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Temperature influences epimerization and composition of flavanol monomers, dimers and trimers during cocoa bean roasting

Lisa Kothe [a], Benno F. Zimmermann [a,b], Rudolf Galensa [a,*]

[a] Department of Nutrition and Food Sciences – Food Chemistry, University of Bonn, Endenicher Allee 11-13, 53115 Bonn, Germany
[b] Institut Prof. Dr. Georg Kurz GmbH, Eupener Straße 161, 50933 Köln, Germany

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ABSTRACT

Cocoa consumption is suggested to promote many health benefits, since cocoa is a rich source of flavanols; but amounts and profiles of flavanols depend strongly on the bean type, origin and manufacturing process. Roasting is known as a crucial step in technical treatment of cocoa, which leads to flavanol losses and modifications, especially the epimerization of (−)-epicatechin to (−)-catechin. This study monitors the influence of cocoa bean roasting on the composition of flavanol monomers to trimers, with special focus on epimerization, which was quantified for procyanidin dimers, and also observed for trimers for the first time. Five dimeric and two trimeric potential epimerization products were detected and the extent of epimerization during cocoa roasting was shown to be a function of temperature. The data also showed remarkable variations in the change of flavanol content. The quantified flavanols decreased about 50% in Java beans and increased about 30% in Ivory Coast beans, despite being roasted under equal conditions.

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1. Introduction

Cocoa (*Theobroma cacao* L. Malvaceae) contains high concentrations of various phenolic compounds, with a total polyphenolic content between 6 to 8% by weight of the dry fermented bean (Crozier, Preston, Hurst, Payne, & Mann, 2011). Consumption of cocoa products is connected with numerous positive health benefits, often related to cardiovascular effects, due to the potential of lowering blood pressure (Buijsse, Weikert, Drogan, & Bergmann, 2010), improving endothelial function (Heiss, Keen, & Kelm, 2010), inhibiting platelet aggregation (Khawaja, Gaziano, & Djoussé, 2011) and reducing inflammatory response (Monagas et al., 2009). Polyphenolic composition of cocoa is mainly dominated by flavanols (catechins and procyanidins) and thus they are held to be responsible for these effects (Tomás-Barbéran, Borges, & Crozier, 2011). This evidence arises from data which shows a strong relationship between the intake of cocoa flavanols, their resulting plasma levels, and physiological effects (Ellinger, Reusch, Stehle, & Helfrich, 2012; Schroeter et al., 2006).

The amounts of flavanols and other phenolic substances ingested with chocolates or cocoa powders differ substantially (Gu, House, Wu, Ou, & Prior, 2006). From the fresh harvested cocoa to its products, a number of processing stages are required to develop flavor or flavor precursers. Composition and amounts of polyphenols in cocoa products vary strongly with bean type, origin and especially with manufacturing processes. While unfermented cocoa presents high flavanol levels, fermenting, roasting and alkalizing led to a dramatic loss of flavanols (Wollgast & Anklam, 2000). Cocoa bean fermenting is the most critical step, which can reduce more than 90% of the initial flavanol concentrations (Elwers, Zambrano, Rohsius, & Lieberei, 2009; Kim & Keeney, 1984). Roasting of cocoa is essential for the formation of the typical chocolate aroma from the precurser compounds formed during fermentation (Arlorio et al., 2008). Time and temperature of the roasting process depends on several factors, such as cocoa material (beans, nibs or liqour roasting), final cocoa product (dark or milk chocolates) and type of cocoa (Criollo or Forastero). For cocoa beans the roasting conditions range from 15 to 45 min with temperatures from 130 to 150 °C (Krysiak, Adamski, & Żyżelewicz, 2013). Since flavanols are heat labile components, roasting results in further flavanol losses (Jolic, Redovnikovic, Markovic, Sipusic, & Delonga, 2011). Alkali treatment of cocoa powders, with the aim to reduce acidity and bitterness and to improve suspension properties, has shown to cause the lowest flavanol contents (related to nonfat cocoa solids) of all cocoa products (Gu et al., 2006).

* Corresponding author. Tel.: +49 228 733798; fax: +49 228 733757.
E-mail address: galensa@uni-bonn.de (R. Galensa).

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Structural modifications, like the epimerization of the flavanol monomers due to the roasting and alkali treatment, has been reported (Hurst et al., 2011). Unfermented cocoa seeds contain the flavan-3-ol monomer (−)-epicatechin and in much lesser concentrations (+)-catechin. The epimerization from (−)-epicatechin to (−)-catechin, and from (+)-catechin to (+)-epicatechin due to technological treatment, has often been postulated. Only a few publications confirmed this reaction by enantioseparation (Fig. 1) (Gotti, Furlanetto, Pinzauti, & Cavrini, 2006; Hurst et al., 2011; Kofink, Papagiannopoulos, & Galensa, 2007). The reaction mechanism is not fully clarified, but it is assumed that ring opening occurs on position C-2 of the oxygenated ring, and reclosing leads to the atypical enantiomers (Ellis, Yeap Foo, & Porter, 1983). High temperatures, particularly when combined with alkaline conditions, accelerate the epimerization reaction. The chiral investigation of chocolates and cocoa powders proved the presence of all four catechins (Cooper et al., 2007; Gotti et al., 2006; Kofink et al., 2007).

