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Aroma chemical composition of *Piper guineense* Schumach. & Thonn. From Lagos, Nigeria: a new chemotype

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ABSTRACT

The essential oil from the bruit (berries) of *Piper guineense* (Piperaceae) from Lagos, Nigeria, was isolated by hydrodistillation and analyzed by gas chromatography – mass spectrometry (GC-MS). A total of 64 compounds were identified in the fruit oil accounting for 99.0% of the composition. The oil was dominated by linalool (52.2%), defining a new chemotype for this plant species. A numerical cluster analysis has revealed, in addition to the linalool chemotype, at least five other chemotypes of *Piper guineense*.

Keywords: Piper Guineense, Essential Oil Composition, Linalool, Chemotype, Cluster Analysis.

1. Introduction

The genus *Piper* is made up of about 1050 species of tropical shrubs, lianas, and small trees, many of which are important as spices and flavoring agents and medicines [1]. Economically important members include *P. nigrum* (black pepper) [2], *P. betle* (betel) [3], *P. methysticum* (kava) [4], and *P. longum* (long pepper) [5]. The essential oils of numerous *Piper* species have been analyzed and examined for biological activity (see, for example: [6-10]).

Piper guineense Shumach. & Thonn. (Ashanti pepper) is an erect herbaceous climbing liana native to tropical Africa, ranging from Guinea to Kenya and south to Zambia [11]. The fruits (berries) of the plant are commonly known in English-speaking countries as "West African black pepper", "*iyeree*" in Yoruba, and "*poivrie*" in French. The fruits are usually sold in Nigerian markets as an edible medicinal plant or additive in foods to offer aroma and flavor [12]. Medicinally, *P. guineense* fruits have been used externally as a counter-irritant or in a stimulating ointment, internally as a stomachic and carminative; the leaves have been used to treat wounds; the stems and twigs used to treat coughs and bronchitis [13, 14]. The essential oils of *P. guineense* from Cameroon [15-17] and from Nigeria [12, 18, 19] have been previously examined, and several chemotypes are apparent. In this work, we present an analysis of the fruit essential oil of *P. guineense* collected from Lagos, southwestern Nigeria.

2. Materials and Methods

2.1 Plant Material

Dried fruits (berries) *Piper guineense* were purchased in March, 2013, from a local market at Ijanikin in Lagos State, Nigeria, and authenticated at the Botany Department, University of Lagos. A sample (350 g) *of P. guineense were* reduced to powder and subjected to hydrodistillation in a Clevenger-type apparatus for 3 h. The yield of oil was 1.34% on a dry weight basis. The oil was dried over anhydrous sodium sulfate and stored in a sealed vial under refrigeration prior to analysis.

2.2 Gas Chromatographic – Mass Spectral Analysis

The volatile oil of *P. guineense* was analyzed by GC-MS using an Agilent model 6890 gas chromatograph with a HP-5ms column and an Agilent 5973 mass selective detector as described previously [20]. Identification of the constituents of the volatile oil was achieved based on their retention data (retention indices) determined with reference to a homologous series of *n*-alkanes and by comparison of their mass spectral fragmentation patterns with those reported in the literature [21] and stored on the MS library [NIST database (G1036A, revision D.01.00) / ChemStation data system (G1701CA, version C.00.01.08)].

2.3 Numerical Cluster Analysis

Ten *Piper guineense* samples were treated as operational taxonomic units (OTUs). The percentage composition of the 33 major essential oil components (α-pinene, sabinene, β-pinene, myrcene, α-phellandrene, δ-3-carene, limonene, (*Z*)-β-ocimene, linalool, safrole, α-cubebene, α-copaene, β-elemene, α-gurjunene, β-caryophyllene, α-humulene, (*E*)-β-farnesene, germacrene D, β-selinene, asaricin, α-zingiberene, (*E*, *E*)-α-farnesene, β-bisabolene, bicyclogermacrene, δ-cadinene, calamenene, *trans*-cadina-1,4-diene, elemol, (*E*)-nerolidol, caryophyllene oxide, guaiol, α-cadinol, and α-bisabolol) was used to determine the chemical relationship between the different *P. guineense* essential oil samples by cluster analysis using the NTSYSpc software, version 2.2 [22]. Correlation was selected as a measure of similarity, and the unweighted pairgroup method with arithmetic average (UPGMA) was used for cluster definition.

3. Results and Discussion

The *P. guineense* fruit essential oil was a pale yellow liquid with the characteristic pungent and aromatic odor of *Piper* plants. The oil content, based on dried fruits was 1.34% (w/w). GC-MS analysis of the fruit essential oil of *P. guineense* (Table 1) revealed 64 identifiable components comprising 99.0% of the composition. The oil was composed largely of the monoterpenoid alcohol linalool, representing 52.2% of the oil. The composition of P. guineense fruit oil from this study is remarkably different from those reported earlier from Cameroon [15-17] or from Nigeria [12, 18, 19], and represents a new chemotype.

A cluster analysis (Figure 1) of the essential oil compositions of *P. guineense* fruits reveals at least six different chemotypes: (1) a linalool-rich chemotype from Nigeria, represented by this present work, (2) an asaricin-rich chemotype from Nigeria [18], (3) a β-caryophyllene/germacrene-D chemotype from Nigeria [12], an α/β-pinene-rich chemotype from Cameroon [15] and from Nigeria [19], a β-caryophyllene/limonene/pinene chemotype from Cameroon [17], and a β-caryophyllene-rich chemotype from Cameroon [16].

