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Online measurement of volatile organic compounds released during roasting of cocoa beans

Jana Diab [a], Romy Hertz-Schünemann [a], Thorsten Streibel [a,*], Ralf Zimmermann [a,b]

[a] Joint Mass Spectrometry Centre (JMSC), University of Rostock (UR), Dr.-Lorenz Weg 1, Rostock 18059, Germany
[b] Joint Mass Spectrometry Centre (JMSC), Helmholtz Zentrum München (HMGU), German Research Center for Environmental Health (GmbH), Comprehensive Molecular Analytics (CMA), Postfach 1129, Neuherberg D-85758, Germany

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ABSTRACT

The gaseous species evolving during the roasting of cocoa beans were analyzed by a newly developed technique, a micro-probe–photo-ionization–time-of-flight mass spectrometer system. A lot of volatile roasting products and typical aroma compounds, such as methylbutanal, phenylacetaldehyde and pyrazines, could be online detected. The differences between the roast gas composition inside and outside the bean were pointed out. Two additional signals at *m/z* 266 and 294 with resonance-enhanced multi-photon ionization (REMPI), which argues for an aromatic character, and a higher methanethiol signal with single photon ionization (SPI) could have been identified at first glance for the measurements inside the bean. Principal component analysis (PCA) and difference spectra revealed and confirmed these findings. Higher concentrations of theobromine and fatty acids are present outside and more caffeine inside the bean. With both ionization techniques, the changes in the PCA are more prominent at the beginning of the roast courses, which are mostly explained by caffeine and theobromine. Following the courses of these characteristic compounds showed the same results as obtained with the PCA and revealed that caffeine is always released before theobromine. The new analytical technique proved to be a fast, reliable and non-labor intensive method, which could therefore be a practical technique for the online analysis and monitoring of the cocoa roasting process.

1. Introduction

The composition of cocoa beans is highly variable, depending on growing conditions, genetics, post-harvest fermentation, drying, and handling during shipment and storage (Afoakwa, Paterson, Fowler, & Ryan, 2008; Humston, Knowles, McShea, & Synovec, 2010). The quality and the flavor of the end product (chocolate bars, cocoa-based beverages) depend not only on this composition of the raw material but also on post-harvest treatment and on the processing conditions of these treatments (Cambrai et al., 2010; Humston et al., 2010; Owusu, Petersen, & Heimdal, 2012; Torres-Moreno, Tarrega, Costell, & Blanch, 2012).

Main compound classes in raw beans are polyphenols, specifically catechins (flavan-3-ols), proanthocyanidins and anthocyanins, which provide precursors for flavor formation. They are already present in the fresh bean and are also formed during subsequent treatment by enzymatic reactions (Afoakwa et al., 2008; Krysiak, 2006; Oliviero, Capuano, Cämmerer, & Fogliano, 2009).

Post-harvest treatment includes fermentation, drying and roasting, in which fermentation and roasting are the most important steps of the manufacturing treatment (Ramli, Hassan, Said, Samsudin, & Idris, 2006). Flavor compounds are formed during the roasting step from precursors formed during fermentation and drying such as free amino acids, short-chain peptides (provided by proteolysis of enzymes) and reducing sugars, revealing a direct relationship between these two steps (Afoakwa et al., 2008; Bailey, M., D.G., Bazinet, & Weurman, 1962; Frauendorfer & Schieberle, 2008). Important factors are the content of polyphenols, polysaccharides and proteins in the raw material. During roasting, non-enzymatic browning (Maillard reaction) takes place. Thereby, the reaction between reducing sugars and amino acids plays the major role. Typical Maillard reaction products include dicarbonyls (e.g., diacetyl), heterocyclic compounds (e.g., pyrazines, pyroles, pyridines, furans and thiazoles), aldehydes formed by Strecker degradation (e.g., phenylacetaldehyde and benzaldehyde), ketones, esters, alcohols and phenolic compounds (Bailey et al., 1962; Baltes, 1980; Cambrai et al., 2010; Frauendorfer & Schieberle, 2008).

Furthermore, acidity is reduced during roasting by release of volatile acids (such as acetic acid) (Afoakwa et al., 2008). The beans get their final texture and color due to oxidation, condensation and complexation of polyphenolic compounds (Krysiak, 2006; Oliviero et al., 2009; Vitzthum, Werkhoff, & Hubert, 1975).

