Changes in key aroma compounds during cocoa powder process

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Abstract

Changes of selected odorants were followed in entire cocoa powder process. Contribution of the intrinsic aroma content of fermented cocoa and the impact of individual processing steps such as preheating, alkalization, roasting and pressing on the odorant content was evaluated. The intrinsic aroma content of raw cocoa beans together with pre-heating before breaking and winnowing appeared to be the most important source of odorants in cocoa powder. Roasting and alkalization surprisingly showed low impact on *Maillard* derived odorants probably due to the depletion of precursors during preliminary processing. It was observed that the distribution of odorants after cocoa pressing is driven by the polarity of the odorant; polar odorants were predominantly retained in cocoa powder while nonpolar odorants in cocoa butter.

Introduction

Cocoa powder is the product obtained by grinding the solids remaining after cocoa butter have been pressed out of cocoa liquor. Cocoa powder has gained a significant attention in industry, not only because of its volatile price, but also because of the increasing number of its applications including confectionary, biscuits, powdered beverages, dairy, ice cream, cereals and bakery segments. Approximately half of cocoa bean production is used for manufacturing cocoa powder and cocoa butter.

Flavour character of cocoa powder originates from genotype and origin of cocoa tree, post-harvest treatments (fermentation and drying) and from the manufacturing processes such as alkalization, roasting and pressing. Twenty-four key aroma active compounds were identified in cocoa powder by a sensomics study comprising odorants formed by biosynthesis, during the fermentation and in *Maillard* reaction upon heat treatment [1]. Changes in key aroma compounds during the cocoa bean roasting [2] as well as the impact of alkalization-roasting interaction [3, 4] on the aroma content were described. Yet, there is no comprehensive study clarifying the origin of key cocoa odorants in whole cocoa powder process. Moreover, the majority of reported studies were performed under laboratory conditions that do not exactly match the conditions of the industrial process.

The objective of the study was to evaluate the contribution of the intrinsic aroma content of fermented cocoa and the impact of individual processing steps on the aroma content in cocoa powder.

Experimental

Materials

Fermented and dried cocoa beans (Ivory Coast origin) and corresponding cocoa nibs (pieces of de-shelled cocoa beans) were obtained from Nestlé La Penilla factory. Potassium carbonate was purchased from Univar (Bradford, United Kingdom). Standards of aroma compounds were purchased from Sigma-Aldrich (Buchs, Switzerland);

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isotopically labelled standards were obtained either from Aroma Lab (Planegg, Germany) or upon customized synthesis from AtlanChim Pharma (Saint Herblain, France).

Alkalization and roasting

Alkalization and roasting of cocoa nibs (14 kg batch) were conducted in the pilot plant at Bühler Barth (Germany). Alkalization was conducted with 3% potassium carbonate in CN50 alkalizer under pressure of 1.5 bar (128°C) for 30 min. The nibs were then dried under vacuum for 10 min. The roasting was conducted in RSX Tornado rotating drum roaster with convective heating under a drum pressure of -0.5 bar. The temperature was first set to 90°C and held for 15 min and then raised to 122°C and held for 10 min. At temperature of 110°C, water was injected for the purpose of debacterization. A small scale roasting was performed under ambient pressure with 1.4 kg nibs using a laboratory drum roaster (Probatino S) that operated with the same roasting profile as used during pilot plant trial.

Production of cocoa powder

Cocoa powder was produced using laboratory equipment. Cocoa nibs were ground into cocoa liquor a using planetary ball mill (Retsch PM 400 CM) and then pressed in 1/400 GSR cocoa press. The kibble cake was broken using G10S GSR breaker and finally pulverized into powder in ultra-centrifugal mill ZM200 (Retsch).

Aroma analysis

The content of fifteen odorants was determined using Head Space Solid Phase Micro Extraction in combination with Gas Chromatography and tandem Mass Spectrometry (HS-SPME-GC/MS/MS). Quantification was accomplished by Stable Isotope Dilution Assay (SIDA). HS-SPME was conducted with 50 mg cocoa sample (original or grinded) in 5 mL water and 100 µL methanol solution of internal standards using DVB-CAR-PDMS fibre of 2cm (Supelco). GC separations were achieved on column DB-624-UI 60 m x 0.25 mm i.d., and film thickness 1.4µm (J&W Scientific).

Results and discussion

There are several processes for the production of cocoa powder varying mainly in the stage where alkalization (also known as “Dutching”) is applied. Alkalization can be applied either before or after the roasting and can be performed with cocoa nibs, cocoa liquor, cocoa cake or cocoa powder. The process addressed in this study (Figure 1) is the most common one. It starts with cleaning and preheating of cocoa beans followed by breaking and winnowing that result in cocoa nibs. Cocoa nibs are alkalized and then roasted, debacterized and finally ground into cocoa liquor. The liquor is then pressed to obtain cocoa butter and cocoa cake that is further broken and pulverized into cocoa powder. Fifteen key aroma compounds were selected based on literature data [1] and their content was measured in five different stages of the process as indicated by numbers in Figure 1.