The chemical variability in *P. guineense* is particularly important in light of its use both as a flavoring agent and a medicinal agent; the flavor profile and medicinal efficacy is expected to vary widely depending on the chemotype utilized. Linalool is a well-known fragrance and flavoring agent with very limited toxicity [23, 24]. It is a major component of the oils of lavender [25], basil [26], and coriander [27], and is an important constituent of floral fragrance and floral pollination biology [28, 29]. Linalool has been shown to impart a soothing, comforting effect on humans as well as anxiolytic effects in laboratory animals [30], but is largely devoid of antimicrobial or cytotoxic activities [31].

Table 1: Chemical composition of *Piper guineense* fruit essential oil.

RI	Compound	%		RI	Compound	%
935	α-Thujene	tr		1420	(*E*)-Caryophyllene	2.0
941	α-Pinene	1.6		1453	α-Humulene	1.0
953	Camphene	tr		1457	(*E*)-β-Farnesene	0.6
976	Sabinene	0.1		1461	Alloaromadendrene	0.3
980	β-Pinene	3.8		1473	*trans*-Cadina-1(6),4-diene	0.1
992	Myrcene	0.2		1477	γ-Muurolene	0.2
1004	α-Phellandrene	0.2		1481	Germacrene D	1.4
1009	δ-3-Carene	0.3		1486	β-Selinene	0.9
1016	α-Terpinene	tr		1491	*trans*-Muurola-4(15),5-diene	0.1
1024	*p*-Cymene	0.7		1495	*epi*-Cubebol	1.3
1029	Limonene	2.2		1500	α-Muurolene	0.2
1030	1,8-Cineole	tr		1505	Germacrene A	0.4
1038	(*Z*)-β-Ocimene	0.6		1511	β-Bisabolene	2.1
1048	(*E*)-β-Ocimene	0.2		1517	Cubebol	0.8
1057	γ-Terpinene	0.1		1524	δ-Cadinene	2.1
1087	Terpinolene	0.1		1531	*trans*-Cadina-1,4-diene	0.2
1102	Linalool	52.2		1542	α-Calacorene	0.3
1149	Camphor	0.8		1550	Elemol	0.6
1159	Isoborneol	0.2		1555	Germacrene B	0.7
1165	Pinocarvone	0.1		1559	Elemicin	0.5
1168	Borneol	0.2		1565	(*E*)-Nerolidol	2.4
1175	*cis*-Pinocamphone	0.1		1581	Spathulenol	1.2
1180	Terpinen-4-ol	0.8		1585	Caryophyllene oxide	1.8

1193	α-Terpineol	1.4		1600	Guaiol	1.6
1251	Piperitone	0.3		1609	Humulene epoxide II	0.8
1254	Geraniol	0.3		1617	Junenol	0.3
1349	α-Cubebene	0.1		1625	Dill apiole	2.1
1376	α-Copaene	0.7		1642	Cubenol	0.2
1389	β-Cubebene	0.1		1646	α-Muurolol (= Torreyol)	0.4
1391	β-Elemene	0.7		1655	α-Cadinol	1.5
1406	Methyl eugenol	0.6		1666	Bulnesol	0.3
1408	α-Gurjunene	0.2		1686	*epi*-α-Bisabolol	1.7
					Total Identified	99.0

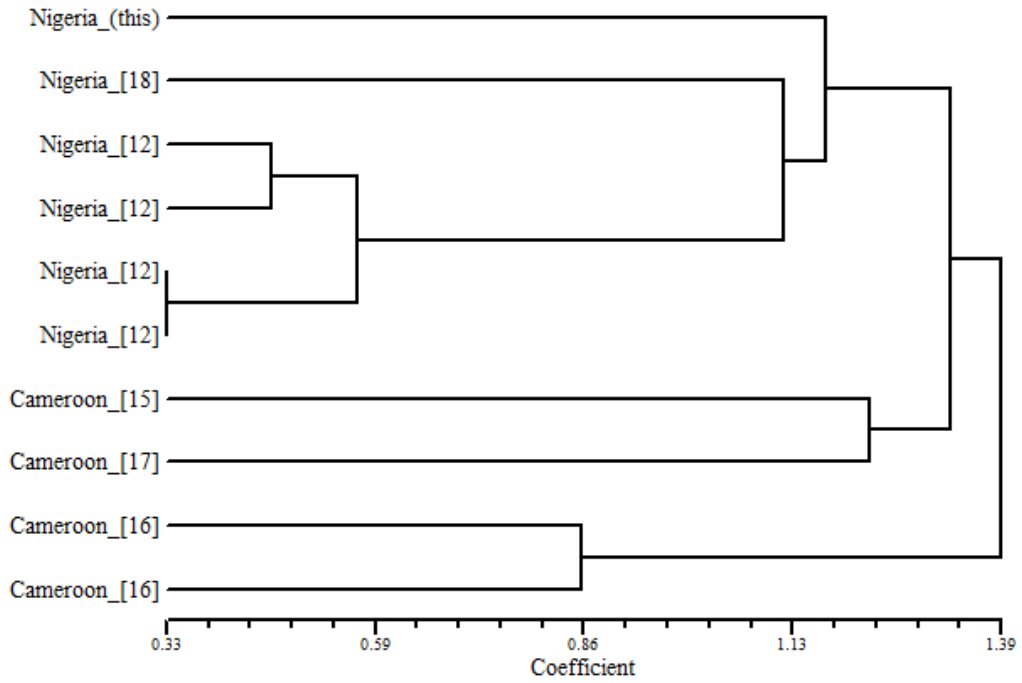

Fig 1: Dendrogram obtained by cluster analysis of the percentage composition of essential oils from *Piper guineense* samples, based on correlation and using the unweighted pair-group method with arithmetic average (UPGMA).

4. Conclusions

GC-MS analysis of *Piper guineense* fruit essential oil from Lagos, Nigeria, is dominated by linalool, and represents a new chemotype of this plant. A cluster analysis shows five other distinct chemotypes.

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