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**VOLATILE COMPOUNDS IN SELECTED
SPICES COMMONLY USED IN
GHANA**

(An FRI Technical Report)

BY

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3	MATERIALS AND METHODS	12
3.1	Materials	12
3.2	Methods	12
3.2.1	Extraction of aroma components	12
3.2.2	GC-MS Analysis	14
4	RESULTS AND DISCUSSION	15
4.1	Volatile compounds identified in seven local Ghanaian spices	15
4.2	Volatile compounds identified in Cloves	16
4.3	Volatile compounds identified in Chili pepper	16
4.4	Volatile compounds identified in Anise seed	17
4.5	Volatile compounds identified in Garlic	17
4.6	Volatile compounds identified in Fennel	18
4.7	Volatile compounds identified in Anise Fruit	18
4.8	Volatile compounds identified in White Pepper	18
6	CONCLUSION	22
6	REFERENCES	23

CONTENTS

ACKNOWLEDGEMENT	I
CONTENTS	II
ABSTRACT	III
1 INTRODUCTION.....	1
2 LITERATURE REVIEW.....	3
2.1 Spice Categories and their functional properties.....	3
2.2 Essential oils of spices.....	4
2.2.1 Nutmeg oil.....	5
2.2.2 Clove oil.....	6
2.2.3 Garlic oil.....	7
2.2.4 Anise seed oil.....	7
2.3 Isolation of aroma compounds.....	8
2.4 Solvent extraction and distillation techniques.....	9
2.4.1 Direct Solvent extraction of aqueous samples.....	9
2.4.2 Steam distillation followed by solvent extraction.....	9
2.4.3 Simultaneous steam distillation/extraction.....	10
2.5 Solid-Phase Microextraction (SPME)	10
3 MATERIALS AND METHODS.....	13
3.1 Materials	13
3.2 Methods	13
3.2.1 Extraction of aroma components	13
3.2.2 GC-MS Analysis.....	14
4 RESULTS AND DISCUSSION	15
4.1 Volatile compounds identified in seven local Ghanaian spices....	15
4.2 Volatile compounds identified in Cloves	15
4.3 Volatile compounds identified in Ethiopia pepper	16
4.4 Volatile compounds identified in Anise seed	17
4.5 Volatile compounds identified in Garlic.....	17
4.6 Volatile compounds identified in Nutmeg.....	18
4.7 Volatile compounds identified in Aidon fruit	18
4.8 Volatile compounds identified in White Pepper.....	19
5 CONCLUSION	22
6 REFERENCES.....	23

ABSTRACT

The volatile compounds in seven spices commonly used in Ghana were investigated by GC-MS using the Likens-Nickerson Simultaneous Distillation-Extraction (SDE) technique. A total of sixty three volatile compounds were found in Ethiopia pepper (*Xylopiya aethiopia*), twenty one in Aidon fruit (*Tetrapleura tetraptera*), forty two in White pepper (*Aframomum melegueta*), fifty five in cloves (*Syzygium sp*), fifty four in nutmeg (*Monodora myristica*), thirty four in Anise seed (*Pimpinella anisum*) and sixteen in garlic (*Allium sativum*). Essential oils were the most common of the volatiles found in these spices and garlic was found to have high amounts of sulphur compounds. Ethiopia pepper contained the highest number of essential oils (63%) while garlic had the least (6.25%). Compounds resulting from the oxidation of hydrocarbons (i.e. alcohols, aldehydes and ketones) as well as derivatives of benzene were also found.

1.0 INTRODUCTION

Spices are substances of plant origin that are commonly used as condiments or other purposes on account of their fragrance. They may be obtained from the bark, fruits, leaves, flowers, rhizomes, roots, seeds, stigmas and styles of the plant.

The ability of this important group of agricultural commodities to contribute to the aroma, flavor, pungency, color and agreeable taste to foods has rendered them virtually indispensable in the culinary art. Due to their potency, it is easy to use these products in small quantities to impart the desired aroma or flavor to the food product.

Various volatile compounds are responsible for the aromatic and pungent properties of spices. These compounds are found in the spices' essential oils and oleoresins. While the characteristic aroma of spices is the direct consequence of the essential oil component, the oleoresin (non-volatile) component is responsible for the typical flavor and taste associated with spices (Pruthi, 1980; Merory, 1960).

As part of their work on the composition of foods commonly used in Ghana, Eyeson and Ankrah (1975) documented the proximate as well as some macro and microelement composition of a few local spices. There is however, no documentation on the aroma profile of spices commonly used in Ghana. The present study was therefore, undertaken to investigate the volatile compounds that may be associated with the characteristic aroma of seven local spices widely used in Ghana, viz: Ethiopia pepper, Anise seed, Nutmeg, Garlic, Cloves, Aidon fruits (dried) and White pepper.

