REVIEW: NOVELTY OF SPECIAL COCOA FLAVOR IN MALAYSIAN RENAISSANCE COCOA STUDY

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ABSTRACT - *Cocoa flavour originates from fermentation, roasting, and drying of cocoa beans. Cocoa bean is a part of the cocoa fruits and as a main ingredient in chocolate making. At the same time, cocoa flavour is an important value in cocoa commodity in the world. It has been known as the main reason in chocolate grading and chocolate qualities. Cocoa with unique and special flavours will increase their value and quality. Commercial cocoa flavour in markets show strong basic cocoa flavour notes, where fine varieties with superior cocoa planting material with genetic improvements show aromatic, floral, or smoother flavour characteristics. About hundred various compounds (alcohols, carboxylic acids, aldehydes, ketones, esters, and pyrazines) have been identified as uniques cocoa compounds in fermented and unfermented cocoa beans. The cocoa flavour arises from complex biochemical and chemical reactions during the post-harvest processing of raw beans, and from many influences of the cocoa genotype, chemical make-up of raw seeds, environmental conditions, farming practices, processing, and manufacturing stages. There has been much research on cocoa flavour components. This paper provides an overview on the existence of specialty cocoa flavour in on-odour volatile compounds group, are reviewed.*

Key words: Cocoa, flavour, specialty cocoa beans, chocolate, compound

INDTRODUCTION

The Maya people who were probably the first to cultivate the cacao plant and produce chocolate. The early chocolate drink, considered a "drink of the Gods" was mixed with cinnamon and pepper, tasting bitter and strong, and was most appreciated for its invigorating and stimulating effects than for its taste and flavour.

From the 1800s to the 20th century, it evolved from a drink to its current pleasurable varieties (such as fondant, Gianduja, milky and white chocolate), gaining much momentum in industry and also made great impact as a romantic item and art form. Important components in chocolate are flavour notes, polyphenol (antioxidants), cocoa butter, caffeine, theobromine and phenylethylamine.

Several factors/trends contribute to the chemistry compound has been discovered to focus on pharmacological and flavour development in chocolate. In the current global cacao industry, where more focus is on direct and transparent trade, sustainability, single origin and high quality cacao beans, more attention has been directed to activities performed at the country of origin.

Thus, there is increasing understanding of the effect of genetics and growing conditions and post-harvest processes, performed at the country of origin, on flavour development of cacao beans and the potential application of the cocoa flavour improvement concept to the chocolate industry. More attention has thus been paid to optimization of crop genetics, agricultural practices, and post-harvest processes. Once the cacao beans are ready for processing, other factors related to optimization of chocolate formulation and processing become important especially in flavour aspect.

The use of novel special cocoa flavour in chocolate formulation and production requires optimization of processing to develop desires such as cocoa planting materials and producing premium cocoa beans. The use of specialty cocoa flavour to contrast the cocoa flavour development of cocoa butter via natural cocoa flavour formations, or to develop chocolate with desired flavour characteristics, has increased flavour properties in several types of flavour and pharmacological aspect with increased interest in flavour and pharmacological development or cocoa quality changes.

Lastly, the increase in special cocoa flavour properties and pharmacological in cocoa beans, related to cocoa plant materials, has increased the interest in farmers and entrepreneurs in chocolate, requiring modification of the cocoa genetic, cocoa plant materials with potential changes in flavour and pharmacological development.

Currently, Malaysian beans are discounted due to their low chocolate flavour. Producing is also currently low in Malaysia. Producing beans with novel and exceptional properties can revive and revolutionize the Malaysian cocoa industry.
The objectives of this review were to provide an overview on cocoa flavour from a flavour composition in chemistry aspect and a sensory perspective. The non-volatile and volatile chemical components of cocoa and chocolate flavour, and their sensory properties correlated to the main influences involved in flavour formation, are reviewed.

Volatile components that contribute to cocoa flavor
Cocoa volatiles are derived from aroma precursors generated during fermentation and bean drying. The typical chocolate flavor is obtained during the roasting stage through Maillard reactions and the Strecker degradation of flavor precursors and their intermediates (Afoakwa and others 2008). About 600 volatiles have been identified in cocoa flavor (Ziegleder 2009).

