Alkylpyrazines and Other Volatiles in Cocoa Liquors at pH 5 to 8, by Selected Ion Flow Tube-Mass Spectrometry (SIFT-MS)

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ABSTRACT: Cocoa beans were alkalized before or after roasting and made into cocoa liquor before analyzing by SIFT-MS. In both alkalized-before-roasting and alkalized-after-roasting samples, there were significantly higher concentrations of alkylpyrazines for the samples with pH above 7 than pH below 7. At pH 8, the concentrations of 2,3-, 2,5-, and 2,6-dimethylpyrazine (DMP), 2,3,5-trimethylpyrazine (TrMP), 2,3,5,6-tetramethylpyrazine (TMP), and 2,3-diethyl-5-methylpyrazine (EMP) in the samples alkalized-before-roasting were higher than those in the samples alkalized-after-roasting. Volatiles increased under conditions that promoted the Maillard reaction. The partition coefficient was not significantly affected by pH from 5.2 to 8. The ratios of TrMP/DMP and DMP/TMP increased while the ratio of TMP/TrMP decreased as the pH increased. The concentrations of Strecker aldehydes and other volatiles followed a similar pattern as that of the alkylpyrazines. High pH favors the production of alkylpyrazines and Strecker aldehydes.

Practical Applications: Cocoa beans alkalized-before-roasting had higher levels of many important chocolate aroma volatiles than those alkalized-after-roasting. Thus, alkalizing before roasting should produce a stronger cocoa aroma. The higher the pH, the higher the concentrations of these important volatiles. There was little change in volatile concentration at acid pH. Above pH 7, volatile levels increased rapidly with increasing pH. To maintain the recommended ratio of tetramethylpyrazine to trimethylpyrazine, a longer roasting time or higher temperature is needed for cocoa liquor with a pH below 6.5, while a shorter roasting time or lower temperature is needed for cocoa liquor with a pH above 7.

Keywords: alkalization, alkylpyrazine, cocoa, Maillard reaction, volatile

Introduction

Chocolate is one of the most aromatic foods. The distinctive flavor characteristics of chocolate are related to the cocoa bean genotype and growing environment (Clapperton 1994). However, chocolate flavor does not exist naturally in the beans; it is generated by a series of procedures that begins with the postharvest fermentation of the beans and continues through roasting (Martin 1987). Fermentation is an important procedure to reduce off-notes such as sourness, bitterness, and astringency in cocoa beans (Meyer and others 1989; Biehl and others 1990). It is also a key step in the formation of reducing sugars and amino acids, which are the precursors of the Maillard reaction during roasting. Roasting is an essential process in developing chocolate flavor from the precursors formed during fermentation. The flavors produced during roasting include alkylpyrazines, aldehydes, ethers, thiazoles, phenols, ketones, alcohols, furans, and esters (Dimick and Hoskin 1981).

Amino acids and peptides are released from proteins during fermentation of the cocoa beans. Fructose and glucose, derived from sucrose hydrolysis (Lopez and others 1978), are the most abundant reducing sugars in cocoa beans (Bonvehí and Coll 2002). These key precursors of flavor compounds interact during roasting and develop volatile heterocyclic compounds. The formation of these heterocyclic compounds is not fully understood but it is generally ac-cepted that aldol condensation and cyclization lead to the formation of alkylpyrazines (Afoakwa and others 2008). The actual structure of the alkylpyrazines is dictated based on the side group of the dioxo compounds, one of the intermediates of the Maillard reaction, and amino acids (Dimick and Hoskin 1999).

Heterocyclic aroma compounds are important volatiles to cocoa aroma (Bonvehí 2005). Among these heterocyclic compounds, the most dominant volatiles are the alkylpyrazines, which contribute to the desirable chocolate aroma (Counet and others 2002; Stark and Hofmann 2005). 2,3-Dimethylpyrazine has the sensorial attribute of caramel and cocoa; 2,5-dimethylpyrazine and 2,3,5-trimethylpyrazine (TrMP) are cocoa and roasted nuts; 2,6-dimethylpyrazine is nutty, coffee, and green; 2,3,5,6-tetramethylpyrazine (TMP) is chocolate, cocoa, and coffee (Bonvehí and Coll 2002).

Alkalization is a treatment of the cocoa nib or liquor with alkali solutions. The primary aim of alkalization is to enhance the solubility of cocoa powders, but it also influences the color and flavor of the cocoa because pH influences the formation of intermediates in the Maillard reaction: acidic conditions favor 3-deoxyhexuloses while basic or neutral pH favor the formation of dehydroreductone intermediates in cocoa (Afoakwa and others 2008). The dehydroreductone compounds are critical for flavor formation since they can produce smaller dicarbonyl molecules or contribute to Strecker degradation (Dimick and Hoskin 1999).

