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Impact of roasting on the flavan-3-ol composition, sensory-related chemistry, and *in vitro* pancreatic lipase inhibitory activity of cocoa beans

Todd H. Stanley[a], Charlene B. Van Buiten[a], Scott A. Baker[a], Ryan J. Elias[a], Ramaswamy C. Anantheswaran[a], Joshua D. Lambert[a,b,*]

[a] Department of Food Science, The Pennsylvania State University, University Park, PA 16802, United States
[b] Center for Molecular Toxicology and Carcinogenesis, The Pennsylvania State University, University Park, PA 16802, United States

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ABSTRACT

Roasting is an important cocoa processing step, but has been reported to reduce the polyphenol content in the beans. We investigated the impact of whole-bean roasting on the polyphenol content, aroma-related chemistry, and *in vitro* pancreatic lipase (PL) inhibitory activity of cocoa under a range of roasting conditions. Total phenolics, (−)-epicatechin, and proanthocyanidin (PAC) dimer – pentamer content was reduced by roasting. By contrast, roasting at 150 °C or greater increased the levels of catechin and PAC hexamers and heptamers. These compounds have greater PL inhibitory potency. Consistent with these changes in PAC composition and this previous data, we found that roasting at 170 °C time-dependently increased PL inhibitory activity. Cocoa aroma-related compounds increased with roasting above 100 °C, whereas deleterious sensory-related compounds formed at more severe temperatures. Our results indicate that cocoa roasting can be optimized to increase the content of larger PACs and anti-PL activity, while maintaining a favorable aroma profile.

1. Introduction

Cocoa, derived from the seeds of *Theobroma cacao* L. (Malvaceae), is a rich source of polyphenolic compounds and may account 12–18% of the dry mass of the beans (Miller et al., 2009; Rusconi & Conti, 2010). These compounds include the flavan-3-ols, (−)-epicatechin (**1**), catechin (**2**), and B-type proanthocyanidins (PACs, **3–8**, Fig. 1). Laboratory and human intervention studies have reported a number of putative beneficial health effects related to consumption of cocoa or cocoa polyphenols including mitigation of inflammation, vascular dysfunction, and metabolic syndrome (Bitzer et al., 2015; Dorenkott et al., 2014; Gu, Yu, & Lambert, 2014; Monahan, 2012). Previous studies in our laboratory have shown that cocoa-derived PACs can inhibit pancreatic lipase (PL) and secreted phospholipase A_2 (PLA_2) *in vitro* (Gu, Hurst, Stuart, & Lambert, 2011). These effects correlated with prevention of fatty liver disease and mitigation of inflammation in high fat-fed mice (Dorenkott, 2014; Gu, Yu, & Lambert, 2014; Gu, Yu, Park, Harvatine, & Lambert, 2014). The inhibitory potency of the individual cocoa PACs was directly proportional to the compound's degree polymerization (DP) (Gu et al., 2011).

A limited number of studies have examined the impact of processing on the biological effects of cocoa, but available data to suggests that variation in the phytochemical composition of cocoa powders can have significant impact on the biological effect of the powder (Dorenkott et al., 2014; Gu et al., 2011). For example, we have found that polyphenol-rich extracts of alkali-treated cocoa powder had reduced PL inhibitory potency compared to extracts from unalkalized and *Lavado* (unfermented) cocoa (Gu et al., 2011). Similarly, two recent papers compared the *in vitro* inhibitory activity of roasted and unroasted cocoa, and fermented and unfermented cocoa against a panel of digestive enzymes (Ryan et al., 2017; Ryan et al., 2016). They found that both processes impacted enzyme inhibitory potency and that the effect was not simply due to measured decreases in total phenolic content. Although these studies are interesting, the results are somewhat preliminary because a limited number of samples were examined and the approach to processing was not systematic.

Roasting is an important step in cocoa bean processing and results in the production of desirable flavor and aroma compounds, as well as color changes (Beckett, 2017). In addition, roasting can act as a pasteurization step (Beckett, 2017; Copetti, Iamanaka, Pitt, & Taniwaki,

Abbreviations: Cat, catechin; CEAS, coulochem electrode array system; DP, degree of polymerization; EC, (−)-epicatechin; ECD, electrochemical detection; GC–MS, gas chromatography–mass spectrometry; MSD, mass selective detector; PAC, proanthocyanidin; PL, pancreatic lipase; SPME, solid phase microextraction; TPC, total phenolic content

* Corresponding author at: Department of Food Science, Center for Molecular Toxicology and Carcinogenesis, The Pennsylvania State University, University Park, PA 16802, United States.
E-mail address: jdl134@psu.edu (J.D. Lambert).

