LWT - Food Science and Technology 159 (2022) 113198

Contents lists available at ScienceDirect

LWT

journal homepage: www.elsevier.com/locate/lwt

Flavor diversification of dark chocolate produced through microwave roasting of cocoa beans

Valérie Lemarcq[a,*], Viena Monterde[a], Emmy Tuenter[b], Davy Van de Walle[a], Luc Pieters[b], Eleni Sioriki[a,**], Koen Dewettinck[a]

[a] *Food Structure & Function Research Group (FSF), Department of Food Technology, Safety and Health, Faculty of Bioscience Engineering, Ghent University, Belgium*
[b] *Natural Products & Food Research and Analysis (NatuRA), Department of Pharmaceutical Sciences, University of Antwerp, Belgium*

ABSTRACT

The impact of microwave roasting cocoa beans on the aroma and phytochemical profile of dark chocolates (70% cocoa) was studied. Three chocolates produced from microwave roasted beans (450 W–55 min, 600 W–35 min, 900 W–20 min) were compared with a chocolate produced from convectively roasted beans (130 °C–30 min). Aroma analysis via HS-SPME-GC-MS indicated that microwave roasting of cocoa beans resulted in chocolate with a distinctive aroma profile, compared to the chocolate produced from convectively roasted beans. Increased power input seems the main inducer of elevated levels of aroma compounds. Interestingly, the impact of the four treatments on the phytochemical profile, measured via LC-HRMS, of the chocolates was rather comparable. Microwave roasting of cocoa beans was more prone to oxidation, but still within acceptable limits. The results validate that microwave roasting is a promising alternative technique that can be used effectively for chocolate production.

1. Introduction

The flavor of chocolate is the most relevant factor influencing consumers' acceptance and is determined by a combination of smell, taste, and trigeminal sensations perceived during consumption (Afoakwa, 2010). A complex interplay of intrinsic characteristics of cocoa beans, such as origin and variety, as well as postharvest practices are responsible for this unique flavor. Among these postharvest practices, roasting is an essential heat treatment for flavor development. This energy-intensive process typically requires high temperatures of approximately 120–140 °C for a duration of 10–35 min (Aprotosoaie et al., 2016). The typical cocoa flavor is mainly formed due to the Maillard reaction taking place during roasting and by which cocoa aroma compounds such as methylpyrazines and Strecker aldehydes are formed (Febrianto & Sari, 2019; Hoskin et al., 1980). Additional flavor compounds can be formed via oxidation of cocoa butter or organic molecules such as alcohols (Parker, 2015), while certain volatile molecules like acetic acid are (partially) eliminated through evaporation (Aprotosoaie et al., 2016). Moreover, bitterness and astringency of cocoa beans is generally reduced through oxidation of flavan-3-ols (Aprotosoaie et al., 2016).

In traditional drum roasters, hot air heats the outer layer of the cocoa bean via convection. The heat produced is subsequently transferred via conduction towards the beans' core (Vadivambal & Jayas, 2010). Therefore, a significant temperature gradient will exist between the surface and core of the bean (Krysiak, 2011; Ryynänen, 2002). This non-homogenous bean heating, *i.e.* over-roasting of the beans' outer parts and under-roasting of the beans' center, could result in a potential enhanced bitterness due to the extended thermal treatment that the outer bean layer experiences. Moreover this relatively time-consuming roasting process leads to the transfer of a respectable amount of cocoa butter to the outer shell which is economically disadvantageous.

Despite the widespread use of convection roasting, the above-mentioned concerns cannot be ignored and therefore investigating alternative roasting techniques is necessary in alleviating issues derived from convective heating. A different, but straightforward, technique can be applied through employing electromagnetic radiation in the form of microwaves, which have frequencies between 300 MHz and 300 GHz (Singh & Heldman, 2014). Microwave processing, although already widely used in domestic households, is gaining popularity in the industry due to the lower cost, faster heating, and a more uniform temperature within the product compared to products heated through traditional means (*i.e.* convective and conductive heat transfer mechanisms). These advantages can be attributed to ionic polarization, which occurs due to acceleration and collision of ions when placed in an electrical field, and dipole rotation, which causes friction due to

---

* Corresponding author.
** Corresponding author.
E-mail addresses: valerie.lemarcq@ugent.be (V. Lemarcq), eleni.sioriki@ugent.be (E. Sioriki).

https://doi.org/10.1016/j.lwt.2022.113198
Received 1 March 2021; Received in revised form 23 January 2022; Accepted 4 February 2022

continuous realignment of the polar molecules (Singh & Heldman, 2014). The behavior of foods exposed to microwaves largely depends on their dielectric properties, which are influenced by the amount of free water, ions, and fat present in the matrix (Teferra, 2019). Although cocoa beans have rather poor dielectric properties, they also have a low specific heat and density due to their high fat content. These properties improve their heating tendencies, and thus make them a good candidate for microwave heating (Hebbar & Rastogi, 2012).

Research concerning the effect of microwave roasting of cocoa beans regarding flavor development is rather limited. Moreover, no previous study has examined the flavor of chocolate produced from microwave roasted beans. Therefore, the goal of this research was to produce dark chocolates from Ecuadorian cocoa beans that have been subjected to different microwave roasting conditions (*i.e.* varying power input and time combination) and to subsequently investigate the effect of such roasting parameters on the flavor profile of the final dark chocolates by analyzing both volatile and non-volatile compounds produced therein.

2. Materials and methods

2.1. Cocoa bean quality and roasting procedure

Fermented and dried cocoa beans of mixed variety from Ecuador were provided by Cargill (Schiphol, The Netherlands). A bean cut test was performed by counting the amount of fully brown cotyledons in a batch of 150 cocoa beans. The fermentation index was determined as described in Rottiers et al. (2019) with a slight modification (*i.e.* homogenization of 1 min and refrigeration of 30 min). The quality of the raw beans was deemed acceptable based on the bean cut test (~70% fully brown beans) and fermentation index (0.87).

2.1.1. Convection roasting

Eight kilograms (8 kg) of raw Ecuadorian cocoa beans were convectively roasted in a drum roaster (Roaster 102, Selmi Group, Santa Vittoria d'Alba, Italy) for 30 min at 130 °C in batches of 2 kg. The beans were loaded into the roasting chamber where they were heated via an air cyclone system. After each cycle, the roasted beans were automatically dropped to the external ventilated tank where they were cooled for 5 min. Afterwards, the roasted beans were cooled further to room temperature prior winnowing.

2.1.2. Microwave roasting

An MC32K7085KT Samsung Combi Microwave oven of 32 L capacity (Samsung, Seoul, South Korea) was used for microwave roasting (MR). Preliminary trials were performed to ensure reproducibility of the microwave roasting set-up (*i.e.* dry matter contents with coefficient of variance below 20%) and to determine appropriate roasting times for each corresponding microwave power input (i.e dry matter content of 97–98% w/w).

The three selected microwave roasting conditions that met the previously mentioned criteria were: 450 W–55 min (MR1), 600 W–35 min (MR2), and 900 W–20 min (MR3). In one microwave roasting batch, approximately 900 g of cocoa beans were distributed over two glass trays, each containing a single layer cocoa beans. The central part of both trays was kept free of beans to prevent them from over-roasting. The first tray was placed at the default position in the microwave oven while the second tray, which was supported by a tripod, was placed above the first tray. Between every roasting batch, a 15-min rest period was done to cool the microwave oven chamber. In total, eleven batches of cocoa beans per microwave condition were roasted and then pooled to achieve the necessary amount for the subsequent chocolate production at Cacaolab (Desteldonk, Belgium).

2.2. Chocolate production process

The roasted cocoa beans were winnowed to separate the shells from the cocoa nibs. These final cocoa nibs were subjected to a coarse grinding and fine grinding step to produce cocoa liquor as described in Lemarcq et al. (2020). The cocoa liquors were then used to produce 70% cocoa dark chocolate on a 5 kg scale with the following composition: 30% sugar, 64.65% cocoa liquor, 5% cocoa butter (CB), and 0.35% soy lecithin. The chocolate production process consisted of mixing, refining, conching, tempering, and molding steps similar to the ones used for the production of choc 1 as described in the research paper of Hinneh et al. (2019).

2.3. Chemical characterization of roasted cocoa beans and cocoa liquor

2.3.1. Dry matter of roasted cocoa beans

Dry matter content (% w/w) of the roasted cocoa beans was determined via oven-drying according the official method AOAC 931.04 (Flanyak, 1995). During the preliminary microwave roasting trials, quintuplicate measurements were performed to check the reproducibility of the roasting method.

2.3.2. Fat content and fat oxidation degree of cocoa liquors

The total fat content of the produced cocoa liquors was measured according to the official Weibull-Soxhlet extraction method, as described in AOAC 963.15 with minor modifications (Flanyak, 1995). Prior the analysis, liquor was melted at 52 °C for 1 h to guarantee homogenous sampling. Five grams (5 g) of sample was weighed and acid digested. Afterwards, extraction with petroleum ether (Extra pure, Thermo Fisher scientific, Loughborough, UK) via a Soxhlet extraction protocol was performed. After, the extracted lipids were measured gravimetrically. The analysis was done in duplicate.