Numerous studies have measured cocoa and chocolate volatiles using gas chromatography-mass spectrometry, frequently with solid phase microextraction or tenax trapping to concentrate the

volatiles. Selected ion flow tube-mass spectrometry (SIFT-MS) allows highly sensitive, real-time analysis of complex mixtures of volatile compounds without trapping or preconcentration (Spanel and Smith 1999). Thus, artifacts or changes in relative proportions are not introduced by the preconcentration steps. SIFT-MS has been used in the analysis of volatiles in coffee, onion, garlic, banana (Smith and Spanel 2005), tomatoes (Xu and Barringer 2009), and oxidation of olive oil (Davis and McEwan 2007).

The purpose of this study is to investigate the effect of alkalization of cocoa beans before or after roasting on the formation of alkylpyrazines and other volatiles in cocoa liquors with different pH values.

Materials and Methods

Cocoa liquor samples

Fermented cocoa beans from the Dominican Republic (Hispaniola '07, Chocolate Alchemy Co.) were used. The cocoa beans were weighed (1 kg) and roasted in a convection oven (Doyon model JA 14, Dayton, Ohio, U.S.A.) at 150 °C for 20 min. After cooling to room temperature, the cocoa beans were cracked with a crankandstein cocoa mill, winnowed by an air gun (Model HG 201 B, Master Appliance Corp., Racine, Wis., U.S.A.) and ground by a juicer (The Champion, Plastaket Mfg. Inc., Lodi, Calif., U.S.A.) at 1725 R.P.M. to cocoa liquor. The alkalized-before-roasting cocoa liquor was prepared by soaking the cocoa beans in 700 mL potassium carbonate (Sigma-Aldrich, Inc., St. Louis, Mo., U.S.A.) aqueous solution for 30 min, then removing the alkali solution by passing through a screen, and drying at 70 °C for 2 h before roasting. The concentration of the alkali solution varied from 42 g/L to 204 g/L depending on the desired final pH. The cocoa liquors were sealed and stored in a −18 °C freezer before testing. The alkalized-after-roasting cocoa liquor was prepared in the same way except the alkalization step occurred after the roasting step.

Commercial cocoa powders (ADM Co. Cocoa Div., Milwaukee, Wis., U.S.A.) N-11-N (pH 5.74), D-11-A (pH 7.07), D-11-V (pH 7.39), D-11-S (pH 7.84), and D-11-R (pH 8.04) with different degrees of alkalization were also analyzed. N-11-N is natural cocoa without alkalization; D-11-A is lightly alkalized; D-11-V is brown with medium alkalization; D-11-S powder is deep red made by a red alkalization process; and D-11-R is dark red. All these cocoa powders are claimed to have a rich flavor and a fat percentage of 10% to 12%.

To determine the effect of pH on the partition coefficient, the unalkalized cocoa liquor (20 g) was alkalized by addition of 50 mL potassium carbonate solution to create different pH values. The samples were warmed in a water bath at 40 or 70 °C for 2h before being tested.

The pH of the sample was measured by placing cocoa liquor (20 g) or cocoa powder (10 g) in a 150 mL beaker, slowly adding with stirring 90 mL boiling hot distilled water, filtering, cooling to 20 to 25 °C, and then measuring with a pH meter (Accumet model 10, Denver Instrument Co., Denver, Colo., U.S.A.). The cocoa liquor sample size was larger to keep the nonfat solids content the same for all samples.

SIFT-MS

Each cocoa liquor sample (20 g) or cocoa powder sample (20 g) was weighed without melting, transferred into 500 mL sealed bottles (Pyrex 1395, Corning, N.Y., U.S.A.), and warmed at 70 °C in a water bath (Circulating bath model 260, Precision Inc., Winchester, Va., U.S.A.) for 1 h. The sample bottle was shaken and immediately transferred into a temperature-protecting sleeve, where the cap of the bottle was changed to a polytetrafluoroethylene-faced silicone

septa (Pyrex 1395-45TS, Corning, N.Y., U.S.A.) so that the inlet needle of the SIFT-MS (Voice 100, Syft Technologies Ltd., Christchurch, New Zealand) could pierce the cap and draw volatiles from the headspace. The SIFT-MS instrument was described by Smith and Spanel (2005). The inlet needle (14 gauge) had been passivated to minimize reactions with the surface. Another long needle (14 gauge) was put at the bottom of the sample to circulate air inside the sample bottle.

In the SIFT-MS, analysis was performed using selected ion mode (SIM) scans, and the concentrations of volatile compounds were quantified from their reactions with the precursor ions H_3O^+, O_2^+, or NO^+ based on known kinetic parameters (Table 1). Applying the predetermined reaction rate constant for the volatile with the precursor ion, and accounting for dilution of the sample gas into the carrier gas, the concentration of the volatile was calculated (Smith and Spanel 1996). Calibration is performed each morning with a known concentration of benzene, toluene, ethylbenzene, and xylene.

Different volatiles can produce the same mass/charge (m/z) value, which creates conflicts that must be removed otherwise the results must be reported as a mixture. Thus, the m/z values produced by reaction with one of the 3 precursor ions were carefully chosen based on published data for each compound (Table 1). The m/z values in Table 1 were chosen because they were not produced by other compounds in the sample and, thus, uniquely measured the stated compound, with the exceptions of 2,3-, 2,5-, and 2,6-dimethylpyrazine (DMP); and 2- and 3-methylbutanal, which were reported as mixtures. Compounds without known reaction kinetics, and compounds that had conflicts, except the ones just mentioned, were not reported in this study.