1. Introduction

The specific objectives of the study are:

- ◆ To determine the volatile compounds in the selected spices using the GC-MS and
- ◆ To tentatively document the compounds which contribute to the characteristic aroma of spices according to literature.

Table 1: Spice Groups and their Functional Properties

Organic Name	Examples	Functional Properties
Roots	Cinnamon	Flavor
Stems	Claves	Flavor and Aroma
Bulbs	Garlic, Onions	Flavor and Aroma
Fruits	Almond Fruit, Ashanti Pepper, Cayenne Pepper	Flavor, Aroma, and Color
Seeds	Anise Seed, Nutmeg	Flavor and Aroma
Rhizomes	Ginger and Turmeric	Flavor and Aroma
Herbs	Rosemary, Mint, Thyme	Flavor and Aroma

2.0 LITERATURE REVIEW

2.1 Spice Categories and their Functional Properties

The use of spices date back to ancient times. Archaeological excavations have revealed that prehistoric man used leaves of certain plants to enhance the flavor of half-cooked food (Borget, 1993). When the queen of Sheba visited Jerusalem in Bible times to witness the fame and wisdom of King Solomon, she brought among other things spices in such profusion that there was never an occasion in the king's life that such amount of spices were brought as gifts. Spices come in various types and though they have diverse uses, they are more often used because of their functional properties to enhance the flavor, aroma and sometimes color of the food. Table 1 shows the various grouping of spices and their functional properties of.

Table 1: Spice Groups and their Functional Properties

Group Name	Example	Functional Properties
Barks	Cinnamon	Flavor
Buds	Cloves	Flavor and Aroma
Bulbs	Garlic, Onions	Flavor and Aroma
Fruits	Aidon Fruit, Ashanti Pepper, Cayenne Pepper	Flavor, Aroma and Color
Seeds	Anise Seed, Nutmeg	Flavor and Aroma
Rhizomes	Ginger and Tumeric	Flavor and Aroma
Herbs	Rosemary, Mint, Thyme	Flavor and Aroma

In his work on the useful plants of Ghana, Abbiw (1990) observed that the consumption of a particular spice in an area was mostly influenced by its local availability. White pepper, for example, was cultivated around the Obuasi area in the villages of Sikamang, Mensonso, and then Brofoyedru in Adansi Ashanti while the aidon fruit was commonly used in the forest regions, particularly among the Ashantis. , Other areas of white pepper production were found to be Mim Goaso area in the Brong Ahafo Region and Dunkwa in the central Region, with gross national production of about 600 – 800 bags weighing between 21.6 and 28.2 tonnes (Abbiw, 1990). The role of commerce can, however, not be overruled.

2.2 Essential Oils of Spices

Spices contain cellulose, proteins, lipids, starch and minerals. However, their most significant composition is their essential oil fraction which is not present in all vegetables and which confer on spices their specific characteristic flavour, aroma and smell (Borget, 1993).

Essential oils were regarded as commodities and became significant when distillation was discovered and then it became possible to separate the flavor chemical mixture from the botanical material of the spices (Wright, 1999). They are typically liquids and possess an aromatic fragrance owing to their volatilization upon contact with air (Schery, 1954). Oils extracted from spices are composed chemically of complex organic substances – a mixture of various aromatic hydrocarbons and their oxygenated derivatives. The aromatic

hydrocarbons, belonging to a group of cyclic hydrocarbons with complex structures called terpenes, have the structural formula which are multiples of two, three or four of C_5H_8 (an isoprene group). The monoterpenes have multiples of two, sesquiterpenes have multiples of three and diterpenes have multiples of four (Borget, 1993). In addition to terpenes, they may also contain derivatives of benzene and other straight-chained compounds which sometimes contain sulfur or nitrogen atoms (Schery, 1954). The terpenes have been given names which are generally suggestive of the plant from which they were first found, e.g. Pinene (present in the essential oils of pepper and nutmeg) and limonene (found in the essential oil of cardamom). Due to the presence of a pair of double bonds in its structure, the isoprene group $[CH_2=CH - C(CH_3)=CH_2]$ can bond with itself and polymerize resulting in the presence of a mixture of terpenes in each spice (Borget, 1993).

