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Pod storage with roasting: A tool to diversifying the flavor profiles of dark chocolates produced from 'bulk' cocoa beans? (part I: aroma profiling of chocolates)

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ABSTRACT

The impact of pod storage (PS) and roasting temperature (RT) on the aroma profiles of dark chocolates were evaluated. Cocoa liquor samples comprised of ten different combinations of PS and RT, whilst keeping the roasting time fixed at 35 min. Additionally, commercial cocoa liquors from renowned origins (Ecuador, Madagascar, Venezuela, Vietnam, Ivory Coast and Ghana) were acquired for comparison. From these, 70% dark chocolates were produced under the same conditions after which they were subjected to headspace solid-phase microextraction-gas chromatography–mass spectrometry (HS-SPME-GC–MS) analysis. Although both PS and RT were found to influence the aroma volatile concentrations, the impact of RT over PS seemed to be greater. An agglomerative hierarchical clustering (AHC) of all chocolates on the basis of their aroma profiles revealed a similar impact as earlier observed, where major clustering of the chocolates was in accordance with the intensity of the roasting process applied. However, within each group, the dissimilarities owing to PS among the chocolates was clearly depicted. Comparatively, chocolates with low (100–120 °C), instead of moderate to high (135–160 °C) RT's, rather showed a low dissimilarity with those from the commercial cocoa liquors of the different origins. Although from the same beans, the diversity of aroma profiles of these chocolates as well as the similitude of some treatments to some chocolates from commercial grade cocoa liquors, unequivocally underscores the possibility for steering diverse distinct flavors from 'bulk' cocoa through PS and roasting, with beneficial implications, both from an application and an economic point of view.

1. Introduction

The cocoa bean is the main raw material of chocolate. As such, its flavor potential is key in determining the final flavor of the chocolate. The variations in flavor precursors contained within the bean have been identified to be greatly linked to its origin, soil type, age of cocoa tree and the genotype or variety (Kongor et al., 2016). From the latter, two main classifications are often discussed in relation to the cocoa flavor; 'fine' and 'bulk' or 'basic' cocoa (Afoakwa, 2016). The 'fine' flavor cocoa are generally known, among others, by their fruity, floral and spicy notes. They are mainly of the *Criollo*, *Trinitario* and *Nacional* varieties. However, the 'bulk' flavor cocoa mainly consists of the *Forastero* variety. It is generally characterized by its typically strong acidic, astringent, intense cocoa and less fruity/floral notes, and constitutes 95% of global cocoa production. For their unique aroma and flavor characteristics, 'fine' flavor cocoa are highly sought after and thus, attract a high premium price in comparison to 'bulk' cocoa. Yet, the soaring global demand for cocoa and chocolate products exhibiting more diverse and distinct flavor profiles, can be partly addressed through various cost-effective and sustainable technological interventions by

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which not only 'fine' flavor cocoa, but also 'bulk' cocoa can be valorized to meet this ever-growing demand.

Through decades of investigations, the impact of various postharvest and processing techniques on the final flavor of the end-product has been established (Aculey et al., 2010; Afoakwa, 2010; Afoakwa, 2014; Beckett, 2009; Frauendorfer & Schieberle, 2008; Hinneh et al., 2018; Kadow, Bohlmann, Phillips, & Lieberei, 2013; Meyer, Biehl, Said, & Samarakoddy, 1989; Sulaiman, Yang, & Ariffin, 2017). Thus, offering various possibilities through which the flavor of cocoa/chocolate can be tuned. Spanning from bean to bar, a range of such postharvest/processing factors can be envisioned; including pod storage (PS), fermentation, drying, alkalization, roasting (temperature and time) and conching. Of these, the possible synergistic impact of PS and roasting temperature is yet to be explored.

Pod storage is an on/off-farm practice of storing harvested cocoa pods under specific conditions for a specified duration of time prior to fermentation (Hinneh et al., 2018). This technique has become a common practice in some cocoa-producing countries, although previously very little was known about its impact on the flavor potential of the cocoa beans. For instance, as observed by Duncan (1984), Ghanaian farmers unknowingly practiced PS as a means of reducing labor cost by first gathering enough ripe pods over a period of days before organizing family and friends to assist in splitting them. Meanwhile, in Malaysia, this was adopted as an intervention for curbing the problem of overacidity in their fermented cocoa beans (Meyer et al., 1989). It is evident that a series of biochemical changes occurring during the PS including pulp volume and moisture content reductions have consequent impact on the chemical composition of the beans (Afoakwa, Quao, Budu, Takrama, & Saalia, 2011b; Saltini, Akkerman, & Frosch, 2013). In dealing with Ghanaian cocoa beans, Afoakwa, Quao, Budu, Takrama, and Saalia (2011a) reported that PS duration between three and seven days along with adequate fermentation resulted in appreciable reductions in nib acidification, sugars (non-reducing and total sugars) and protein with resultant increase in reducing sugars and acceptable free fatty acid levels. In agreement, Hinneh et al. (2018) recently reported detailed analyses of some flavor precursors (sugars and free amino acid profiles), where they observed an increasing total concertation of precursors with increasing PS. More so, of the Maillard reaction-related aroma volatiles investigated, PS up to seven days was associated with more than twice the total concentration of aroma volatiles compared to the reference. Thus, it is possible to boost or modify the aroma of cocoa through PS.

After fermentation and drying, a very crucial stage which ensures the formation of desirable flavor volatiles from precursors (sugars and free amino acids) through the Maillard reaction is the roasting process (Counet, Callemien, Ouwerx, & Collin, 2002; Frauendorfer & Schieberle, 2008; Nazaruddin, Seng, Hassan, & Said, 2006). Here, the free amino acids interact with the reducing sugars through a series of chemical reactions to form the Amadori compounds. This is a precursor for the formation of 3-deoxyhexuloses and 2,3-enediol with dehydroreductone intermediates under acidic and basic/neutral conditions, respectively. From the latter, α-dicarbonyl compounds are formed, which undergoes Strecker degradation and heterocyclization to give rise to various kinds of aldehydes, ketones, pyrazines, pyrroles and pyridines among others (Afoakwa, Paterson, Fowler, & Ryan, 2008; Aprotosoaie, Luca, & Miron, 2016). For this reason, roasting is also regarded as one of the most important stages in the processing of cocoa beans, especially, in the context of the flavor quality of the end product.

To the best of our knowledge, in spite of the immense contributions of PS and roasting temperature (RT) on the cocoa/chocolate flavor, the impact of both processes on the aroma profile of the final chocolate has not been investigated. Thus, the aim of this study was to explore the potential of PS with RT for the diversification and/or tuning of the aroma profiles of dark chocolates produced from 'bulk' cocoa beans. This was done by applying different pre-selected treatments of PS and RT and thereafter, the production of 70% dark chocolates from these beans. These chocolates were then assessed on the basis of the uniqueness of their aroma profiles with respect to the applied treatments as well as in comparison to equally manufactured chocolates from commercial cocoa liquors of recognized origins.

2. Materials and methods

2.1. Preliminary trials for sample selection

A preliminary study on the impact of PS and RT on the aroma profiles of Ghanaian cocoa liquors was performed to select the PS and RT to be applied in the present study. In this preliminary study, a 3 × 5 full factorial experiment comprising of PS; 0, 3 and 7 days and roasting conditions; 100, 120, 135, 140 and 160 °C each with a constant roasting duration of 35 min was used. Cocoa liquors from these samples were analyzed using headspace solid-phase microextraction-gas chromatography–mass spectrometry (HS-SPME-GC–MS) to identify and quantify the volatile compounds related to aroma. Ten out of these fifteen cocoa liquors were then selected for the present study. The basis for this selection was the interest to identify cocoa liquors of the treatments showing diverse and distinct aroma profiles from the others. However, in order to understand the influence of the factors on possibly identified trends, the following criteria was also considered; (1) for each selected PS – RT combination, a corresponding reference with unstored pods (0PS) was also present, (2) the impact of PS or RT could be traced among the samples given that at least one RT (*ie.* 135 °C) or PS (*ie.* 0PS) was fixed respectively. Table 1 shows a summary of these ten selected PS – RT combinations to be investigated in this present study.

Finally, by means of situating the different liquors samples in a typical industrial context, six extra cocoa liquors from renowned origins (Ecuador, Ghana, Ivory coast, Madagascar, Venezuela and Vietnam) were obtained from a commercial supplier. Information as obtained from the supplier are summarized in Table 2. It must be indicated that for these commercial cocoa liquors, information concerning PS, specific type and conditions of roasting were not provided. However, within the framework of this study, they were viewed as representation of the typical industrial grade liquor. As such, the basis of comparison of these with our liquor samples, given the goal of this study, was irrespective of the specifics of the applied industrial process. Hitherto, the basic idea was to see, of the diverse aroma profiles of our samples, if some of these chocolates could mimic typical aroma profiles of those from a commercial grade liquor given the same manufacturing processing conditions. From all sixteen cocoa liquors, 70% dark chocolates were then produced and thereby compared on the basis of their aroma profiles using the HS-SPME-GC–MS analytical technique.

2.2. From pod storage to roasted cocoa liquor

Ripe cocoa pods were harvested during the September–October peak season from a cocoa farm in Jachere, Ghana (N7.088525, W2.110127833333333). This was representative of a cluster of farms

Table 1
Pod storage and roasting conditions of selected samples.

Pod storage (day)	Temperature (°C)
0	100
0	120
0	135
0	140
0	160
3	120
3	135
7	100
7	135
7	160

Table 2
Information about commercial cocoa liquors as received from supplier.

Origin	Variety	Fermentation	Drying	Roasting
Ecuador	*Nacional*	Box	Combined drying	Nib roasting
Ghana	*Forastero*	Heap	Solar drying	Nib roasting
Ivory coast	*Forastero*	Heap	Solar drying	Nib roasting
Madagascar	*Forastero* + *Criollo* + *Trinitario*	Box	Combined drying	Nib roasting
Venezuela	*Criollo* + *Trinitario*	Box	Combined drying	Nib roasting
Vietnam	*Trinitario*	Box	Solar drying	Nib roasting

demonstrating high potential for quality cocoa beans following an earlier survey in this region (Kongor et al., 2017). Cocoa trees were approximately 31 years old. The pods were stored in small heaps (ca 80–100 pods) on the farm for three different storage times (0, 3, and 7 days), at ambient temperature (28–30 °C) and relative humidity of 77–85%. At the end of each duration of PS, the pods were opened, beans were gathered in heaps (ca 45 kg) and covered with fresh banana leaves to begin the spontaneous heap fermentation process. This occurred for six days with two turnings at 48 h intervals as recommended for local farmers by the Cocoa Research Institute of Ghana (CRIG). After this, the fermented cocoa beans were sun-dried on raised platforms until the required moisture content of < 7% was achieved, as described by Afoakwa (2010). The dried beans were then stored in jute bags of 64 kg gross weight. They were then air-freighted to the Faculty of Bioscience Engineering, Ghent University, Belgium. Here, the bags were stored in a cool well-ventilated room on odorless wooden racks. Roasting and winnowing (2 kg per batch) were carried out in the Selmi roaster (Selmi-group, Italy) and Winn-15 Winnower (Cacao Cucina, U.S.A), respectively. Cocoa nibs (1.5 kg per batch) were first pre-broken using the Stephan mixer at 45 °C. First, 8 min at 50% speed, then, 6 min at 75% speed. Thereafter, the ECGC-12SLTA melanger (CocoaTown, Roswell, USA) was used to further grind the nibs into liquor. For this, about 300 min grinding time was required to obtain liquor of particle size; D (v,0.9) of 21 μm. The particle size was determined using a Malvern Mastersizer according to Saputro et al. (2017).

2.3. Chocolate production

Sixteen batches of 70% dark chocolate (total fat = 43%) consisting of 30.00% pre-broken sugar (Barry Callebaut Belgium, Wieze, Belgium), 64.65% cocoa liquor, 5.00% cocoa butter (Puratos - Belcolade, Erembodegem, Belgium) and 0.35% soy lecithin (Soya International Ltd., Cheshire, U.K.) were produced on a 5 kg scale. Mixing was carried out using the VEMA BM 30/20 planetary mixer (Machinery Verhoest NV/Vema Construct, Izegem, Belgium) for a duration of 20 min at 45 °C. The mixed ingredients (27% fat) was refined with the Exakt 80S 3-roll refiner (Exakt Technologies, inc., USA) at gap setting 2–1, roller speed of 400 rpm and temperature of 35 °C. The refined chocolate mass was then conched in a Bühler ELK'olino conche (Richard Frisse GmbH, Bad Salzuflen, Germany) in two phases. The dry phase was carried out at 60 °C with 1200 rpm for two hours (clockwise) and 80 °C with 1200 rpm for four hours (anti-clockwise). At the liquid phase, calculated amounts of pre-conched cocoa liquor, cocoa butter and the soy lecithin were added, such that, the final fat content of the chocolate was 43%. Here, the process was carried out as follows; 45 °C with 2400 rpm for 15 min (clockwise) and 15 min (anti-clockwise). Pre-conching of part of the cocoa liquor was necessary since the entire amount of cocoa liquor required to produce final chocolate consisting of 70% cocoa could not be included in the recipe prior to the dry conching phase. Hence, for each batch, equal amounts of cocoa liquor was previously dry-conched using the same dry conching procedure, of which specific required amounts were later added at the stage of liquid conching in order to make up for this final concentration. This production method was inspired by the Cocoa of Excellence Program.