The degree of fat oxidation was determined on the fat phase of the cocoa liquors, extracted via petroleum ether. Primary and secondary fat oxidation products were estimated in triplicate via the peroxide value (PV) and *para*-anisidine value (*p*-AV), using standardized procedures of the official AOAC 956.33 and AOCS Cd 18–90 methods, respectively (Flanyak, 1995). In addition, total oxidation values (TOTOX), which are assumed to give an indication on total oxidation state, were calculated (Min & Ellefson, 2010):

$$\mathrm{TOTOX} = (2 \times \mathrm{PV}) + (p - \mathrm{AV})$$

2.4. Phytochemical and aroma profile of chocolates

2.4.1. Non-volatiles

Chocolate tablets from each treatment were cooled with liquid nitrogen, milled, and sieved (2 mm mesh). Of each chocolate, 1 g was defatted with *n*-hexane, according to the method of Tuenter et al. (2020). Next, 0.1 g of the defatted samples were extracted in triplicate, according to Lemarcq et al. (2020). The obtained extracts were 10-fold and 1000-fold diluted with methanol/40 mM ammonium formate buffer (60/40% w/w) prior to analysis. A selected set of 52 reference compounds was prepared and analyzed under the same conditions in concentrations ranging from 2 ng/mL to 1 μg/mL. An overview of these compounds can be consulted in the supplementary information S1. All samples were analyzed on an Acquity UPLC-HRMS (XEVO G2-XS QTOF MS) system, as described previously (Tuenter et al., 2020).

2.4.2. Volatiles

Semi-quantitative concentrations of aromatic volatiles present in the chocolate samples were measured in triplicate via HS-SPME-GC-MS. A

Table 1

Dry matter content (% w/w) of cocoa beans roasted under different conditions and tetramethylpyrazine/trimethylpyrazine (TMP/TrMP) ratio of the corresponding chocolates (n = 3). Conditions: convection roasted (CR: 130 °C −30 min), microwave roasted (MR1: 450 W–55 min, MR2: 600 W–35 min, MR3: 900 W–20 min).

	CR	MR1	MR2	MR3
Dry matter content (% w/w)	97.74 ± 0.11^{b}	97.43 ± 0.07^{a}	97.69 ± 0.04^{b}	97.33 ± 0.05^{a}
TMP/TrMP	2.14 ± 0.11^{a,b}	2.43 ± 0.10^{b}	2.05 ± 0.06^{a}	2.29 ± 0.01^{a,b}

Significant differences ($p < 0.05$) within one row are indicated with different superscripts (a-b), following one-way ANOVA with post-hoc tests.

similar Method described in Lemarcq et al. (2020) with some adaptations was applied. Molten chocolate (1 g) was mixed with 4-methylpyridine (1.045 μL of 0.957 mg/mL) which was used as internal standard and poured into 20 mL vials. These vials were agitated at 250 rpm and 60 °C for 10 min prior analysis. Afterwards volatiles present in the headspace of the samples were exposed to a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber. Adsorbed volatiles were subsequently desorbed at the GC inlet for 5 min at 270 °C with a split ratio (3:1) and separated on a polar DB-WAX UI column (60 m × 250 μm, 0.25 μm) (Agilent Technologies Belgium NV, Diegem, Belgium). Two different approaches were applied in order to identify the detected volatiles. Firstly, experimentally determined Kovats indices (KI_{exp}) were compared with those described in literature (KI_{lit}). Secondly, the mass spectra of each compound were compared with data reported in the NIST14 library (Agilent Technologies Belgium NV, Belgium).

2.5. Statistical analysis

All data of the physicochemical characterization of the roasted beans and cocoa liquors, with the exception of total fat content (measurements in duplicate), were statistically analyzed in SPSS 25 (IBM, New York, United States) by one-way analysis of variance (ANOVA) after checking the fulfillment of normality and homogeneity of variance assumptions. In addition, aroma compounds detected by HS-SPME-GC-MS that were above the limit of quantification (LOQ) (signal-to-noise ratio >10) were statistically analyzed via the same tool. A significance level of 0.05 was set and *post-hoc* tests were completed if significant differences were detected. If equal variances could be assumed based on the Levene test ($p > 0.05$), a Tukey test was conducted. In the other case, a Dunnett's T3 test was used as *post-hoc* test.

The data acquired from the UPLC-HRMS (non-volatile phytochemicals investigation) were processed using MassLynx V.4.1, while GraphPad Prism 8 (GraphPad Software, California, United States) was used to make the calibration curves and to perform statistical analysis (one-way ANOVA with Bonferroni *post-hoc* test). The limit of detection (LOD) and limit of quantification (LOQ) were determined for each compound, according to the "blank sample" method, as described by Mani et al. (2012).

Two bi-plots were created to visualize the potential different flavor profiles of the chocolate samples. All measured concentrations of molecules potentially contributing to the final flavor profile (56 volatiles and 13 non-volatiles) were used as variables to run two separate principal component analyses (PCA) in SPSS 25 via a factor analysis. Data were reduced into fewer principal components (PC). After applying a Varimax rotation, a rotated component matrix with Kaiser normalization was obtained, wherefrom the loadings of the main principal components were extracted for each variable. Afterwards, these loadings were plotted together with the obtained components scores of the chocolate samples in biplots created via Excel software.

3. Results and discussion

3.1. Roasting treatment indicators

The measured ratio of tetramethylpyrazine to trimethylpyrazine (TMP/TrMP) in the headspace of the chocolate samples was used as indicator to determine the roasting degree. All treatments resulted into well-roasted cocoa beans according to the reported range of 2.5–1.5 in literature (Beckett et al., 2017). The measured TMP/TrMP ratio was the lowest for the MR2 chocolate (2.053) and the highest for the MR1 chocolate (2.429), implying that these treatments received most likely the most and least intensive roasting treatment, respectively. Nevertheless, compared to CR, no significant differences ($p < 0.05$) were detected between the TMP/TrMP ratios of the distinct chocolates, demonstrating that all roasting treatments were roasted to a similar extent. Aside from the TMP/TrMP ratio, dry matter content (DM) was used as additional roasting degree indicator. A DM in the range of 97–98% w/w of the cocoa beans was observed after roasting for all treatments, resulting from an extensive evaporation of mainly water (Table 1). The slightly higher but significant ($p < 0.05$) DM measured in the convectively roasted beans (CR = 97.74% w/w) and the microwave roasted beans at 600 W for 35 min (MR2 = 97.69% w/w), imply a

Table 2

Fat content and fat oxidation degree (PV, p-AV and TOTOX) measured for cocoa liquors) produced from cocoa beans roasted under varying conditions (n = 3, unless otherwise indicated). Convectional roasted (CR: 130 °C −30 min), microwave roasted (MR1: 450 W–55 min, MR2: 600 W–35 min, MR3: 900 W–20 min).

	CR	MR1	MR2	MR3
Liquor				
Fat content (% w/w) (n = 2)	53.88 ± 0.01	53.51 ± 0.09	53.71 ± 0.32	53.70 ± 0.51
Fat oxidation				
Peroxide value (PV)	1.26 ± 0.29^{a}	3.82 ± 0.43^{b}	3.04 ± 0.30^{b}	3.06 ± 0.30^{b}
p-Anisidine value (*p*-AV)	1.61 ± 0.55^{a,b}	1.85 ± 0.28^{b}	1.41 ± 0.12^{a,b}	0.85 ± 0.06^{a}
TOTOX value (TOTOX)	4.13 ± 0.68^{a}	9.49 ± 0.68^{c}	7.48 ± 0.44^{b}	6.97 ± 0.43^{b}

Significant differences ($p < 0.05$) within one row are indicated with different superscripts (a-c), following one-way ANOVA with post-hoc tests.

slightly more intense roasting treatment compared to the other microwave roasting treatments (MR1 = 97.43% w/w and MR3 = 97.33% w/w).

