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Extended Abstract

Evaluation of Changes in Alkyl Pyrazines, Color and Sensory Properties of Cocoa Powder under Different Roasting Conditions

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Abstract
Cocoa is an important product in the world and the raw material for the production of cocoa powder, which is widely used in the chocolate and food industries. Its value and quality are related to its unique and complex flavor combinations. The most important of these compounds are pyrazines, which are known to be the key components of the cocoa flavor. Since roasting is one of the most important steps in the process of producing cocoa powder, in the present study, the effect of roasting temperature (120, 130 and 140 °C) and time (20, 30 and 40 min) on flavor (alkyl pyrazines), color and sensory properties of cocoa powder were studied as the most important characteristics of cocoa quality and acceptability. Alkyl pyrazine compounds were analyzed by gas chromatography-mass spectrometry. The results showed that by changing the roasting temperature and time, the browning index (OD_{460}/OD_{525}) ($P \leq 0.05$) as well as the amount of alkyl pyrazines changed significantly ($P \leq 0.01$). Roasted cocoa powder at 140 °C for 40 min showed the highest browning index, tetra-methyl pyrazine to tri-methyl pyrazine (TMP/TrMP) ratio and sensory evaluation score compared to other samples.

Keywords: Alkyl pyrazine, Cocoa powder, Color, Roasting

Introduction
Cocoa is a product of significant economic importance in the world and a key raw material in *cocoa powder and chocolate manufacturing* (Kongor *et al.*, 2016). There are several indicators to measure the quality of cocoa beans but the most important ones are the amount and type of flavor compounds (Krähmer *et al.*, 2015; Magi, Bono, & Di Carro, 2012). To date, more than 600 flavor compounds of cocoa beans and cocoa products have been identified (Crafack *et al.*, 2014), including aldehydes and ketones, pyrazines, pyrroles, esters, alcohols, hydrocarbons, nitriles and sulphides, ethers, furans, thiazoles, pyrones, acids, phenols, imines, amines, and oxazoles (Kongor *et al.*, 2016). About 80 pyrazine compounds contribute to the overall cocoa flavor and tetramethylpyrazine and trimethylpyrazine are the most important compounds (Afoakwa, Paterson, Fowler, & Ryan, 2008). The concentration ratio of tetramethylpyrazine (TMP)/trimethylpyrazine (TrMP) has been suggested as an indicator of roasting degree (Ziegleder, 2017). Roasting is one of the important steps which

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affects the quality characteristic of cocoa beans during industrial processing (Oracz & Nebesny, 2014; ZZaMan & Yang, 2013) and determines the chemical and physical processes that occur inside the beans, as well as the quality of the final products (Afoakwa, Budu, Mensah-Brown, Takrama, & Ofosu-Ansah, 2014; Krysiak, 2006; Krysiak & Motyl-Patelska, 2006). Numerous studies confirmed that temperature and duration of roasting have considerable effect on the physical and chemical changes of cocoa beans. The optimal temperature for cocoa bean roasting is 15 to 45 min and temperatures range from 130 to 150 °C (Ramli, Hassan, Said, Samsudin, & Idris, 2006).One other factor which affects the final quality of cocoa powder is the color. The color change occurs due to the presence of compounds made from epicatechin that may combine during various processes like fermentation, drying, and roasting. These compounds increase the intensity of molecule color and make cocoa darker. The pH, humidity, time and temperature of roasting need to be determined accurately and carefully, as different types of color are likely to form (Beckett, 2009), studies have shown that during the processing of cocoa beans and making cocoa powder, there appear to be a number of problems such as aroma reduction, unpleasant odors like cigarette smoke, and alkaline flavor and aroma. In present research, changes in flavor volatile compounds (alkyl pyrazines) and color as important quality properties as well as changes in polyphenols and sensory properties of cocoa in different conditions are studied in order to obtain optimal conditions for the process.