2.4. Aroma profiling of chocolates

The aroma analysis was carried out using HS-SPME-GC–MS according to Tran et al. (2015) and modified by Hinneh et al. (2018). Identification of aroma volatiles in the headspace was performed by comparing the MS-spectrum of each peak to those from the Wiley 275 library. The identification was verified by determination of Kovat indices (KI's) after injection of a series of n-alkane homologues (C5 – C13). From these, the Kovat indices of the confirmed aroma compounds were calculated based on their respective retention times and compared with Kovat indices from literature.

The semi-quantitative concentrations of the identified volatile compounds were expressed as nanograms of the internal standard equivalents per gram of cocoa liquor and calculated as the area of the compound of interest divided by the response factor of the internal standard. For each chocolate, isolation, separation, identification and quantification of the aroma volatiles were performed in triplicate. Finally, in order to evaluate a volatile's contribution to the overall flavor profile of the cocoa liquor, odor activity values (OAV's) were calculated using odor threshold values (OTV's) documented in literature. Here, the OTV in oil media were used since chocolate is a fat continuous suspension (43% fat). These values were sourced from Van Gemert (2011). From these, OAV's were calculated by dividing the detected headspace concentration by their respective OTV's. Hitherto, a volatile with OAV ≥ 1 may be considered as an odor-active volatile and *vice versa*. It is worth mentioning that depending on its OTV, a volatile with a relatively higher headspace concentration may not necessarily contribute to the overall flavor profile of a particular liquor. Moreover, as can be seen from Table 4a, 4b, not all OTV references were found. Hence, not all potentially odor-active volatiles could be elucidated. Thus, even though the calculated OAV's may provide some insight, they must be interpreted with caution.

2.5. Statistical analysis

The concentrations of the various volatile compounds as well as their totals were subjected to Analysis of Variance (ANOVA) at a 5% significance level. Assumptions of normality and equality of variance were tested prior to the analysis using Kolmogorov-Smirnov test and Modified Levene's test, respectively. Where assumptions were fulfilled, a post-hoc Tukey's test was used to investigate significant differences among samples. However, when assumption was not fulfilled, a non-parametric alternative, Welch was used along with Games Howell post-hoc test. ANOVA was performed with Minitab 18 (Minitab Inc., USA). Agglomerative Hierarchical Clustering (AHC) of the chocolates on the basis of their aroma volatiles was carried out using XLSTAT 2014.5.03 (Addinsoft, USA).

3. Results and discussion

Table 3a and 3b display the full list of aroma volatiles identified in all 16 chocolates. The odor activity values (OAV's) were calculated in order to estimate the contribution of each volatile to the overall aroma of the chocolates (Table 4a and 4b). Furthermore, dendrograms (Fig. 2a and b) were also constructed by agglomerative hierarchical clustering

Table 3a
Concentrations (ng/g cocoa) of aroma volatiles identified from dark chocolates produced from cocoa beans of different pod storage – roasting conditions.

N-o.	Volatile	0PS-100 °C	7PS-100 °C	0PS-120 °C	3PS-120 °C	0PS-135 °C	3PS-135 °C	7PS-135 °C	0PS-140 °C	0PS-160 °C	7PS-160 °C
	Acids										
1	Acetic acid	2822.26 ± 195.13^{CDE}	2090.90 ± 95.39^{FG}	2834.36 ± 86.31^{CD}	2169.45 ± 81.26^{FG}	3609.52 ± 217.97^{B}	2107.52 ± 70.26^{FG}	3516.61 ± 204.88^{B}	2902.55 ± 33.42^{C}	3885.59 ± 109.66^{B}	4312.15 ± 110.39^{A}
2	Isovaleric acid	213.77 ± 3.21^{CD}	171.26 ± 24.58^{DE}	380.86 ± 43.62^{A}	231.45 ± 15.04^{CD}	331.45 ± 40.25^{AB}	223.73 ± 15.88^{CD}	277.98 ± 62.96^{BC}	381.40 ± 32.92^{A}	261.07 ± 26.23^{BCD}	268.21 ± 19.97^{BC}
3	Oxalic acid DITMS	152.88 ± 28.94^{AB}	167.32 ± 30.71^{AB}	104.78 ± 9.42^{BC}	102.78 ± 4.04^{BC}	115.95 ± 14.20^{BC}	157.78 ± 6.79^{AB}	139.82 ± 65.83^{ABC}	101.33 ± 10.93^{BC}	175.87 ± 19.13^{AB}	218.59 ± 54.44^{A}
	Total	3188.91 ± 221.50^{C}	2429.48 ± 78.04^{D}	3319.99 ± 111.11^{C}	2503.68 ± 70.44^{D}	4056.93 ± 261.98^{B}	2489.03 ± 53.32^{D}	3934.42 ± 173.43^{B}	3385.27 ± 75.86^{C}	4322.53 ± 122.78^{B}	4798.95 ± 122.95^{A}
	Alcohols										
4	Amyl alcohol	40.99 ± 0.89^{BC}	39.49 ± 7.88^{BC}	46.64 ± 3.11^{AB}	41.43 ± 2.77^{BC}	34.38 ± 2.02^{CD}	34.84 ± 0.73^{CD}	25.26 ± 0.77^{EF}	18.77 ± 2.57^{F}	19.24 ± 1.33^{EF}	23.20 ± 1.61^{EF}
5	1-Hexanol	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}
6	2,3-Butanediol	71.89 ± 7.07^{DEF}	133.42 ± 29.33^{BC}	46.00 ± 10.13^{EF}	50.81 ± 13.40^{DEF}	164.02 ± 21.11^{B}	106.29 ± 12.63^{BCD}	410.45 ± 39.94^{A}	104.53 ± 19.09^{CDE}	434.76 ± 30.24^{A}	433.56 ± 30.92^{A}
7	1,3-Butanediol	116.55 ± 19.76^{EF}	103.57 ± 6.30^{F}	169.21 ± 8.20^{BCDE}	189.85 ± 18.88^{BCD}	351.41 ± 49.75^{A}	184.09 ± 7.25^{BCD}	368.60 ± 6.89^{A}	218.97 ± 45.64^{B}	227.35 ± 27.38^{B}	200.75 ± 16.73^{BC}
8	Benzyl alcohol	126.46 ± 10.48^{BCDE}	128.10 ± 7.78^{BCDE}	120.06 ± 12.48^{CDEF}	145.05 ± 13.47^{ABC}	142.20 ± 3.49^{BCD}	108.49 ± 34.35^{CDEF}	121.10 ± 14.39^{CDEF}	170.75 ± 33.19^{AB}	122.76 ± 6.91^{CDEF}	188.15 ± 14.47^{A}
9	2-Phenylethyl alcohol	382.59 ± 21.94^{EF}	98.05 ± 3.62^{H}	510.18 ± 14.16^{D}	296.66 ± 34.00^{F}	887.19 ± 22.30^{B}	361.74 ± 9.94^{EF}	397.44 ± 55.17^{E}	828.68 ± 37.29^{B}	1083.60 ± 59.08^{A}	614.51 ± 36.63^{C}
	Total	738.48 ± 46.57^{E}	502.64 ± 15.13^{FG}	892.08 ± 43.02^{D}	723.81 ± 75.55^{E}	1579.19 ± 53.37^{B}	795.46 ± 28.18^{DE}	1322.85 ± 98.80^{C}	1341.70 ± 94.88^{C}	1887.71 ± 14.89^{A}	1460.17 ± 17.57^{BC}
	Aldehydes										
10	2-Methylbutanal	12.87 ± 2.36^{DEF}	13.63 ± 1.07^{CDEF}	18.58 ± 1.32^{BCDE}	14.78 ± 2.85^{CDEF}	19.73 ± 1.46^{BC}	25.11 ± 3.21^{B}	18.83 ± 2.86^{BCDE}	24.48 ± 0.72^{B}	44.77 ± 2.94^{A}	40.71 ± 4.05^{A}
11	3-Methylbutanal	47.18 ± 4.76^{EFG}	39.76 ± 3.71^{GH}	89.00 ± 3.45^{D}	61.16 ± 8.44^{E}	113.90 ± 6.01^{BC}	104.47 ± 2.92^{CD}	96.20 ± 3.84^{D}	125.18 ± 4.12^{AB}	138.82 ± 2.11^{A}	121.71 ± 8.29^{B}
12	Pentanal	128.54 ± 6.19^{BC}	135.89 ± 6.09^{B}	115.66 ± 5.25^{BCD}	104.88 ± 4.09^{CDE}	110.01 ± 5.29^{CDE}	89.10 ± 0.95^{E}	113.41 ± 13.36^{BCDE}	128.79 ± 6.44^{BC}	95.52 ± 3.86^{DE}	117.33 ± 7.99^{BCD}
13	Hexanal	191.78 ± 14.84^{DEF}	162.76 ± 4.62^{FGH}	178.35 ± 8.71^{EFG}	153.03 ± 3.27^{GHI}	138.56 ± 11.29^{HIJ}	128.82 ± 2.46^{IJ}	155.26 ± 15.99^{GHI}	178.77 ± 11.87^{EFG}	113.75 ± 5.49^{J}	135.14 ± 8.35^{HIJ}
14	Heptanal	24.46 ± 2.11^{FGH}	19.72 ± 1.18^{H}	27.89 ± 0.37^{CDEFG}	21.93 ± 2.49^{GH}	24.34 ± 2.46^{FGH}	24.15 ± 2.59^{FGH}	27.06 ± 2.66^{EFGH}	33.97 ± 0.91^{BCDE}	27.44 ± 3.63^{DEFG}	30.54 ± 2.21^{BCDEF}
15	Octanal	29.99 ± 0.73^{EFG}	22.40 ± 1.00^{G}	38.97 ± 1.00^{BC}	36.77 ± 3.53^{CDE}	38.93 ± 1.22^{BC}	36.89 ± 5.74^{CDE}	37.63 ± 4.40^{CDE}	40.63 ± 1.77^{BC}	38.71 ± 3.36^{BCD}	30.67 ± 0.40^{DEF}
16	Nonanal	58.80 ± 6.31^{BC}	41.50 ± 4.00^{C}	67.74 ± 6.13^{BC}	52.21 ± 8.14^{BC}	46.94 ± 2.26^{BC}	83.12 ± 27.26^{ABC}	66.21 ± 18.27^{BC}	61.49 ± 6.52^{BC}	131.49 ± 27.89^{A}	63.11 ± 6.44^{BC}
17	Benzaldehyde	86.48 ± 3.83^{EFGH}	81.56 ± 6.82^{FGH}	110.03 ± 2.86^{BCD}	89.33 ± 8.18^{EFGH}	112.20 ± 4.36^{ABC}	99.05 ± 5.63^{CDEF}	114.24 ± 8.22^{ABC}	115.94 ± 4.16^{ABC}	126.94 ± 13.90^{AB}	130.59 ± 4.14^{A}
18	Benzeneacetaldehyde	163.81 ± 12.86^{C}	40.34 ± 1.96^{F}	207.65 ± 5.54^{B}	82.21 ± 8.73^{E}	264.64 ± 14.95^{A}	77.04 ± 3.08^{E}	110.05 ± 16.04^{D}	229.86 ± 8.14^{B}	159.16 ± 8.52^{C}	79.04 ± 2.12^{E}
19	Methyl phenyl pentenal	16.69 ± 2.22^{FG}	11.30 ± 2.05^{GH}	24.84 ± 2.14^{EF}	32.45 ± 3.07^{DE}	45.69 ± 4.68^{B}	35.78 ± 4.74^{CD}	37.16 ± 4.19^{CD}	42.45 ± 1.24^{BC}	50.40 ± 2.05^{AB}	55.38 ± 3.77^{A}
20	5-Methyl-2-phenyl-2-hexenal	74.90 ± 7.82^{EF}	41.61 ± 8.94^{FG}	126.73 ± 9.41^{DE}	151.65 ± 35.42^{CD}	307.41 ± 47.56^{A}	170.50 ± 14.16^{CD}	184.43 ± 22.13^{BC}	228.96 ± 13.64^{B}	135.34 ± 11.14^{CD}	162.10 ± 11.41^{CD}
	Total	835.52 ± 43.38^{E}	610.47 ± 34.10^{F}	1005.42 ± 10.46^{BC}	800.40 ± 56.86^{E}	1222.36 ± 34.22^{A}	874.03 ± 31.49^{DE}	960.50 ± 35.84^{BCD}	1210.53 ± 41.90^{A}	1062.34 ± 73.68^{B}	966.34 ± 26.49^{BCD}
	Ketones										
21	2-Heptanone	28.56 ± 2.89^{CDEF}	32.25 ± 1.05^{BCDE}	27.84 ± 2.30^{CDEF}	28.27 ± 2.08^{CDEF}	23.96 ± 2.47^{F}	25.87 ± 1.69^{DEF}	25.12 ± 4.18^{EF}	26.23 ± 2.16^{DEF}	31.63 ± 3.09^{BCDEF}	35.78 ± 4.03^{BC}
22	3-Octanone	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}
23	3-Hydroxy-2-butanone	57.44 ± 4.51^{A}	56.38 ± 6.04^{A}	34.93 ± 4.85^{B}	27.48 ± 2.14^{BC}	0.00 ± 0.00$^{\#}$	0.00 ± 0.00$^{\#}$	0.00 ± 0.00$^{\#}$	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}
24	2-Octanone	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}
25	3-Octen-2-one	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	28.39 ± 1.16^{D}	24.58 ± 3.67^{D}	65.88 ± 3.71^{B}	47.87 ± 6.46^{C}	55.02 ± 2.41^{C}	70.41 ± 2.63^{B}	96.63 ± 4.61^{A}	70.86 ± 4.19^{B}
26	2-Nonanone	14.52 ± 0.27^{C}	15.90 ± 0.42^{C}	20.76 ± 0.91^{B}	21.58 ± 1.55^{B}	0.00 ± 0.00$^{\#}$	0.00 ± 0.00$^{\#}$	0.00 ± 0.00$^{\#}$	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}
27	Acetophenone	28.73 ± 1.48^{EFGH}	32.36 ± 0.99^{CDEF}	39.31 ± 0.64^{BCDE}	45.30 ± 4.68^{BCD}	48.47 ± 1.59^{B}	54.49 ± 5.07^{B}	53.99 ± 1.23^{B}	47.05 ± 2.50^{BC}	86.02 ± 9.08^{A}	76.51 ± 14.98^{A}
	Total	129.25 ± 2.05^{C}	136.89 ± 6.00^{C}	151.22 ± 4.16^{C}	147.21 ± 11.83^{C}	138.31 ± 6.90^{C}	128.23 ± 12.49^{C}	134.14 ± 5.59^{C}	143.69 ± 7.29^{C}	214.27 ± 16.41^{A}	183.15 ± 22.94^{B}
	Pyrazines										
28	Methylpyrazine	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	12.84 ± 1.35^{B}	15.13 ± 1.81^{B}	16.13 ± 2.80^{B}	22.79 ± 3.16^{B}	38.57 ± 11.87^{A}	22.46 ± 3.57^{B}
29	2,5-Dimethylpyrazine	0.00 ± 0.00^{H}	0.00 ± 0.00^{H}	12.99 ± 0.49^{FG}	10.44 ± 1.65^{G}	19.63 ± 1.18^{DE}	18.71 ± 1.44^{E}	26.12 ± 0.80^{C}	22.21 ± 0.89^{D}	33.41 ± 2.59^{B}	40.19 ± 1.67^{A}
30	2,6-Dimethylpyrazine	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	17.53 ± 0.65^{B}	19.62 ± 1.53^{B}	18.57 ± 1.89^{B}	19.30 ± 1.59^{B}	37.12 ± 3.49^{A}	33.76 ± 1.97^{A}

