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Inline roasting hyphenated with gas chromatography–mass spectrometry as an innovative approach for assessment of cocoa fermentation quality and aroma formation potential

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ABSTRACT

Today, the cocoa industry is in great need of faster and robust analytical techniques to objectively assess incoming cocoa quality. In this work, inline roasting hyphenated with a cooled injection system coupled to a gas chromatograph–mass spectrometer (ILR-CIS-GC–MS) has been explored for the first time to assess fermentation quality and/or overall aroma formation potential of cocoa. This innovative approach resulted in the in-situ formation of relevant cocoa aroma compounds. After comparison with data obtained by headspace solid phase micro extraction (HS-SPME-GC–MS) on conventional roasted cocoa beans, ILR-CIS-GC–MS data on unroasted cocoa beans showed similar formation trends of important cocoa aroma markers as a function of fermentation quality. The latter approach only requires small aliquots of unroasted cocoa beans, can be automatated, requires no sample preparation, needs relatively short analytical times (<1 h) and is highly reproducible.

1. Introduction

Roasting is a highly important processing step, resulting in the formation of desirable aroma and flavor properties in a wide variety of food products. Roasting induces value-added chemical and physical alterations, of which unique colour, aroma and texture are most important (Demir, Celayeta, Cronin, & Abodayeh, 2002; Ioannone et al., 2015). Additionally, roasting influences beneficial water loss, changes in the content of tannins and their transformation, alteration of bioactive compounds, the destruction of cellular structures or vegetative forms of microorganisms and spores (Żyżelewicz et al., 2014). Roasting is crucial in the processing of seeds, cocoa beans, coconuts, coffee beans, nuts, soybean, wheat, barley, green gram, hazelnuts, peanuts and sesame seeds (Youn & Chung, 2012). Next to the properties and quality of the starting material, it is mainly the temperature, time and air flow that influences the complex physical and chemical chemistry during roasting. Maillard reactions are of utmost importance during roasting, and initiate reactions between reducing sugars and amino acids. Typical Maillard reaction products include dicarbonyls (e.g., butanedione), heterocyclic compounds (e.g., pyrazines, pyrroles, pyridines, furans and thiazoles), aldehydes formed by Strecker degradation (e.g., phenylacetaldehyde), ketones, esters, alcohols and phenolic compounds (Ioannone et al., 2015). Furthermore, roasting also affects the release of volatile acids (such as acetic acid) (Afoakwa, Paterson, Fowler, & Ryan, 2008). Additionally, oxidation, condensation and complexation reactions of polyphenolic compounds occur during the roasting process (Diab, Hertz-Schünemann, Streibel, & Zimmermann, 2014).

In recent years many research papers have focused on the differences in quality of cocoa varieties, geographic origin and fermentation quality. Other studies indicated the impact of processing steps on the aroma and flavour properties of the final product. In practice however all aforementioned aspects are correlated. Indeed, the demand for high quality chocolate can only be fulfilled if interactions of both ingredient and process parameters are considered. Hue et al. (2016) described, for example, how the fermentation process of cocoa beans determines the type and concentration of cocoa flavor precursors, mainly free amino acids and peptides under proteolysis. Other factors affecting the aroma potential of unroasted cocoa are harvesting time, location and treatment after fermentation (Misnawi, Jinap, Jamilah, & Nazamid, 2004). During roasting these flavour precursors undergo Maillard reactions to develop a characteristic cocoa flavor. Differences in the fermentation quality have a significant impact on the types and concentrations of flavour and aroma compounds. Indeed, Aculey et al. (2010) described how unfermented cocoa beans did not generate cocoa flavour upon roasting. Not only the

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fermentation degree, but also the genotype and/or origin is known to result in formation of unique aroma properties after roasting. Oracz and Nebesny (2014) illustrated how the type of cocoa cultivar significantly affects the level of biogenic amines. Farah, Zaibunnisa, Misnawi, and Zainal (2012) studied the formation rate of acrylamide and pyrazines in different origin cocoa beans each roasted at 116 °C for 23 min. Papua New Guinea cocoa beans contained around 3 times more acrylamide compared to cocoa beans from Cameroon. Kothe, Zimmermann, and Galensa (2013) showed remarkable variations in the change of flavanol content during roasting of cocoa from different regions. The selection of cocoa processing parameters also has a decisive influence on the nature of chemical and physical changes in the cocoa bean (Żyżelewicz et al., 2014). Ioannone et al. (2015) described how deviations in roasting conditions significantly influence flavanol and proanthocyanidin contents and antioxidant activity. In a similar veiny, Ramli, Hassan, Said, Samsudin, and Idris (2006) measured large deviations in the aroma composition of commercial Malaysian cocoa beans that were roasted in a forced-airflow drying oven for 20 min, 30 min, 40 min and 50 min at 120 °C, 130 °C, 140 °C, 150 °C, 160 °C and 170 °C.