3.2. Fat content and fat oxidation degree of cocoa liquors

No clear differences were detected in the total fat content among the different liquors produced from beans with various roasting treatments. Regarding the quality of the cocoa butter, the peroxide values (PV) of the liquors produced from microwave roasted beans (MR1, MR2 and MR3) were significantly higher than that of the reference liquor (CR) (Table 2). This finding is consistent with other studies stating that microwave processing increases the susceptibility of food products to fat oxidation (Jittrepotch et al., 2010; Krysiak, 2011). Suomela et al. (2016) postulated that this could be due to the residual microwave energy, resulting from only partial absorption of microwave energy, especially in dry products like cocoa beans, and the rapid movement of triacylglycerols allowing them to readily react with oxygen. The formed peroxides are highly reactive and may undergo scission to form various secondary oxidation products including aldehydes, ketones, organic acids, and hydrocarbons (Hashim et al., 1997). These secondary oxidation products were estimated by quantifying α- and β-unsaturated aldehydes through determination of the *para*-anisidine value (*p*-AV) (Min & Ellefson, 2010). The cocoa liquors made from beans with comparable roasting times (i.e. CR and MR2) had similar *p*-AVs. Furthermore, MR1 (450 W–55 min) had a significantly higher *p*-AV than MR 3 (900 W–20 min). This outcome suggests that a prolonged microwave roasting time resulted in a more intensive oxidation. The TOTOX value, which gives a more complete view of the oxidation state, was the lowest for the CR treatment (4.13) and the highest for the MR1 treatment (9.49). The significantly higher TOTOX values measured in all microwave roasting treatments compared to the CR treatment is in line with the results reported by Krysiak (2011). A possible explanation for this phenomena could be the fact that during microwave roasting, heat is generated throughout the entire bean resulting in a more pronounced oxidation at the center of the cocoa bean. Although all TOTOX values of the microwave roasting treatments were significantly higher than the convectively roasted beans, they were still below the threshold value of 10. This number is set as an acceptable limit, whereby rancidity of fats is estimated as rather low (Matthäus, 2010). Hence, the negative impact of increased fat oxidation during microwave roasting of cocoa beans is expected to be limited. This likely limited fat oxidation might be attributed to the composition of cocoa butter, consisting of relatively high amounts of saturated fatty acids and low amount of poly-unsaturated fatty acids resulting in a lower susceptibility towards fat oxidation (Zyzelewicz et al., 2014). However, oxidation of lipids might be perceived as beneficial due to the formation of certain volatiles that could contribute to the final flavor profile of cocoa (Hashim et al., 1997). The potential effects of these oxidative phenomena on long-term quality was not studied in the scope of this study.

3.3. Phytochemical profile

The UPLC-HRMS analysis of the chocolates led to the quantification of 18 compounds, including flavan-3-ols, proanthocyanidins, methylxanthines, amino acids, and biogenic amines (Table 3). In general, the analyzed phytochemicals in the four different samples were present in very similar concentrations. The same was observed in chocolates processed from beans that had been convectively roasted with varying duration and temperature during roasting, in that they showed generally similar concentrations of these phytochemicals (Lemarcq et al., 2020). Despite the somewhat similar phytochemical levels found this present study, some significant differences ($p < 0.05$) between concentrations of certain compounds were found. For instance, the flavan-3-ol epicatechin was present in a significantly lower level in MR2 compared to CR ($p = 0.0146$), while catechin was less abundant in MR1 compared to CR ($p = 0.0223$). In samples MR2 and MR3, less procyanidin B2 was present compared to CR. During roasting, epimerization of (−)-epicatechin into (−)-catechin can take place, leading to a reduction of epicatechin (Hurst et al., 2011; Kothe et al., 2013; Lemarcq et al., 2020). Also for procyanidin B2, epimerization has been reported, which is more significant when more intensive roasting treatments are applied (Kothe et al., 2013; Lemarcq et al., 2020). Thus, the lower level of epicatechin and procyanidin B2 in sample MR2 may indicate that this treatment was somewhat more intense compared to the CR treatment. This hypothesis is supported by the calculated TMP/TRMP ratio which was the lowest for the MR2 chocolate.

Dark chocolate CR also contained more cyanidin-3-O-galactoside compared to the MR2 chocolate. Luteolin was present in a significantly higher level in CR as in MR1 and MR2.

As for the methylxanthines (theobromine and caffeine), no significant differences ($p > 0.05$) were found among the different roasting treatments. Theophylline was also detected, although its level in all chocolates was below the LOQ of 3.3 μg/g defatted chocolate. Thus, the level of this compound in the chocolates was not statistically compared (not included in Table 3). Overall, it thus seems that roasting does not affect methylxanthine levels, which is in line with previous reports in literature (Lemarcq et al., 2020; Shively & Tarka, 1984; Timbie et al., 1978).

With regard to the amino acids (L-tryptophan, L-tyrosine, L-α-phenylalanine) and biogenic amines (tryptamine, tyramine, 2-phenylethylamine and salsolinol), no significant differences ($p > 0.05$) were found as well, except for serotonin, which was more abundant in the CR chocolate compared to the MR2 chocolate. One type of reaction which can occur during roasting is the decarboxylation of amino acids, resulting in formation of the corresponding biogenic amines (Oracz & Nebesny, 2014). Since the levels of amino acids and biogenic amines in general did not differ significantly, the CR and MR had a comparable impact on these compounds and decarboxylation most probably has taken place to the same extent.

The currently available reports on microwave roasting of cocoa are limited. In view of our work, the most relevant data are presented by Supriyanto and Haryadi (2007), who roasted ground cocoa nibs by convection roasting (140 °C, 40 min) and microwave roasting (20% of the full power of a 900 W microwave, 5 min) and compared the total polyphenolic content. Their results indicated that the phenolic content of the cocoa products which received these two treatments did not differ. Although the experimental conditions of their set-up are not directly comparable to the current set-up, our data seem to agree with their findings as both studies indicate that a shorter microwave roasting treatment does not result in a better retention of polyphenolic compounds.

Given the similar levels of most non-volatile compounds in the different chocolates, microwave roasting can provide an adequate alternative to convection roasting. More specifically, treatments MR1 and CR resulted in highly comparable chocolates with regard to the phytochemical composition.

Table 3

Concentrations (µg/g defatted chocolate) of flavan-3-ols, methylxanthines, biogenic amines and their precursors, as analyzed by UPLC-HRMS for different roasting treatments (n = 3) and taste thresholds of these compounds found in literature. Conditions: Convectional roasted (CR: 130 °C –30 min), microwave roasted (MR1: 450 W–55 min, MR2: 600 W–35 min, MR3: 900 W–20min).

	Taste (Threshold (mM))	CR	MR1	MR2	MR3
Monomeric flavan-3-ols					
Catechin	Bitter (1), Astringent (0,6)[1]	2771.0 ± 280.6^{b}	2111.7 ± 224.9^{a}	2570.0 ± 85.9^{a,b}	2654.3 ± 150.7^{a,b}
Epicatechin	Bitter (0,8), Astringent (0,8)[1]	9263.3 ± 878.3^{b}	8181.0 ± 307.8^{a,b}	7019.3 ± 173.6^{a}	7900.7 ± 835.6^{a,b}
Polymeric flavan-3-ols					
Procyanidin B1	Bitter (0,4), Astringent (0,24)[2]	437.9 ± 71.6^{a}	384.3 ± 51.9^{a}	416.6 ± 51.9^{a}	404.9 ± 77.8^{a}
Procyanidin B2	Bitter (0,485), Astringent (0,19)[2]	4782.7 ± 472.0^{c}	4071.3 ± 72.5^{b,c}	3044.3 ± 196.0^{a}	3696.7 ± 434.6^{a,b}
Methylxanthines					
Theobromine	Bitter (0,8)[1]	29761.3 ± 3195.9^{a}	28798.7 ± 771.2^{a}	25405 ± 1484.5^{a}	26699.0 ± 3265.3^{a}
Caffeine	Bitter (0,75)[1]	3889.5 ± 420.4^{a}	3807.6 ± 80.7^{a}	3294.3 ± 159.5^{a}	3452.0 ± 343.5^{a}
Flavanoids					
Luteolin	Bitter	4.7 ± 0.4^{b}	4.8 ± 0.3^{b}	4.6 ± 0.3^{a,b}	3.7 ± 0.3^{a}
Quercetin	Bitter	49.5 ± 4.1^{a}	53.3 ± 2.4^{a}	55.2 ± 2.1^{a}	47.6 ± 4.4^{a}
Amino acids					
L-Tryptophan	Bitter (5)[3]	69.0 ± 8.6^{a}	64.7 ± 5.2^{a}	54.6 ± 3.2^{a}	55.9 ± 8.0^{a}
L-Tyrosine	Bitter (5)[3]	338.0 ± 64.2^{a}	306.4 ± 23.7^{a}	258.3 ± 11.8^{a}	254.5 ± 36.1^{a}
L-alpha-Phenylalanine	Bitter (58)[3]	579.1 ± 31.6^{a}	571.3 ± 34.6^{a}	467.6 ± 53.4^{a}	510.2 ± 52.7^{a}
2-Phenylethylamine	Fishy[4]	4.7 ± 0.5^{a}	4.8 ± 0.47^{a}	5.4 ± 0.3^{a}	4.3 ± 0.7^{a}
Biogenic amines					
Tryptamine	N.A.	4.9 ± 0.6^{a}	4.6 ± 0.5^{a}	3.8 ± 0.6^{a}	3.9 ± 0.6^{a}
Serotonin	N.A.	41.7 ± 3.7^{b}	36.9 ± 3.5^{a,b}	29.1 ± 1.9^{a}	32.6 ± 4.7^{a,b}
Tyramine	Savory[4]	4.7 ± 0.6^{a}	3.9 ± 0.4^{a}	4.1 ± 0.6^{a}	3.8 ± 0.2^{a}
Salsolinol	N.A.	53.4 ± 6.2^{a}	47.5 ± 3.3^{a}	41.6 ± 2.5^{a}	42.0 ± 5.2^{a}
Anthocyanidin-3-o-glycosides					
Cyanidin-3-O-galactoside	N.A.	43.0 ± 4.1^{a,b}	49.9 ± 3.5^{b}	37.3 ± 1.5^{a}	45.4 ± 7.7^{a,b}
Cyanidin-3-O-arabinoside	N.A.	37.7 ± 3.9^{a}	44.2 ± 3.0^{a}	32.7 ± 2.3^{a}	39.9 ± 5.5^{a}

Significant differences ($p < 0.05$) within one row are indicated with different superscripts (a-c), following one-way ANOVA with post-hoc tests. Taste thresholds derived from literature: 1. (Hufnagel & Hofmann, 2008)*; 2.* (Stark et al., 2006)*; 3.* (Dagan-Wiener et al., 2017)*; 4.* https://pubchem.ncbi.nlm.nih.gov.