2.2.1 Nutmeg Oil

The chemistry of nutmeg, particularly that of its essential oils, has been the subject of many investigations over a considerable number of years. Reports of analyses on nutmeg have been published since the early nineteenth century. (Baldry *et al*, 1976). Its major constituents have been found to be monoterpene hydrocarbons with little amounts of oxygenated hydrocarbons and aromatic ethers. The oil, on extraction, is a pale-yellow to almost water-white liquid with a fresh, warm, spicy and aromatic odor possessing a rich, sweet-spicy body note (Purseglove *et al*, 1981). The monoterpene

2. Literature Review

hydrocarbon components include sabinene (light, peppery, herbaceous note), alpha-pinene (light, peppery note), gamma-terpene (light, citrus, herbaceous note) and limonene (weak, light citrus note). Purseglove *et al* (1981) found the following additional monoterpenes: camphene, delta-3-carene, alpha and beta-phellandrene, alpha-thujen, alpha-terpinene and terpinolene. The only oxygenated monoterpene found in the oil by Wright (1999) was 1,8-cineole which possesses a fresh, eucalyptous flavor note. Additional compounds in this category documented by Perseglove *et al* (1981) are camphor, methone, borneol, citronellol, geraniol, linalool cis-2-menth-2-en-ol, cis-piperitol, alpha and beta-terpineol, terpinen-4-ol, cis and tran-sabinene hydrate, bornyl acetate, geranyl acetate, linalyl acetate, menthyl acetate and terpinene acetate. The essential oil component that falls under the aromatic ether category include: safrole (warm, sweet sasafras note) and myristicin (warm, woody balsamic note) according to Wright, 1999. While the monoterpene hydrocarbon fraction has alpha and beta-pinene as well as sabinene as the predominant constituents, myristicin is the major constituents of the aromatic ether fraction.

2.2.2 Clove Oil

Clove oil can be derived from three sources, namely, the buds, leaves and stem. (Schery, 1954). A number of studies on the composition of the clove bud oil were undertaken between the late nineteenth century and early twentieth century in which the identification of 18 components were reported. The major component of the oil is eugenol (Purseglove *et al.*, 1981;

Wright, 1999) although its percentage composition differs with higher values being observed for oil distilled from whole spices in contrast to the comminuted spice. Apart from eugenol which has a strong, warm, clove aroma note, other components of the oil that contribute to the characteristic aroma have been identified as caryophyllene (spicy, woody note), alpha-humulene (woody note), and eugenyl acetate (warm, spicy note) Wright (1999).

2.2.3 Garlic Oil

Garlic, a widely consumed spice, is known mainly for its flavor and odor. In recent times however, many medicinal properties have been attributed to it, including anticarcinogenic, antiatherosclerotic, and antithrombotic properties (Abbiw, 1990; Bonsu, 2002). The oil from garlic derives its aroma characteristics from sulfide compounds. According to Wright (1999), the major volatile compounds that contribute to the characteristic aroma of garlic are diallyl disulfide (strong, garlic note), diallyl trisulfide (strong, heavy, garlic note) and diallyl sulfide (strong, fresh garlic note). Similar findings were made by Calvo *et al*, (2004). They identified forty seven compounds in garlic oil with the most abundant being diallyl disulfide and diallyl trisulfide.

2.2.4 Anise Seed Oil

Anise Seed oil was found to consist mainly of anethole, trans-anethole (strong, sweet anise note) and methyl chavicol (strong, sweet terragon note)

Schery (1954) and Wright (1999).

2.3 Isolation of aroma compounds

Analysis of food aromas using modern techniques such as gas chromatography and mass spectrometry has resulted in the isolation and identification of hundreds of volatile constituents (Meyer, 1960)

In order to be perceived, aroma compounds must leave the food matrix and travel through the air. This characteristic makes them ideal for analysis by gas chromatography, which involves the analysis of compounds that exist in the gaseous phase at typical gas chromatography operating temperatures of between 40 – 300°C (Wampler, 1997). Two most common procedures reported in literature for the isolation of aroma compounds are headspace and distillation/extraction methods (Parliment, 1997). Although it is preferable to take advantage of the volatility of these compounds and rely on techniques of headspace analysis, it is possible, and sometimes most appropriate, to isolate and then concentrate the compounds from the food matrix through solvent extraction and/or distillation.

Schery (1954) emphasized distillation as the most important process for obtaining essential oils from plant products. With the essential oil thus obtained, the GC-MS can be used to investigate their chemical composition and where possible, chemical synthesis of compounds can be affected. According to Parliment (1997) essential oils are best analysed by direct injection of the sample into the GC and in some cases the sample may have

to be diluted with a solvent to obtain a response within the limits of the detector.

