1994; Wollgast & Anklam, 2000; Jalil & Ismail, 2008; Nazaruddin, Seng, Hassan, & Said, 2006) reports that the richest in the phenolic compounds are cocoa beans of bulk *Forastero* variety used for mass production.

It has been shown that processes such as fermentation, drying, alkalization and roasting contribute to the degradation of phenolic compounds (Counet, Ouwerx, Rosoux, & Collin, 2004; Jorgensen, Marin, & Kennedy, 2004; Ortega et al., 2008; Schinella et al., 2010; Di Mattia et al., 2013; Albertini et al., 2015). A review of the literature indicates that changes in polyphenol content in cocoa bean during convective roasting were investigated in terms of temperature. It has been shown that with increasing heat treatment, especially above 130 °C, the level of polyphenols in cocoa beans is significantly reduced. However, only a few works (Jolic, Redovnikovic, Markovic, Sipusic, & Delonga, 2011; Kothe et al., 2013; Tamrin, Harijono, Yuwono, Estiasih, & Santoso, 2012; Zzaman, Bhat, & Yang, 2014; Ioannone et al., 2015) describe the effect of temperature and roasting time on the changes in the content of phenolic compounds in the cocoa beans.

In the literature, there is no study taking into account the effects of other highly important process parameters, such as relative humidity and air flow rate and application of modulating process parameters over time on the level of degradation of phenolic compounds. Additionally, checking the possibility to reduce the energy expenditure for running the roasting process was in mind. The demonstration that the application of modulating process parameters over time contribute to maintaining a greater stability of phenolic compounds would enable the cost reduction of the roasting process. The impact of cocoa beans particle size on the kinetics of changes of polyphenol content was also not analyzed. Among the numerous works on the impact of methods for preparation of chocolate to change the content of polyphenolic compounds can be pointed studies conducted by Di Mattia et al. (2014).

Consequently, it was considered purposeful to undertake research that would enable:

- defining the influence of roasting parameters such as temperature, roasting time, air flow rate and relative humidity on the kinetics of changes in the content of phenolic compounds in whole beans and in cocoa nibs of different particle size; and
- choice of the conditions of roasting of whole beans and cocoa nibs, which will provide chocolates products with the highest content of phenolic compounds.

2. Material and methods

2.1. Chemicals and reagents

Standards of (±)-catechin (≥99%), (−)-epicatechin (≥98%), epigallocatechin (≥90%), procyanidin B2 (≥90%), procyanidin C1 (≥75%), quercetin (≥95%), quercetin-3-O-glucoside (≥98%), quercetin-3-O-galactoside (≥97%), quercetin-3-O-arabinoside (≥95%), gallic acid (≥99%), caffeic acid (≥98%), chlorogenic acid (≥99%), acetonitrile of HPLC grade (≥99.9%), formic acid for LC–MS (~98%) were all obtained from Sigma-Aldrich (St. Louis, MO, USA). All other reagents used were of analytical grade and purchased from POCH (Gliwice, Poland). Ultrapure water was obtained from a Millipore Milli-Q Plus purification system (Bedford, MA, USA).

2.2. Materials

The raw material was a bulk variety of cocoa beans (*Forastero*) originating from Togo (Togo) and purchased from polish company "Union Chocolate" (Żychlin, Poland). Before roasting, cocoa beans were segregated in order to standardize the thermal conditions of the process. The size of the beans was maintained in the range of 20.2 to 24.0 mm.

2.3. Roasting of cocoa bean and nibs

Roasting was carried out in a convective tunnel with a possibility to regulate the process parameters (T — temperature, v — roasting air flow rate, RH — roasting air relative humidity), also during the process of heat treatment. Tunnel roaster made of stainless steel consists of pipes connected to each other in a closed circuit with adjustable degree of recirculation. Fan with a capacity of 0.13 m^3/s provides in a measuring section the air velocity in the range of 0.5–4.0 m/s and forces air circulation. The air is heated to a given temperature in the heater, and using the heater switches located on the control panel it is possible to regulate temperature in each section. The temperature is maintained at a constant level by the heater and controlled by a temperature controller. The heated air flows through a pipe with a circular cross-section to a pipe with rectangular cross-section consisting of several sections of different lengths and functions. The first section is responsible for the control of the air parameters. The next sections are used to even out the velocity profile and to determine the parameters of roasting process. The most important part of the tunnel roaster is the measuring section, in which the proper implementation and control of the heat treatment process is conducted.

The air leaving the measuring section flows to the air removing section and then through air off taking pipe into the outside. This is when air is not re-circulated. The tunnel roaster may, however, be also adapted to work when part of the air undergoes re-circulation. To reduce heat losses to the surrounding, the apparatus is covered with a layer of the insulating mat with a thickness of 5 mm. In order to eliminate the impact of vibration on the measurement section and weight readouts, a rubber connection between fan and tunnel and rubber pads under the load-bearing construction is introduced. Tunnel roaster allows also conducting the roasting process in air with increased humidity. Steam produced in steam generator is led through the main heater and valve serves for adjusting its amount. Scheme of tunnel is included in the article of Żyżelewicz, Krysiak, Budryn, Oracz and Nebesny (2014).

2.3.1. Cocoa bean

The whole cocoa beans were roasted by modulating the process parameters over the time and by keeping constant conditions for comparison.

In order to determine the changes of the concentration of cocoa beans phenolic compounds during roasting, independent roasting processes were carried out for each tested time-temperature-air flow rate-relative humidity combination, so to reflect the actual sampling of beans without changing the thermal conditions. All applied roasting process conditions are included in Table 1. Each time of ignition, 200 g of cocoa beans were unfolded in a single layer. The product mass to internal volume of roasting tunnel ratio was 0.168 kg/m^3. The beans were roasted until 2% water content (final sample).

After each roasting process, the beans were cooled to around 20 °C, dehusked and crushed.