(*continued on next page*)

Table 3a (*continued*)

N-o.	Volatile	0PS-100 °C	7PS-100 °C	0PS-120 °C	3PS-120 °C	0PS-135 °C	3PS-135 °C	7PS-135 °C	0PS-140 °C	0PS-160 °C	7PS-160 °C
31	2-Ethyl-6-methylpyrazine	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	6.01 ± 0.45^{DE}	4.50 ± 0.69^{DE}	14.58 ± 1.34^{C}	9.76 ± 1.66^{CD}	14.57 ± 1.51^{C}	15.95 ± 1.35^{C}	38.41 ± 1.78^{B}	34.98 ± 3.79^{B}
32	2-Ethyl-5-methylpyrazine	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	37.81 ± 1.16^{BC}	31.82 ± 2.89^{C}	41.74 ± 1.51^{B}	45.71 ± 2.77^{B}	69.77 ± 2.64^{A}	74.19 ± 9.10^{A}
33	Trimethylpyrazine	10.95 ± 0.97^{H}	13.71 ± 1.10^{GH}	25.76 ± 0.81^{EFGH}	21.08 ± 1.65^{FGH}	63.77 ± 4.13^{C}	47.84 ± 3.03^{CDE}	134.19 ± 2.70^{B}	63.11 ± 5.09^{C}	151.72 ± 8.46^{B}	345.28 ± 28.80^{A}
34	2,6-Diethyl-3-ethylpyrazine	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	209.63 ± 19.22^{C}	116.82 ± 23.22^{E}	183.51 ± 31.55^{CD}	166.80 ± 8.52^{D}	349.66 ± 19.98^{B}	488.17 ± 15.51^{A}
35	Tetramethylpyrazine	178.26 ± 23.40^{FG}	581.62 ± 9.37^{C}	197.79 ± 8.92^{EF}	150.22 ± 29.12^{FGH}	277.23 ± 3.21^{DE}	103.26 ± 7.94^{GH}	966.32 ± 63.36^{B}	223.28 ± 7.86^{DEF}	306.64 ± 27.86^{D}	1467.80 ± 79.11^{A}
36	3,5-Diethyl-2-methylpyrazine	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	20.13 ± 0.90^{DE}	13.15 ± 2.25^{E}	39.37 ± 5.40^{B}	27.13 ± 1.21^{CD}	36.67 ± 4.64^{BC}	35.74 ± 0.76^{BC}	87.60 ± 10.30^{A}	78.01 ± 6.40^{A}
37	2,3,5-Trimethyl-6-ethylpyrazine	30.72 ± 3.87^{D}	37.24 ± 2.06^{D}	49.86 ± 1.72^{D}	36.29 ± 2.13^{D}	107.94 ± 1.38^{C}	36.58 ± 5.38^{D}	136.54 ± 7.28^{B}	95.57 ± 4.69^{C}	154.58 ± 14.28^{B}	305.20 ± 21.20^{A}
38	2,5-Dimethyl-3-n-pentylpyrazine	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	35.15 ± 8.84^{C}	24.88 ± 1.34^{C}	34.45 ± 1.24^{C}	27.22 ± 8.81^{C}	64.47 ± 8.92^{B}	99.42 ± 18.32^{A}
	Total	219.93 ± 22.79^{GH}	632.58 ± 11.08^{E}	312.54 ± 11.95^{G}	235.69 ± 30.95^{GH}	835.48 ± 24.91^{D}	451.54 ± 41.22^{F}	1608.82 ± 63.47^{B}	737.68 ± 20.06^{DE}	1331.95 ± 53.81^{C}	2989.47 ± 134.56^{A}
	Esters										
39	Methyl acetate	32.38 ± 3.61^{BCD}	25.70 ± 5.58^{DEF}	19.85 ± 0.88^{F}	20.32 ± 2.76^{EF}	24.70 ± 1.97^{DEF}	25.57 ± 1.94^{DEF}	26.39 ± 2.05^{DEF}	28.72 ± 2.71^{CDEF}	54.67 ± 3.99^{A}	41.19 ± 3.62^{B}
40	Ethyl octanoate	11.68 ± 1.34^{CD}	9.67 ± 0.69^{DE}	17.82 ± 0.38^{A}	15.95 ± 1.74^{AB}	0.00 ± 0.00^{G}	0.00 ± 0.00^{G}	0.00 ± 0.00^{G}	0.00 ± 0.00^{G}	0.00 ± 0.00^{G}	0.00 ± 0.00^{G}
41	Methyl phenyl acetate	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	18.67 ± 3.84^{B}	22.67 ± 7.43^{B}	17.72 ± 3.64^{B}	20.17 ± 0.43^{B}	44.66 ± 0.97^{A}	46.71 ± 2.91^{A}
42	Ethyl phenyl acetate	40.35 ± 4.46^{EFG}	56.45 ± 3.51^{CDE}	44.85 ± 3.86^{EF}	49.32 ± 13.73^{DEF}	70.12 ± 9.51^{C}	65.55 ± 7.59^{CD}	97.99 ± 5.01^{B}	75.15 ± 5.65^{C}	74.31 ± 9.27^{C}	118.35 ± 7.06^{A}
43	Phenyl ethyl acetate	99.28 ± 6.74^{EFGH}	83.45 ± 5.60^{FGHI}	103.91 ± 2.26^{DEFG}	64.51 ± 12.44^{IJ}	123.59 ± 7.07^{BCDE}	53.24 ± 2.37^{J}	106.95 ± 14.60^{DEF}	109.98 ± 8.94^{DEF}	128.75 ± 8.61^{BCD}	139.89 ± 9.72^{BC}
44	Amyl benzoate	56.76 ± 6.76^{BCDE}	71.27 ± 6.35^{ABC}	51.16 ± 1.52^{CDEF}	76.55 ± 11.67^{ABC}	57.74 ± 5.01^{BCDE}	70.54 ± 7.15^{BCD}	78.73 ± 14.05^{AB}	60.22 ± 3.42^{BCDE}	73.90 ± 15.46^{ABC}	97.22 ± 12.84^{A}
	Total	240.45 ± 8.11^{DEFG}	246.54 ± 4.44^{DEF}	237.59 ± 8.03^{EFGH}	226.65 ± 39.62^{FGH}	294.81 ± 9.20^{CD}	237.58 ± 20.76^{EFGH}	327.78 ± 37.45^{BC}	294.24 ± 12.20^{CDE}	376.30 ± 8.23^{B}	443.37 ± 17.32^{A}
	Terpenes and terpenoids										
45	Delta-3-carene	9.96 ± 1.26^{ABCD}	8.28 ± 0.10^{BCDE}	12.00 ± 0.49^{AB}	8.28 ± 1.52^{BCDE}	7.32 ± 0.32^{DE}	8.30 ± 0.59^{BCDE}	7.35 ± 1.06^{CDE}	10.11 ± 0.61^{ABCD}	13.20 ± 1.35^{A}	12.84 ± 4.02^{A}
46	Myrcene	5.85 ± 1.19^{EF}	6.41 ± 0.45^{DEF}	10.24 ± 0.84^{A}	8.12 ± 0.61^{BCD}	8.65 ± 0.46^{ABC}	8.85 ± 0.89^{AB}	8.58 ± 0.47^{ABC}	10.06 ± 1.47^{AB}	9.66 ± 0.89^{AB}	10.58 ± 0.17^{A}
47	Limonene	14.94 ± 1.03^{CDE}	10.78 ± 1.15^{EF}	11.49 ± 0.28^{DEF}	10.30 ± 2.38^{F}	9.66 ± 1.01^{F}	12.68 ± 0.79^{DEF}	11.28 ± 0.73^{EF}	12.18 ± 1.46^{DEF}	19.84 ± 1.49^{B}	17.73 ± 0.84^{BC}
48	Cis-ocimene	11.23 ± 1.44^{E}	11.10 ± 0.90^{E}	19.15 ± 1.64^{BC}	16.29 ± 0.90^{CD}	20.69 ± 2.14^{ABC}	21.24 ± 2.63^{AB}	22.15 ± 1.00^{AB}	22.73 ± 2.16^{AB}	24.43 ± 0.73^{A}	24.22 ± 1.77^{A}
49	Trans-ocimene	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	5.37 ± 0.58^{AB}	4.88 ± 0.84^{AB}	6.28 ± 1.02^{AB}	6.11 ± 0.19^{AB}	5.03 ± 0.26^{AB}	5.24 ± 0.59^{AB}	5.13 ± 1.60^{AB}	10.67 ± 8.56^{A}
50	Linalool oxide	23.55 ± 6.49^{CD}	22.62 ± 1.82^{CD}	27.84 ± 4.07^{ABC}	37.33 ± 8.99^{ABC}	43.25 ± 11.46^{A}	25.47 ± 2.59^{BCD}	32.30 ± 5.09^{ABC}	28.99 ± 6.78^{ABC}	29.15 ± 7.83^{ABC}	39.76 ± 2.41^{AB}
51	Dihydromyrcenol	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}
52	Linalool	74.91 ± 10.99^{CD}	69.19 ± 3.91^{D}	93.47 ± 7.97^{BCD}	91.92 ± 5.17^{BCD}	113.34 ± 5.72^{AB}	93.09 ± 7.36^{BCD}	117.01 ± 5.72^{AB}	99.75 ± 6.02^{ABC}	113.72 ± 7.08^{AB}	121.33 ± 24.83^{A}
53	Epoxylinalool	42.23 ± 5.69^{B}	36.47 ± 9.42^{B}	31.81 ± 3.30^{B}	39.04 ± 8.06^{B}	40.66 ± 3.60^{B}	30.64 ± 7.39^{BC}	39.56 ± 5.60^{B}	36.16 ± 6.58^{B}	45.82 ± 5.16^{B}	62.66 ± 8.17^{A}
	Total	182.68 ± 22.76^{DEF}	164.85 ± 13.77^{EF}	211.37 ± 8.13^{CD}	216.16 ± 10.99^{BCD}	249.85 ± 14.42^{BC}	206.38 ± 16.13^{CDE}	243.26 ± 6.83^{BC}	225.21 ± 9.30^{BCD}	260.95 ± 14.76^{AB}	299.79 ± 41.18^{A}
	Furans, furanones, pyrans, pyrones										
54	2-Pentyl furan	47.17 ± 2.38^{GH}	53.87 ± 5.08^{GH}	65.96 ± 3.08^{DEF}	43.10 ± 1.69^{H}	43.54 ± 4.84^{H}	55.82 ± 2.24^{FG}	45.82 ± 3.46^{GH}	69.68 ± 5.13^{CD}	70.44 ± 3.83^{CD}	68.91 ± 0.50^{CD}
55	Rose oxide	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	65.26 ± 1.53^{D}	52.58 ± 5.05^{D}	134.24 ± 12.68^{B}	114.38 ± 10.77^{C}	138.39 ± 7.35^{B}	147.14 ± 5.55^{B}	211.72 ± 10.45^{A}	202.66 ± 12.08^{A}
56	γ-Butyrolactone	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	24.64 ± 10.57^{CDE}	19.47 ± 5.04^{DE}	47.40 ± 16.72^{BCD}	58.54 ± 20.59^{B}	54.64 ± 25.01^{BC}	39.62 ± 1.13^{BCD}	99.05 ± 9.43^{A}	93.96 ± 15.95^{A}
57	Furfuryl alcohol	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	49.85 ± 2.49^{D}	52.63 ± 13.64^{CD}	76.58 ± 4.99^{BC}	78.92 ± 7.49^{B}	94.76 ± 5.52^{AB}	86.39 ± 9.57^{B}	114.05 ± 5.63^{A}	91.61 ± 9.93^{AB}
58	5-Ethyl-2(5H)-furanone	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}
59	Tetrahydro-2H-pyran-2-one	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	27.68 ± 4.92^{BC}	24.72 ± 3.45^{C}	33.34 ± 4.94^{B}	29.81 ± 3.17^{BC}	55.34 ± 1.47^{A}	31.94 ± 1.13^{B}
60	Pantoic lactone	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	36.09 ± 1.41^{CDE}	35.06 ± 4.09^{CDE}	30.63 ± 4.00^{CDE}	23.68 ± 1.54^{E}	50.54 ± 23.16^{BC}	46.25 ± 2.93^{BCD}	65.80 ± 2.22^{B}	101.24 ± 5.52^{A}