N.A.: not applicable.

Table 4

Semi-quantitative concentrations (ng 4-methylpyridine equivalents/g chocolate) of volatiles detected above LOQ ($S/N > 10$) measured via HS-SPME-GC-MS for the four different chocolate samples ($n = 3$) produced from cocoa beans roasted at different conditions, odor descriptions and calculated Kovat indices (KI_{exp}) and those reported in literature (KI_{lit}). Conditions: Convectional roasted (CR: 130 °C –30 min), microwave roasted (MR1: 450 W–55 min, MR2: 600 W–35 min, MR3: 900 W–20 min).

	Odor description	CR	MR1	MR2	MR3	KI_{exp}	KI_{lit}
Acids							
Acetic acid	Sour, Vinegar	1391 ± 776^{a}	3127 ± 390^{b}	3498 ± 332^{b}	3579 ± 78^{b}	1428	1450
Propanoic acid	Fat, Fruit, Pungent, Silage, Soy	N.D.	20.7 ± 1.9	N.D.	N.D.	1508	1468–1492
Isobutyric acid	Burnt, Butter, Cheese, Sweat	156 ± 62^{a}	N.D.	368 ± 38^{a}	N.D.	1534	1574
Isovaleric acid	Cheese, Pungent	330 ± 164^{a}	644 ± 84^{a}	827 ± 54^{a}	853 ± 19^{a}	1622	1665
Pentanoic acid, 4-methyl	Floral	34 ± 8^{a}	$46 \pm 4^{a,b}$	59 ± 10^{b}	62 ± 2^{b}	1729	1813–1824
Pentanoic acid	Cheese, Pungent	N.D.	N.D.	238 ± 17^{a}	201 ± 3^{a}	1761	1713–1780
Octanoic acid	Cheese, Fat, Grass, Oil	87 ± 31^{a}	78 ± 20^{a}	67 ± 7^{a}	62 ± 4^{a}	1917	2083
Nonanoic acid	Green fat	225 ± 86^{a}	206 ± 104^{a}	N.D.	N.D.	1980	2202
Alcohols							
2-Pentanol	Fuel Oil, Green	178 ± 50^{a}	289 ± 27^{b}	299 ± 35^{b}	374 ± 45^{b}	1111	1105–1138
1-Butanol, 2-methyl-	Fish Oil, Green, Malt, Onion, Wine	N.D.	53 ± 14	N.D.	N.D.	1196	1180–1197
1-Butanol, 3-methyl-	Burnt, Cocoa, Floral, Malt	106 ± 24^{a}	182 ± 11^{b}	180 ± 5^{b}	214 ± 24^{b}	1198	1225
1-Pentanol	Balsamic, Fruit, Green, Pungent, Yeast	31 ± 8^{a}	$45 \pm 6^{a,b}$	52 ± 2^{b}	70 ± 3^{c}	1241	1255–1261
2-Heptanol	Citrus, Earth, Fried, Mushroom, Oil	464 ± 102^{a}	656 ± 20^{b}	$719 \pm 87^{b,c}$	847 ± 13^{c}	1313	1307
1-Octen-3-ol	Mushroom	N.D.	58 ± 4^{a}	72 ± 5^{b}	60 ± 2^{a}	1435	1445–1456
1-Hexanol, 2-methyl	Rose, Green	N.D.	98 ± 7^{a}	89 ± 8^{a}	N.D.	1472	1470–1507
2-Nonanol	Citrus, Fruity, Lemon, Grass	98 ± 19^{a}	$117 \pm 6^{a,b}$	139 ± 12^{b}	141 ± 2^{b}	1501	1535
Benzyl alcohol	Sweet, Floral	90 ± 29^{a}	165 ± 6^{b}	$199 \pm 16^{b,c}$	225 ± 3^{c}	1786	1877–1886
Phenylethyl alcohol	Floral, Honey	2601 ± 826^{a}	4102 ± 136^{b}	$5193 \pm 353^{b,c}$	5713 ± 100^{c}	1813	1925
Terpenes							
Linalool	Floral, Rose, Sweet, Green, Citrus	$< LOQ$	$< LOQ$	37 ± 3^{a}	36 ± 1^{a}	1522	1537
Esters							
Acetic acid, methyl ester	Green	89 ± 25^{a}	161 ± 27^{b}	178 ± 29^{b}	171 ± 6^{b}	878	810–828
Propyl acetate	Pears aroma	N.D.	N.D.	678 ± 133	N.D.	906	980
Acetic acid ethenyl ester	Aromatic, Brandy, Contact Glue, Grape	N.D.	N.D.	555 ± 51^{b}	570 ± 21^{b}	906	878
Propanoic acid, ethyl ester	Apple, Pineapple, Rum, Strawberry	N.D.	588 ± 89	N.D.	N.D.	962	966
1-Butanol, 3-methyl-, acetate	Apple, Banana, Glue, Pear	N.D.	131 ± 14^{a}	130 ± 22^{a}	93 ± 58^{a}	1107	1117
Octanoic acid, ethyl ester	Apricot, Brandy, Fat, Floral, Pineapple	50 ± 18^{a}	75 ± 2^{a}	88 ± 8^{a}	79 ± 3^{a}	1422	1436
Decanoic acid, ethyl ester	Waxy	N.D.	41 ± 2^{a}	N.D.	51 ± 2^{b}	1603	1643
Benzeneacetic acid, methyl ester	Sweet, Honey, Jasmine	N.D.	16.60 ± 0.66	N.D.	N.D.	1718	1749
Benzeneacetic acid, ethyl ester	Fruity, Sweet	83 ± 14^{a}	82 ± 5^{a}	116 ± 8^{b}	116 ± 3^{b}	1717	1776–1784
Acetic acid, 2-phenylethyl ester	Honey, Floral	474 ± 85^{a}	$563 \pm 48^{a,b}$	641 ± 50^{b}	661 ± 5^{b}	1741	1771–1821
Dodecanoic acid, ethyl ester	Floral, Fruit, Leaf	N.D.	N.D.	N.D.	38 ± 1	1767	1849–1856
Ketones							
2-Butanone	Fruity	96 ± 32^{a}	183 ± 29^{b}	$211 \pm 5^{b,c}$	261 ± 40^{c}	913	881–900
2-Pentanone	Fruit, Pungent	298 ± 92	N.D.	N.D.	N.D.	968	984
2,3-Butanedione	Buttery	N.D.	576 ± 19^{a}	N.D.	570 ± 21^{a}	968	971–980
3-Penten-2-one	Fruity	N.D.	N.D.	N.D.	140 ± 2	1107	1126–1127
2-Heptanone	Fruity, Coconut, Cheesy, Floral	208 ± 57^{a}	305 ± 26^{b}	304 ± 36^{b}	326 ± 13^{b}	1168	1170
Acetoin	Butter, Creamy, Green Pepper	73 ± 28^{a}	145 ± 17^{b}	157 ± 13^{b}	173 ± 5^{b}	1270	1287
2-Nonanone	Fruity, Fresh, Sweet	136 ± 45^{a}	163 ± 10^{a}	181 ± 16^{a}	191 ± 11^{a}	1378	900
Ethanone, 1-(2-furanyl)-	Sweet, Balsamic, Slightly coffee	122 ± 39^{a}	207 ± 12^{b}	261 ± 22^{b}	233 ± 2^{b}	1479	1457–1514
Pyrazines							
Pyrazine, methyl-	Nutty, Chocolate, Cocoa, Roasted nuts	109 ± 36^{a}	188 ± 9^{b}	349 ± 35^{c}	314 ± 12^{c}	1253	1176
Pyrazine, 2,5-dimethyl-	Cocoa, Roasted nuts	178 ± 54^{a}	258 ± 24^{a}	530 ± 42^{b}	475 ± 9^{b}	1312	1274–1358
Pyrazine, 2,6-dimethyl-	Nutty, Coffee, Green	84 ± 29^{a}	146 ± 12^{b}	261 ± 23^{c}	237 ± 7^{c}	1318	1280–1370
Pyrazine, ethyl-	Peanut butter, Musty Nutty	39 ± 11^{a}	54 ± 5^{a}	100 ± 9^{c}	75 ± 1^{b}	1322	1354
Pyrazine, 2,3-dimethyl-	Caramel, Cocoa	65 ± 20^{a}	120 ± 12^{b}	167 ± 14^{c}	152 ± 3^{b}	1336	1315–1344
Pyrazine, 2-ethyl-6-methyl-	Green, Nuts, Roasted	56 ± 18^{a}	87 ± 5^{a}	175 ± 17^{b}	146 ± 7^{b}	1375	1381–1414
Pyrazine, trimethyl-	Roast, Potato, Must	276 ± 80^{a}	445 ± 34^{b}	696 ± 58^{c}	631 ± 11^{c}	1394	1395
Pyrazine, 3-ethyl-2,5-dimethyl-	Potato, Roasted	111 ± 25^{a}	136 ± 4^{a}	267 ± 20^{b}	243 ± 7^{b}	1432	1435
2,3-Dimethyl-5-ethylpyrazine	Burnt, Green bean, Popcorn	60 ± 15^{a}	92 ± 4^{b}	148 ± 12^{c}	126 ± 1^{c}	1448	1460
Pyrazine, tetramethyl-	Cocoa, Coffee, Green, Mocha, Roast	583 ± 138^{a}	1078 ± 49^{b}	1428 ± 108^{c}	1445 ± 26^{c}	1461	1438–1474
2,3,5-Trimethyl-6-ethylpyrazine	Candy, Sweet	52 ± 10^{a}	70 ± 2^{a}	116 ± 6^{b}	104 ± 3^{b}	1496	–
Aldehydes							
Propanal, 2-methyl	Burnt, Caramel, Cocoa, Green, Malt	360 ± 337^{a}	236 ± 25^{a}	279 ± 43^{a}	270 ± 16^{a}	872	801–812
Butanal, 2-methyl-	Chocolate	373 ± 111^{a}	592 ± 63^{b}	685 ± 38^{b}	669 ± 87^{b}	921	864–936
Butanal, 3-methyl-	Chocolate	560 ± 153^{a}	859 ± 24^{a}	842 ± 53^{a}	727 ± 83^{a}	924	912–936
Hexanal	Grass, Tallow, Fat	63 ± 13^{a}	N.D.	60 ± 15^{a}	61 ± 8^{a}	1063	1078–1094
Nonanal	Fat, Floral, Green, Lemon	45 ± 14^{a}	N.D.	N.D.	56 ± 2^{a}	1381	1390–1400
Benzaldehyde	Sweet, Bitter, Almond Cherry	1323 ± 365^{a}	1906 ± 52^{b}	$2418 \pm 212^{b,c}$	2644 ± 35^{c}	1495	1470–1568
Benzeneacetaldehyde	Honey, Floral	1466 ± 282^{a}	1751 ± 411^{a}	1697 ± 648^{a}	1576 ± 90^{a}	1597	1646–1650