Table 1 summarizes the compounds thought to be main contributors to cocoa flavor. They include several chemical classes such as aldehydes, ketones, esters, alcohols, pyrazines, quinoxalines, furans, pyrones, lactones, pyrroles, and diketopiperazines (Figure 3). Different cocoa types may exhibit various and specific flavors since the concentration and sensory character of these compounds vary significantly.

Alcohols
These compounds occur during fermentation as a result of microbial activity. Also, they may result from heat degradation of amino acids. During drying and roasting, the concentration of alcohol decreases through chemical degradation or volatilization. High temperatures (160 °C to 170 °C) and the prolonged heat duration promote the loss of alcohols (Ramli and others 2006).

Alcohols confer a fruity, green, floral aroma. High alcohol contents are desirable in order to obtain cocoa products with flowery and candy notes (Rodriguez-Campos and others 2012). 2-Heptanol imparts a fruity, herbaceous, flowery, and spicy aroma. Linalool and 2-phenylethanol are major alcohols in roasted nibs (Jinap and others 1998). Also, 2-phenylethanol is the most odoractive compound in dried and fermented cocoas (RodriguezCampos and others 2012).

Flavor-grade cocoas from South America (Ecuador and Venezuela) and Trinidad contain important concentrations of linalool and other terpenoids (1.6 to 3.8 mg/kg), which confer a flowery, leafy, and tea-like aroma. On the other hand, the level of linalool is very low in basic cocoas from West

Basic cocoas from Ghana have a medium content of linalool (0.2 to 0.8 mg/kg; Ziegleder 1990). Africa (0 to 0.5 mg/kg) or Malaysia (0 to 0.2 mg/kg; Ziegleder 1990; Biehl and Ziegleder 2003a). During roasting, the linalool content slightly decreases, but the difference between flavor and basic grade cocoas remains. The ratio of linalool/benzaldehyde may be used as a flavor index. A value higher than 0.3 indicates typical fine-grade cocoas (Ziegleder, 1990).

Aldehydes and ketones
The carbonylic compounds of aldehyde type are crucial for the development of good cocoa flavor. A high concentration of aldehydes as well as of ketones is favorable for cocoa quality (Rodriguez-Campos and others 2012). Usually, they are formed by Strecker degradation of free amino acids during roasting.
However, low concentrations of aldehydes may arise even during fermentation and drying. 2-Methylbutanal and 3-methylbutanal arising during fermentation produce malty and chocolate notes in unroasted and roasted cocoa (RodriguezCampos and others 2012).

Desirable aldehydes and ketones are obtained during the stage of fermentation of 6 to 8 d and drying at 70°C (Rodriguez-Campos and others 2012). High temperatures and a longer roasting decrease the content of aldehydes. Aldehydes are not only flavor components but also important reactants involved in the formation of heterocyclic compounds (pyrazines; Ziegleder 2009).

They generate, *via* aldol condensation, phenylalk-2-enals with a typical flowery note fairly reminiscent of cocoa/chocolate (Biehl and Ziegleder 2003a). 5-Methyl- 2-phenyl-2-hexenal exhibits a deep bitter cocoa note (Ramli and others 2006). Among the ketones, acetophenone determines sweet, floral notes, and acetoin appears to be a precursor of tetramethylpyrazine, an important odor-active component of cocoa flavor (Rodriguez-Campos and others, 2012).

Esters
Esters are the second most important class of volatiles after pyrazines. Ethyl-, methylesters, and acetates predominate (Ramli and others 2006; Rodriguez-Campos and others 2011). They confer a fruity flavor and are the typical aroma components (mainly

acetates) in unroasted cocoas that arise from amino acids (Biehl and Ziegleder 2003a). 2-Phenylethyl Acetate has flowery and honey notes and it is mainly responsible for the characteristic aroma of Asian cocoa liquor (Jinap and others 1998).

It has been found in unroasted and roasted cocoa, and it can also results from yeast metabolism. Also, ethyl-2-methylbutanoate is an important flavor generated during fermentation (Afoakwa and others 2008). The formation of amyl acetates during fermentation must be avoided. They are considered as indicators of flavour defects (Rodriguez-Campos and others 2012).

A summary of main aroma-damaging compounds to the cocoa flavor is provided in Table 2. High levels of 2-phenylethyl acetate and low concentrations of 3-methyl-1-butanol acetate are important for an aromatic quality of cocoa (Rodriguez-Campos and others 2012). High temperatures during roasting negatively affect the content of esters (Ramli and others, 2006).