(*continued on next page*)

Table 3a (*continued*)

N-o.	Volatile	0PS-100 °C	7PS-100 °C	0PS-120 °C	3PS-120 °C	0PS-135 °C	3PS-135 °C	7PS-135 °C	0PS-140 °C	0PS-160 °C	7PS-160 °C
61	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	39.70 ± 10.27^{CD}	0.00 ± 0.00^{E}	37.31 ± 3.15^{CDE}	33.62 ± 4.31^{DE}	53.44 ± 20.49^{BCD}	170.03 ± 40.69^{A}	74.26 ± 8.79^{BC}	82.10 ± 11.52^{B}
	Total	47.17 ± 2.38^{H}	53.87 ± 5.08^{H}	281.51 ± 17.41^{EF}	202.85 ± 22.45^{FG}	397.38 ± 14.30^{CD}	389.67 ± 29.31^{D}	470.92 ± 76.68^{C}	588.92 ± 49.31^{B}	690.66 ± 11.12^{A}	672.44 ± 9.31^{A}
	Pyrroles										
62	Isoamyl-2-formyl pyrrole	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	44.46 ± 8.60^{BC}	25.37 ± 10.37^{D}	37.03 ± 3.18^{BCD}	31.64 ± 4.27^{CD}	52.19 ± 10.01^{B}	148.55 ± 11.52^{A}
63	2-Acetylpyrrole	19.29 ± 0.65^{E}	19.29 ± 0.70^{E}	42.71 ± 1.02^{CD}	43.39 ± 2.88^{CD}	87.08 ± 3.59^{B}	55.29 ± 1.74^{C}	92.22 ± 10.26^{B}	83.22 ± 4.08^{B}	116.65 ± 6.07^{A}	126.93 ± 7.92^{A}
64	2-Formylpyrrole	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	64.31 ± 16.11^{A}	44.13 ± 4.46^{B}	61.95 ± 8.81^{A}	51.82 ± 2.56^{AB}	59.49 ± 2.71^{AB}	57.90 ± 7.57^{AB}
	Total	19.29 ± 0.65^{G}	19.29 ± 0.70^{G}	42.71 ± 1.02^{FG}	43.39 ± 2.88^{FG}	195.85 ± 26.16^{BC}	124.79 ± 14.78^{D}	191.20 ± 16.15^{C}	166.68 ± 6.52^{C}	228.33 ± 17.33^{B}	333.38 ± 22.10^{A}
	Others										
65	Dimethyldisulfide	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	13.23 ± 0.77^{B}	12.74 ± 1.75^{B}	13.01 ± 1.45^{B}	15.18 ± 1.47^{B}	14.42 ± 1.63^{B}	13.24 ± 0.73^{B}	24.45 ± 2.40^{A}	22.52 ± 1.47^{A}
66	o-Xylene	9.17 ± 2.01^{ABCD}	8.77 ± 0.38^{ABCDE}	9.43 ± 2.27^{ABCD}	7.74 ± 1.79^{BCDE}	7.50 ± 0.13^{CDE}	8.41 ± 1.11^{ABCDE}	6.50 ± 0.62^{DE}	13.30 ± 2.40^{A}	12.47 ± 2.96^{AB}	12.36 ± 2.93^{ABC}
67	Pyridine	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	3.35 ± 0.87^{ABC}	2.81 ± 0.79^{BC}	2.82 ± 1.07^{BC}	2.60 ± 0.85^{BC}	2.53 ± 0.34^{C}	2.90 ± 0.33^{BC}	4.94 ± 0.79^{A}	4.44 ± 0.92^{AB}
68	2-Methoxyphenol	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	24.13 ± 7.85^{BC}	16.93 ± 3.97^{C}	29.61 ± 1.95^{BC}	31.66 ± 4.91^{B}	36.85 ± 1.64^{B}	52.07 ± 15.80^{A}
69	Pyrrolidinone	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	31.44 ± 2.88^{C}	25.84 ± 1.96^{CD}	30.17 ± 3.72^{C}	29.51 ± 4.29^{CD}	65.10 ± 10.05^{B}	125.96 ± 36.43^{A}
	Total	9.17 ± 2.01^{G}	8.77 ± 0.38^{G}	26.01 ± 1.37^{FG}	23.29 ± 4.25^{FG}	78.90 ± 5.01^{CD}	68.97 ± 5.12^{CDE}	83.23 ± 2.69^{CD}	90.61 ± 3.59^{C}	143.81 ± 9.76^{B}	217.33 ± 44.99^{A}
	Grand total	5610.87 ± 346.36^{F}	4805.39 ± 123.78^{G}	6480.46 ± 124.59^{E}	5123.13 ± 244.52^{FG}	9049.06 ± 400.27^{C}	5765.68 ± 182.63^{EF}	9277.11 ± 458.77^{C}	8184.53 ± 174.66^{D}	10,518.86 ± 283.81^{B}	12,364.38 ± 86.20^{A}

For each row different alphabets represent significant differences (α = 0.05) among samples. ($^{\#}$) peak was present but too small to be integrated.

(AHC) to illustrate the (dis)similarities between the different chocolates in terms of their aroma profiles. Hereby, Fig. 1a and b represent clustering on the basis of all identified volatiles and odor-active volatiles, respectively.

3.1. Acids

The fermentation of cocoa beans facilitates the formation of both volatile and non-volatile acids which imparts sourness and astringency with inimical implications on the flavor quality of cocoa/chocolates (Afoakwa et al., 2008; Frauendorfer & Schieberle, 2008). Table 3a and 3b show the concentrations of aroma volatiles identified from both sample chocolates and those from commercial cocoa liquors respectively. Generally, chocolates from unstored pods expressed higher total acid concentrations than those from stored pods. Hinneh et al. (2018) attributed this to the impact of pulp volume reduction on the quality of the fermentation process, thus, resulting in minimal acid production after PS. However, for a rise in acidity between 3PS and 7PS, they attributed this to the additional consequence of an onset of cellular degradation of both pod and pulp (fermentation-like process), in which case it was associated with a gradual rise in acidity. This trend was consistent at all temperatures with an exception of RT of 160 °C where a leveling-off effect was observed, probably due to the influence of this elevated temperature. Generally, the total concentration of volatile acids increased insignificantly ($p > .05$) with increasing RT, except at temperatures of 135 °C and 160 °C where a significant increase ($p < .05$) was observed. Through the mechanism of volatilization, the roasting processes has been claimed to reduce acidity in cocoa beans (Afoakwa et al., 2008; Rodriguez-Campos et al., 2012). However, it is likely that the heating process may have resulted in unlocking these volatiles from the matrix, thereby making them more 'available' in the liquor and subsequently in the chocolate. Afoakwa (2016), described the impact of roasting on the structural changes within the bean, whereby, the extensive loss of moisture ultimately renders the beans friable, accompanied with loose and a porous matrix. Therefore, the degree of change along with the liberation of volatiles from the matrix can be said to be proportional to the roasting intensity. Meanwhile, the chocolates from the commercial cocoa liquors possessed generally lower concentrations of volatile acids. Of these, the Ghanaian, Vietnamese and Madagascan chocolates possessed significantly similar ($p > .05$) level of acids with 3PS-120 °C, 3PS-135 °C and 7PS-100 °C chocolates. Meanwhile, both Venezuelan and Ivorian chocolates recorded the lowest ($p < .05$) total acid concentrations. Among the identified acids, only acetic acid and isovaleric acid were identified as odor-active volatiles (Table 4). However, due to its higher concentrations, the major contribution of acetic acid to the overall sourness of the chocolates could be suspected.

3.2. Alcohols

The trend in the total alcohol concentration was similar to the volatile acids, where, for any given RT, chocolates with pod stored cocoa beans possessed significantly lower ($p < .05$) total alcohol concentration compared to chocolates from the unstored pods (Table 3a). For the same reason aforementioned, the significant rise ($p < .05$) in total alcohols from 3PS to 7PS was also logical. High alcohol contents are essential in developing chocolates with flowery and candy notes (Rodriguez-Campos et al., 2012). Thus, the results suggest that very minimal or no PS may be ideal in conserving more alcohols for any RT. Likewise, a significant increasing ($p < .05$) trend in total alcohol with increasing RT was also observed. Apart from the possible impact of roasting on the liberation of volatiles as suggested earlier, Ramli, Hassan, Said, Samsudin, and Idris (2006) also observed an increasing linear relationship between alcohol concentration and RT. Of these, they speculated that alcohols such as 2-heptanol and linalool may be recognized as volatiles of thermally degradable amino acids.

Additionally, they also noted that the prolonged heat duration of roasting may be responsible for the volatilization of some alcohols, yet, this was only observed within the range of 160 °C to 170 °C. Comparing the chocolates from the commercial cocoa liquors to the sample chocolates, significantly lower ($p < .05$) concentrations of the alcohols were recorded. Furthermore, of these chocolates from the commercial liquors, the differences were insignificant ($p > .05$), except for Ghana and Venezuela. Among all the alcohols, 2-phenylethyl alcohol was the only odor-active volatile, thus, it is expected to impart its typical floral note to the chocolates (Tables 4a and 4b).

3.3. Aldehydes and ketones

Aldehydes and ketones which are formed from the Strecker degradation reaction during roasting, are crucial for the expression of good cocoa flavor. Table 3a shows a similar trend of total aldehydes with PS as seen for the alcohols. Hereby, the concentrations of the aldehydes were higher in chocolates of 0PS compared to other days of PS for any given RT, except at 160 °C where no significant ($p > .05$) difference was seen for the unstored and stored pods. More so, the impact of the RT was also seen as the aldehyde concentration increased with increasing RT until a peak between 135 and 140 °C. Between 140 °C and 160 °C, the total concentration declined, possibly, due to the higher temperature. Accordingly, Aprotosoaie et al. (2016), stated that high temperatures and a longer roasting conditions are known to decrease the content of aldehydes. It can be seen from Tables 3a and 3b that a total of eleven aldehydes were identified. Of these, key aldehydes, namely; 2-methylbutanal and 3-methylbutanal, which were both dominant in 0PS-160 °C chocolate, increased trivially with increasing RT. Both aroma volatiles were also found to be odor-active and most likely to impart their characteristic cocoa and chocolate notes to the final flavor (Frauendorfer & Schieberle, 2008). It is worth mentioning that despite registering generally lower concentrations in other key aldehydes, the concentrations of odor-active hexanal and heptanal were generally higher in the chocolates from commercial cocoa liquors than in the sample chocolates. Here, the Ecuadorian chocolate recorded significantly higher ($p < .05$) concentrations for both volatiles. Not only was the Madagascan chocolate also dominant with respect to heptanal, but together with the Ecuadorian chocolate, also recorded the highest total concentration of the aldehydes among the chocolates from the commercial liquors.

Except at a temperature of 160 °C, both RT and PS had no significant ($p > .05$) effect on the total concentration of ketones. For the sample chocolates, identified ketones including; 2-nonanone and 3-hydroxy-2-butanone, appeared dominant in chocolates with lower RT's. For these volatiles, quantifiable amounts were observed at 100 °C and 120 °C. This may be attributed to the high volatility of these aroma compounds. On the contrary, acetophenone and 3-octen-2-one were produced in abundance at higher temperatures. Although the trend underlying the effect of both PS and RT were indefinite, the highest concentrations of the ketones were obtained at higher temperatures (~ 160 °C) for 0PS. From Table 3b, the Ghanaian chocolate was found to possess higher total concentration of ketones among the chocolates from commercial liquors.