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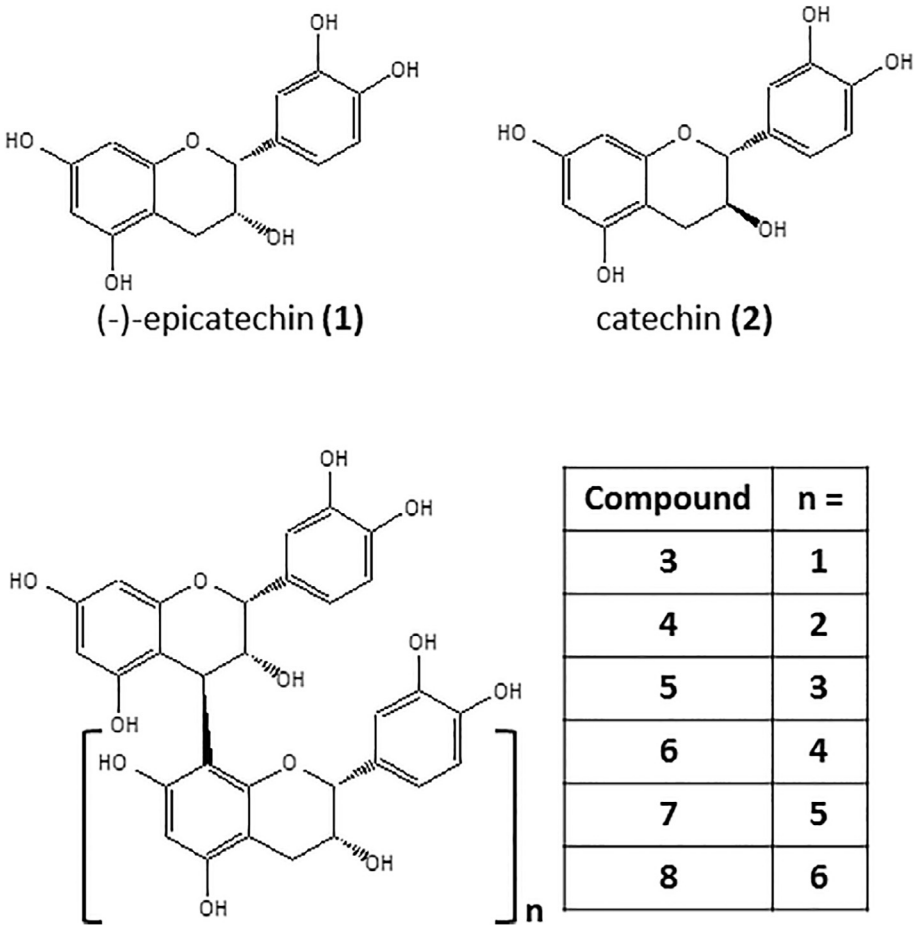

Compound	n =
3	1
4	2
5	3
6	4
7	5
8	6

Fig. 1. Structures of cocoa polyphenols under investigation.

2014; do Nascimento, Brum, Pena, Berto, & Efraim, 2012). A number of studies have examined the effects of roasting on antioxidant activity and the levels of **1–3** in cocoa (Arlorio et al., 2008; Hurst et al., 2011; Kothe, Zimmermann, & Galensa, 2013). For example, it has been reported that roasting at temperatures greater than 70 °C leads to substantial decreases in both **1** and **2** (Payne, Hurst, Miller, Rank, & Stuart, 2010). The authors also reported that roasting led to epimeric conversion of **1–2** (Payne et al., 2010). A second study by the same group reported that roasting at 163 °C for up to 25 min time-dependently reduced the levels of **1** but increased levels of **2** (Hurst et al., 2011). To date, a limited number of studies have examined the effect of roasting on PAC levels in cocoa. One study reported that roasting at 140–150 °C for 20 min reduced TPC by 14% and PAC dimer levels by 30–57% (Jolic, Redovnikovic, Markovic, Sipusic, & Delonga, 2011). More recently, the impact of roasting on PACs of higher DP was examined (Ioannone et al., 2015). These authors found that roasting at temperatures of up to 125–145 °C reduced levels of PACs in a time and temperature-dependent manner. The results of this study are interesting, but the use of a relatively narrow temperature range limits the predictive values of the results.

The goal of the present study was to examine the time-temperature impact of roasting across a wide range of roasting temperatures, including those relevant to industry and more extreme temperatures, on the TPC and flavan-3-ols (**1**, **2**) and PACs (**3–8**), as well as on the PL inhibitory potency of the resulting cocoa. In addition, we determined the effect of the same roasting conditions on a range of roasting-related volatile components to provide a "quality" context for the observed changes in polyphenol composition.

2. Materials and methods

2.1. Materials

Cocoa beans were sourced through Taza Chocolate Co. (Somerville, MA). Trinitario beans were harvested at *El Vesia* farm (*Hato Mayor* Province, Dominican Republic). Prior to shipment, beans were fermented for 5 d and dried. Beans were stored at −20 °C prior to the start of experiments. All chemicals were of the highest grade commercially-available.

2.2. Roasting conditions

Cocoa beans were selected with the following criteria: mass between 1.0 and 2.0 g, firm, not flat, and with intact shells. Cocoa beans that did not fall within these parameters were excluded in order to maintain uniformity of samples. Cocoa beans (100 g) were roasted on a fine wire mesh tray in a BD-53 Binder oven (Tuttlingen, Germany) preheated for 20 min to 100, 130, 150, 170, or 190 °C. Samples were roasted for 10, 20, 30, or 40 min. A full-factorial experimental design was employed and each treatment was repeated three times. Internal bean temperature was monitored during roasting. In brief, 15 beans were selected in each treatment, a one-millimeter hole was drilled into the center of each bean and an OMEGA Type T thermocouple (Stamford, CT) was fitted into the hole. The thermocouple was then sealed with fast-drying superglue. Internal bean temperature and oven temperature were monitored using a CR3000 data logger (Campbell Scientific, Logan, UT) with a 15 s sample rate. Upon removal from the oven, samples were immediately cooled in liquid nitrogen and beans were stored in heat-sealed polyester/polyethylene bags (ProAmpac, Cincinnati, OH) at