Significant differences ($p < 0.05$) within one row are indicated with different superscripts (a-d), following one-way ANOVA with post-hoc tests.
N.D.: non detected.
Odor descriptions derived from (Aprotosoaie et al., 2016; Rottiers, 2019) & http://www.flavornet.org/flavornet.html.
KI_{lit} derived from (Rottiers, 2019), *C20M on* http://www.flavornet.org/flavornet.html *& NIST14 library (*https://webbook.nist.gov).

3.4. Aroma profile

According to Parker (2015), most of the aroma components generated during heating processes such as roasting are formed via three main processes: Maillard and side reactions, lipid oxidation or thermal breakdown of components. Therefore, a reduction of certain volatiles can be expected due to consumption of the precursors via these reactions as well as evaporation of aroma compounds. As reported by Ibrahim et al. (2012), microwave roasting is capable of developing similar compounds as during convection roasting, with the difference of promoting certain reactions above others. In this present research, a HS-SPME-GC-MS analysis of the four chocolates resulted in a semi-quantification of 56 volatile compounds above the LOQ which could be categorized into the following chemical classes: acids, alcohols, esters, terpenes, ketones, pyrazines and aldehydes (Table 4). In the following paragraphs, the trends observed for these volatiles are discussed based on the potential difference on the impact on the main processes by varying the roasting conditions.

3.4.1. Maillard and side reactions

Pyrazines are typical products formed during the latter stages of the Maillard reaction. Higher concentrations of pyrazines were measured in the chocolates from microwave roasted beans. Despite the non-significant differences ($p > 0.05$), a trend of highest pyrazine concentration was observed for MR2 chocolate (with exception of 2,3,5-trimethyl-6-ethylpyrazine). A possible explanation may be that not only the power input or duration are responsible for this trend, but more likely the combination of both, as the highest roasting degree (lowest TMP/TrMP) was measured in MR2, followed by MR3 and MR1. Since pyrazines are formed during the Maillard reaction, microwave roasting of cocoa beans might possibly favor this reaction. As stated by Datta (2001), a microwave heat treatment could accelerate several reactions including cyclization reactions necessary to produce pyrazines. In addition, the difference in heat transfer could be beneficial for pyrazine formation during microwave roasting. As previously mentioned, convection roasting faces a temperature gradient from outside towards the center of the bean, which could result in a burned crust and a relatively cooler center (Agila & Barringer, 2012). During microwave roasting the entire bean is affected equally and therefore more aromas might have been generated simultaneously in the entire bean, resulting in a more intensive aroma profile. Additionally during microwave heating where the outer bean layer is hypothesized to be less intensely roasted as it would have been during a non-uniform convective heating, the formation of undesired products, such as acrylamide – a known carcinogen, could also have occurred to a lesser extent. Though, additional measurements should be done to confirm this hypothesis. A limiting factor, addressed in literature, is that microwave roasting usually requires less time, which might not be sufficient to allow complex reactions consisting of several consecutive steps, such as Maillard reaction, to be completed (Datta, 2001). However, it seemed that a microwave roasting treatment of at least 20 min (MR3) was sufficiently long for flavor development, as still more pyrazines were formed compared to the chocolate made from convectively roasted beans.

Aldehydes are mainly formed via Strecker degradation reactions during the Maillard reaction. The concentrations of 2-methylbutanal were significantly higher in chocolates produced from microwave roasted beans compared to the chocolate from convectively roasted beans (+59%, +84% and +79% for MR1, MR2 and MR3, respectively, compared to CR). This aldehyde, derived from the amino acid isoleucine, is known for its strong chocolate aroma, Therefore, the significantly higher concentrations suggest that microwave roasting could result in a more intense cocoa aroma (Afoakwa et al., 2008). Likewise, 2-methylbutanal, levels of benzaldehyde, a compound formed via the aldol condensation of acetaldehyde and 3-methylbutanal, were significantly higher for MR chocoaltes compared to CR. The other measured aldehydes were present in non-significantly different amounts in chocolates produced from microwave roasted and convectively roasted beans. This outcome is supported by solvent-mediated Maillard model systems whereby microwave roasting until a similar temperature as convection roasting resulted in an increased formation of Strecker aldehydes (Steinke et al., 1989).