The parameters of the SIFT-MS were set as: inlet flow rate 120 cm³/min, scan time 60 s, calculation delay time 5 s, product sample period 100 ms, precursor sample period 20 ms, heated inlet temperature 120 °C, carrier gas argon pressure 200 kPa, helium pressure 30 psi. The flow tube vacuum pressure was 0.038 ± 0.003 Torr.

Statistical analysis

One-way analysis of variance (ANOVA) with Tukey's honestly significant difference (HSD) was performed to analyze for statistical differences between samples with different pH values, and a t-test was used to compare the samples alkalized-before-roasting and alkalized-after-roasting but having similar pH values. Significance was defined as $P < 0.05$.

Results and Discussion

Alkylpyrazines and aldehydes are among the main compounds formed through the Maillard reaction and Strecker degradation during roasting, and both are major contributors to chocolate flavor (Dimick and Hoskin 1999; Bonvehí and Coll 2002). Many of these volatile compounds have relatively low threshold levels (Table 2), have an important influence on chocolate flavor, and can be used as aroma quality indicators for chocolate products.

Alkylpyrazines in cocoa liquors

When the pH was above 7, there was a significant increase in the concentration of all the alkylpyrazines for both alkalized-before-roasting and alkalized-after-roasting cocoa liquors, because alkali conditions favor the formation of alkylpyrazines (Figure 1 and 2). The Maillard reaction can be divided into 3 stages: sugar-amine condensation and Amadori rearrangement; sugar dehydration and

fragmentation and amino acid degradation; and formation of heterocyclic nitrogen compounds (Davies and Labuza 1997). Reducing sugars in the open-chain configuration and amino groups in the -NH$_2$ form are active reactants for the 1st stage of the Maillard reaction (Martins and others 2001). Basic conditions were more effective than acid in promoting the open ring formation of the reducing sugar at 70 °C (Yaylayan and others 1993). Also, basic condition facilitates the deprotonation of the amino group on the protein into the more reactive –NH$_2$ form (Davies and Labuza 1997). Therefore, the increase of the reactants (open-chain reducing sugar and amine in -NH$_2$ form) under alkali conditions accelerates the 1st stage reaction.

The alkali pH also alters which intermediates are formed during the 2nd stage. Basic pH favors the formation of dehydroreductone intermediates (1-deoxyhexuloses) and fission products including acetol, pyruvaldehyde, and diacetyl (Martins and others 2001). These dicarbonyls react with amino acids to yield the Strecker aldehydes and aminoketones that are converted via dimerization to alkylpyrazines (Davies and Labuza 1997). Thus, at high pH the 1st stage is accelerated and more alkylpyrazine precursors are formed in the 2nd stage so more alkylpyrazines are formed than at low pH.

In the basic pH range, both alkalized-before-roasting and alkalized-after-roasting samples have increased levels of volatiles, but there is a greater increase in the alkalized-before-roasting samples (Figure 1 and 2). Comparing the samples around pH 8, there are significantly higher levels of volatiles in the alkalized-before-roasting samples. Most alkylpyrazines form during the Maillard reaction, which is accelerated at temperatures above 100°C (Koehler and Odell 1970). An increase in temperature leads to an increase in the reactivity between the sugar and the amino group (Martins and others 2001), thus the roasting process at 150 °C promotes this reaction. During roasting, the pH of the alkalized-after-roasting sample was only 5.2, which is the natural pH of cocoa beans,

Table 1 — Information of selected volatile compounds for SIFT-MS analysis.