Pyrazines

These compounds are the main class of heterocyclic volatiles and the key odor components in cocoa aroma. They display nutty, earthy, roasty, and green aromas (Semmelroch and Grosch 1996; Wagner and others 1999; Czerny and Grosch 2000; Czerny and others 2008).

About 80 pyrazines contribute to the overall cocoa flavour (Afoakwa and others 2008). They are alkylpyrazines with different substituents (methyl-, ethyl-, propyl-, furyl-, vinyl-, and methoxy; Ziegleder 2009), and tetramethylpyrazine and trimethylpyrazine are the most important. These pyrazines exhibit nutty, grassy, and persistent cocoa notes, and tetramethylpyrazine has cocoa flavor enhancer properties (Ramli and others 2006).

It has been reported that tetramethylpyrazine constitutes about 90% of the total pyrazines (Rodriguez-Campos and others 2012). Well-fermented cocoa from Ghana has higher levels of pyrazines (698 μg/100 g) than Mexican cocoas (142 μg/100 g; Afoakwa and others 2008).

Generally, the Criollo cultivar shows high levels of pyrazines while Nacional/Arriba cocoa has the lowest concentrations of pyrazines (Afoakwa and others 2008; Giacometti and others 2015). Most of the pyrazines originate from α-aminoketones by Strecker degradation and Maillard reactions during roasting (Rodriguez-Campos and others 2012).

Temperature and duration of thermal reactions are critical factors that influence the concentration of pyrazines. Tetramethylpyrazine reaches high concentrations (7 mg/kg) at medium roasting conditions (Ziegleder 2009). The concentration ratio of tetramethylpyrazine (TMP)/trimethylpyrazine (TrMP) has been proposed as an indicator of roasting degree.

For a normal degree of roasting, the ratio TMP/TrMP ranges from 1.5 to 2.5, and for an overroasting degree, the value is below 1 (Ziegleder 2009). Tetramethylpyrazine could occur during fermentation as a metabolic product of *Bacillus subtilis* (Ramli and others 2006). However, the fermentation of cocoa beans in the absence of yeasts and their subsequent roasting leads to less pyrazines and a less chocolaty character of the final flavor (Ho and others 2014). Also, pyrazines may arise during the drying process via Maillard reactions initiated by a drop in moisture content and temperatures of 30 °C to 50 °C (Puziah and others 1999).

Acids

During fermentation the concentration of organic acids increases as a result of sugar metabolism. Acetic acid with sour and vinegar-like aroma is considered the highest odor-active compound in fermented and unroasted beans. Besides acetic acid, other short-chain carboxylic acids (isobutyric, isovaleric, and propionic) predominate in fermented cocoa beans.

They produce off-odor notes (rancid, butter, and hammy) and they are eliminated during the roasting and conching stages. A prolonged fermentation (over 6 d) increases the level of organic acids and their off-flavor notes (Rodriguez-Campos and others 2012). Drying reduces the content of volatile fatty acids such as acetic, propionic, butyric, and isobutyric acids (Paramo and others 2010), and 70% of acetic acid is removed during roasting (Rodriguez-Campos and others 2012).

Phenols

Phenols (phenol, 2-methoxyphenol) are compounds with aroma-damaging properties, producing smoky and undesirable notes. They arise during drying or storage by contamination from burning wood or charcoal smoke.

The roasting of cocoa beans at 110 °C to 140 °C for 5 to 30 min increases the level of phenols. A high-quality cocoa should be mostly free of them (Jinap and others 1998).

Other components

Furanones and pyrones are generated during drying and roasting via degradation of monosaccharides. Moderate temperatures and relative high humidities favor their formation (Ziegleder 2009; Rodriguez-Campos and others 2012). Roasting at 130 °C for 20 min is the optimal condition for the production of pyrones and furanones (Ziegleder 1991).

The most important compounds are furaneol [4-hydroxy-2,5-dimethyl 3(2H)furanone], hydroxymaltol (3,5- dydroxy-6-methyl-4-pyrone), dyhydroxymaltol, and cyclotene (2- hydroxy-3-methyl-2-cyclopentene-1-one). They confer pleasant caramel notes and enhance the flavor impression.