2.4 Solvent Extraction and Distillation Techniques

2.4.1 *Direct solvent extraction of aqueous samples*

When relatively large amounts of aqueous samples are available separatory funnels or commercial liquid-liquid extractors may be employed using diethyl ether, diethyl ether/pentane mixtures in order to obtain the extract for analysis. The technique is applied to carbonated beverages, fruit juices and caffeinated beverages (Parliment, 1997). Extraction is followed by concentration of the solvent on a steam bath and drying it over sodium sulphate or magnesium sulphate.

2.4.2 *Steam distillation followed by solvent extraction*

Steam distillation followed by solvent extraction has as its primary advantage, the separation of the volatiles through distillation, from the non-volatiles. It works best for compounds that are slightly volatile and water insoluble (Parliment, 1997). Steam distillation may involve direct, indirect or vacuum steam distillations. Indirect distillation is fast and eliminates scorching of samples. It therefore reduces the decomposition of samples since the samples are not directly heated. However, if sample decomposition remains a problem, steam distillation may be done under vacuum (Parliment, 1997). After condensation, the aroma compounds may be extracted by use of semi-micro extractors e.g. Mixxer apparatus described by Parliment (1986) or by use of a suitable direct solvent method.

2.4.3 Simultaneous Steam Distillation/Extraction

The simultaneous steam distillation/extraction (SDE) apparatus, first described by Likens and Nickerson (1986) is one valuable technique in flavor analysis. The apparatus comprises mainly a sample flask of 500 ml to 5 liter capacity, a pear shaped flask of 10-50 ml capacity and a central extracting U-tube fitted with a condenser. This ensures a simultaneous condensation of the steam distillate and an immiscible organic solvent, continuous recycling of both liquids and transfer of the steam distillable soluble compounds from the aqueous phase to the solvent (Parliment, 1997).

Varigar, *et al* (1997) used this technique to isolate the essential oils of fresh ginger rhizomes gamma irradiated (60 Gy) for sprout inhibition and non-irradiated rhizomes. Compounds present were identified by GC-MS and GLC.

2.5. Solid – Phase Microextraction (SPME)

Solid –phase Microextraction is one of the relatively new techniques used for the rapid, solventless extraction or pre-concentration of volatile and semi – volatile organic compounds (Harmon, 1997). It employs the partitioning of organic components between a bulk aqueous or vapour phase and the thin polymeric films coated onto fused silica fibres in the SPME apparatus. In their studies on the sensitivity of methods for the collection of aroma compounds, Peterson *et al.* (2000) found SPME to be the least sensitive method compared to dynamic headspace with thermal desorption and the Likens – Nickerson distillation extraction, both of which were found to be most sensitive.

The method is, however, advantageous because it requires no solvent, it is independent of the form of matrix (liquids, solids and gases can easily be sampled) and since heating is optional, the formation of artifacts is reduced and in some cases eliminated entirely (Harmon, 1997). Jirovetz *et al*, (2002) investigated the aroma compounds of the essential oils of dried fruits of black pepper (*Piper nigrum*) and black and white Ashanti pepper (*Piper guineense*) from Cameroon using the Solid State Micro Extraction (SPME) to identify the odorous target components responsible for the characteristic aroma of these valuable spices. Using GC-flame ionization detection (GC-FID) and GC-MS, the main compounds and corresponding peak areas of SPME headspace extracts of the above mentioned spices were found to be germacrene D (11.0%), limonene(10.26%), β -pinene (10.02%), α -phellandrene(8.59%), β -caryophyllene(7.29%), α -pinene(6.40%), and cis- β -ocimene. Compounds in SPME extracts of *P. guineense* (black) were identified as .beta-caryophyllene (57.59%), .bea-elemene(5.10%), bicyclogermacrene (5.05%) and .alpha-humulene (4.86%) and finally, those constituting the essential oil of *P. guineense* (white) were .beta-caryophyllene (51.75%), cis- β -ocimene (6.61%), limonene (5.88%), β -pinene (4.56%), linalool (3.97%) and alpha-humulene (3.29%).

The problem with SPME as a method for aroma analysis is the difficulty in obtaining accurate quantitation during extraction. This is because the method is an equilibrium technique and each component behaves differently as the following factors are altered: polarity, volatility, organic/water partition coefficient, volume of the sample or volume of the headspace, the rate of agitation, the pH of the solution and temperature.

Excellent quantitative correlations are, however, usually obtained with the incorporation of an internal standard into the matrix and adhering to specific sampling times (Harmon, 1997).