A relative contribution of intrinsic aroma of raw nibs and a contribution of two processing steps, alkalization and roasting, to the aroma content of alkalized-roasted nibs is depicted in Figure 2. The contribution of the alkalization and the roasting was assessed based on changes (increase or decrease) of odorant concentrations during these two processes.

Surprisingly, carry over from raw cocoa nibs had the highest impact on the aroma of alkalized-roasted nibs followed by alkalization and roasting. The impact of these two processing steps was rather low.

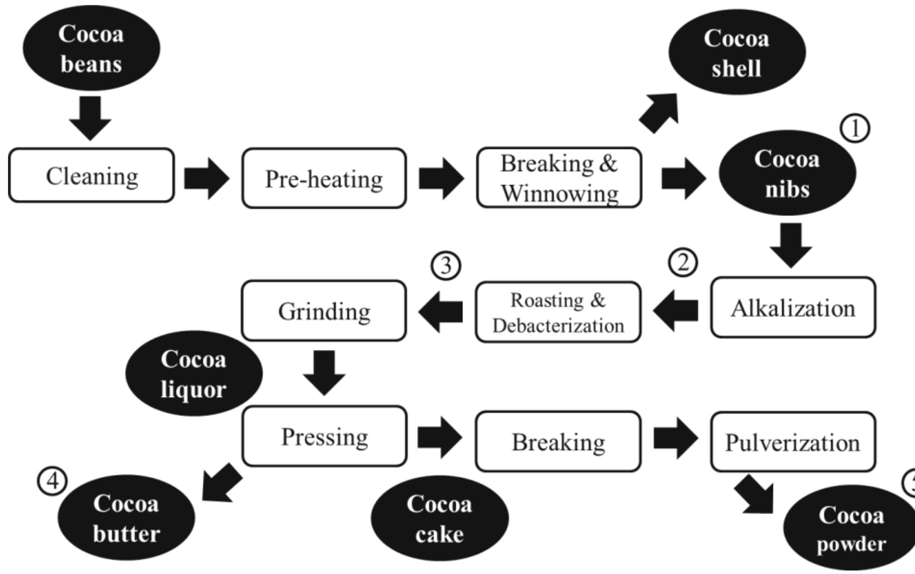

Figure 1: Cocoa powder process (numbers indicate sampling points)

Impact of alkalization on aroma content

Alkalization has traditionally several purposes: neutralize acidity, decrease bitterness, reduce astringency, modify the colour and improve dispersability of cocoa powder in beverages. Impact of alkalization on aroma compounds is not yet fully understood.

Alkalization revealed a decrease of the majority of the odorants, usually by 30% to 40% as compared to raw nibs. Amounts of 2,3-butanedione (-62%) and dimethyltrisulfide (-81%) were reduced more significantly. Surprisingly, 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone (HDMF) did not change after the alkalization. Only three odorants increased after the alkalization; phenylacetaldehyde that doubled its amounts and guaiacol and 2,3-pentanedione that increased by a factor 6. Yet, the levels of the latter two odorants were very low, thus this increase is less sensory relevant. The decrease of odorants during the alkalization process can be explained either by degradation in basic pH or by stripping of the odorants during vacuum drying applied at the end of alkalization (probably facilitated by water evaporation). It is possible that the generation of certain aroma compounds takes place during alkalisation, however it is outbalanced by the degradation or stripping.

Impact of roasting on aroma content

Roasting is considered as an important step for flavour development during cocoa processing. Several studies have shown significant increase of *Maillard* derived odorants upon cocoa roasting [2-5].

In order to evaluate changes of odorants during roasting, aroma content of alkalized nibs before and after the roasting was compared. Surprisingly, roasting of alkalized cocoa nibs had only limited and for majority of the odorants negative impact on the aroma content (Figure 2). More significant changes were detected only for 2,3-pentanedione that decreased by 63% and for dimethyltrisulfide that increased by 77% after the roasting.

Our results are in contradiction with literature data [2-4]. The reason for this could be that published data come exclusively from the trials conducted in a laboratory scale (either with a small coffee roaster or with an oven). In order to understand this phenomenon, a small scale roasting employing only 1.4 kg of alkalized cocoa nibs and a laboratory drum roaster operating with the same roasting profile as used during the pilot plant roasting was conducted. The results were indeed surprising as after small scale roasting a significant increase of many odorants was detected; especially *Maillard* derived odorants such as Strecker aldehydes, HDMF, dimethyltrisulfide and pyrazines increased by 2 to 10 folds.

