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Volatile chemical profile of cacao liquid smoke

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Abstract

Liquid smoke is a food additive derived from pyrolysed biomass which conveniently provides a smoked flavor and aroma to marinated food items. A variety of plant sources has been utilized to develop liquid smoke since the properties, such as the odor, are dependent on the source. Recently, liquid smoke derived from discarded cacao pod husks was produced in an effort to utilize this major agricultural waste from cacao farming. In this paper, we report the volatile chemical profile of cacao liquid smoke using gas chromatography mass-spectrometry. Chemical composition analysis of liquid smoke is an integral part of ensuring compliance to regulatory standards, which ultimately leads to consumer safety and protection. The major components of the cacao liquid smoke were found to be the typical biomass pyrolysis products. In addition, functional compounds such as an arenofuran and a pyrazine were observed which may provide antifungal properties to the cacao liquid smoke, in addition to a distinct flavor and aroma. Efforts must be made during processing in order to lessen the presence of the polyaromatic hydrocarbons detected in order to further promote the development of liquid smoke out of the cacao pod husk as value added products from agricultural waste.

Introduction

Liquid smoke is a food additive that imparts a smoked flavor and aroma to meats, poultry, and seafood. The popularity of liquid smoke emanates from the convenience it offers since the tedious task of smoking the food item is no longer necessary in acquiring a smoked taste. This convenience does not sacrifice taste since a recent consumer preference study showed that people could not tell the difference between sausages that were actually smoked and from those marinated in liquid smoke (Martinez and Machado, 2016). Liquid smoke treatment, at some cases can also be viewed as a healthier alternative compared with traditional smoking. This is because the polyaromatic hydrocarbon (PAH) content of liquid smoke treated food item is much lower compared with that of gas smoking (Hattula *et al*., 2001). In addition, liquid smoke can also safeguard meats from food borne pathogens such as *Listeria monocytogenes* (Faith *et al*., 1992), *Escherichia coli* (Estrada-Munoz *et al*., 1998), and *Aeromonas hydrophilia* (Sunen *et al*., 2001), thereby prolonging their storage life.

Liquid smoke is derived through heating (450 – 600^{0}C) wood or similar biomass materials in an oxygen starved environment in a process commonly referred to as pyrolysis (Underwood and Graham, 1989). The smoke produced from the process is collected through condensation, separated and diluted wherein the final fraction represents the liquid smoke. Each type of liquid smoke has a unique aroma and flavor which is dependent from the plant in which the liquid smoke was produced. It is therefore not surprising that liquid smoke preparations utilizing a variety of plants sources have been widely documented. Some of these plant sources include oak (Guillen and Manzanos, 2002), sage (Guillen and Manzanos, 1999), thyme (Guillen and Manzanos, 1999), among others.

In this paper, we report the chemical profile of liquid smoke produced from cacao pods using gas chromatography – mass spectrometry. Chemical composition analysis of liquid smoke is an integral part of ensuring compliance to regulatory standards, which ultimately leads to consumer safety and protection (Simon *et al*., 2005). Moreover, knowledge on the chemical composition of a specific type of liquid smoke will facilitate a deeper understanding on its function and appropriate application (Montazeri *et al*., 2013).

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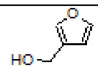
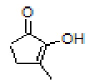
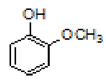
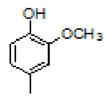
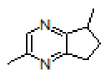
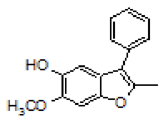
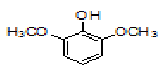
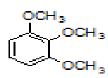
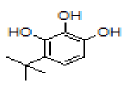
Table 1. The major volatile chemical components of the cacao liquid smoke

Entry	Retention Time (minutes)	Chemical Compound	Structure	% Composition	Molecular Weight
A	5.81	3-furanmethanol		10.81	98.10
B	12.07	2-vinylfuran		11.00	94.11
C	14.33	2-hydroxy-3-methyl-2-cyclopenten-1-one		4.36	112.13
D	17.27	2-methoxyphenol		36.39	124.14
E	23.80	2-methoxy-4-methylphenol		4.96	138.16
F	25.66	2,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine		8.59	148.21
G	32.81	Isoparvifuran		2.18	254.28
H	34.60	2,6-dimethoxyphenol		16.22	154.16
I	40.15	1,2,3-trimethoxybenzene		4.11	168.19
J	44.66	5-tertbutylpyrogallol		1.37	182.22