- Blackberry (*Rubus fruticosus*)
- Apple (*Malus domestica*)
- Orange (*Citrus aurantium*)
- Lemon (*Citrus limon*)
- Dried Apple (*Malus domestica*)
- White grape (*Vitis rotundifolia*)
- Raisin (*Vitis vinifera*)

2.2. Methods

2.2.1. Extraction of volatile components

The volatile components of the spices were extracted using the Likens-
Nikerson steam distillation and extraction technique (Likens and Likens, 1959; Davis, 1982; SDE, Chrompack, Middleburg,
The Netherlands). Two grams of the crushed spice were mixed with 400 ml of
distilled water to give a slurry of 0.5% w/v. One millilitre of internal standard
solution (50 ppm 4-methyl-1-pentanol in water) was added to the slurry in a 1

3.0 MATERIALS AND METHODS

3.1 Materials

Seven local spices were bought from a local retailer in Accra. These were

- ◆ Ethiopia pepper (*Xylopiya aethiopia*)
- ◆ Anise seed (*Pimpinella anisum*)
- ◆ Nutmeg (*Mondora myristica*)
- ◆ Cloves (*Syzygium sp*)
- ◆ Dried Aidon fruit (*Tetrapleura tetraptera*)
- ◆ White pepper (*Aframomum melegueta*)
- ◆ Garlic (*Allium sativum*)

They were thoroughly cleaned to remove dirt and crushed with a laboratory mortar and pestle. Extraction of volatile compounds was conducted immediately or samples were sealed in airtight containers and stored in the refrigerator (4°C) for later extraction and analysis.

3.2 Methods

3.2.1 Extraction of volatile components

The volatile components of the spices were extracted using the Likens-Nickerson simultaneous steam distillation and extraction technique. (Nickerson and Likens, 1966). Using (Micro-SDE, Chrompack, Middelburg, The Netherlands). Two grams of the crushed spice were mixed with 400ml of distilled water to give a slurry of 0.5% (w/v). One millilitre of internal standard solution (50ppm, 4-methyl-1-pentanol in water) was added to the slurry in a 1

3. Materials and Methods

litre Erlenmeyer flask and six millilitre of a pentane and dimethyl ether mixture (1:1) transferred into a 9 ml pear-shaped solvent flask. Both flasks were appropriately connected a micro-scale steam distillation low-density solvent extraction device and the solutions brought to the boil. Extraction of volatiles was carried out for 30 minutes, from the beginning of condensation of vapour on the walls of the condenser. The solvent/water collected in the pear-shaped flask was placed in the freezer to freeze-out the water phase. The solvent extract was poured off, dried over approximately 2g of Na_2SO_4 and concentrated to about 100 mg by gently blowing N_2 gas over the surface. The concentrated extract was analyzed for volatile compounds using the GC-MS.

3.2.2 GC-MS Analysis

Separation and Identification of volatiles in the spice extract was carried out on a Hewlett- Packard G1800A GCD System (GC-MS, Hewlett- Packard, Palo Alto, CA, USA). The instrument was equipped with a Hewlett-Packard DB-WAX column (30m x 0.25 μm i.d; x 0.25mm film thickness). Two microlitre extract were injected (split ratio 1:20) using the temperature program: 10min at 40°C, increased to 240°C at 6°C min^{-1} , and held constant at 240°C for 30 minutes. Identification of volatile compounds was determined in the Total Ion mode scanning a mass to charge ration (m/z) of range between 25 and 550. Further identification was obtained by probability- based matching with mass spectra in the G1033A NIST PBM Library (Hewlett-Packard) containing 75000 reference spectra.

4.0 RESULTS AND DISCUSSIONS

4.1 Volatile compounds identified in seven local Ghanaian spices

Volatile compounds identified in cloves, Ethiopian pepper, Anise seed, garlic, nutmeg, aidon fruit and white pepper are shown in Tables 1 – 7, respectively.