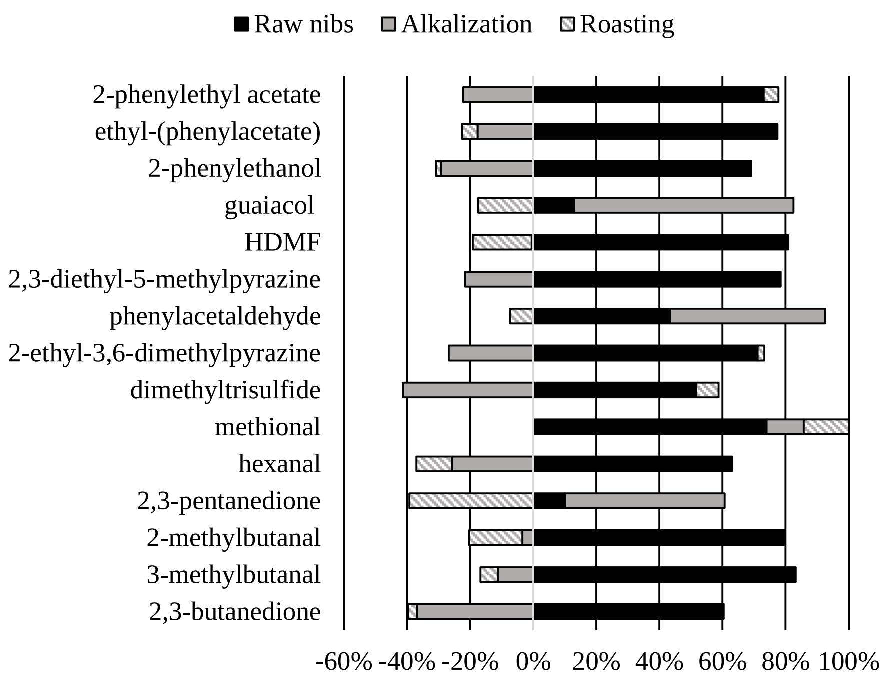

Figure 2: Origin of odorants in alkalized-roasted cocoa nibs: relative contribution of intrinsic aroma content of raw nibs and two processes alkalization and roasting

Small scale roasting also resulted in a substantial decrease of esters. Obtained results thus indicate that larger scale roasting influences the flavour development in a much lower extent as compared to small scale roasting (scale-up effect). This is likely linked to heat transfer that depends on batch size and type of heating (conductive heating in a small roaster versus convective heating in a pilot plant roaster).

Intrinsic aroma content in raw nibs

Carry over from raw cocoa nibs had by far the highest impact on the aroma of alkalized-roasted nibs (Figure 2). This finding was especially surprising for *Maillard* derived odorants whose formation typically requires higher temperatures. There are theoretically four ways how these odorants can originate in raw cocoa nibs: (i) biosynthesis in cocoa plant, (ii) fermentation, (iii) drying and (iv) preheating before breaking and winnowing. Temperature during fermentation and drying is rather low (between 25°C to 65°C), but both processes can last very long (up to eight days each), thus the formation of odorants by *Maillard* reaction cannot be excluded. In our study, the focus was put on pre-heating before breaking and winnowing as the most likely process for generation of *Maillard* odorants. During preheating cocoa beans are exposed to temperatures between 90 to 100°C for 20 to 30 min. These thermal conditions are comparable to those applied by Frauendorfer & Schieberle [2] in their roasting study. The authors reported that roasting of cocoa beans in a laboratory coffee roaster (95°C/14min) triggers significant increase of *Maillard* odorants. The highest increase was reported for phenylacetaldehyde (85 folds), HDMF (71 folds) and 3-methylbutanal (21 folds).