The alkalization process destroys those compounds (Rodriguez-Campos and others 2012). 2-Acetyl-1-pyrrole is produced during drying and roasting *via* Maillard reactions and Strecker degradation starting from the amino acid proline. It confers caramel, chocolate, and roasty desirable notes (Rodriguez-Campos and others 2012).

Table 1: Specialty cocoa flavour existed in on-odour volatile compounds group

On-odor volatile compounds group	**Specialty cocoa flavor**	**Compound name**	**Researcher**
Alcohols and phenols	Fruity, grape Fruity	2-Methyl-1-butanol	Ramos and others (2014)
	Fruity, green Fruity, herbal	1-Hexanol	Bonvechi (2005)
	Fruity, green Fruity, herbal	2-Hexanol	
	Citrusy Fruity	2-Heptanol	Rodriguez-Campos and others (2012)
	Honey, floral Floral	1-Phenylethanol	
	Honey, floral Floral	2-Phenylethanol	
	Sweet, floral Floral	Benzyl alcohol	
Aldehydes and ketones	Honey, floral Floral	2-Phenyl acetaldehyde	
	Floral Floral	2-Phenylpropanal	Bonvechi (2005)
	Fruity Fruity	2-Pentanone	Rodriguez-Campos and others (2011)
	Fruity, floral Fruity, floral	2-Heptanone	
	Floral Floral	Acetophenone	
	Heavy floral, herbaceous Floral, herbal	2-Hydroxy acetophenone	Bonvechi (2005)
	Fruity, floral Fruity, floral	4-Methyl acetophenone	
Acids	Floral Floral	2-Methylpropionic acid	Krings and others (2006)
	Sweet, rose Floral	3-Phenylpropionic acid	Bonvechi (2005)
	Honey, floral Floral	Cinnamic acid	
Esters	Pineapple Fruity	Ethyl acetate	Rodriguez-Campos and others (2012)
	Floral, jasmine Floral	Benzyl acetate	
	Fruity Fruity	Isobutyl acetate	
	Fruity, banana Fruity	Isoamyl acetate	Ramos and others (2014)
	Sweet, cinnamon-like Sweet chocolate	Ethyl cinnamate	Rodriguez-Campos and others (2012)
	Balsamic, strawberry Fruity	Methyl cinnamate	Bonvechi (2005)
	Bitter-almond Nutty	Methyl salicylate	
	Sweet, honey, jasmine Floral	Methylphenyl acetate	
	Balsam, sweet Floral	Isoamyl benzoate	Rodriguez-Campos and others (2012)
	Fruity, floral Fruity, floral	Ethyl laurate	Bonvechi (2005)

	Pear, grape Fruity	Ethyl decanoate	Rodriguez-Campos and others (2012)
	Fruity, floral Fruity	Ethyl octanoate	
	Fruity Fruity	Ethyl hexanoate	
	Fruity, apple Fruity	Ethyl valerate	Bonvechi (2005)
	Fruity Fruity	Ethyl 3-methylbutanoate	Rodriguez-Campos and others (2012)
	Fruity, sweet Floral	Ethylphenyl acetate	
	Honey, floral Floral	2-Phenylethyl acetate	
	Pineapple Fruity	Ethyl butyrate	Ramos and others (2014)
	Fruity Fruity	Ethyl lactate	Rodriguez-Campos and others (2012)
	Pleasant aroma Floral	Diethyl succinate	Ramos and others (2014)
	Fruity Fruity	Ethyl 2-methylbutanoate	Rodriguez-Campos and others (2012)
Amines, amides, nitriles, purines	Essences Floral	N-(2-phenethyl) formamide	Bonvechi (2005)
	Almond Nutty	Benzonitrile	
Lactones	Coconut Nutty	δ-Octenolactone	Afoakwa (2012)
	Peach Fruity	γ -Decalactone	
Terpenoids	Geraniol	Floral, rose, fruity Floral, fruity	Bonvechi (2005)
	Geranyl acetate	Rose, lavender Floral	
	α-Terpenyl formate	Herbaceous, citrus Herbal, fruity	
	Linalool (cis-pyranoid)	Floral, green Floral, herbal	
	Linalool (trans-pyranoid)	Floral Floral	
	Linalool oxide (cis-furanoid)	Nutty Nutty	
	Linalool oxide (trans-furanoid)	Floral, citrus Fruity, floral	
Furans, furanones, pyrans, pyrones	2-Furfural	Almond Nutty	
	2-Furfuryl acetate	Fruity, banana Fruity	Ramos and others (2014)
	2-Acetyl-5-methylfuran	Strong nutty Nutty	Bonvechi (2005)
	2-Furfuryl propionate	Spicy, floral Floral	
	5-(1-Hydrohyethyl)-2-furanone	Red fruit, jam, green notes Fruity, herbal	Krings and others (2006)
	Dihydro-3-hydroxy-4,4-dimethyl-2-furanone	Coconut Nutty	
	4-Hydroxy-2,5-dimethyl-3-furanone (furaneol)	Fruity, strawberry, hot sugar Fruity, nutty	Bonvechi (2005)
	3-Hydroxy-2-methyl-4-pyrone (maltol)	Roasted nuts Nutty	
	5,6-Dihydro-6-pentyl-2-pyrone	Coconut Nutty	Krings and others (2006)
Pyrroles	Pyrrole	Nutty Nutty	Bonvechi (2005)
	2-Acetylpyrrole	Chocolate, hazelnut Sweet chocolate	Rodriguez-Campos and others (2012)
	Pyrrole-2-carboxaldehyde	Nutty Nutty	Krings and others (2006)
	2-Methylpyrazine	Nutty, chocolate, cocoa, roasted-nuts Sweet chocolate, nutty	
	2-Ethylpyrazine	Peanut butter, musty nutty Nutty	