Besides these compounds, also less typical products can be formed

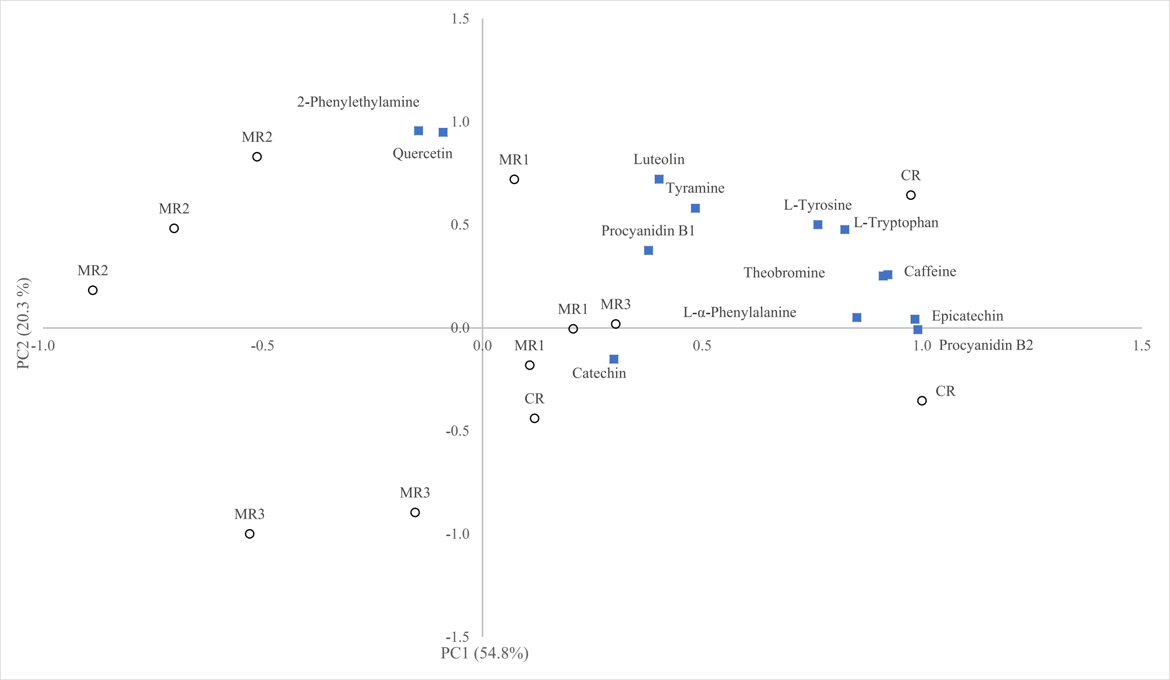

Fig. 1. PCA biplot of potential flavor contributing compounds (13 non-volatile compounds (blue ■)) plotted together with the factor loadings of the four chocolate samples (black ○)) (n = 3). Conditions: Convectional roasted (CR: 130 °C - 30 min), microwave roasted (MR1: 450 W–55 min, MR2: 600 W–35 min, MR3: 900 W–20 min). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

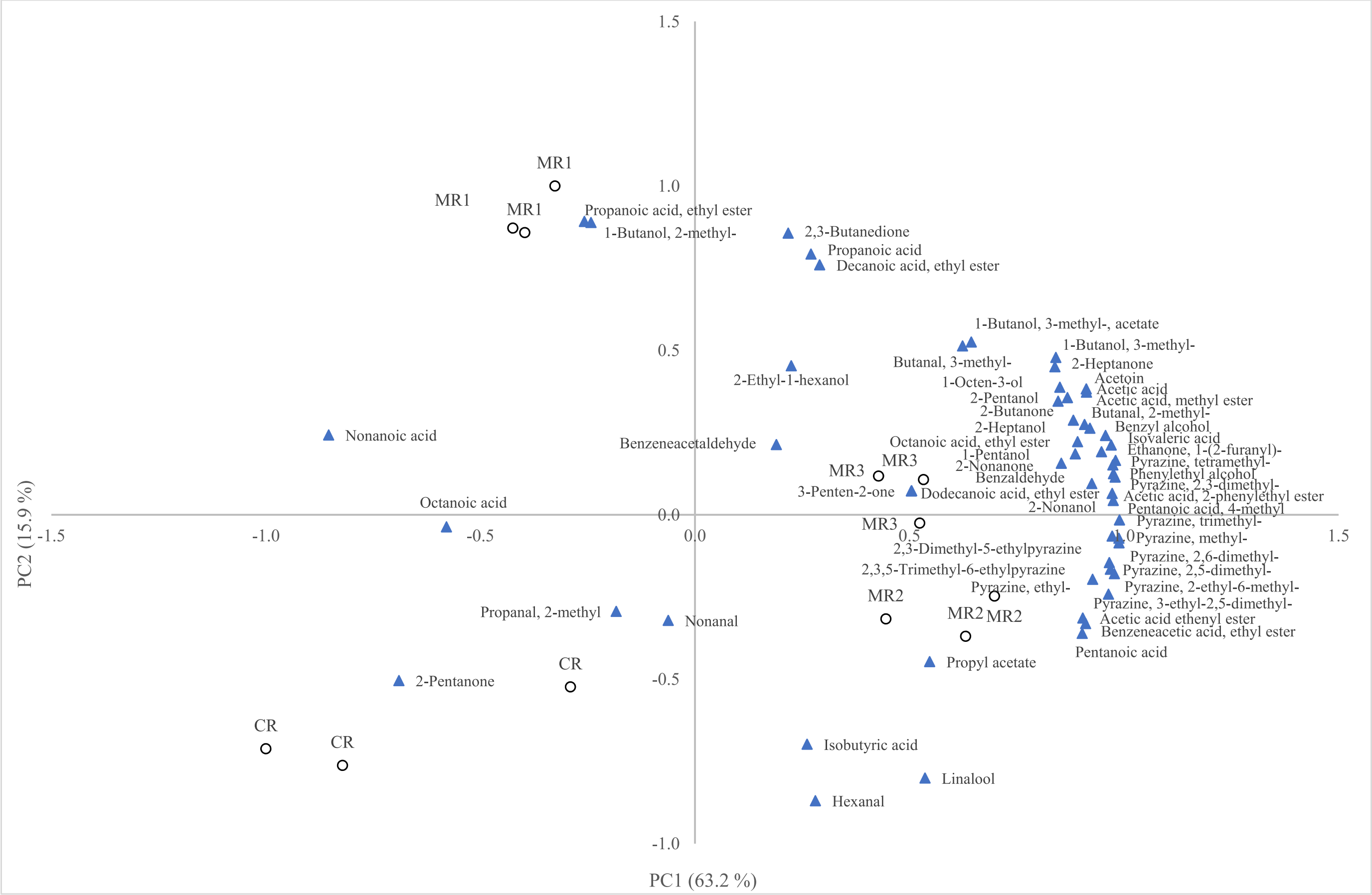

Fig. 2. PCA biplot of potential flavor contributing compounds (56 volatile compounds (blue ▲)) plotted together with the factor loadings of the four chocolate samples (black ○) (n = 3). Conditions: Convectional roasted (CR: 130 °C - 30 min), microwave roasted (MR1: 450 W–55 min, MR2: 600 W–35 min, MR3: 900 W–20 min). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

during the Maillard reaction. For example, as described by Parker (2015), acetic acid could be formed during the Maillard reaction by several cleavage reactions of the highly reactive dicarbonyls. Considering a more intensive Maillard reaction that took place during microwave roasting, higher levels of acetic acid in the MR chocolates could be expected.

3.4.2. Oxidation of lipids and other compounds

Lipid oxidation contributes to an increased aroma profile as was stated by Hashim et al. (1997), whereby the oxidation of cocoa butter resulted in the formation of several volatile compounds such as aldehydes, ketones, heterocyclic compounds, esters, alcohols, and organic acids.

Our research showed that microwave roasting resulted in chocolates with higher levels of alcohols compared to the chocolate produced from convectively roasted cocoa beans. Here, lipid oxidation might have served as a plausible cause for this observed increase. Higher alcohol levels were observed at higher power input during microwave roasting. Specifically, a significantly higher concentration 1-pentanol, 2-heptanol, benzylalcohol and phenylethylalcohol (57%, 29%, 37% and 39%, respectively) was observed in MR1 (450 W for 55 min) than in MR3 (900 W for 55 min). A possible explanation might be that the formed alcohols were oxidized themselves into secondary oxidation products such as aldehydes and/or ketones when a prolonged microwave roasting treatment was applied. This hypothesis could be supported by the higher *p*-AV in MR1 chocolate than in MR3, indicating a higher concentration of secondary oxidation products in the former. Linalool, a terpene alcohol, was only detected above LOQ in the microwave roasting treatments with high power input (MR2 – 600 W and MR3 – 900 W). The microwave treatment with longer time (MR1 450 W for 55 min) was likely too extensive to retain this compound.

Besides the formation of aldehydes via the oxidation of alcohols, aldehydes can be formed as a result from lipid oxidation. Hexanal is frequently selected as an indicator for lipid oxidation (Hashim et al., 1997). In the aroma profiles of the different chocolates, no significant difference ($p > 0.05$) was detected between the measured hexanal concentrations, except in chocolate MR1 (450 W for 55 min), where this compound was not detected. The extensive roasting time could have resulted in the entire evaporation of this compound.

On top of promoting the formation of aldehydes, the presence of oxygen might also result in the reduction of aldehydes by further oxidation into acids (Hofmann et al., 2000). Assuming that these types of reactions are promoted by microwave roasting, higher values of organic acids in chocolates of microwave roasted beans could be expected.

With regard to esters, these compounds could be formed via oxidative esterification of carboxylic acids with alcohols or lipid oxidation (Datta, 2001; Lemarcq et al., 2020). Similar as in the case for alcohols, microwave roasting also resulted in elevated concentrations of esters with the highest concentrations measured in chocolates produced from beans roasted under MR3 conditions (900 W for 20 min). These findings are in agreement with lab-scale experiments whereby it was proven that esterification reactions between benzoic acid and 2-butanol were accelerated during microwave roasting (Gedye et al., 1991).