Material and methods

In the current study, fermented and dried Cameron cocoa beans (Forastero cultivar, Cameroon) were prepared from Shirin Asal Food Industrial Group (Tabriz, Iran). In the factory, Cameroon cocoa beans were cleaned, dried at 100 °C, broken into cocoa nibs and stored. At this stage, a sufficient amount of Cameroon cocoa beans, which had undergone the cleaning step (cleaning, drying in 100 °C for 320 s) was taken from Shirin Asal Company and the alkalization process (by NaOH 1.5% + K_2CO_3 0.5%) was performed on nibs. The roasting process was performed by adjusting the oven to the desired temperature (120, 130 and 140 °C). 75 g nibs were spread as a single layer on aluminum foil, placed in the oven and baked for the intended time (for 20, 30, 40 min). Prior to testing, the samples were milled and pulverized in a laboratory mill (Made in Germany and IKA brand) at room temperature (27 °C) for 45 s in order to obtain homogeneous samples. The liqueurs were homogenized by mixer (CJJ-2 / 2A Series). The aromatic compounds were identified and confirmed by GC-MS. For the purpose of GC-MS analysis, an Agilent 7890 A gas chromatograph coupled to a 5975A mass spectrometer using a HP-5 MS capillary column (5% The standards of five pyrazine compounds (2-methylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,3,5-trimethylpyrazine, and 2,3,5,6-tetramethylpyrazine) had been previously injected into the GC-MS. Finally, the identification of the alkylpyrazines compounds was carried out by comparing their retention time with the standards. Color determination was evaluated according to Bonvehi & Coll (1997) .The absorbance was determined at 460 and 252 nm (OD_{460} and OD_{525}) using UV/Visible spectrophotometer (HACH, DR/4000U, USA). Sensory evaluation was performed by the method (Bonvehí, 2005).

Statistical analysis

Qualitative experiments were performed in three replications using factorial in a completely randomized design. The analysis of variance (ANOVA) was performed , using Mstatc 11 software (Michigan State University). Duncan test was used to compare the difference between the mean values at a significance level ($P \leq 0.01$).

Results and discussion

Many volatile aromatic materials included alcohols, acids, aldehydes, esters, ketones, , and pyrrole compounds (Table 1), which. According to previous studies, pyrazines are the most effective compounds in creating the cocoa products' flavor. Based on the statistical results, the amount of alkylpyrazines and TMP/TrMP ratio of the samples in different treatments had a statistically significant difference ($P \leq 0.01$). The concentration of pyrazines increased with increasing temperature from 120 to 140 °C. Roasted cocoa powder at 140 °C for 40 min, had the highest amount of tetramethylpyrazine and trimethylpyrazine (and roasted cocoa powder at 120 °C for 20 min indicated the lowest amount of these compounds (Table 1). According to various researches, it has been determined that the degree of cocoa roasting is normal when the TMP/TrMP ratio is equal to or about 1, in which case the cocoa products show the desired aroma and flavor quality. A ratio lower than 1 indicates the overdevelopment of trimethylpyrazine, the high temperature of the cocoa roasting process, and the presence of a burnt odor. This ratio can be used to evaluate the optimum temperature in cocoa processing (Bonvehi & Coll, 1997; Hashim & Chaveron, 1994; Huang & Barringer, 2010). This ratio was between 1 and 1.26 in all samples of the present study. Color is widely used as an indicator of the development of browning reactions in cocoa beans, and temperature is the main cause of these changes (Krysiak, 2006; Shakerardekani, Karim, Ghazali, & Chin, 2011; Żyżelewicz, Krysiak, Nebesny, & Budryn, 2014). In the present study, the results of experiments showed (Table 1) that with increasing temperature and roasting time, the intensity of color increased significantly ($P \leq 0.05$) and only in samples at 140 °C and 30 and 40 min the increase was not significant. The highest color quality was obtained during roasting at 140 °C for 40 min. The increase in browning index with increasing roasting time was probably due to increase in brown pigment formation from Maillard reactions, thermal oxidation and polymerization of polyphenols to form tannins (Patras, Brunton, O'Donnell, & Tiwari, 2010) and Strecker degradation reactions (Krysiak, 2006; Nebesny & Rutkowski, 1998) during the roasting process. In this study, due to the fact that different roasting conditions mainly affect the flavor, color and aroma of products and these features are among the most important features effective in quality acceptance by consumers, in the sensory evaluation of produced cocoa powders, these properties were investigated. The results obtained from analysis of variance of the samples indicated that the effect of temperature and roasting time on flavor, color and aroma of cocoa was significant, but the interaction of temperature and time on color was not significant ($P > 0.05$), while it was significant on flavor and aroma ($P < 0.01$), Fig. (1).