Table 1: Volatile compounds identified in Cloves

Essential Oils	Carbonyls and Alcohols	Esters and Acids	Miscellaneous Aliphatics	Others
Monoterpene	2-heptanone	Ethyl ester hexanoic acid	Cyclohexadecane	Toluene
Hydrocarbons:	(Z) 2-heptenal	Ethyl ester octanoic acid	Tricosane.	Butylated hydroxytoluene
.alpha-Pinene	6-methyl-5-heptene-2-one.	Ethylbenzoate	3, 7-dimethyl-(Z)-1, 3, 6-octatriene.	p-Xylene
.beta-Pinene	2-nonanone	Phenyl methyl ester acetic acid		1, 3-dimethyl benzene
.alpha-Phellandrene	Nonanal	Methyl salicylate		Chlorobenzene
.alpha-Terpinene	2-furancarboxy-aldehydes.	4-allylpheny acetate		Styrene.
.gamma-Terpinene	Benzaldehyde	Methyl linolaidate		5-(1-propenyl)-1, 3-benzodioxole.
Limonene	Acetophenone	Methyl linolate		N, N-bis (2-hydroxy ethyl)-dodecanamide.
Sabinene	(S)-2-heptanol.	Benzyl benzoate		
Terpinolene	3, 7-dimethyl-1, 6-octadien-3-ol.	Dibutyl phthalate		
		Tetradecanoic acid		
Oxygenated				
Monoterpenes:				
Linalyoxide				
Sesquiterpene				
Hydrocarbons:				
.alpha-Cubebene				
Ylangene				
Copaene				
Caryophyllene				
.alpha-Farnesene				
Calamene				
Oxygenated				
Sesquiterpenes:				
d-Nerolidol				
Aromatic Ethers				
Eugenol				
Isoeugenol				
4-(2-propenyl)-phenol				
Miscellaneous				
Essential oils:				
Eucalyptol				
Paracymenyl				
Durene				
Germacrene				
Anethole				

Table 2: Volatile compounds identified in Ethiopia Pepper

Essential Oils	Carbonyls and Alcohols	Esters and Acids	Miscellaneous Aliphatics	Others
Monoterpene	Benzaldehyde	Hexadecanoic acid.	Cyclotetracosane.	Thymol
Hydrocarbons:	isopinocampone	(Z)-, methyl ester-9	1,3,5,7-Cycloocta-	Butylated Hydroxytoluene
(+)-2-Carene	(+)-Nopinone	-octadecanoic acid.	Tetradecane.	o-Isopropenyltoluene
(+)-Carene	Sabina Ketone		7,7-dimethyl-2	p-xylene
.alpha-Phellandrene	Cuminic aldehydes		-methylene-bicyclo	.alpha-dimethyl styrene
.alpha-Pinene	.alpha-Campholenal.		[2.2.1] heptane.	Methyl-(methylene)-benzene
.alpha-Terpinene	4-(1-methylethenyl)			
.alpha-Terpinolene	-1cyclohexene-1			
.beta-Limonene	-carboxyaldehyde.			
.beta-Pinene	Hexanal			
.beta-Thujen	Fenchyl alcohol			
.delta-Cadinene	Cuminol			
.gamma-Terpinene	(-)-Spatulenol			
Camphene				
p-Cymene				
Sabinene				
Thujen				
Oxygenated				
monoterpenes:				
.alpha-Terpineol				
Camphor				
Cis-linaloxide				
L-4-Terpineol				
Linalyoxide				
Trans-Carveol				
Sesquiterpene				
Hydrocarbons:				
.alpha- Elemene				
.alpha-Cubebene				
.alpha-Gurjenene				
.beta-Cubebene				
.delta-Elemene				
.delta-selinene				
calamene				
Caryophyllene				
Copaene				
Ylangene				
Oxygenated				
Sesquiterpenes:				
Caryophyllene oxide				
Aromatic Ethers:				
Carvacrol				
Eugenol				
Isoeugenol				
Miscellaneous				
Essential Oils:				
Cyrene				
Dehydro-p-cymene				
D-verbenone				
Eucalyptol				
Germacrene B				
Germacrene D				
Thujone				

4. Results and Discussion

Table 3: Volatile compounds identified in Anise Seed

Essential Oils	Carbonyls and Alcohols	Esters and Acids	Miscellaneous Aliphatics	Others
Monoterpene Hydrocarbons: .alpha-Terpinene D-limonene Limonene	Nonanal Benzaldehyde Trans-2-heptenal p-methoxypropionphenone. 4-methoxy-benzaldehyde. 1-(4-methoxyphenyl) -2-propanone. 1-octanol (-)-spathulenol	Hexadecanoic acid Butyl methyl ester-1,2 -benzenecarboxylic acid. 3,5-dimethoxy-methyl ester benzoic acid.	1-Decene Cyclodecane (-)-9-Tricosene	p-Xylene Chlorbenzene
Oxygenated Monoterpenes: Linalool				
Aromatic Monoterpenes: p-cymene				
sesquiterpene hydrocarbons: .beta-Cubebene caryophyllene Copaene Ylangene				
Aromatic ethers: 2,6-bis (1,1-dimethyl ethyl)-Phenol Eugenol				
Miscellaneous Essential Oils: .alpha-bisabolol .alpha-Himachalene .alpha-Longipinene .beta-Himachalene Anethole Apiol Zingiberene				