Ketones followed the same trend with esters. However, differences in concentrations were not significant ($p > 0.05$), with the exception of 2-butanone, 2,3-butanedione and 3-penten-2-one, which were different among the different microwave conditions. The higher levels of ketones in chocolates produced from microwave roasted cocoa beans might be the result of increased oxidation reactions of cocoa butter or alcohols. On the one hand, the higher levels of ketones, alcohols and esters of the chocolates produced from microwave roasted cocoa beans, might potentially result in a more intense fruity and floral flavor perception compared to chocolate produced from convectively roasted cocoa beans. On the other hand, the increased levels of organic acids might be experienced as less pleasant.

3.4.3. Evaporation of volatiles

Microwave roasting would be expected to result in an increased evaporation of volatiles. Steam distillation of aroma compounds, caused by water vapor pressure created internally in the bean during microwave roasting, could potentially result in a depletion of the developed aroma. In addition, during convection roasting, evaporation is impeded via crust formation as a result of dehydration of the external surface of the bean which is not the case when microwave roasting (Datta, 2001; Ibrahim et al., 2012). Specifically, low molecular weight polar molecules like alcohols and aldehydes and short chain organic acids are expected to evaporate at increased rates resulting from the steam distillation occurring during microwave roasting. With regard to the chocolates of the microwave treatments, no significant differences ($p > 0.05$) were observed on the levels of the organic acids. However, for the more volatile organic acids such as acetic acid, a prolonged microwave roasting time was observed to be related to a lower acetic acid concentration, which might have been due to an increased evaporation of these compounds. In general, a similar pattern was seen for alcohols and esters. Although it was expected that microwave roasting would promote evaporation, no clear reduction in the concentration of volatile organic compounds were measured in chocolates produced from microwave roasted beans compared to those from convectively roasted beans. This discrepancy could have three probable reasons Firstly, due to the relative low water content of dried and roasted cocoa beans, the impact of steam distillation of aroma molecules might have been rather limited (Datta, 2001). Secondly, a higher flavor retention might have been achieved due to the high fat content in the matrix, as was suggested in a study related to cakes (de Roos & Graf, 1995). Thirdly, the shell itself – although probably not as crusted as in convectively roasted beans – could still constitute a physical barrier that might still limit aroma release.

3.5. Flavor profile

Two biplots were created to visualize the outcome of a PCA analysis of flavor compounds, one for non-volatile phytochemicals (13 non-volatile compounds) and one for aroma molecules (56 volatile compounds). Data of these flavor compounds were reduced into principal components and plotted, together with the component scores of the chocolate samples (Fig. 1 and Fig. 2). By looking at the differences in flavor profile caused by non-volatile compounds as illustrated in Fig. 1, it could be noticed that more than 50% of the variance between the chocolates is explained by PC1. High positive loadings on PC1 indicate the presence of rather high levels of non-volatile compounds such as methylxanthines (theobromine, caffeine) and major flavan-3-ols (epicatechin and procyanidin B2). Although the effect of microwave roasting on non-volatile phytochemicals present in cocoa beans was rather similar to convection roasting, some differences were noticed. The highly positive loadings on PC1 for the chocolate from convectively roasted cocoa beans (CR) indicate that these chocolate might be perceived slightly more bitter and astringent compared to MR2 and MR3 chocolate samples, which are negatively loaded for PC1. When focusing on the aroma molecules, the different chocolate samples were plotted in a different quadrant, implying distinctive aroma profiles (Fig. 2). More than 60% of the variance was explained by the first principal component (PC1), while roughly another 15% was explained by the second principal component (PC2). It could be concluded that the aroma profile of MR1 chocolate is the most resembling to the CR chocolate sample due to the negative values for PC1. These negative values are corresponding to a relative lower presence of aroma molecules. In contrast to CR chocolate, MR2 chocolate samples were positively loaded on PC1, indicating a higher aromatic flavor profile, mainly dominated by pyrazines. MR3 was characterized with both positive loadings of PC1 and PC2, which besides cocoa aromas (pyrazines), was also dominated by fruity and floral aroma compounds (organic acids, alcohols, esters, ketones). The high levels of aroma compounds for MR2 and MR3 indicated that a higher power input resulted in an increased aroma profile. Generally, it could be concluded that microwave roasting of cocoa beans could modify the flavor profile of corresponding dark chocolates. Based on a similar moisture content and TMP/TrMP ratio, MR2 resulted in an intensified aroma profile, while a slightly less intense microwave roasting treatment (MR1), resulted in a chocolate with increased aroma and relatively unaffected phytochemical profile compared to the CR. Moreover, a combined high-power short-time microwave roasting treatment like MR3, might result in a lower energy consumption, while still being able to produce chocolates of good quality (supplementary information S2) and flavor. In the future, it will be prominent to study whether these distinctive flavor profiles can be distinguished sensorially and on which differences their flavor perception can be attributed.

4. Conclusions

The purpose of the current study was to investigate if microwave roasting could be applied as an alternative technique to roast cocoa beans, which can be used for the subsequent chocolate production. The results showed that chocolates with more intense aroma profiles were obtained through microwave roasting cocoa beans, compared to convectively roasted cocoa beans (130 °C–30 min). A possible explanation for this phenomena might be that microwave roasting heats the cocoa beans in a more uniform way. Furthermore, varying the microwave roasting conditions (450 W–55 min, 600 W–35 min, 900 W–20 min) resulted in distinctive aroma profiles. The degree of oxidation, based on the measurement of primary and secondary oxidation products, was estimated to be too limited to induce rancidity for both convectively and microwave roasted samples. Meanwhile, the slightly higher degree of oxidation measured in liquors produced from microwave roasted cocoa beans, might even benefit the final aroma profile as this process could have promoted additional formation of aromatic compounds. In addition, no substantial differences were detected between the non-volatile phytochemical profiles of the chocolates produced from microwave or convectively roasted beans. Taken together, these findings not only indicate that microwave roasting could serve as a potential alternative towards convection cocoa bean roasting, but also suggest that flavor diversification could be achieved by varying the microwave roasting conditions. However, further research is required to fully explore the sensory characteristics of chocolates produced from microwave roasted cocoa beans.

Funding source

Funding: This work was supported by the Fund for Scientific Research (Flanders) (Grant number S004617N) in the framework of the REVICO project (Revisiting Cocoa: Exploiting the full potential of cocoa raw materials through novel processing).

‘Declarations of interest: none’

The authors (Valérie Lemarcq, Viena Monterde, Emmy Tuenter, Davy Van de Walle, Luc Pieters, Eleni Sioriki and Koen Dewettinck) of “Flavor diversification of dark chocolate produced through microwave roasting of cocoa beans” declare that they have no conflict of interest.

CRediT authorship contribution statement

Valérie Lemarcq: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft. **Viena Monterde:** Conceptualization, Investigation, Formal analysis, Writing – original draft. **Emmy Tuenter:** Conceptualization, Methodology, Investigation, Formal analysis, Writing – review & editing. **Davy Van de. Walle:** Conceptualization, Methodology, Writing – review & editing, Supervision. **Luc Pieters:** Conceptualization, Writing – review & editing, Funding acquisition, Resources. **Eleni Sioriki:** Conceptualization, Methodology, Writing – review & editing, Project administration, Supervision. **Koen Dewettinck:** Conceptualization, Writing – review & editing, Funding acquisition, Supervision, Resources.

Acknowledgment

We would like to thank the lab technicians Benny, Corine, Griet and Paul for their assistance during the chocolate production and the chemical analyses. In addition we would like to thank Cargill for providing cocoa beans and Belcolade (Puratos) and Cacaolab bv for the availability of their cocoa processing equipment.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2022.113198.

References

Afoakwa, E. O. (2010). *Chocolate science and technology* (2nd ed.). John Wiley & Sons Inc.

Afoakwa, E. O., Paterson, A., Fowler, M., & Ryan, A. (2008). flavor formation and character in cocoa and chocolate: A critical review. *Critical Reviews in Food Science and Nutrition, 48*(9), 840–857.

Agila, A., & Barringer, S. (2012). Effect of roasting conditions on color and volatile profile including HMF level in sweet almonds (Prunus dulcis). *Journal of Food Science, 77*(4), 461–468. https://doi.org/10.1111/j.1750-3841.2012.02629.x

Aprotosoaie, A. C., Luca, S. V., & Miron, A. (2016). Flavor chemistry of cocoa and cocoa products - an overview. *Comprehensive Reviews in Food Science and Food Safety, 15*(1), 73–91.

Beckett, S. T., Fowler, M., & Ziegler, G. R. (2017). *Industrial chocolate manufacture and use* (5th ed.). John Wiley \& Sons Inc.

* Datta, A. K. (2001). Generation and release of food aromas under microwave heating. In V. A. Yaylayan, & D. D. Roberts (Eds.), *Handbook of microwave technology for food application*. CRC Press.

Febrianto, N. A., & Sari, A. B. T. (2019). Roasting equipment for cocoa processing. In C. L. Hii, & F. M. Borém (Eds.), *Drying and roasting of cocoa and coffee* (pp. 47–60). CRC Press, Taylor & Francis Group.

Flanyak, J. R. (1995). Cacao bean and its products. In *AOAC official methods of analysis* (pp. 1–17).