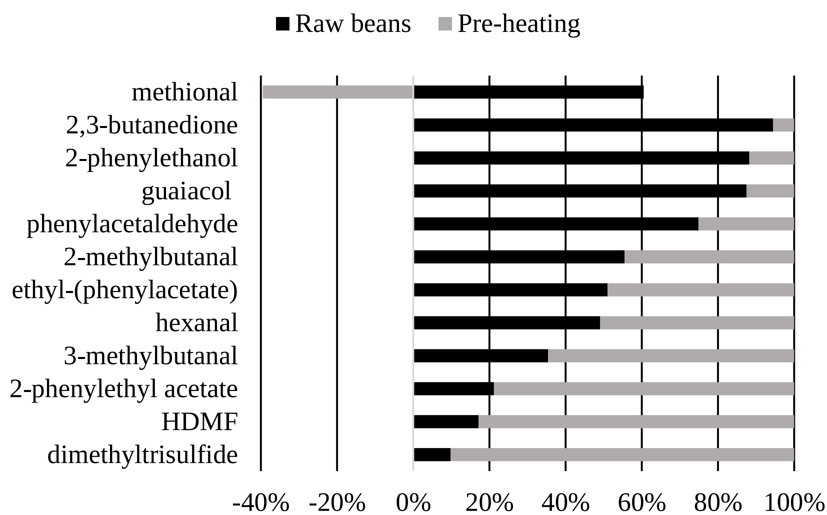

Figure 3: Origin of odorants in cocoa nibs: relative contribution of intrinsic aroma content in raw cocoa beans and pre-heating applied during breaking and winnowing

Inspired by this finding the fermented and dried cocoa beans and de-shelled cocoa nibs produced from the same batch were sampled and analysed. Aroma content in both samples was compared in order to evaluate origin of odorants in the nibs (Figure 3). The sniffing of both samples already pointed out the huge difference in aroma quality (non-heated beans possessed beany and earthy notes, while the nibs had already a strong cocoa aroma). The analytical results indeed confirmed that pre-heating applied during breaking and winnowing leads to substantial increase of the odorants, yet intrinsic aroma of raw cocoa still contributes significantly. The odorants in the nibs can be classified into those predominantly carried over from raw cocoa including 2,3-butanedione, 2-phenylethanol, but surprisingly also some Strecker aldehydes like phenylacetaldehyde and 2-methylbutanal and those that are predominantly generated during the preheating including 3-methylbutanal, 2-phenylethylacetate, HDMF and dimethyltrisulfide. Methional was the only odorant whose amount decreased during the preheating.

Distribution of odorants between cocoa powder and cocoa butter after pressing

The relative distribution of odorants between cocoa powder and cocoa butter after the pressing of cocoa liquor is depicted in Figure 4. The distribution was established from odorant concentration determined in cocoa powder and cocoa butter and mass ratio between these two products. The distribution was driven mainly by the polarity of the odorants. More polar odorants like Strecker aldehydes, diketones and HDMF were predominantly retained in the powder, while less polar odorants like esters, pyrazines, dimethyltrisulfide and hexanal were predominantly retained in butter. The distribution of the odorants after the pressing is a final step that determines the concentration ratios between the odorants and consequently flavour signatures of both cocoa powder and cocoa butter.

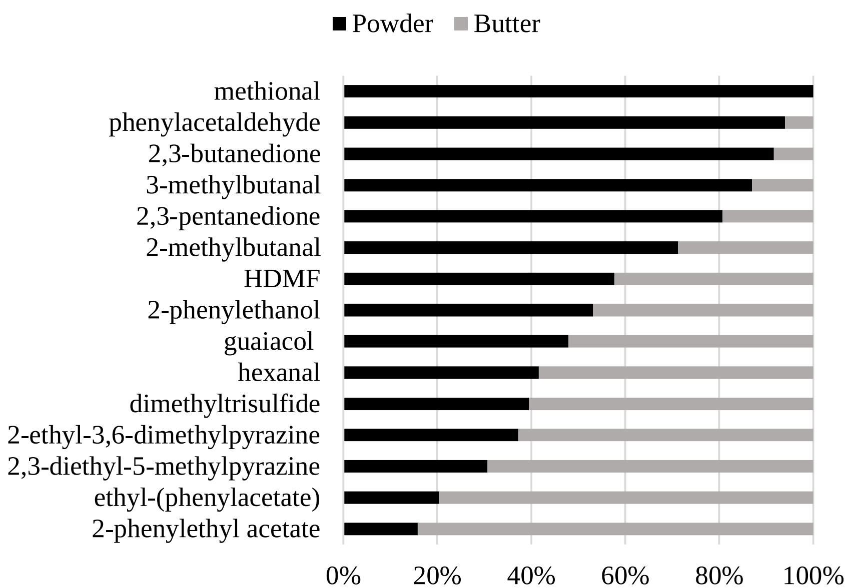

Figure 4: Relative distribution of odorants between cocoa powder and cocoa butter after pressing cocoa liquor

In conclusion, the intrinsic aroma content of raw cocoa beans together with preheating before breaking and winnowing appeared to be the most important source of odorants in cocoa powder produced from Ivory Coast cocoa. Roasting and alkalization surprisingly showed low impact on Maillard derived odorants probably due to the depletion of precursors during preliminary processing. Distribution of the odorants after cocoa pressing is driven by the polarity of the odorant. More studies are required to understand the generation of *Maillard* derived odorants during post-harvest processing such as fermentation and drying as well as the impact of cocoa origin.

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