Materials and Methods

The cacao liquid smoke sample was sourced from the Cocoa Foundation of the Philippines, Incorporated. Three milliliters of cacao liquid smoke was repeatedly extracted with analytical grade dichloromethane (DCM). The DCM extract was then treated with sodium sulfate to yield a clear, yellowish solution after filtration. One microliter of the resulting solution was then subjected to gas chromatography-mass spectrometry (GC-MS) using a Perkin Elmer Clarus 500 Tandem GC-MS. The column used was a 30 m, 0.25 mm ID 5MS WCOT 5% phenylsiloxane. Helium was used as the carrier gas and the initial temperature of the column was set at 50^{0}C for 0.5 minutes, which increased by 2^{0}C per minute until 280^{0}C is reached. The injector and detector temperatures were 250^{0}C and 280^{0}C, respectively. The percent composition of the compounds was based on the peak are of each identified compound.

Results and Discussion

Cacao pods are considered waste products during processing wherein their disposal presents a serious problem for the industry (Ntiamoah and Afrane, 2008), such as source of plant pathogens for succeeding fruiting season. A viable solution to this problem is to create value added products out of cacao pod husk which will not only increase the value of this crop but also lessen the adverse environmental impact that accompanies cacao production and processing. Thus, the utilization of cacao pod husks as biomass sources for creating liquid smoke is a good and sustainable agricultural practice beneficial both to the farmers and the environment. In order to further develop the production of cacao liquid smoke, identifying the chemical profile is necessary. The volatile chemical profile of cacao liquid smoke is presented in Table 1 and the chromatogram of the analysis is shown in Figure 1. The chemical profile

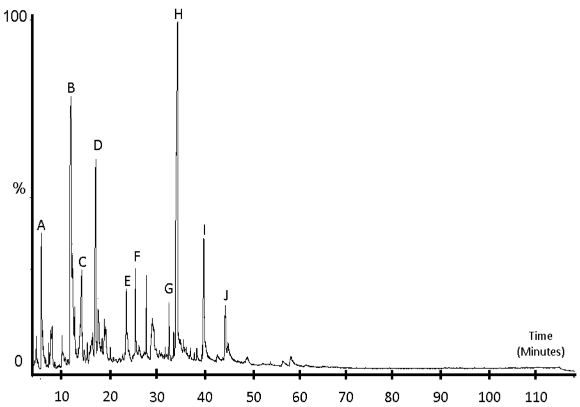


Figure 1. Gas chromatogram of the cacao liquid smoke. The identity and structure of each compound are shown in Table 1.

of cacao liquid smoke exhibits expected compounds, which are common pyrolysis products. On the other hand, several interesting compounds were observed which may provide a distinct character with respect to flavor and aroma to the cacao liquid smoke. The major component of cacao liquid smoke is 2-methoxyphenol or guaiacol. This compound is a common pyroloysis product of lignin, along with the observed 2,6-dimethoxyphenol (syringol) (Bai *et al*., 2014). Guaiacol is responsible for the overall smoky odor (Akakabe *et al*., 2006). The other regular lignin pyrolysis products observed include 1,2,3-trimethoxybenzene (Saiz-Jimenez and De Leeuw, 1985) and 2-methoxy-4-methylphenol (Jiang *et al*., 2010). The compounds 2-hydroxy-3-methyl-2-cyclopenten-1-one (Sipila *et al*., 1998) and 5-tertbutylpyrogallol (Chen *et al*., 2012) are typically present in oil-based by-products of biomass pyrolysis while 3-furanmethanol is observed in cellulose pyrolysis (Nowakowski *et al*., 2007).

Interesting compounds observed from the chemical profile of cacao liquid smoke include 2,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine which is also present in the scent of roasted peanuts (Walradt *et al.*, 1971) and filberts (Kinilin *et al.*, 1972). The occurrence of this compound in cacao liquid smoke may therefore impart a roasted and nutty aroma and flavor to food items marinated with this food additive. The compound 2-vinylfuran is found in various tobacco species (Adam *et al*., 2005) which generally have a floral fragrance. Finally, the compound isoparvifuran is an important natural product that exhibits potent antifungal properties (Muangnoicharoen and Frahm, 1981; Kumar *et al*., 2013).

Conclusion

In conclusion, the volatile chemical profile of cacao liquid smoke was determined. The compounds present were typical pyrolysis products, which were mostly polyaromatic hydrocarbons. Functional compounds such as an arenofuran and a pyrazine were observed which may provide antifungal properties to the cacao liquid smoke, in addition to a distinct flavor and aroma. Efforts must be made during processing in order to lessen the presence of the polyaromatic hydrocarbons detected in order to further promote the development of liquid smoke out of the cacao pod husk.

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