Volatile compounds	Precursor ion	k (10^{-9} cm^3/s)	m/z	Product ion	Reference
Pyrazines					
2,3-, 2,5-, and 2,6-dimethylpyrazines (DMP)	O$_2^+$	2.7	108	C$_6$H$_8$N$_2^+$	Syft 2009
2,3,5-trimethylpyrazine (TrMP)	O$_2^+$	2.5	122	C$_7$H$_{10}$N$_2^+$	Syft 2009
2,3,5,6-tetramethylpyrazine (TMP)	O$_2^+$	2.5	136	C$_8$H$_{12}$N$_2^+$	Syft 2009
2,3-diethyl-5-methylpyrazine (EMP)	O$_2^+$	2.5	150	C$_9$H$_{14}$N$_2^+$	Syft 2009
Aldehydes					
phenylacetaldehyde	NO$^+$	2.5	120	C$_8$H$_8$O$^+$	Syft 2009
2- and 3-methylbutanal	H$_3$O$^+$	3.7	69 + 87	C5H9$^+$, C$_5$H$_{11}$O$^+$	Spanel and others 2002
2-methylpropanal	O$_2^+$	3.0	72	C$_4$H$_8$O$^+$	Spanel and others 2002
2,4(6)-nonadienal	NO$^+$	2.5	168	C$_9$H$_{14}$O $\bullet$ NO$^+$	Syft 2009
2,4-decadienal	NO$^+$	4.2	151	C$_{10}$H$_{15}$O$^+$	Spanel and others 2002
2-nonenal	NO$^+$	3.8	169	C$_9$H$_{15}$O $\bullet$ NO$^+$	Spanel and others 2002
Heptanal	NO$^+$	3.3	113	C$_7$H$_{13}$O$^+$	Spanel and others 2002
Nonanal	O$_2^+$	3.2	138	C$_{10}$H$_{18}^+$	Syft 2009
Furans					
furaneol	NO$^+$	2.5	128	C$_6$H$_8$O$_3^+$	Syft 2009
5-methylfurfural	NO$^+$	3.1	110	C$_6$H$_6$O$_2^+$	Wang and others 2004b
Ketones					
delta-decalactone	NO$^+$	2.5	200	C$_{10}$H$_{18}$O$_2$ $\bullet$ NO$^+$	Syft 2009
acetone	NO$^+$	1.2	88	C$_3$H$_6$O $\bullet$ NO$^+$	Spanel and others 1997
2-nonanone	NO$^+$	2.7	172	C$_9$H$_{18}$O $\bullet$ NO$^+$	Smith and others 2003
2-heptanone	NO$^+$	3.4	144	C$_7$H$_{14}$O $\bullet$ NO$^+$	Smith and others 2003
acetoin	NO$^+$	2.5	118	C$_4$H$_8$O$_2$ $\bullet$ NO$^+$	Syft 2009
Alcohol					
n-amyl alcohol	NO$^+$	2.5	87	C$_5$H$_{11}$O$^+$	Spanel and Smith 1997
maltol	NO$^+$	2.5	156	C$_6$H$_6$O$_3$ $\bullet$ NO$^+$	Syft 2009
guaiacol	NO$^+$	2.5	124	C$_7$H$_8$O$_2^+$	Syft 2009
Nitrogen Compounds					
benzonitrile	H$_3$O$^+$	5.3	122	C$_6$H$_5$CN $\bullet$ H$^+$	Spanel and Smith 1998a
3-methylindole	NO$^+$	2.5	131	C$_9$H$_9$N$^+$	Wang and others 2004b
indole	H$_3$O$^+$	3.3	118	C$_8$H$_8$N$^+$	Wang and others 2004b
Sulfur Compounds					
dimethyl trisulfide	O$_2^+$	2.2	126	C$_2$H$_6$S$_3^+$	Wang and others 2004a
Hydrocarbons					
toluene	NO$^+$	1.7	92	C$_7$H$_8^+$	Spanel and Smith 1998b
phenol	NO$^+$	2.0	94	C$_6$H$_6$O$^+$	Spanel and Smith 1997

Table 2 — Odor thresholds in water of some alkylpyrazines and aldehydes.

Compounds	Odor description	Threshold level (ppb)	Reference
2,3-dimethylpyrazine	Nutty	80	Mihara and Mssuda 1988
2,5-dimethylpyrazine	Strong nutty	38	Fors and Olofsson 1985
2,6-dimethylpyrazine	Green nutty	57	Fors and Olofsson 1985
2,3,5-trimethylpyrazine	Musty, nutty, caramel, sweet	38	Fors and Olofsson 1985
2,3,5,6-tetramethylpyrazine	Walnuts, green	120	Fors and Olofsson 1985
2,3-diethyl-5-methylpyrazine	Earthy, bitter, green, tallow	4	Fors and Olofsson 1985
2-methylbutanal	Malty	140	Rychlik and others 1998
3-methylbutanal	Malty	13	Rychlik and others 1998
2-methylpropanal	Malty	0.1–2.3	Fors 1988
phenylacetaldehyde	Honey, sweet	4	Buttery and others 1988

thus the formation of alkylpyrazines is slow. However, in the alkalized-before-roasting samples, the pH is above 7 during roasting, and the high pH accelerates the 1st stage and favors the formation of alkylpyrazines in the 2nd stage of the Maillard reaction (Martins and others 2001). Therefore, higher concentrations of alkylpyrazines were detected in alkalized-before-roasting cocoa liquors than alkalized-after-roasting liquors.

The Maillard reaction occurs rapidly at the high temperature of roasting, but this reaction also occurs at relatively moderate temperatures when basic conditions are present, for example, during drying (70 °C for 2 h) after alkalization. Thus, in the alkalized-after-roasting samples, the cocoa liquors with a pH higher than 7 have higher concentrations of alkylpyrazines than those with a pH lower than 7 (Figure 1 and 2). The Maillard reaction is known to be significant at moderate temperature and high pH. For instance, the rate of formation of Amadori products at 80 °C increased as the pH increased above 7 (Ge and Lee 1997). At 75 °C, the rates of pyrazine formation and the number of types of alkylpyrazines increased as pH increased from 5 to 9 (Leahy and Reineccius 1989). At 72 °C, the level of the volatiles produced by the Maillard reaction increased from pH 6 to 8 (Blank and others 2003).

When the pH was below 7, no significant differences were found in the concentrations of alkylpyrazines in cocoa liquors alkalized-before-roasting and alkalized-after-roasting (Figure 1 and 2). Since the formation of alkylpyrazines is slow at acidic pH, there was no significant difference between the samples.