Gedye, R. N., Rank, W., & Westaway, K. C. (1991). The rapid synthesis of organic compounds in microwave ovens. *Canadian Journal of Chemistry, 69*(4), 706–711. https://doi.org/10.1139/v91-106

Hashim, L., Hudiyono, S., & Chaveron, H. (1997). Volatile compounds of oxidized cocoa butter. *Food Research International, 30*(3–4), 163–169. https://doi.org/10.1016/S0963-9969(97)00039-2

Hebbar, H. U., & Rastogi, N. K. (2012). Microwave heating of fluid foods. In *Novel thermal and non-thermal Technologies for fluid foods* (pp. 369–409). Elsevier Inc. https://doi.org/10.1016/B978-0-12-381470-8.00012-8.

* Hinneh, M., Van de Walle, D., Tzompa-Sosa, D. A., Haeck, J., Abotsi, E. E., De Winne, A., Messens, K., Van Durme, J., Afoakwa, E. O., De Cooman, L., & Dewettinck, K. (2019). Comparing flavor profiles of dark chocolates refined with melanger and conched with Stephan mixer in various alternative chocolate production techniques. *European Food Research and Technology, 245*(4), 837–852. https://doi.org/10.1007/s00217-018-3221-2.

Hofmann, T., Münch, P., & Schieberle, P. (2000). Quantitative model studies on the formation of aroma-active aldehydes and acids by Strecker-type reactions. *Journal of Agricultural and Food Chemistry, 48*(2), 434–440. https://doi.org/10.1021/jf990954c

Hoskin, J. M., Dimick, P. S., & Daniels, R. R. (1980). Scanning electron microscopy of the theobroma cacao seed. *Journal of Food Science, 45*(6), 1538–1540.

Hufnagel, Jan Carlos, & Hofmann, Thomas (2008). Orosensory-directed identification of astringent mouthfeel and bitter-tasting compounds in red wine. *Journal of Agricultural and Food Chemistry, 56*(4), 1376–1386. https://doi.org/10.1021/jf073031n

Hurst, W. J., Krake, S. H., Bergmeier, S. C., Payne, M. J., Miller, K. B., & Stuart, D. A. (2011). Impact of fermentation, drying, roasting and Dutch processing on flavan-3-ol stereochemistry in cacao beans and cocoa ingredients. *Chemistry Central Journal*. https://doi.org/10.1186/1752-153X-5-53

Ibrahim, G. E., El-Ghorab, A. H., El-Massry, K. F., & Osman, F. (2012). Effect of microwave heating on flavour generation and food processing. In *The development and application of microwave heating*. Intech.

Jittrepotch, N., Kongbangkerd, T., & Rojsuntornkitti, K. (2010). Influence of microwave irradiation on lipid oxidation and acceptance in peanut (Arachis hypogaea L.) seeds. *International Food Research Journal, 17*, 173–179.

* Kothe, L., Zimmermann, B. F., & Galensa, R. (2013). Temperature influences epimerization and composition of flavanol monomers, dimers and trimers during cocoa bean roasting. *Food Chemistry, 141*(41), 3656–3663.

Krysiak, W. (2011). Effects of convective and microwave roasting on the physicochemical properties of cocoa beans and cocoa butter extracted from this material. *Grasas y Aceites, 62*(4), 467–478. https://doi.org/10.3989/gya.114910

* Lemarcq, V., Tuenter, E., Bondarenko, A., Van de Walle, D., De Vuyst, L., Pieters, L., Sioriki, E., & Dewettinck, K. (2020). Roasting-induced changes in cocoa beans with respect to the mood pyramid. *Food Chemistry, 332*(127467).

Mani, D. R., Abbatiello, S. E., & Carr, S. A. (2012). Statistical characterization of multiple-reaction monitoring mass spectrometry (MRM-MS) assays for quantitative proteomics. *BMC Bioinformatics, 13*(S9), 1–18. https://doi.org/10.1186/1471-2105-13-S16-S9

Matthäus, B. (2010). Oxidation of edible oils. In E. A. Decker, R. J. Elias, & D. J. McClements (Eds.), *Oxidation in foods and beverages and antioxidant applications* (pp. 183–238). Woodhead Publishing. https://doi.org/10.1533/9780857090331.2.183.

Min, D. B., & Ellefson, W. C. (2010). Fat analysis. In *Food analysis* (pp. 117–132). Boston, MA: Springer. https://doi.org/10.1007/978-3-319-45776-5_17.

Oracz, J., & Nebesny, E. (2014). Influence of roasting conditions on the biogenic amine content in cocoa beans of different Theobroma cacao cultivars. *Food Research International, 55*, 1–10. https://doi.org/10.1016/j.foodres.2013.10.032

* Parker, J. K. (2015). Thermal generation or aroma. In *Flavour development, analysis and perception in food and beverages* (pp. 151–185). Woodhead Publishing. https://doi.org/10.1016/b978-1-78242-103-0.00008-4.

de Roos, K. B., & Graf, E. (1995). Nonequilibrium partition model for predicting flavor retention in microwave and convection heated foods. *Journal of Agricultural and Food Chemistry, 43*, 2204–2211. https://doi.org/10.1021/jf00056a045

Rottiers, H., Tzompa Sosa, D. A., De Winne, A., Ruales, J., De Clippeleer, J., De Leersnyder, I., De Wever, J., Everaert, H., Messens, K., & Dewettinck, K. (2019). Dynamics of volatile compounds and flavor precursors during spontaneous fermentation of fine flavor Trinitario cocoa beans. *European Food Research and Technology, 245*(9), 1917–1937. https://doi.org/10.1007/s00217-019-03307-y

Rottiers, Hayley (2019). A multipronged flavor comparison of Ecuadorian CCN51 and Nacional cocoa cultivars. *European Food Research and Technology, 245*(11), 2459–2478. https://doi.org/10.1007/s00217-019-03364-3

Ryynänen, S. (2002). *Microwave heating uniformity of multicomponent prepared foods*. University of Helsinki.

Shively, C. A., & Tarka, S. M. (1984). Methylxanthine composition and consumption patterns of cocoa and chocolate products. *Progress in Clinical & Biological Research, 158*, 149–178. https://doi.org/10.1201/9780429126789-7

Singh, R. P., & Heldman, D. R. (2014). *Introduction to food engineering* (5th ed.). Academic Press.

Steinke, J. A., Frick, C. M., Gallagher, J. A., & Strassburger, K. J. (1989). Influence of microwave heating on flavor. In *Thermal generation of aroma* (pp. 519–525). American Chemical Society.

Suomela, J.-P., Tarvainen, M., & Kallio, H. (2016). *Effects of microwave vs. convection oven heating on the formation of oxidation products in canola (Brassica rapa subsp. oleifera) oil*. https://doi.org/10.1051/ocl/2017015

Supriyanto, M., & Haryadi. (2007). Microwave roasting of ground cocoa nib to produce cocoa liquor and chocolate paste. *Proceedings of the International Agricultural Engineering Conference*, 1–8.

Teferra, T. F. (2019). Engineering properties of food materials. In *Handbook of farm, dairy and food machinery engineering* (pp. 45–89). Elsevier. https://doi.org/10.1016/b978-0-12-814803-7.00003-8.

Timbie, D. J., Sechrist, L., & Keeney, P. G. (1978). Application of high-pressure liquid chromatography to the study of variables affecting theobromine and caffeine concentrations in cocoa beans. *Journal of Food Science, 43*(2), 560–565.

Tuenter, E., Delbaere, C., De Winne, A., Bijttebier, S., Custers, D., Foubert, K., Van Durme, J., Messens, K., Dewettinck, K., & Pieters, L. (2020). Non-volatile and volatile composition of West African bulk and Ecuadorian fine-flavor cocoa liquor and chocolate. *Food Research International, 130*, 108943.

Vadivambal, R., & Jayas, D. S. (2010). Non-uniform temperature distribution during microwave heating of food materials-A review. *Food and Bioprocess Technology, 3*(2), 161–171. https://doi.org/10.1007/s11947-008-0136-0

Zyzelewicz, D., Budryn, G., Krysiak, W., Oracz, J., Nebesny, E., & Bojczuk, M. (2014). Influence of roasting conditions on fatty acid composition and oxidative changes of cocoa butter extracted from cocoa bean of Forastero variety cultivated in Togo. *Food Research International, 63*, 328–343. https://doi.org/10.1016/j.foodres.2014.04.053

Datta (2008) provides much info on the flavor formation during microwave roasting.

Hinneh (2019) describes the chocolate production process that was performed in a similar way during this research.

Krysiak (2011) is one of first qualitative research papers that mentioned microwave roasting of cocoa beans as an alternative roasting treatment.

Lemarcq (2020) describes the methods used for HS-SPME-GC-MS and UPLC-MS analyses in detail.

Parker (2015) discusses aroma formation when applying a heat treatment and stresses the importance of aroma formed via oxidation reactions.