Table 4: Volatile compounds identified in Garlic

Sulphur Compounds	Essential Oils	Carbonyls & Alcohols	Acids & Esters	Miscellaneous Aliphatics	Others
Allyl methyl sulfide Dimethyl -Disulfide Dimethyl-Trisulfide Allyl Sulfide	Aromatic ether: 2,6- bis (1,1-dimethylethyl) -Phenol	Methional Ethanol	Elaol Hexadecanoic acid	1-Octadecene Heneicosene Heptadecane (E)-3-Eicosene. 2,6,10,15-tetra-methyl-heptadecane.	p-Xylene Chlorbenzene

Table 5: Volatile compounds identified in Nutmeg

Essential Oils	Carbonyls and Alcohols	Esters and Acids	Miscellaneous Aliphatics	Others
Monoterpene	Trans-2-heptenal.	Eicosyl ester oleic acid	8-Heptadecene	p-xylene
Hydrocarbons:	Cyclohexanone.	L-Bornylacetate	2-methyl-5-(1-methyl ethyl)-bicyclo [3.1.1] hex-2-ene.	2-ethyl-aniline
(+)-2-carene	2-methyl-5-(1-methyl ethyl)-(S)-cyclohexanone.	Linyl propanoate	6, 6-dimethyl-2-methylene, 1(S)-bicyclo [3.1.0] hexane.	2-ethyl-6-methyl benzenamine
1, 3, 6-p-menthatriene	4-(1-methylethyl) - benzaldehyde..	Dicarboxylic acid		Butylated Hydroxytoluene
3-carene	4-methoxy-Benzaldehyde.	Hexadecanoic acid		
Camphene	6,6-dimethyl-bicyclo [3.1.1] hept-2-ene-carboxaldehyde.	Octadecanoic acid		
E.beta-ocimene	Cuminol	Oleic acid		
Sabinene	3,7-dimethyl-1,6-octadien-3-ol.	Linoleic acid		
		Cuminic acid		
Oxygenated		9,12-octadecadienoic acid (Z, Z).		
Monoterpenes:		Methyl ester-12-octadecenoic acid.		
.alpha-cardinol		Butyl-2-methylpropyl ester-1, 2-benzene.		
Carvacrol				
Sesquiterpene				
Hydrocarbons:				
.alpha-caryophyllene				
.alpha-cubebene				
.beta-cubenene				
caryophyllene				
Copaene				
Aromatic ethers				
Eugenol				
Myristicin				
2, 4-bis (1, 1-dimethyl) -Phenol				
Miscellaneous				
Essential Oils:				
.alpha-Phellandrene-epoxide				
.alpha-santelene				
Allocimene				
Anethole				
Cis-linaloxide				
Eucalyptol				
Germacrene D				
Para-cymenyl				
Perillene				
Spathulenol				

Table 6: Volatile compounds identified in Aidon Fruit

Essential Oils	Carbonyls and Alcohols	Esters and Acids	Miscellaneous Aliphatics	Others
Aromatic Ethers:	Tetradecanal	Hexadecanoic acid	1-Decene	m-Xylene
Eugenol	1-Octanol		Docosene	Chlorobenzene
	1-Hexadecanol		(E)-9-Eicosene	Naphthalene
			(Z)-13-Octadecenyl	Butylated Hydroxytoluene
			1-Pentadecene	5-ethyl-2-methylthiazole
			Tricosane	
			Tetracosane	
			Docosane	
			Hexadecane.	
			6-Propenyl-tridecane	
			2,6,10,15-tetramethyl-heptadecane.	

4. Results and Discussion

Table 7: Volatile compounds identified in White Pepper

Essential Oils	Carbonyls and Alcohols	Esters and Acids	Miscellaneous Aliphatics	Others
Monoterpene Hydrocarbons: .alpha-Pinene .beta-Pinene sabinene D-limonene	Heptanone. Hexanal. Octadecenal. 2-Heptanone. 2-Nonanone. 1-Octanol. 2-Heptanol.	Octyl ester acetic acid Hexadecanoic acid	7-Hexadecene- (Z). Hexadecane. Docosane. 3-Hexadecene-(Z). Pentadecane. 2-Methyl tricosane. 12,16-dihydroxy-4, 7,14,20-tetraoxa-1, 10-diaza bicyclo [8.7.5]-docosane.	p-Xylene Chlorobenzene Bulnesol Butylated Hydroxytoluene
Oxygenated Monoterpenes: Linalool oxide	3,7-dimethyl-1,6- octadien-3-ol.			
Sesquiterpene Hydrocarbons: .alpha-cubebene .beta-cubebene Elemene Caryophyllene Copaene alpha-Gurjunene Ylangene				
Oxygenated Sesquiterpenes: Caryophyllene oxide Nerolidol				
Aromatic Ethers: Eugenol Myristicin 2, 4-bis (1, 1-dimethyl- ethyl)-Phenol				
Miscellaneous Essential Oils: Guaiol .alpha-Bisabolol .alpha-Bergamotene .alpha-Fenchene				