The effect of pH on partition coefficient

When cocoa liquor was alkalized and held at 40 °C, there was no significant change in the concentration of alkylpyrazines with pH from 5.2 to 8. Given that alkylpyrazines are basic, it would seem logical that volatility would decrease at low pH, but in this study, pH itself, without an increase in temperature to create the Maillard reaction products, did not produce a significant effect on volatile concentrations in the gas phase. When samples were held at 70 °C, TrMP, 2- and 3-methylbutanal, and phenylacetaldehyde increased when pH increased above 7 (Figure 3), indicating that the Maillard reaction occurred rapidly in alkali conditions at this temperature. The other compounds did not change. However, the concentrations of the alkylpyrazines and Strecker aldehydes in the alkalized cocoa

liquor samples were much lower than that in the alkalized cocoa bean samples, because the beans were heated much longer than the liquor, promoting the Maillard reaction.

The effect of pH on the ratios between alkylpyrazines

In the alkalized-before-roasting cocoa liquors, the ratio of TrMP to DMP increased from 0.79 to 2.29, and the ratio of DMP to TMP increased from 0.3 to 2.3 when the pH increased from 5.9 to 7.9 (Figure 4). The same trend was found in alkalized-after-roasting samples, where the ratio of TrMP to DMP and DMP to TMP increased when the pH increased from 6 to 8.4 (Figure 5). The change in the ratio of the different alkylpyrazines demonstrates that increasing pH favors the formation of TrMP and DMP, followed by TMP. Either the precursors or intermediates for forming TrMP and DMP must be more available than those for forming TMP as pH increases. Many of the amino acids have been shown to be precursors to TrMP and DMP, but not many are precursors for TMP. TrMP and DMP can be formed from alanine, valine, leucine, phenylalanine, and threonine (Arnoldi and others 1988; Amrani-Hemaimi and others 1995). TrMP can also be formed from glycine and DMP from lysine, asparagine, and glutamate. However, leucine is the only identified amino acid precursor for TMP (Arnoldi and others 1988). Bonvehí and Coll (2002) found the ratio of TMP to TrMP increased as the pH increased, opposite to our results. However, they used a different variety of cocoa beans, removed most of the cocoa butter, added water, and then roasted at a lower temperature for a longer time. Thus, the variety and/or exact conditions during roasting greatly affect the rate of formation of different alkylpyrazines.

Sensory evaluation has determined that the degree of roasting is normal if the ratio of TMP/TrMP is close to 1, in which case the cocoa liquors show a normal aromatic quality (Hashim and Chaveron 1994). If this ratio is greater than 1, the cocoa aromatic quality is poor because the concentration of TMP has not yet declined and not enough TrMP has developed (Hashim and Chaveron 1994). A ratio less than 1 indicates trimethylpyrazine is overdeveloped and a burnt flavor is present (Hashim and Chaveron 1994). No one has tested whether this ratio also works for alkalized cocoa, but if it does, the roasting conditions need to be adjusted for pH changes. For the samples with a pH below 6.5, a longer roasting time or higher temperature is necessary to increase the concentration of
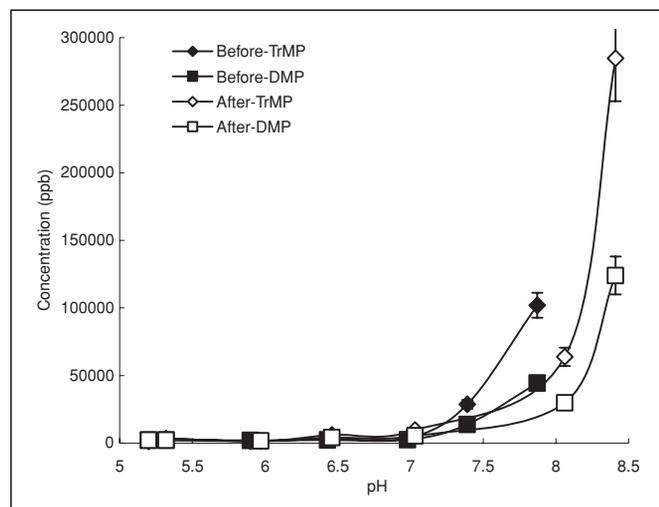

Figure 1 — 2,3-, 2,5-, and 2,6-dimethylpyrazines (DMP) and 2,3,5-trimethylpyrazine (TrMP) in cocoa liquors alkalized-before-roasting or alkalized-after-roasting to different pH values, with 95% confidence interval error bars.
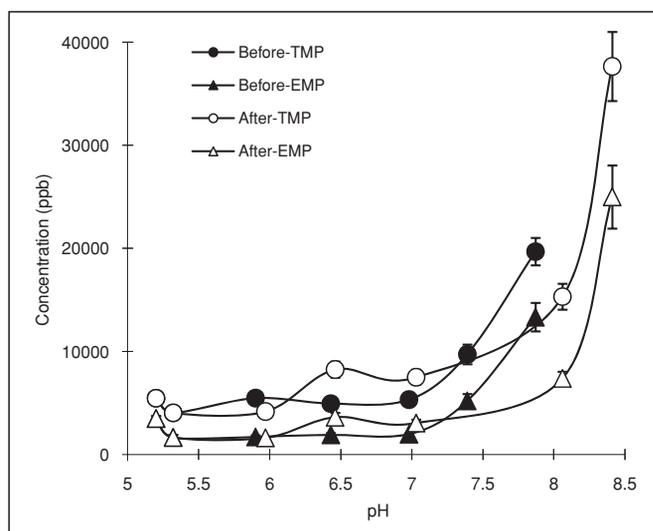