Wrong handling during all manufacturing processes leads to off-flavors, for example, moisture damage leads to growth of bacteria and mold (Humston et al., 2010).

* Corresponding author.
E-mail address: thorsten.streibel@uni-rostock.de (T. Streibel).

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Most studies comprise the analysis of key flavor compounds or constituents of roasted cocoa beans or the end products, such as chocolate, by using steam or high-vacuum distillation or solvent extraction or a combination of both, to excavate the aroma and Maillard reaction compounds. The extraction or distillation is mostly followed by a gas chromatography–mass spectrometry (GC-MS) analysis or an aroma extract dilution analysis (AEDA) (Cambrai et al., 2010; Counet, Callemien, Ouwerx, & Collin, 2002; Frauendorfer & Schieberle, 2008; Gill, Macleod, & Moreau, 1984; Ramli et al., 2006; Schieberle & Pfnuer, 1999; Schnermann & Schieberle, 1997; Van Praag, Stein, & Tibbetts, 1968; Vitzthum et al., 1975; Ziegleder & Stojacic, 1988).

Since the identification of Linalool and fatty acid esters as constituents of cocoa by Bainbridge and Davies (1912), a lot of studies dealt with the identification of volatile compounds of cocoa and their products (Gill et al., 1984; Humston, Zhang, Brabeck, McShea, & Synovec, 2009; Ramli et al., 2006; Van Der Wal, Kettenes, Stoffelsma, Sipma, & Semper, 1971; Van Praag et al., 1968; Vitzthum et al., 1975). Most of these compounds, released by unroasted and roasted beans, have been identified by using solvent extraction techniques followed by gas chromatography, solid phase micro-extraction followed by comprehensive 2D gas chromatography coupled with time-of-flight mass spectrometry (SPME-GCxGC-TOFMS) and solvent extraction followed by gas chromatography coupled to mass spectrometry (SE-GC-MS) (Gill et al., 1984; Humston et al., 2009; Ramli et al., 2006). These techniques therefore helped to reveal the complexity of the aroma of roasted cocoa beans. Major compound classes are pyrazines, alcohols, aldehydes, esters, amines, acids, ketones and hydrocarbons (Afoakwa et al., 2008; Gill et al., 1984), whereby aldehydes and pyrazines are the major compounds formed during roasting and the most important contributors to the chocolate aroma (Vitzthum et al., 1975). Key flavor-active compounds are 3-methylbutanal, 2-methylbutanal, 2- and 3-methylbutanoic acid, phenylacetaldehyde, 2-ethyl-3,5-dimethylpyrazine, 1-octen-3-one, 2,3-diethyl-5-methylpyrazine, 2-nonenal, 2-methyl-3-(methyldithio)furan and 2-phenylethanol, with 2-methylbutanal and 3-methylbutanal contributing most to the chocolate character (Afoakwa et al., 2008; Frauendorfer & Schieberle, 2008; Schieberle & Pfnuer, 1999; Schnermann & Schieberle, 1997).

Since most techniques use extraction methods, such as solvent extraction, high vacuum distillation or steam distillation to extract the roast products from the bean (Vitzthum et al., 1975), the extractable products of roasted cocoa beans are well analyzed. However, a continuous real-time online monitoring of the process of cocoa roasting is not possible with such extractive off-line techniques but requires a fast analytical method with high time resolution. Such an approach could be very helpful to get a better understanding of the dynamics of flavor generation and could form the basis for future quality control measures.

Photo-ionization time-of-flight mass spectrometry (PI-TOFMS) is a potential tool for the investigation of cocoa roasting. On the one hand, photo-ionization is a very soft (almost fragment free) technique for generating ions in mass spectrometry, i.e., only molecular ions are obtained and bulk gases such as oxygen or nitrogen are not ionized, which leads to an increase in sensitivity and avoids interferences or saturation effects at the detector. In addition, depending on the actual realization of photo-ionization a certain selectivity of analyzed compounds is achievable. Resonance enhanced multi-photon ionization (REMPI), where molecules are ionized by absorption of at least two UV-photons, is very selective for aromatic and poly-aromatic compounds. Single photon ionization (SPI) employing VUV-photons, on the other hand, is more universal and suitable for a wide range of organic compounds but excluding all species with higher ionization energy than the applied wavelength. Time-of-flight mass spectrometry enables fast detection of ionized components of complex gaseous mixtures, yielding a complete mass spectrum with every ionization event.