With the knowledge that incoming cocoa bean quality changes continuously, the cocoa processing industry is in need for a faster and automatable analytical method enabling prediction of the aroma potential of cocoa beans as a solid base to adapt and fine-tune the roasting conditions. Such an adaptation of roasting conditions, depending on the batch quality of the incoming cocoa beans, is seldom done. The degree of fermentation of incoming cocoa beans can be determined by, for example, a quantitative analysis of polyphenols. Based on measurements on cocoa beans from different treatments of fermentation namely; post-harvest pod storage, bean spreading and pressing, Nazaruddin, Seng, Hassan, and Said (2006) concluded that polyphenols could be useful indicators of fermentation quality, due to their oxidation, condensation and complexation during cocoa fermentation. Typically, the more fermented beans contain lower total content of polyphenols and/or epicatechin levels (Caligiani, Cirlini, Palla, Ravaglia, & Arlorio, 2007). Besides phenolic substances, aroma precursors formed through fermentation, i.e. free amino acids, short-chain peptides and reducing sugars, can be linked to cocoa flavour potential of cocoa beans (Afoakwa et al., 2008). Youn and Chung (2012) used response surface methodology, based on physicochemical quality indicators, to find the most optimal roasting conditions.

Despite the potential of aforementioned approaches to evaluate the fermentation quality and/or to determine optimal roasting conditions, most of them are labour and time intensive. Indeed, typically multiple small-scale roasting experiments have to be done, followed by intensive analytical work. Consequently, today the chocolate industry is in need of more simple and faster screening techniques to determine the aroma potential of cocoa beans, taking into account type, origin, fermentation and drying characteristics. As a result, increasing research attention is given to the development of such analytical techniques. Diab et al. (2014) connected a micro-probe to a photo ionization time-of-flight mass spectrometry (PI-TOFMS) to determine the volatile compounds released during the roasting of a coffee bean. In this manner the evolved compounds generated during the roasting process could be identified over the roasting period. Similar, Gloess et al. (2014) concluded that direct on-line analysis of the roasting of different coffees might give insights into the dynamics and quality of aroma formation. Wei et al. (2012) reported a hydrogen and carbon 13 nuclear magnetic resonance (NMR)-based comprehensive analysis of coffee bean extracts of different degrees of roast. Multivariate data analysis indicated that some components, such as sucrose, chlorogenic acids, quinic acids, and polysaccharides, could serve as chemical quality markers in coffee beans. The composition-based quality analysis as described by Wei et al. (2012) seems to be a promising method and suggests useful chemical markers to control and characterise the coffee-roasting process.

The aforementioned techniques however are most applicable for mechanistic studies. The goal of this work is to suggest a relatively simple, however unexplored, methodology to quantify the fermentation degree and to estimate whether the cocoa beans will produce a satisfactory level of organoleptical important cocoa aroma components (e.g., pyrazines and aldehydes) in a fast and objective manner. For the first time inline roasting hyphenated with a cooled injection system and followed by GC–MS analysis (ILR-CIS-GC–MS) is explored in the field of cocoa processing. ILR-CIS-GC–MS involves an inline controlled heat treatment of small aliquots of grounded cocoa beans during which similar reactions as occurring during traditional roasting are induced. Produced aroma products are trapped on a cooled sorbent medium. Following a standard GC–MS analysis, markers can be quantitatively measured enabling assessment of the overall potential of the cocoa beans. This work may be of great importance for the cocoa processing industry, since ILR-CIS-GC–MS will enable faster product control prior to purchase, and has the potential to become a sound basis to select optimal roasting conditions for individual cocoa batches.

2. Materials and methods

2.1. Cocoa samples

Dried and fermented cocoa beans were collected from two different origins, Ghana and Tanzania. Samples from Ghana were fermented under guidance of the University of Ghana. The collected cocoa was unfermented, or fermented in optimal circumstances for 6 days. Both fermented and unfermented Ghanaian cocoa batches were dried, packed and shipped under the same conditions. Cocoa samples from Tanzania were externally supplied. Specific information on fermentation and drying conditions for the other origins is not available, as this information was kept confidential by its suppliers. However, based on a cut-test and determination of fermentation index on these samples, the Tanzanian cocoa samples proved to be 'medium-fermented' and 'poor fermented'. The cut-test involved cutting a selection of 100 cocoa beans lengthwise through the middle, followed by an inspected under artificial light of their colour (brown to purple). For determination of fermentation index cocoa nibs were ground and 5 g were weighed and homogenized in 50 mL methanol: HCl (97:3) solution at 4 °C overnight, followed by measuring the ratio of 430 nm and 530 nm absorbance. From the moment of arrival the dried cocoa beans were manually deshelled and stored in sealed glass recipients under cooled and dark circumstances until further sample preparation and analysis.

For each batch a part was roasted separately at 150 °C for 30 min in a hot air oven (Termaks, Lien 79, N-5057 Bergen, Norway) (Tran et al., 2015).

2.2. Chemical-analytical aroma profiling of roasted cocoa beans

The volatile aroma profiles were recorded by HS-SPME-GC–MS based on methods as described in Tran et al. (2015) and Ducki, Miralles-Garcia, Zumbé, Tornero, and Storey (2008). The isolation of the volatiles released was performed in a Multi-Purpose Sampler (Gerstel, Mülheim an der Rur, Germany) equipped with an HS-SPME unit as follows: 2 g of cocoa bean were cut and blended with 3 μL internal standard undecane at a concentration of 0.36 μg μL^{-1} in hermetically sealed 20-mL vials and incubated for 10 min at