3.4. Pyrazines

Pyrazines are a major group of volatiles which are formed through various heterocyclization reactions following the Strecker degradation reaction during the roasting process. They are typically known to confer cocoa, chocolate and nutty flavor notes. From the sample chocolates in Table 3a, a trend revealing a direct relationship between PS and the total pyrazine concentration was found, except for the short duration of PS (*ie.* 0–3 days) where the opposite was found. This was synonymous with the findings of Hinneh et al. (2018) who demonstrated the modification of aroma precursors (reducing sugars and free amino acids) in the beans due to PS and its link with the abundance of pyrazines formed during the roasting process. Remarkably, the concentration of pyrazines in 7PS increased over two folds at most RT's. Suggestively, the prolonged period of PS may have facilitated the formation of more precursors which enhanced the formation of these pyrazines during the subsequent roasting process. More so, the same increasing effect of RT on the pyrazine concentration was observed. Apart from tetramethylpyrazine and trimethylpyrazine which are reported to partly evolve from microbiological activities during fermentation (Jinap, Siti, & Norsiati, 1994; Schwan & Wheals, 2004), the majority of pyrazines originate from the Strecker degradation in the Maillard reaction. Temperature as well as abundance of aroma precursors are critical factors that influence their concentrations (Afoakwa et al., 2008; Aprotosoaie et al., 2016). This may explain why the RT appeared to play a substantial role in in the concentration of the pyrazines. Tetramethylpyrazine was the most dominant pyrazine in all chocolates with its highest concentration observed in 7PS-160 °C. Nevertheless, the contributing effect of this volatile to the flavor quality of the cocoa was negligible due to its low OAV (Table 4a and 4b). Trimethypyrazine was odor-active exclusively in 7PS-160 °C chocolate. Methylpyrazine and 2,6-dimethyl pyrazine were among the pyrazines absent in chocolates whose initial cocoa beans were roasted at temperatures below 135 °C. This is likely due to the lower concentrations of the volatiles produced in the liquors after roasting, more so, the heating effect and the processing conditions during the conching may have enhanced their complete elimination from these chocolates. Some pyrazines were absent in many of the chocolates from the commercial liquors. Of these, the Ghanaian and Vietnamese chocolates were marked among the origins as they exhibited significantly higher ($p < .05$) total pyrazine concentration (Table 3b).

3.5. Esters, terpenes and terpenoids

Esters are associated with fruity/floral notes and represent the second most important group of volatile compounds after pyrazines in roasted cocoa nibs (Jinap, Wan-Rosli, Russly, & Nordin, 1998). Apart from methyl acetate, ethyl octanoate and phenyl ethyl acetate, 7PS-160 °C chocolates exhibited the highest concentrations of all other esters (Table 3a). Ethyl octanoate was exclusive to the chocolates from commercial liquors and sample chocolates with lower RT's (100–120 °C). Ethyl octanoate was significantly pronounced ($p < .05$) in both 0PS-120 °C and 3PS-120 °C chocolates. It was odor-active and thus expected to contribute to the final chocolate flavor (Table 4a and 4b). Phenyl ethyl acetate was the most abundant ester, being more pronounced in the Vietnamese chocolate (Table 3b). This volatile confers honey and floral notes (Rodriguez-Campos et al., 2012), but was only odor-active in the Ecuadorian, Vietnamese and 7PS-160 °C chocolates. It is worth mentioning that most esters occur as microbial metabolites which may arise from the fermentation process (Aprotosoaie et al., 2016). Yet, it seemed that both the PS and the RT impacted the concentrations of these esters as they may have promoted their formation and release respectively. However, these effects were significant above 135 °C, beyond which the abundance of esters associated with 7PS chocolate was conspicuous. More so, the abundance of esters in the chocolates from commercial liquors were fairly comparable to the sample chocolates. Of the former, the Vietnamese chocolate recorded generally higher concentration of esters.

No significant effect ($p > .05$) of PS on the total concentration of terpenes and terpenoids was found. Likewise, a trivial increase in the total concentration these volatiles with RT was also found (Table 3a). Apart from linalool, other terpenes occurred in minimal amounts in the chocolates with 7PS-160 °C chocolate recording the highest total concentration. It also increased with increasing RT. Just like the other terpenes, it is probable that linalool became less bound within the matric following an increase in temperature. It was identified as odor-active in most chocolates and likely to impart its characteristic floral

Table 3b

Concentrations (ng/g cocoa) of aroma volatiles identified from dark chocolates produced from commercial cocoa liquors.

No.	Volatile	Ecuador	Ghana	Ivory coast	Madagascar	Venezuela	Vietnam	Description*	KI
	Acids								
1	Acetic acid	3000.67 ± 118.90^{C}	2405.33 ± 180.97^{EF}	1479.63 ± 95.61^{H}	2433.68 ± 199.92^{DEF}	1821.11 ± 134.11^{GH}	2478.24 ± 106.48^{DEF}	Sour, vinegar	1418.21
2	Isovaleric acid	47.69 ± 3.58^{F}	177.29 ± 54.46^{D}	14.14 ± 0.33^{F}	56.29 ± 9.63^{F}	53.28 ± 7.09^{F}	86.37 ± 18.30^{EF}	Sweat, rancid	1607.91
3	Oxalic acid DITMS	112.94 ± 10.25^{BC}	124.14 ± 1.84^{BC}	113.91 ± 24.46^{BC}	112.13 ± 21.25^{BC}	67.35 ± 8.08^{C}	132.23 ± 5.63^{BC}	–	1357.99
	Total	3161.30 ± 130.83^{C}	2706.76 ± 235.68^{D}	1607.69 ± 120.28^{E}	2602.10 ± 172.15^{D}	1941.73 ± 133.99^{E}	2696.84 ± 127.92^{D}		
	Alcohols								
4	Amyl alcohol	36.04 ± 1.23^{CD}	54.43 ± 1.01^{A}	41.98 ± 4.25^{BC}	27.58 ± 2.91^{DE}	35.64 ± 0.87^{CD}	20.94 ± 1.53^{EF}	Banana	1236.36
5	1-Hexanol	8.87 ± 0.17^{B}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	9.74 ± 0.15^{A}	7.65 ± 0.16^{C}	7.70 ± 0.79^{C}	Fruity, green	1340.18
6	2,3-Butanediol	21.89 ± 2.25^{F}	68.92 ± 19.15^{DEF}	69.53 ± 9.71^{DEF}	42.55 ± 0.68^{F}	55.12 ± 0.85^{DEF}	56.95 ± 3.69^{DEF}	Cocoa butter	1507.95
7	1,3-Butanediol	87.29 ± 7.23^{F}	137.10 ± 14.34^{CDEF}	132.89 ± 19.34^{DEF}	115.32 ± 11.16^{EF}	83.34 ± 2.39^{F}	138.52 ± 5.14^{CDEF}	Sweet, flowery, caramel	1540.13
8	Benzyl alcohol	86.16 ± 1.28^{EFGH}	96.63 ± 7.36^{EFGH}	55.05 ± 9.91^{GH}	97.78 ± 6.92^{DEFG}	53.07 ± 1.98^{H}	79.02 ± 3.54^{FGH}	Sweet, floral	1767.54
9	2-Phenylethyl alcohol	181.16 ± 6.36^{GH}	190.10 ± 6.88^{G}	137.21 ± 33.00^{GH}	134.11 ± 17.90^{GH}	119.80 ± 9.29^{GH}	174.42 ± 3.38^{GH}	Floral	1793.64
	Total	421.41 ± 3.43^{FG}	547.18 ± 43.20^{F}	436.66 ± 68.35^{FG}	427.08 ± 14.70^{FG}	354.60 ± 12.08^{G}	477.55 ± 10.43^{FG}		
	Aldehydes								
10	2-Methylbutanal	12.79 ± 1.85^{EF}	16.25 ± 1.37^{CDEF}	19.41 ± 1.57^{BCD}	12.72 ± 1.25^{EF}	11.96 ± 0.67^{F}	16.49 ± 1.55^{CDEF}	Cocoa, chocolate	915.12
11	3-Methylbutanal	37.77 ± 3.40^{GH}	58.12 ± 6.46^{EF}	43.97 ± 0.81^{FGH}	33.14 ± 6.68^{GH}	31.17 ± 2.80^{H}	55.64 ± 7.24^{EF}	Cocoa, chocolate	917.15
12	Pentanal	186.76 ± 7.65^{A}	164.55 ± 0.67^{A}	89.50 ± 7.30^{E}	162.26 ± 23.68^{A}	96.15 ± 1.91^{DE}	122.76 ± 3.15^{BC}	Pungent	953.13
13	Hexanal	376.68 ± 14.26^{A}	253.21 ± 6.34^{C}	171.20 ± 6.38^{FG}	325.30 ± 19.30^{B}	207.47 ± 1.46^{DE}	212.98 ± 0.63^{D}	Green	1047.75
14	Heptanal	52.01 ± 2.39^{A}	35.84 ± 1.45^{B}	34.75 ± 5.17^{BCD}	54.36 ± 1.94^{A}	37.32 ± 1.90^{B}	35.09 ± 2.15^{BC}	–	1158.50
15	Octanal	50.89 ± 2.29^{A}	34.25 ± 2.89^{CDEF}	32.57 ± 3.58^{CDEF}	46.12 ± 2.32^{AB}	33.59 ± 1.21^{CDEF}	28.22 ± 1.28^{FG}	Fatty, waxy	1268.20
16	Nonanal	71.80 ± 1.95^{BC}	66.53 ± 11.96^{BC}	84.82 ± 36.40^{ABC}	97.86 ± 36.06^{AB}	77.37 ± 10.63^{BC}	54.70 ± 4.54^{BC}	Soapy	1372.10
17	Benzaldehyde	71.53 ± 5.23^{HI}	104.33 ± 2.62^{CDE}	93.61 ± 6.65^{DEFG}	75.47 ± 5.85^{GHI}	62.85 ± 1.42^{I}	71.47 ± 0.70^{HI}	Almond, burnt sugar	1477.26
18	Benzeneacetaldehyde	16.44 ± 1.06^{G}	36.31 ± 3.49^{FG}	17.33 ± 3.46^{FG}	26.46 ± 3.48^{FG}	16.75 ± 1.59^{G}	31.71 ± 1.43^{FG}	Honey, sweet, rose, flora	1804.38
19	Methyl phenyl pentenal	8.62 ± 0.78^{GH}	10.74 ± 0.77^{GH}	8.90 ± 1.19^{GH}	16.50 ± 3.53^{FG}	7.55 ± 0.93^{H}	10.05 ± 1.23^{GH}	Cocoa	1814.71
20	5-Methyl-2-phenyl-2-hexenal	21.11 ± 2.25^{FG}	36.38 ± 4.24^{FG}	15.44 ± 1.20^{G}	60.42 ± 15.84^{FG}	11.13 ± 0.77^{G}	30.47 ± 1.24^{FG}	Cocoa	1908.33
	Total	906.41 ± 25.88^{CDE}	816.50 ± 15.63^{E}	611.51 ± 47.08^{F}	910.62 ± 18.15^{CDE}	593.31 ± 19.65^{F}	669.58 ± 16.43^{F}		
	Ketones								
21	2-Heptanone	36.94 ± 2.59^{B}	33.87 ± 3.96^{BCD}	29.70 ± 2.02^{BCDEF}	48.78 ± 2.64^{A}	24.19 ± 1.19^{EF}	35.33 ± 2.67^{BC}	Fruity, floral	1155.99
22	3-Octanone	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	11.59 ± 1.62^{A}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	–	1233.48
23	3-Hydroxy-2-butanone	7.87 ± 1.11^{E}	26.83 ± 2.13^{C}	19.18 ± 2.58^{D}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	Butter, cream	1254.32
24	2-Octanone	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	9.52 ± 0.62^{A}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	–	1264.97
25	3-Octen-2-one	0.00 ± 0.00^{F}	10.19 ± 0.77^{E}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	–	1343.52
26	2-Nonanone	27.85 ± 1.93^{A}	28.96 ± 1.61^{A}	20.57 ± 3.14^{B}	23.24 ± 0.18^{B}	21.46 ± 2.01^{B}	22.50 ± 0.57^{B}	Milk, green, fruity	1368.61
27	Acetophenone	14.86 ± 1.58^{HI}	30.25 ± 2.82^{DEFG}	15.75 ± 1.60^{GHI}	14.58 ± 2.24^{HI}	13.41 ± 0.40^{I}	22.68 ± 4.42^{FGHI}	Floral, almond	1587.15
	Total	87.52 ± 4.98^{DE}	130.09 ± 6.42^{C}	94.73 ± 5.59^{D}	98.19 ± 4.87^{D}	59.05 ± 1.01^{E}	80.52 ± 6.64^{DE}		
	Pyrazines								
28	Methylpyrazine	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	13.58 ± 5.76^{B}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	Nutty, cocoa, roasted-nuts	1239.39
29	2,5-Dimethylpyrazine	18.21 ± 1.00^{E}	17.69 ± 0.58^{E}	0.00 ± 0.00^{H}	17.57 ± 0.94^{E}	11.80 ± 0.61^{FG}	14.00 ± 0.60^{F}	Cocoa, roasted nuts	1299.09
30	2,6-Dimethylpyrazine	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	12.21 ± 1.06^{C}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	Nutty, coffee, green	1304.66
31	2-Ethyl-6-methylpyrazine	3.66 ± 0.57^{DE}	121.96 ± 4.93^{A}	4.37 ± 0.59^{DE}	3.84 ± 0.61^{DE}	2.90 ± 0.25^{DE}	124.64 ± 7.75^{A}	Roasted, coffee, hazelnut	1362.22
32	2-Ethyl-5-methylpyrazine	0.00 ± 0.00^{D}	4.51 ± 0.37^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	6.12 ± 0.57^{D}	Nutty, raw potato	1368.64
33	Trimethylpyrazine	45.73 ± 3.57^{CDE}	41.71 ± 3.66^{CDEF}	19.31 ± 1.04^{FGH}	35.10 ± 2.57^{DEFG}	28.92 ± 0.80^{EFGH}	54.90 ± 1.72^{CD}	Cocoa, roasted nuts, sweet, smoky	1381.21
34	2,6-Diethyl-3-ethylpyrazine	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	–	1435.11
35	Tetramethylpyrazine	189.34 ± 11.52^{EFG}	626.85 ± 36.22^{C}	76.85 ± 11.61^{H}	65.41 ± 4.68^{H}	104.55 ± 6.30^{GH}	552.69 ± 5.51^{C}	Cocoa, coffee, roasted	1448.42
36	3,5-Diethyl-2-methylpyrazine	18.96 ± 1.68^{DE}	16.44 ± 2.05^{DE}	16.63 ± 4.92^{DE}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	19.56 ± 0.86^{DE}	–	1465.49
37	2,3,5-Trimethyl-6-ethylpyrazine	47.28 ± 3.65^{D}	43.36 ± 1.04^{D}	38.76 ± 7.05^{D}	0.00 ± 0.00^{E}	41.53 ± 1.46^{D}	48.35 ± 2.03^{D}	Candy, sweet	1484.11
38	2,5-Dimethyl-3-n-pentylpyrazine	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	27.63 ± 1.95^{C}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	–	1602.94
	Total	323.18 ± 18.51^{FG}	872.53 ± 45.55^{D}	209.34 ± 27.55^{GH}	121.92 ± 6.70^{H}	189.70 ± 7.54^{GH}	820.26 ± 5.12^{D}		
	Esters								
39	Methyl acetate	25.80 ± 1.22^{DEF}	23.47 ± 3.45^{DEF}	29.29 ± 5.05^{CDE}	25.64 ± 3.61^{DEF}	35.93 ± 0.75^{BC}	25.48 ± 1.17^{DEF}	–	888.28
40	Ethyl octanoate	11.76 ± 1.16^{CD}	12.08 ± 1.18^{C}	8.99 ± 0.98^{EF}	7.11 ± 0.18^{F}	9.45 ± 0.34^{DEF}	14.83 ± 0.83^{B}	Fruity, floral	1415.50