In previous studies, PI-TOFMS has been combined with a novel sampling approach that applied a micro-probe connected to a transfer capillary leading to the ion source of the mass spectrometer (Hertz-Schünemann, Dorfner, Yeretzian, Streibel, & Zimmermann, 2013; Hertz-Schünemann, Streibel, Ehlert, & Zimmermann, 2013; Hertz, Streibel, Liu, McAdam, & Zimmermann, 2012). The tip of the micro-probe could be inserted in a single coffee bean, thus sampling the evolved compounds generated during the roasting process directly at the place of formation.

The aim of this work was to apply this experimental approach to determine the volatile compounds released during the roasting of cocoa beans. Furthermore, the roast products formed inside the cocoa bean are compared to the volatile roast products measured outside the cocoa bean.

2. Materials and methods

2.1. Roasting and sampling

The investigated cocoa beans are organic raw beans from the Dominican Republic. Fig. 1 shows a scheme of the experimental setup of the measurements. It consists of a newly designed μ-probe sampling device and a PI-TOFMS system. The μ-probe was originally designed for the analysis of cigarette smoke inside a burning cigarette (Hertz et al., 2012). It consists of a stainless steel capillary (ID 0.2 mm, OD 0.4 mm). One end sticks out (4 mm) and can be inserted into the cocoa bean, and the other end is located inside a heated aluminum base body and is connected to the transfer capillary via a capillary union. The μ-probe was now applied to the analysis of the processes inside and outside a cocoa bean during roasting. Thereby, compounds formed during the cocoa roasting process are analyzed in two different ways by means of the μ-probe sampling device. In both cases, the roasting process was simulated with a heating gun at 250 °C. For the measurements outside the bean, the bean was roasted inside a glass to avoid the dilution of the roast gases (Fig. 1a).

For the measurements inside the bean, the micro-probe was inserted directly into the bean via a 5 mm deep whole, drilled with a 1 mm drill (see Fig. 1b). The hole in the sample was sealed not vacuum tight with inorganic glue based on zirconium oxide. The temperature was controlled via a thermocouple placed on the surface of the bean. At least 5 replicates were conducted for every distinct experimental setup. The μ-probe is heated continuously via heating cartridges to avoid condensation of volatile compounds. The released compounds were transferred to the ion source of the mass spectrometer via a continuously heated transfer line (deactivated stainless steel, OD 530 μm, ID 280 μm) to avoid condensation and plugging of the capillary. To guarantee the continuous heating, the capillary is located inside a heating hose (2 m, 250 °C). The techniques of SPI and REMPI have already been described in detail elsewhere (Boesl, 2000; Butcher, 1999; Dorfner, Ferge, Yeretzian, Kettrup, & Zimmermann, 2004; Mühlberger, Zimmermann, & Kettrup, 2001); therefore, only a brief description is given in the following. The PI-TOFMS instrument is equipped with a 10 Hz Nd:YAG-laser (Continuum Inc., Santa Clara, CA, USA), which provides 335 nm and 226 nm pulses via harmonic generation for the photo-ionization. The 226 nm beam is directly used for REMPI while the 335 pulse is used to generate the 118 nm for SPI via a third harmonic generation (THG) gas cell filled with xenon. The mass spectrometer is a reflectron TOFMS (Kaesdorf Instrumente, Munich, Germany). The PI-TOFMS system has also been described in detail in the literature (Hertz et al., 2012; Hertz-Schünemann, Dorfner et al, 2013; Hertz-Schünemann, Streibel et al, 2013; Mühlberger, Hafner, Kaesdorf, Ferge, & Zimmermann, 2004; Mühlberger et al., 2001).

2.2. Principle component analysis (PCA)

PCA was applied to reveal differences between the measurements inside and outside the cocoa bean and to analyze the course of roasting. It was performed by the “Unscrambler” program (CAMO Software AS). The data sets were baseline corrected and normalized to the total ion