Figure 2 — 2,3,5,6-tetramethylpyrazine (TMP) and 2,3-diethyl-5-methylpyrazine (EMP) in cocoa liquors alkalized-before-roasting or alkalized-after-roasting to different pH values with 95% confidence interval error bars.
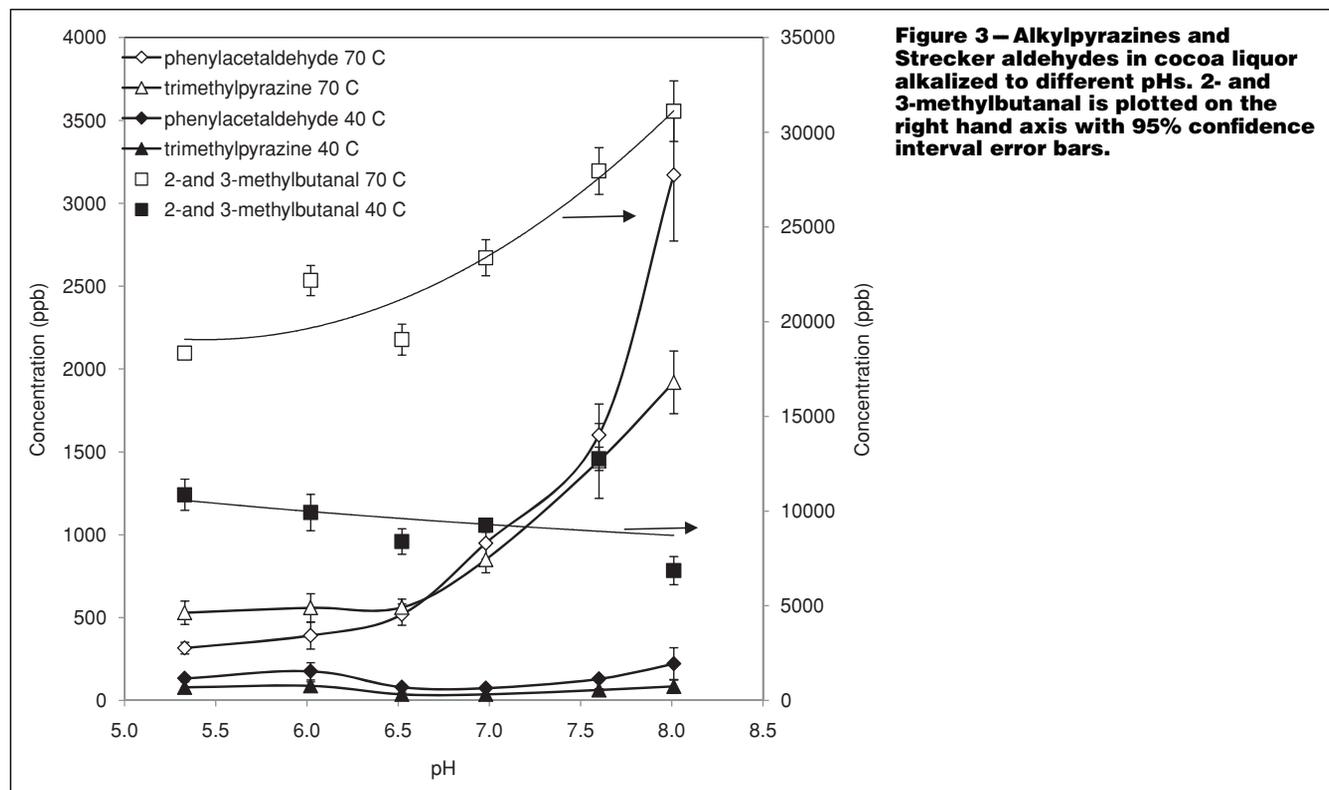
Figure 3 — Alkylpyrazines and Strecker aldehydes in cocoa liquor alkalized to different pHs. 2- and 3-methylbutanal is plotted on the right hand axis with 95% confidence interval error bars.

TrMP. For the samples with a pH above 7, the roasting time should be shorter or the temperature lower.