(*continued on next page*)

Table 3b (*continued*)

No.	Volatile	Ecuador	Ghana	Ivory coast	Madagascar	Venezuela	Vietnam	Description*	KI
41	Methyl phenyl acetate	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	Sweet, honey, jasmine	1678.38
42	Ethyl phenyl acetate	31.12 ± 2.87^{FG}	34.48 ± 1.12^{FG}	0.00 ± 0.00^{H}	39.45 ± 4.68^{EFG}	25.87 ± 2.14^{G}	39.84 ± 1.17^{EFG}	Fruity, sweet	1700.45
43	Phenyl ethyl acetate	143.28 ± 13.05^{B}	114.83 ± 1.19^{CDE}	56.81 ± 12.21^{IJ}	78.61 ± 10.10^{GHIJ}	76.75 ± 5.41^{HIJ}	203.56 ± 8.57^{A}	honey, floral	1722.77
44	Amyl benzoate	38.91 ± 4.43^{EF}	44.57 ± 2.52^{DEF}	36.34 ± 8.27^{EF}	30.14 ± 6.60^{F}	41.21 ± 5.33^{EF}	37.15 ± 9.96^{EF}	Balsam, sweet	1742.59
	Total	250.88 ± 16.37^{DEF}	229.43 ± 5.02^{FGH}	131.43 ± 19.77^{I}	180.94 ± 20.49^{HI}	189.21 ± 12.78^{GH}	320.85 ± 16.91^{BC}		
	Terpenes and terpenoids								
45	Delta-3-carene	11.20 ± 0.44^{ABC}	12.60 ± 0.32^{A}	6.00 ± 0.20^{E}	6.00 ± 0.05^{E}	10.15 ± 1.26^{ABCD}	6.57 ± 0.64^{DE}	–	1115.82
46	Myrcene	4.64 ± 0.30^{F}	6.80 ± 0.12^{CDE}	0.00 ± 0.00^{G}	4.50 ± 0.27^{F}	5.22 ± 0.47^{EF}	0.00 ± 0.00^{G}	Balsamic, must, spicy, sweet	1139.26
47	Limonene	12.56 ± 0.53^{DEF}	11.61 ± 1.61^{DEF}	16.02 ± 2.06^{BCD}	48.47 ± 2.51^{A}	12.21 ± 2.13^{DEF}	9.83 ± 1.90^{F}	Citrus-like	1169.41
48	Cis-ocimene	0.00 ± 0.00^{F}	13.17 ± 1.70^{DE}	10.16 ± 2.18^{E}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	0.00 ± 0.00^{F}	Balsamic, peppery, spicy	1214.52
49	Trans-ocimene	0.00 ± 0.00^{B}	5.38 ± 0.43^{AB}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	Balsamic, must, spicy, sweet	1230.91
50	Linalool oxide	0.00 ± 0.00^{E}	9.89 ± 2.49^{DE}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	Fruity: citrus, floral	1446.42
51	Dihydromyrcenol	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	13.22 ± 1.52^{A}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	–	1452.19
52	Linalool	16.94 ± 2.11^{EF}	70.17 ± 2.59^{D}	38.32 ± 6.16^{E}	0.00 ± 0.00^{F}	16.94 ± 2.10^{EF}	25.66 ± 2.68^{E}	Floral, sweet	1517.66
53	Epoxylinalool	0.00 ± 0.00^{D}	15.47 ± 2.43^{CD}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	Floral	1690.80
	Total	45.33 ± 1.85^{G}	145.09 ± 5.23^{F}	70.50 ± 9.12^{G}	72.19 ± 3.18^{G}	44.52 ± 1.25^{G}	42.07 ± 4.91^{G}		
	Furans, furanones, pyrans, pyrones								
54	2-Pentyl furan	112.91 ± 7.48^{A}	74.65 ± 2.38^{CD}	67.73 ± 6.71^{CDE}	99.34 ± 1.27^{B}	78.65 ± 2.45^{C}	56.70 ± 0.98^{EFG}	Green bean, vegetable	1209.21
55	Rose oxide	0.00 ± 0.00^{F}	27.64 ± 1.62^{E}	0.00 ± 0.00^{F}	9.12 ± 1.45^{EF}	6.79 ± 1.10^{F}	18.47 ± 1.57^{EF}	Floral: geranium-like	1337.81
56	γ-Butyrolactone	25.12 ± 0.87^{CDE}	25.51 ± 0.25^{BCDE}	27.59 ± 2.26^{BCDE}	29.76 ± 5.79^{BCDE}	24.57 ± 6.58^{CDE}	27.42 ± 4.67^{BCDE}	Cheesy	1564.28
57	Furfuryl alcohol	38.44 ± 6.73^{D}	37.00 ± 7.94^{D}	45.80 ± 19.26^{D}	45.12 ± 2.67^{D}	30.95 ± 2.91^{D}	50.72 ± 1.00^{D}	Faint burning	1603.11
58	5-Ethyl-2(5H)-furanone	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	14.32 ± 2.13^{A}	0.00 ± 0.00^{B}	0.00 ± 0.00^{B}	–	1673.04
59	Tetrahydro-2H-pyran-2-one	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	–	1705.16
60	Pantoic lactone	29.68 ± 0.93^{DE}	29.28 ± 3.66^{DE}	30.81 ± 5.18^{CDE}	32.55 ± 3.89^{CDE}	23.45 ± 1.21^{E}	47.21 ± 5.38^{BCD}	–	1874.47
61	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	37.75 ± 7.28^{CDE}	19.57 ± 0.11^{DE}	20.15 ± 6.70^{DE}	55.73 ± 4.91^{BCD}	25.20 ± 0.43^{DE}	35.84 ± 2.52^{DE}	Roasted	2030.28
	Total	243.90 ± 4.68^{EFG}	213.65 ± 8.54^{EFG}	192.08 ± 14.04^{G}	285.94 ± 5.22^{E}	189.61 ± 9.91^{G}	236.36 ± 13.35^{EFG}		
	Pyrroles								
62	Isoamyl-2-formyl pyrrole	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	0.00 ± 0.00^{E}	–	1714.35
63	2-Acetylpyrrole	44.68 ± 2.28^{C}	42.18 ± 2.99^{CD}	29.57 ± 6.49^{DE}	55.11 ± 5.74^{C}	29.77 ± 2.80^{DE}	88.94 ± 4.23^{B}	Caramel	1833.53
64	2-Formylpyrrole	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	–	1867.79
	Total	44.68 ± 2.28^{FG}	42.18 ± 2.99^{FG}	29.57 ± 6.49^{FG}	55.11 ± 5.74^{EF}	29.77 ± 2.80^{FG}	88.94 ± 4.23^{E}		
	Others								
65	Dimethyldisulfide	12.16 ± 0.56^{B}	12.93 ± 0.92^{B}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	0.00 ± 0.00^{C}	13.44 ± 2.22^{B}	Sulfurous	1030.73
66	o-Xylene	12.30 ± 1.06^{ABC}	9.15 ± 0.82^{ABCD}	4.23 ± 0.57^{E}	6.21 ± 0.57^{DE}	5.18 ± 0.72^{DE}	7.22 ± 1.28^{DE}	–	1103.28
67	Pyridine	0.00 ± 0.00^{D}	2.22 ± 0.40^{C}	3.68 ± 0.13^{ABC}	3.08 ± 0.23^{ABC}	2.43 ± 0.16^{C}	3.01 ± 0.98^{BC}	–	1153.16
68	2-Methoxyphenol	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	0.00 ± 0.00^{D}	Smoky	1752.67
69	Pyrrolidinone	42.21 ± 0.59^{BC}	0.00 ± 0.00^{D}	30.58 ± 8.26^{C}	45.76 ± 4.78^{BC}	43.93 ± 0.67^{BC}	45.67 ± 4.83^{BC}	–	1882.01
	Total	66.66 ± 1.21^{CDE}	24.30 ± 1.75^{FG}	38.49 ± 8.89^{EFG}	55.05 ± 4.84^{CDEF}	51.54 ± 1.39^{DEF}	69.35 ± 2.03^{CDE}		
	Grand total	5551.27 ± 64.78^{F}	5727.71 ± 241.74^{F}	3421.99 ± 151.10^{H}	4809.14 ± 160.63^{G}	3643.05 ± 186.94^{H}	5502.32 ± 176.40^{FG}		

For each row different alphabets represent significant differences (α = 0.05) among samples. (*) odor description from Afoakwa et al. (2008), Aprotosoaie et al. (2016), Bonvehi (2005), Rodriguez-Campos et al. (2012) and (Tran, Van de Walle, et al., 2015, Tran, Van Durme, et al., 2015).

Table 4a
Odor activity values of aroma volatiles identified from dark chocolates produced from cocoa beans of different pod storage – roasting conditions.