Volatile compounds found in the seven spices investigated included essential oils (monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpenes and aromatic ethers), aromatic compounds, carbonyls, acids and esters, alcohols, miscellaneous aliphatic hydrocarbons and sulphur-containing compounds. None of the essential oils stated above were found in garlic. The characteristic aroma of garlic is reported to be the result of the breakdown of alliin by alliinase and its conversion to alliin. The unstable alliin molecule is rapidly converted into a series of other odorous

sulphur-containing molecules (Freeman and Koderá, 1995). Calvino *et al* (2004) also found a lot of sulphur compounds in garlic oil. Out of the 47 compounds identified in their study, 18 were linear sulphur-containing compounds, 6 were of non-linear, and 23 were cyclic compounds. The most abundant volatile components they found were diallyl disulfide and diallyl trisulfide.

A total of 58 volatile compounds were found in the clove oil in the present study. Some of the monoterpenes and sesquiterpenes found in this investigation were also identified in earlier work by Deyama and Horiguchi (1971) and Walter (1972). They include Ylangene, Caryophyllene and β -Pinene. Caryophyllene occurs in many essential oils and especially in clove oil (Merck Index, 1989). It has a terpene odor about midway between the odour of cloves and turpentine and is mostly used in perfumery (Merck Index, 1989). β -Pinene is found in oils that contain α -pinene and has a characteristic odour of turpentine (Merck Index, 1989).

In the present study nutmeg was found to contain 50 volatile compounds. They included sabinene and 3-carene, which have also been previously reported by Sandford and Heinz (1971). Camphene another terpene found in this study was also reported in nutmeg by Dann *et al* (1997) and Baldry *et al* (1976). Camphene volatilizes on exposure to air and has an insipid odour (Merck Index, 1989). Eugenol, the only aromatic ether identified in this was also found in studies by Sandford and Heinz (1971). It has the odour of cloves with a spicy, pungent taste and may be used as an insect attractant as well as a source for the production of vanillin (Merck Index, 1989). The sesquiterpenoids capaene and caryophyllene in nutmeg oil found in this study were also found by Sammy and Nawar (1968) and Baldry *et al* (1976).

Dried Aidon fruit contained several aliphatic hydrocarbons and no esters. The only essential oil found in Aidon fruit was eugenol. Ethiopia pepper was found to have the highest number of volatile compounds (65) with over 63% of them being essential oil components including .alpha-Pinene, camphor, ylangene, eugenol and cayrophyllene oxide. Anise seed had 35 volatile compounds while white pepper had 43. Both had a high number of essential oil volatiles components.

Compounds resulting from the oxidation of hydrocarbons were found in all the spices. These are: ketones, aldehydes and esters. Aidon fruit and garlic had relatively few numbers of these oxidation products with no ester present in the former. Derivatives of benzene were also present. These include p-Xylene (and its isomer m-Xylene), Chlorobenzene and Styrene. These benzene derivatives are aromatic in nature. Chorobenzene, for instance, is a colourless and very refractive liquid with a faint, not unpleasant odour; and then Styrene has a penetrating odour; being an oily liquid in nature with its colour falling between colourless to yellow. (Mercks Index, 1989). These compounds of oxidation of hydrocarbons and derivatives of benzene found in the spices may contribute to the aroma and flavour of these spices as well as their delicate nuances.

5.0 CONCLUSION

The volatile compounds found in the seven commonly used spices in Ghana were found to comprise a complex mixture of aromatic hydrocarbons and their oxygenated derivatives, short- and medium -chained hydrocarbons, some sulphur – containing compounds and several essential oils. The results of this study have tentatively identified and documented for the first time volatile compounds that are found in selected spices on the Ghanaian retail market. These documented volatile profiles would help to detect the presence of contaminants or adulterations of these spices. It is recommended however, that further studies including Gas Chromatography Olfactometric analysis (GC-sniffing) be conducted to identify the specific compounds that have an aroma impact on the spices. In order to further authenticate the aroma profiles of the spices, measures have to be taken to obtain samples from their original sources before extraction and analysis.

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