Table 1. Alkylpyrazines* (ppb) with different Roasting condition

Sample		Alkylpyrazine						
Temperature (°C)	Time (min)	2-MP	2,3- DMP	2,5- DMP	2,3,5-TrMP	2,3,5,6- TMP	TMP/TrMP	Total pyrazine
120	20	801.2 ±7.61^{f}	481.6±16.28^{g}	1530.0±11.60^{h}	8402.0±15.77^{h}	10230.0±22.90^{i}	1.21±0.004^{b}	4289±0.54^{c}
	30	793.3±10.62^{f}	836.5±23.72^{e}	2956.0±18.60^{e}	10330.0±14.91^{g}	12870.0±28.94^{d}	1.24±0.00^{a}	5556±7.51^{b}
	40	1297.0±16.98^{b}	960.9±12.46^{d}	2701.0±22.89^{f}	10760.0±16.34^{f}	12480.0±21.94^{g}	1.15±0.004^{ef}	5640±5.18^{b}
130	20	1206.0±19.52^{C}	687.4±24.15^{f}	3587.0±24.60^{c}	10940.0±18.72^{d}	11890.0±27.98^{h}	1.08±0.00^{g}	5661±18.39^{b}
	30	1129.0±27.01^{d}	1623.0±12.82^{b}	6281.0±15.24^{a}	11030.0±31.58^{c}	12670.0±20.13^{f}	1.14±0.004^{f}	6548±2.96^{a}
	40	1085.0±19.57^{d}	1562.0±24.78^{c}	4740.0±22.50^{b}	11770.0±5.30^{b}	14030.0±27.32^{c}	1.19±0.004^{cd}	6637±6.74^{a}
140	20	1471.0±24.26^{a}	1573.0±29.46^{c}	2416.0±16.10^{g}	10840.0±10.25^{e}	12790.0±18.31^{e}	1.17±0.004^{de}	5819±5.53^{b}
	30	1213.0±26.08^{c}	1644.0±10.57^{ab}	3323.0±12.99^{d}	11810.0±16.80^{b}	14930.0±29.20^{b}	1.26±0.00^{a}	6584±7.09^{a}
	40	967.2±22.01^{e}	1678.0±16.39^{a}	2430.0±21.54^{g}	12540.0±24.59^{a}	15070.0±24.08^{a}	1.20±0.00^{bc}	6537±10.63^{a}

MP methylpyrazine, *DMP* dimethylpyrazine, *TrMP* trimethylpyrazine, *TMP* tetramethylpyrazine
*Values are mean ± standard deviation of three separate determinations.

1Mean values with different superscript letters in the same column are significantly different ($P \leq 0.01$).

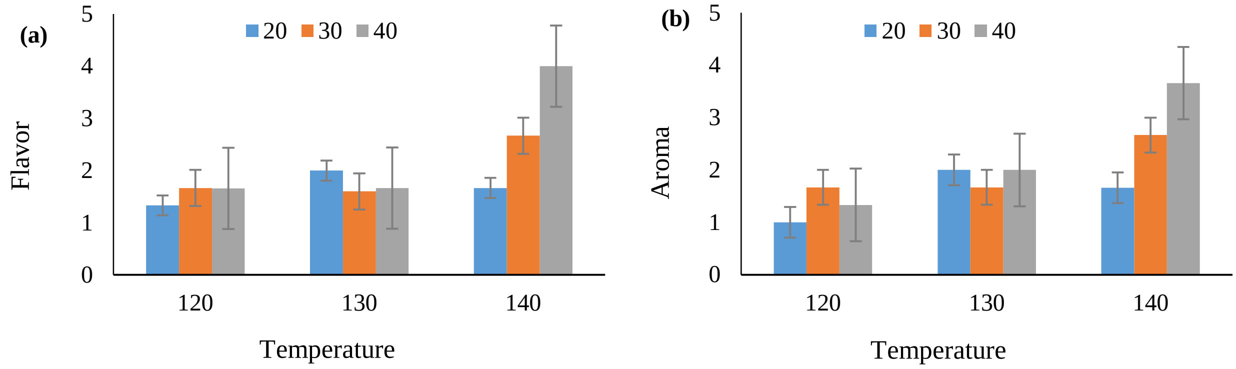

Fig. 1. Effect of different Roasting conditions on the sensory properties of cocoa powder. a. The flavor of cocoa powder. b. The aroma of cocoa powder

Conclusions

The formation of color and flavor combinations during the Maillard reaction depend on the conditions of the roasting process, especially its time and temperature. In the present study, the roasting process affected the alkylpyrazine color and sensory parameters . Increasing the roasting temperature to 140 °C and roasting time to 40 min increased the browning index (OD_{460}/OD_{525}) and a darker color was obtained. Also, this treatment had a high content of total alkylpyrazine and tetramethylpyrazine, but a lower content of polyphenols and humidity, which in general, compared to other treatments, can be considered as a suitable treatment.

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