No.	Volatile	OTV (ng/g)	0PS-100 °C	7PS-100 °C	0PS-120 °C	3PS-120 °C	0PS-135 °C	3PS-135 °C	7PS-135 °C	0PS-140 °C	0PS-160 °C	7PS-160 °C
	Acids											
1	Acetic acid	124–750	3.76–22.76	2.79–16.86	3.78–22.86	2.89–17.50	4.81–29.11	2.81–17.00	4.69–28.36	3.87–23.41	5.18–31.34	5.75–34.78
2	Isovaleric acid	22–1000	0.21–9.72	0.17–7.78	0.38–17.31	0.23–10.52	0.33–15.07	0.22–10.17	0.28–12.64	0.38–17.34	0.26–11.87	0.27–12.19
	Alcohols											
3	Amyl alcohol	470	0.09	0.08	0.10	0.09	0.07	0.07	0.05	0.04	0.04	0.05
4	Hexanol	400	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	Benzyl alcohol	5100–900,000	≤ 0.02	≤ 0.03	≤ 0.02	≤ 0.03	≤ 0.03	≤ 0.02	≤ 0.02	≤ 0.03	≤ 0.02	≤ 0.04
6	2-Phenyl ethyl alcohol	10–590	0.65–38.26	0.17–9.81	0.86–51.02	0.50–29.67	1.50–88.72	0.61–36.17	0.67–39.74	1.40–82.87	1.84–108.36	1.04–61.45
	Aldehydes											
7	2-Methylbutanal	2.2–152	0.08–5.85	0.09–6.19	0.12–8.44	0.10–6.72	0.13–8.97	0.17–11.41	0.12–8.56	0.16–11.13	0.29–20.35	0.27–18.50
8	3-Methylbutanal	5.4–80	0.59–8.74	0.50–7.36	1.11–16.48	0.76–11.33	1.42–21.09	1.31–19.35	1.20–17.82	1.56–23.18	1.74–25.71	1.52–22.54
9	Pentanal	240	0.54	0.57	0.48	0.44	0.46	0.37	0.47	0.54	0.40	0.49
10	Hexanal	75	2.56	2.17	2.38	2.04	1.85	1.72	2.07	2.38	1.52	1.80
11	Heptanal	64.8	0.38	0.30	0.43	0.34	0.38	0.37	0.42	0.52	0.42	0.47
12	Octanal	320	0.09	0.07	0.12	0.11	0.12	0.12	0.12	0.13	0.12	0.10
13	Nonanal	56	1.05	0.74	1.21	0.93	0.84	1.48	1.18	1.10	2.35	1.13
14	Benzaldehyde	60	1.44	1.36	1.83	1.49	1.87	1.65	1.90	1.93	2.12	2.18
15	Benzeneacetaldehyde	22–154	1.06–7.45	0.26–1.83	1.35–9.44	0.53–3.74	1.72–12.03	0.50–3.50	0.71–5.00	1.49–10.45	1.03–7.23	0.51–3.59
	Ketones											
16	2-Heptanone	1500	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
17	2-Octanone	500–510	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	3-Octen-2-one	250	0.00	0.00	0.11	0.10	0.26	0.19	0.22	0.28	0.39	0.28
19	2-Nonanone	100	0.15	0.16	0.21	0.22	0.00	0.00	0.00	0.00	0.00	0.00
20	Acetophenone	5629	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
	Pyrazines											
21	Methylpyrazine	27,000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22	2,5-Dimethylpyrazine	2600–17,000	0.00	0.00	0.00	0.00	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.02
23	2,6-Dimethylpyrazine	1021–8000	0.00	0.00	0.00	0.00	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.04	≤ 0.03
24	2-Ethyl-6-methylpyrazine	320	0.00	0.00	0.02	0.01	0.05	0.03	0.05	0.05	0.12	0.11
25	Trimethylpyrazine	290	0.04	0.05	0.09	0.07	0.22	0.16	0.46	0.22	0.52	1.19
26	Tetramethylpyrazine	38,000	0.00	0.02	0.01	0.00	0.01	0.00	0.03	0.01	0.01	0.04
	Esters											
27	Methyl acetate	3.4	9.52	7.56	5.84	5.98	7.26	7.52	7.76	8.45	16.08	12.11
28	Ethyl octanoate	1.5–5.5	2.12–7.79	1.76–6.44	3.24–11.88	2.90–10.63	0.00	0.00	0.00	0.00	0.00	0.00
29	Phenyl ethyl acetate	137–233	0.43–0.72	0.36–0.61	0.45–0.76	0.28–0.47	0.53–0.90	0.23–0.39	0.46–0.78	0.47–0.80	0.55–0.94	0.60–1.02
	Terpenes and terpenoids											
30	Myrcene	9.18	0.64	0.70	1.12	0.88	0.94	0.96	0.93	1.10	1.05	1.15
31	Limonene	250–14,700	≤ 0.06	≤ 0.04	≤ 0.05	≤ 0.04	≤ 0.04	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.08	≤ 0.07
32	Linalool	37	2.02	1.87	2.53	2.48	3.06	2.52	3.16	2.70	3.07	3.28
	Furans and furanones											
33	2-Pentyl furan	100–2000	0.02–0.47	0.03–0.54	0.03–0.66	0.02–0.43	0.02–0.44	0.03–0.56	0.02–0.46	0.03–0.70	0.04–0.70	0.03–0.69
34	γ-Butyrolactone	35	0.00	0.00	0.70	0.56	1.35	1.67	1.56	1.13	2.83	2.68
	Others											
35	Dimethyldisulfide	12	0.00	0.00	1.10	1.06	1.08	1.26	1.20	1.10	2.04	1.88
36	Pyridine	920–3000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	≤ 0.01	0.00
37	2-Methoxyphenol	10	0.00	0.00	0.00	0.00	2.41	1.69	2.96	3.17	3.69	5.21

Table 4b
Odor activity values of aroma volatiles identified from dark chocolates produced from commercial cocoa liquors.

No.	Volatile	OTV (ng/g)	Ecuador	Ghana	Ivory coast	Madagascar	Venezuela	Vietnam
	Acids							
1	Acetic acid	124–750	4.00–24.20	3.21–19.40	1.97–11.93	3.24–19.63	2.43–14.69	3.30–19.99
2	Isovaleric acid	22–1000	0.05–2.17	0.18–8.06	0.01–0.64	0.06–2.56	0.05–2.42	0.09–3.93
	Alcohols							
3	Amyl alcohol	470	0.08	0.12	0.09	0.06	0.08	0.04
4	Hexanol	400	0.02	0.00	0.00	0.02	0.02	0.02
5	Benzyl alcohol	5100–900,000	≤ 0.02	≤ 0.02	≤ 0.01	≤ 0.02	≤ 0.01	≤ 0.02
6	2-Phenyl ethyl alcohol	10–590	0.31–18.12	0.32–19.01	0.23–13.72	0.23–13.41	0.20–11.98	0.30–17.44
	Aldehydes							
7	2-Methylbutanal	2.2–152	0.08–5.81	0.11–7.38	0.13–8.82	0.08–5.78	0.08–5.44	0.11–7.49
8	3-Methylbutanal	5.4–80	0.47–7.00	0.73–10.76	0.55–8.14	0.41–6.14	0.39–5.77	0.70–10.30
9	Pentanal	240	0.78	0.69	0.37	0.68	0.40	0.51
10	Hexanal	75	5.02	3.38	2.28	4.34	2.77	2.84
11	Heptanal	64.8	0.80	0.55	0.54	0.84	0.58	0.54
12	Octanal	320	0.16	0.11	0.10	0.14	0.10	0.09
13	Nonanal	56	1.28	1.19	1.51	1.75	1.38	0.98
14	Benzaldehyde	60	1.19	1.74	1.56	1.26	1.05	1.19
15	Benzeneacetaldehyde	22–154	0.11–0.75	0.24–1.65	0.11–0.79	0.17–1.20	0.11–0.76	0.21–1.44
	Ketones							
16	2-Heptanone	1500	0.02	0.02	0.02	0.03	0.02	0.02
17	2-Octanone	500–510	0.00	0.00	0.02	0.00	0.00	0.00
18	3-Octen-2-one	250	0.00	0.04	0.00	0.00	0.00	0.00
19	2-Nonanone	100	0.28	0.29	0.21	0.23	0.21	0.22
20	Acetophenone	5629	0.00	0.01	0.00	0.00	0.00	0.00
	Pyrazines							
21	Methylpyrazine	27,000	0.00	0.00	0.00	0.00	0.00	0.00
22	2,5-Dimethylpyrazine	2600–17,000	≤ 0.01	≤ 0.01	0.00	≤ 0.01	0.00	≤ 0.01
23	2,6-Dimethylpyrazine	1021–8000	0.00	0.00	≤ 0.01	0.00	0.00	0.00
24	2-Ethyl-6-methylpyrazine	320	0.01	0.38	0.01	0.01	0.01	0.39
25	Trimethylpyrazine	290	0.16	0.14	0.07	0.12	0.10	0.19
26	Tetramethylpyrazine	38,000	0.00	0.02	0.00	0.00	0.00	0.01
	Esters							
27	Methyl acetate	3.4	7.59	6.90	8.62	7.54	10.57	7.49
28	Ethyl octanoate	1.5–5.5	2.14–7.84	2.20–8.05	1.63–5.99	1.29–4.74	1.72–6.30	2.70–9.89
29	Phenyl ethyl acetate	137–233	0.61–1.05	0.49–0.84	0.24–0.41	0.34–0.57	0.33–0.56	0.87–1.49
	Terpenes and terpenoids							
30	Myrcene	9.18	0.51	0.74	0.00	0.49	0.57	0.00
31	Limonene	250–14,700	≤ 0.05	≤ 0.05	≤ 0.06	≤ 0.19	≤ 0.05	≤ 0.04
32	Linalool	37	0.46	1.90	1.04	0.00	0.46	0.69
	Furans and furanones							
33	2-Pentyl furan	100–2000	0.06–1.13	0.04–0.75	0.03–0.68	0.05–0.99	0.04–0.79	0.03–0.57
34	γ-Butyrolactone	35	0.72	0.73	0.79	0.85	0.70	0.78
	Others							
35	Dimethyldisulfide	12	1.01	1.08	0.00	0.00	0.00	1.12
36	Pyridine	920–3000	0.00	0.00	0.00	0.00	0.00	0.00
37	2-Methoxyphenol	10	0.00	0.00	0.00	0.00	0.00	0.00

and sweet notes to the final flavor. The chocolates from commercial liquors recorded lower concentrations than the sample chocolates although, although among these, the Ghanaian chocolate was significantly highest ($p < .05$). Myrcene being present in marginal concentrations was only odor-active in most sample chocolates.

3.6. Furans, furanones, pyrans, pyrones, pyrroles and others

Generally, these groups of volatiles showed a similar pattern whereby their total concentrations were largely influenced by the RT. It was evident from Table 3a, that these concentrations increased with increasing temperature. Withal, at low to moderate RT's (100–135 °C), no clear trends were seen with respect to PS. However, at 160 °C, 7PS recorded significantly higher ($p < .05$) total concentrations of pyrroles and the other unclassified volatiles. This may be due to their higher reducing sugar and free amino acid contents which are required for the Maillard reaction as reported by Hinneh et al. (2018).

Apart from 2-pentyl furan – which is a product from fat degradation, all other furans, furanones, pyrans and pyrones were absent in chocolates with RT of 100 °C. Arguably, due to the low temperature, most of these volatiles may have been formed in very minimal concentrations which were eventually lost during the chocolate manufacturing process. Rose oxide, which was identified in substantial amounts in the chocolates, is known for its geranium-like floral note (Bonvehí, 2005). It was however not odor-active (Table 4a). γ-Butyrolactone which was most dominant in the chocolates roasted at 160 °C, was also odor-active in some chocolates and is thus expected to confer sweet and caramel notes towards the final flavor. Also, among the chocolates from the commercial liquor, the Madagascan, Ecuadorian, Vietnamese and Ghanaian chocolates recorded the most abundant (but significantly equal) concentrations of this group of volatiles (Table 3b).

The pyrroles were the least abundant group identified. Apart from their absence in the chocolates with lower RT's (< 135 °C), their concentrations seemed to increase as RT increased. Both 0PS and 7PS appeared to have comparable concentrations at RT's below 160 °C. Although, isoamyl-2-formyl pyrrole was the most abundant in 7PS-160 °C chocolate, 2-acetyl pyrrole was the most prevalent pyrrole identified in all the chocolates. The latter is formed from proline

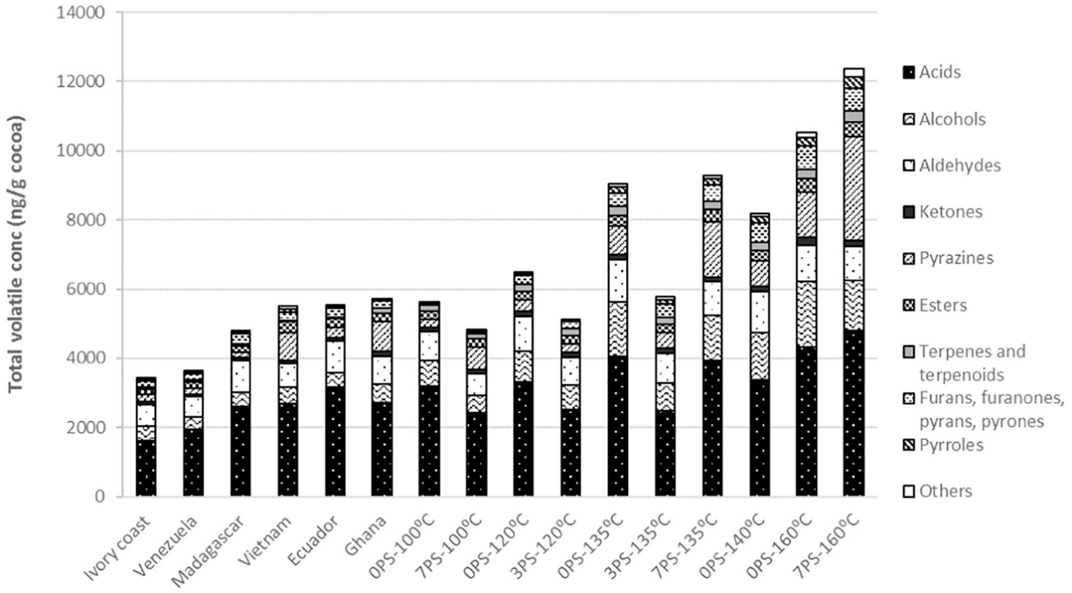

Fig. 1. Total concentrations of various groups of volatiles identified in dark chocolates produced from cocoa beans of different pod storage – roasting conditions and commercial cocoa liquors.

through the Strecker degradation reaction (Afoakwa, Paterson, Fowler, & Ryan, 2009; Mottram, 2007) and is characterized by its caramel flavor notes. Notwithstanding, this volatile was not odor-active (Table 4a). Pyrroles were absent in the chocolates from commercial liquors, except for 2-acetyl pyrrole, which was the highest in the Vietnamese chocolate.