Alkylpyrazines in commercial cocoa powders

Commercial cocoa powder samples followed a similar trend of alkylpyrazines increasing with increasing pH (Figure 6). There was no significant change in the concentrations of alkylpyrazines between the samples at pH 5.74 and 7.07, while the alkylpyrazines increased for the samples at pH 7.39 and 7.84. But the alkylpyrazines at pH 8.04 were not higher than those with lower pH values (Figure 6). The commercial samples cannot be expected to match

the laboratory results exactly since each commercial sample was made by a different, proprietary method unknown to these authors. However, it is known that the cocoa powder sample at pH 5.74 is unalkalized. The samples with pH 7.07, 7.39, 7.84 are probably made with 1% to 6% potassium carbonate at moderate temperatures for 30 to 60 min, while 4% to 6% sodium hydroxide with an oxidizer and compressed air at a higher temperature for 1 h is probably used to produce the pH 8.04 sample (Ellis 1992). The pH 8.04 sample, a dark red cocoa powder, is intentionally made to have less flavor (Ellis 1992), which is shown by the lower level of alkylpyrazines.

Strecker aldehydes in cocoa liquors

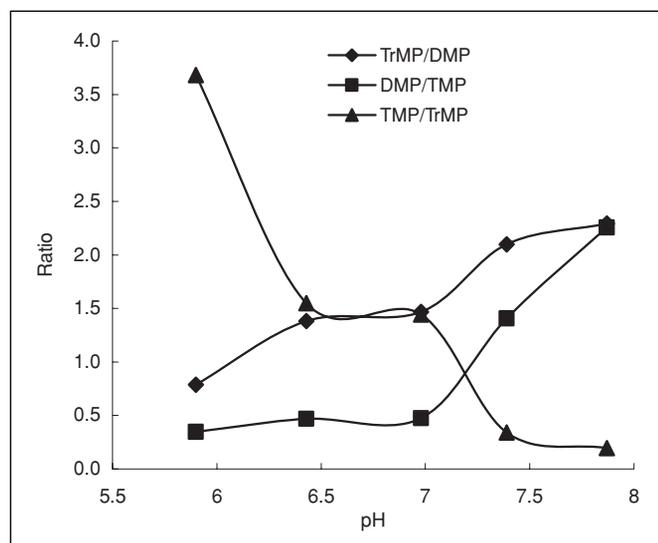Strecker aldehydes such as 2- and 3-methylbutanal, 2-methylpropanal, and phenylacetaldehyde, are products of

Figure 4 — The ratio between alkylpyrazines in cocoa liquors alkalized-before-roasting (DMP-dimethylpyrazines, TrMP-trimethylpyrazine, TMP-tetramethypyrazine).
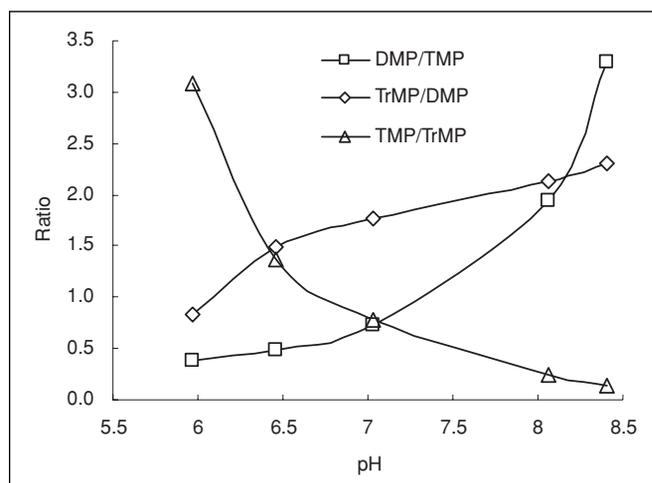

Figure 5 — The ratio between alkylpyrazines in cocoa liquors alkalized-after-roasting (DMP-dimethylpyrazines, TrMP-trimethylpyrazine, TMP-tetramethylpyrazine).
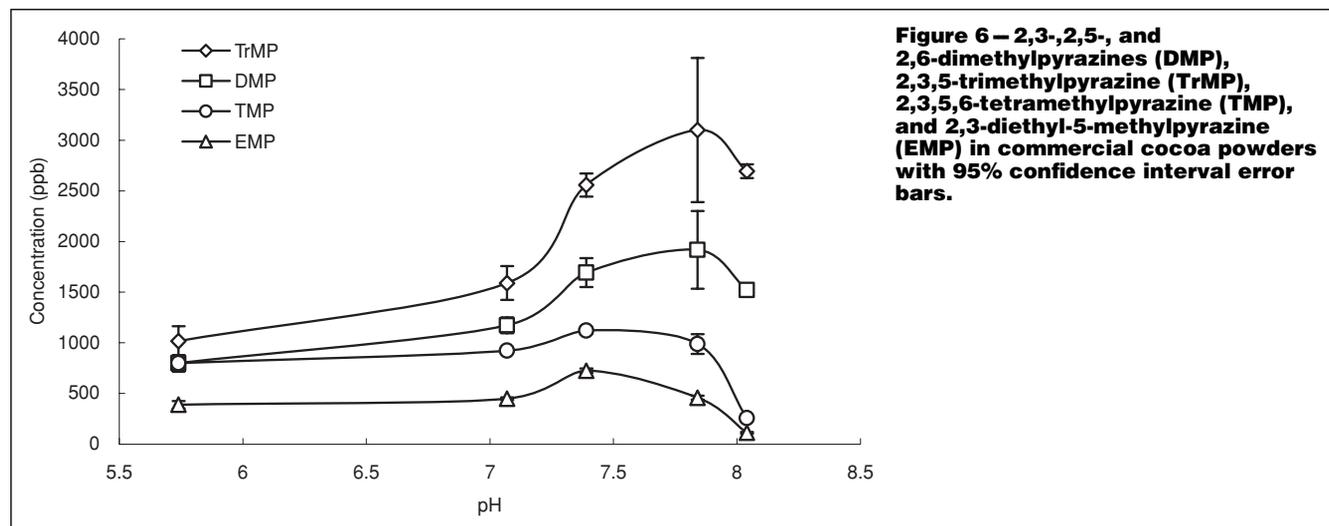
Figure 6 — 2,3-,2,5-, and 2,6-dimethylpyrazines (DMP), 2,3,5-trimethylpyrazine (TrMP), 2,3,5,6-tetramethylpyrazine (TMP), and 2,3-diethyl-5-methylpyrazine (EMP) in commercial cocoa powders with 95% confidence interval error bars.