Human intervention studies suggest that bioavailability of the flavanol monomers in humans is influenced by stereochemical configuration (Ottaviani et al., 2011; Ritter, Zimmermann, & Galensa, 2010). In the case of catechin, the absorption of the (+)-isomer is favoured, compared to the (−)-isomer. These results were the same for catechin derived from pure reference compounds and from alkalized cocoa powder (Ritter et al., 2010). Ottaviani et al. (2011) confirmed these findings for the catechin enantiomers and additionally found a ranking in the absorption for all four catechins in the following order: (−)-epcatechin > (+)-catechin = (+)-epicatechin > (−)-catechin.

As procyanidins are composed of catechin and epicatechin units, they also contain chiral centers where epimerization could occur. Procyanidin B2 and B5 are the main flavanol dimers in cocoa (Fig. 1). These molecules present five stereocenters, two of each monomeric unit (position C-2 and C-3) and one at the interflavan bond (position C-4 of the upper unit). Changes in the stereochemical configuration are only postulated for the C-2 positions and no information exists about changes in configuration of the other stereocenters. Based on this, epimerization can take place at two positions in the procyanidin dimers, leading to three possible epimerization products per dimer (listed in Fig. 1). These epimerization products would be composed of one or two of the atypical (−)-catechin units.

Since not all the stereocenters are converted, epimerization products are diastereomers and analytical separation is possible by reversed phase chromatography, in the same way as for the procyanidins B1, B2, B5, and other epimeric dimers (Santos-Buelga, García-Viguera, & Tomás-Barberán, 2003).

Procyanidin dimers are absorbed into the blood stream (Holt et al., 2002; Ritter et al., 2010; Taubert, Roesen, Lehmann, Jung, & Schömig, 2007). As postulated for the monomers, the absorption of the dimers could be influenced by stereochemical configuration.

Thus, this study was carried out to investigate if epimerization of procyanidins occurs during cocoa bean roasting. Three cocoa bean samples (two batches from Java and one from the Ivory Coast) were roasted using the same time and temperature conditions to compare changes in content and composition. One of these cocoa beans was also roasted at different temperatures to observe flavanol alterations as a function of the temperature. Data from this study may suggest how to conduct the roasting process to preserve the natural profile of the flavanols as much as possible.

The procyanidin dimers B1, B2, B5 and further unknown dimers were investigated by mass spectrometry and quantified by UHPLC–UV. Mass traces of procyanidin B-type dimers and trimers, before and after roasting, were evaluated to investigate the epimerization reaction. The monomers were chirally separated by cyclodextrin-added capillary electrophoresis to reveal the epimerization of the catechins.

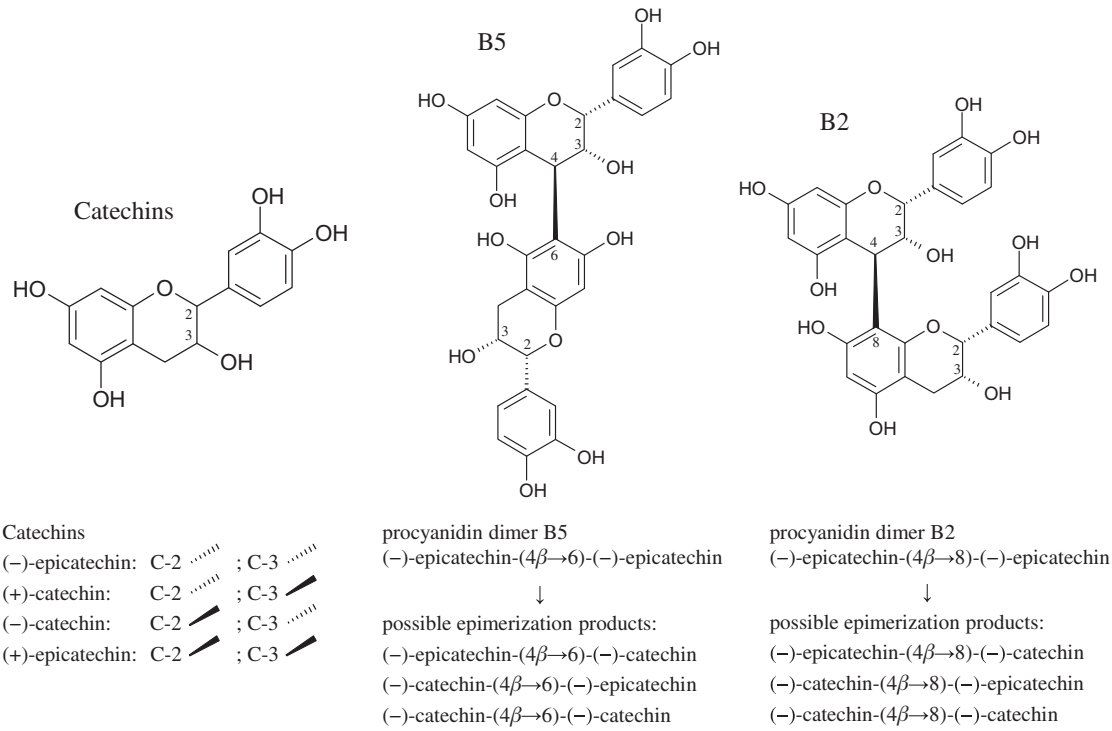

Fig. 1. Stereochemical configurations of the catechins and the main cocoa procyanidin dimers B2 and B5 with possible epimerization products listed beneath.

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