Pyrazines	2,5-Dimethylpyrazine	Cocoa, rusted nuts Sweet chocolate, nutty	Bonvechi (2005)
	2,6-Dimethylpyrazine	Nutty, coffee, green Nutty, herbal	
	2-Ethyl-5-methylpyrazine	Nutty, raw potato Nutty, hernal	
	2,3-Diethylpyrazine	Nutty, hazelnut, cereal Nutty	
	2,3,5-Trimethylpyrazine	Cocoa, rusted nuts, peanut Sweet chocolate, nutty	

Specialty cocoa flavor

Cocoa beans are classified as valuable food that contributed all over around the world. One of the important things that most researcher focus on is concentrating on flavour analysis and investigating their chemical compound that are useful to human beings such as in pharmaceutical industries and food industries.

Special cocoa flavour is a complex process during which numerous chemical reactions occur from fresh cocoa beans, fermented cocoa beans, drying processes of cocoa beans and in chocolate processing levels. The most important processes, involving most of the reactions important for development of the proper cocoa flavour, are fermentation, drying and roasting of cocoa beans, and chocolate conching.

During fermentation, formation of important precursors occurs, which are essential for further chemical reactions in the following processes of chocolate production. Roasting is one of the most important processes due to the occurrence of Maillard's reactions, during which aroma compounds are formed.

Chocolate flavour development involves two complexes processes: fermentation and roasting. During fermentation storage, protein degrades into amino acids and short oligopeptides. They can reach with reducing sugar to produce a complex mixture of compounds during roasting. These compounds are the major contributors to chocolate flavour. Cocoa flavour turned to be low when polyphenols content was high and cocoa flavour was high when polyphenols level was low (Clapperton et al., 1994). This is a common situation when cocoa beans have been fermented and roasted for several days. Chemical changes were shown at the pre-fermentation and after fermentation process.

Besides components that contribute to chocolate flavour, seeds also contain ones that detract from chocolate flavour, notably condensed tannins and methylxanthines (theobromine and caffeine). Tannins reduce percieved chocolate flavour and cause astringency, and methyxanthines are bitter. Along the process, it is producing other cocoa flavours integrated with existing cocoa flavour aromas. It has been called a special cocoa flavour. Special cocoa flavour consisted of nutty flavour, fruity flavour, flowery flavour and spicy flavour.

Microanalysis is a one of powerful techniques that can be used as new tools for cocoa compound analysis.

CONCLUSIONS

Specialty cocoa flavour is unique, complex, and fascinating. There is no single key component that determines the final flavour character. Both non-volatile and volatile chemical components contribute to the special cocoa aroma. Many chemical, biological, and physical factors influence the formation and the development of specialty cocoa flavor. In every single on-odour volatile compound, group, it contains several specialty cocoa beans which can be used for development of new chocolate niches.

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