Table 3 — Concentrations (ppb) of aldehydes and other volatiles in cocoa liquors with different pH values.

	Alkalized-before-roasting					Alkalized-after-roasting				
pH	5.9	6.43	6.98	7.39	7.87	5.97	6.46	7.03	8.06	8.41
Aldehydes										
Phenylacetaldehyde	596	1604	1774	10836	31862	699	3062	4966	22302	51462
2- and 3-methylbutanal	43307	20490	14830	66730	84830	28227	23090	25270	74070	122390
2-methylpropanal	2638	3719	4099	8185	17769	3046	5233	5529	13779	46889
(E,Z)-2,6-nonadienal	183	162	157	315	438	124	270	208	216	274
(E,E)-2,4-decadienal	596	828	924	1030	1281	642	1126	1092	907	882
(E)-2-nonenal	599	511	718	978	990	519	1111	961	820	864
Heptanal	162	176	196	253	352	195	324	266	289	254
Nonanal	13268	13767	15387	44207	89567	11222	22027	23287	67647	203607
Furans										
Furaneol	548	492	567	683	798	478	840	680	596	608
5-methylfurfural	196	217	221	391	1039	207	393	327	480	1009
Ketones										
delta-decalactone	122	105	158	236	281	129	376	188	215	246
Acetone	6627	7564	6522	11684	13010	6637	9200	7192	6662	6608
2-nonanone	358	347	374	511	840	374	692	536	494	603
2-heptanone	735	659	806	913	1091	787	1252	931	921	676
acetoin	5936	4335	4819	6595	8955	7352	10997	6835	6397	5057
Alcohol										
n-amyl alcohol	1300	1737	2039	2205	2367	1396	2417	2331	2265	1765
maltol	724	334	378	1260	1043	400	664	630	603	760
guaiacol	456	635	766	1189	2553	453	1002	1092	1851	3535
Nitrogen Compounds										
benzonitrile	323	974	1011	11331	42479	311	1963	3315	25979	116339
3-methylindole	2971	4609	5181	5167	5513	3497	6153	5793	4853	3469
indole	347	395	386	694	1273	380	492	457	813	2023
Sulfur Compounds										
dimethyl trisulfide	2709	3544	4244	6986	12192	2849	6238	6072	9232	24044
Hydrocarbons										
toluene	1404	947	717	2641	7797	1170	1999	1355	2167	6113
Phenol	2413	2946	3358	3988	5754	2881	5602	5204	5070	6878

roasting but are already present in the unroasted cocoa due to their biochemical formation during growth and fermentation (Granvogl and others 2006). The effect of pH during roasting on the formation of Strecker aldehydes showed a similar pattern to that of alkylpyrazines. In the samples with pH values below 7, there were no significant changes in the concentrations of 2- and 3-methylbutanal, 2-methylpropanal, and phenylacetaldehyde in either alkalized-before-roasting or alkalized-after-roasting samples, while the concentrations of these aldehydes increased when the pH was above 7 (Table 3). Since alkali conditions favor the formation of dicarbonyl compounds during Strecker degradation, a significant increase in Strecker aldehydes was expected in cocoa liquors with a pH above 7.

Other volatiles such as furans, ketones, alcohols, nitrogen compounds, sulfur compounds, hydrocarbons, and phenol also showed an increase in concentration with increasing pH for both alkalized-before-roasting and alkalized-after-roasting cocoa liquors (Table 3). Many of these volatile compounds are formed during the Maillard reaction and hence, are promoted under alkali conditions.

Conclusions

The concentration of alkylpyrazines in cocoa liquor increased as the pH increased, and cocoa liquors with higher pH have a higher concentration of aroma compounds. Altering the pH alone did not affect the concentration of aroma compounds in the gas

phase, except when samples were heated, which promoted the Maillard reaction. The ratios of TrMP/DMP and DMP/TMP increased while the ratio of TMP/TrMP decreased as the pH increased. The roasting conditions may be adjusted based on pH changes to produce optimum aroma.

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