Some other (unclassified) volatiles such as 2-methoxyphenol and dimethyldisulfide were also marked for their notable presence in chocolates (Aprotosoaie et al., 2016). These two volatiles are generated at intense heating processes and thus, associated with undesirable flavor notes. They were odor-active and more dominant in chocolates with beans roasted at 160 °C.

3.7. Trends in the overall aroma concentration of chocolates as influenced by pod storage and roasting temperature

Fig. 1 shows the general trends in the overall aroma volatile concentration in the various chocolates. Overall, the impact of PS and RT on the volatile concentrations were also depicted. Particularly, at lower temperatures (100–120 °C), chocolates with unstored pods possessed higher concentrations than those from stored pods. However, at 160 °C, the opposite was observed. This is probably because of the high rate of Maillard reaction occurring amidst the excess of flavor precursors (reducing sugars and free amino acids) in 7PS (Hinneh et al., 2018). Comparatively, a temperature of 135 °C seemed more optimal for maximal aroma volatile release than at 140 °C. Aside the trend from the overall volatile concentrations, similar observations were made from the total acid and alcohol concentrations. At this temperature (135 °C), both 0PS and 7PS contained significantly similar ($p > .05$) overall volatile concentrations whereas the concentration of 3PS was significantly lower ($p < .05$). Generally, except at lower RT's (100–120 °C), the concentrations of aroma volatiles from the sample chocolates were seen to be higher than those from the commercial cocoa liquors. Whereas this could be due to the type (whole bean roasting for treated samples as opposed to nib roasting for the commercial liquors) and intensities of roasting applied in the latter, difference in the industrial treatments applied from bean to liquor could also be implicated to have had a detrimental impact on the levels of the various volatiles. Consequently, desirable volatiles such as esters, aldehydes, ketones, terpenes and pyrazines which impart the overall aroma expression were either produced at lower concentrations due to lower roasting intensities or lost to the extreme industrial process often applied. Finally, it is also possible that on a mass industrial scale, the mixing together of different cocoa beans of different qualities (in terms of pod storage, fermentation and drying) from the different producers of the beans could have inevitably influenced the aroma quality of these commercial liquors. However, for the purpose of comparison, these liquors, being representative of the typical industrial quality, were accepted and utilized ‘as-is’.

3.8. Comparing chocolates on the basis of their aroma volatile profiles

Clustering analysis can be viewed as a means of grouping a set of data such that the samples in a particular group (here referred to as cluster) do share certain similarities in comparison to others from a different group. AHC uses a bottom-up approach, thus, each sample starts as its own unique cluster, of which pairs of other clusters are merged systematically in a hierarchical order. The process begins by computing the dissimilarity between the available number (N) of samples. Then, two samples with a low dissimilarity that minimizes the given agglomeration criterion are clustered. Next, the dissimilarity between this cluster and the N-2 other samples is also computed according to the same agglomeration criterion. These two samples whose clustering again minimizes the agglomeration criterion are then clustered together. Consequently, the process continues until all samples have been clustered (XLSTAT, 2019). The AHC was therefore useful for exploring the possible existing (dis)similarities among the chocolates in terms of their aroma profiles.

Fig. 2a and 2b depict the similarities between the chocolates, first, taking into consideration all the identified volatiles and next, on the basis of their odor-active volatiles respectively. From Fig. 2a, with a dissimilarity of 400, three main clusters were obtained. The first group comprised of chocolates of various PS with moderate to high RT's (135–160 °C). Remarkably, these were chocolates with generally higher overall aroma volatile concentration, owing to the intensity of roasting (Table 3a). These were further distinguished between chocolates of RT's 135–140 °C on one hand and 160 °C on the other. From these, the different groupings arising from the different PS treatments were also seen. The second major group consisted of chocolates from Madagascar. Suggestively, this separation was as a result of its relatively higher concentrations of aldehydes, furans, furanones, pyrans and pyrroles as well as the lower pyrazine concentration among the chocolates from

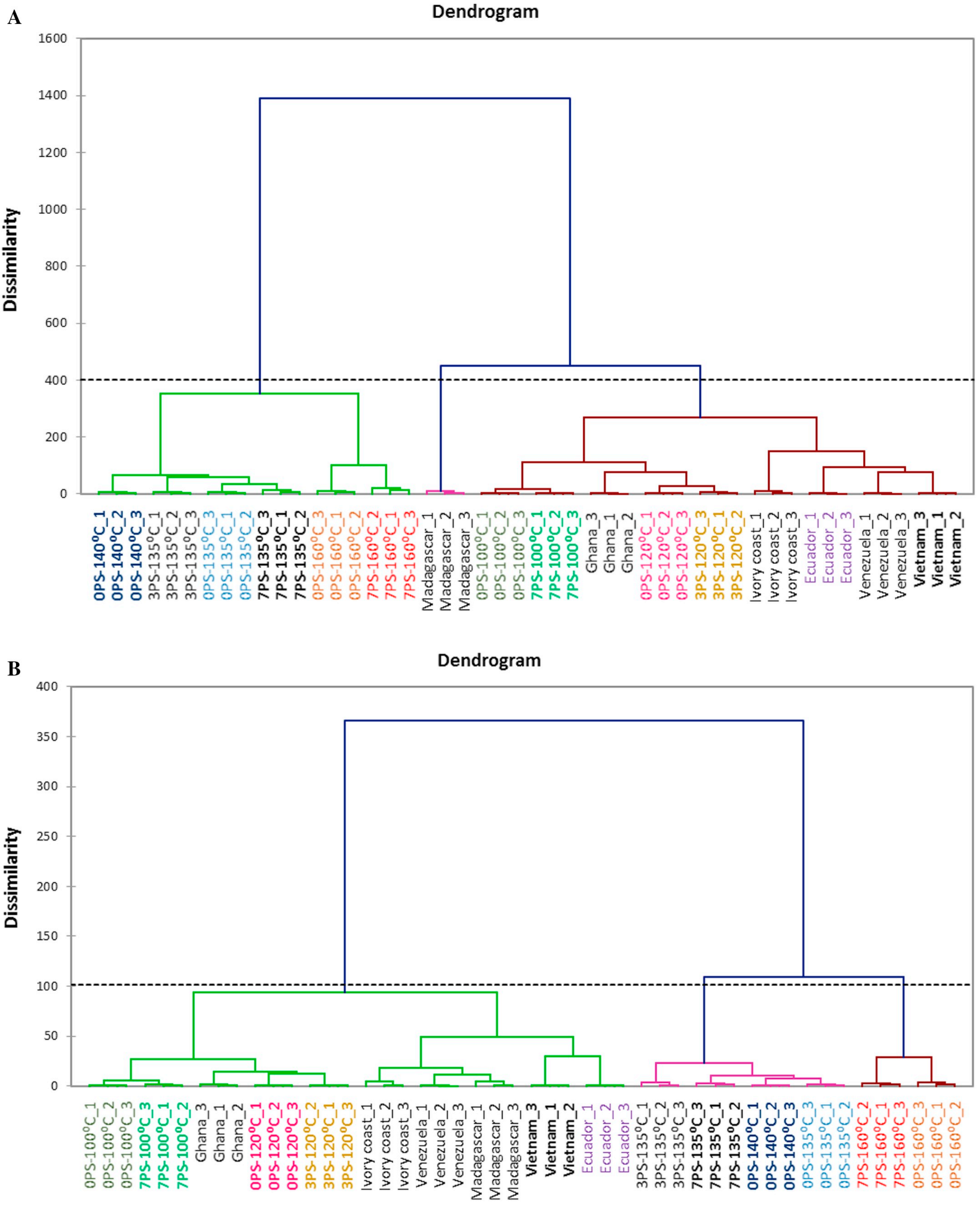

Fig. 2. a. Agglomerative hierarchical clustering of all identified aroma volatiles in various dark chocolates produced from cocoa beans of different pod storage – roasting conditions and commercial cocoa liquors. 2b: Agglomerative hierarchical clustering on the basis of odor activity values of various dark chocolates produced from cocoa beans of different pod storage – roasting conditions and commercial cocoa liquors.

commercial liquors. More so, from Table 2, this was the only chocolate which was produced with liquor comprising of all three major varieties of cocoa (*Forastero, Criollo* and *Trinitario*). However, the final group encompassed all remaining chocolates from commercial liquors including sample chocolates with minimal roasting intensity (100 °C). The chocolates from this cluster where generally known for their lower overall volatile concentrations (Table 3a and 3b). Hitherto, a keen similarity is observed between the Ghanaian chocolate and those roasted at 100 °C and 120 °C. Meanwhile, the Ivorian chocolates, showed more similarity with the Ecuadorian, Venezuelan and Vietnamese chocolates. Given the clear differences in the variety of cocoa beans used to manufacture these chocolates (Table 2), it is possible that the different roasting protocols (time – temperature) applied in each scenario may have play a more important role in fashioning their individual profiles, although unfortunately, this information was not provided by the supplier. Yet, for the sole purpose of comparison within the context of this study, these commercial cocoa liquors were envisioned as representative of what was available on the market irrespective of the specific pre-processing technique applied by the producer. It is, thus clear, that regardless of the cocoa bean variety, it is possible to steer the aroma profiles of chocolates through PS and roasting. However, from these clustering, it seemed that the impact of the latter may have been greater.

From Fig. 2b, the dissimilarities between the chocolates on the basis of their odor-active volatiles were rather low, given that with a dissimilarity of 100, only three clusters were obtained. First, a cluster comprising of chocolates with a high roasting temperature of 160 °C. The second cluster comprised of chocolates within the range of 135–140 °C. Of these, chocolates; 0PS-135 °C and 0PS-140 °C showed a great similarity, followed by chocolates; 7PS-135 °C and 3PS-135 °C. Particularly within this cluster, the distinguishing effect of PS seemed more pronounced than that of the RT. From the third cluster, two main groupings were observed. On the one hand, the Ghanaian chocolate together with sample chocolates with low roasting intensities (100–120 °C), whereas, on the other hand, all the other chocolates from commercial cocoa liquors were grouped. Here, the Ivorian, the Madagascan and the Venezuelan chocolates showed some similarities. However, these were slightly different from both the Vietnamese and Ecuadorian chocolates. The observed similarities may be ascribed to the varieties of beans utilized for the production of the various liquors. However, the closeness of the Venezuelan and Madagascan chocolates to the Ivorian chocolate in spite of their different cocoa varieties, may be due to the additional difference in the roasting process/protocol applied.

4. Conclusions

A decreasing effect of PS on the overall aroma concentration was observed. This has often been ascribed to the partial modification of the pulp leading to reduction in pulp volume during the storage process. However, for long durations of PS (∼ 7 days), an increase in the overall volatile concentration could be attributed to the on-set of an extensive degradation of the pod and pulp material, thus, making available more aroma precursors. RT also contributed significantly ($p < .05$) to an increase in the overall volatile concentration. This increase is either as a result of the unlocking effect of the heating process on the volatiles trapped within the matrix or the promotion of new volatile formation through the Maillard reaction during roasting. From an AHC, chocolates with a moderate to high (135–160 °C) RT's showed high similarity among each other, such that, these chocolates possessed more volatiles with relatively higher concentrations. However, the diversity in the aroma profiles among these chocolates was evident as chocolates from unstored pods were significantly dominant ($p < .05$) in alcohols (fruity/floral), aldehydes (cocoa/chocolate) and ketones (fruity/creamy). Whereas those from prolonged PS (∼ 7 days) were significantly dominant ($p < .05$) in pyrazines (cocoa/nutty/roasted), acids (sour), esters (fruity/floral/sweet), furans (roasted/cheesy/green) and pyrroles (caramel). The latter group of chocolates could also be marked by the significantly higher ($p < .05$) levels of undesirable volatiles such as dimethyldisulfide (sulfurous) and 2-methoxyphenol (smoky). Conversely, all chocolates with low (100–120 °C) RT's including the Ghanaian origin chocolate also showed high similarity. Of these, chocolates from the unstored pods, were significantly higher ($p < .05$) in alcohols (fruity/floral), acids (sour) and aldehydes (cocoa/chocolate), whereas, 7PS chocolates were significantly ($p < .05$) rich in pyrazines. Suggestively, with similar levels of terpenes/terpenoids (fruity/floral/spicy) in both unstored and pod stored chocolates, the latter is likely to express more fruity/floral notes. Generally, at the different RT's applied, 3PS chocolates mostly recorded the lowest volatile concentrations. It is possible that the suppression of some dominant aroma volatiles (such as acids, pyrazines, aldehydes and ketones) due to the limited PS treatment could have led to a more balanced aroma profile, with possible expressions of more subtle volatiles including esters and terpenes/terpenoids. This study, thus, reveals the possibility of harnessing both PS and RT in order to steer the aroma profiles of dark chocolates produced from ‘bulk’ cocoa beans.

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Conflict of interest

The authors declare that they have no conflict of interest.

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