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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 |

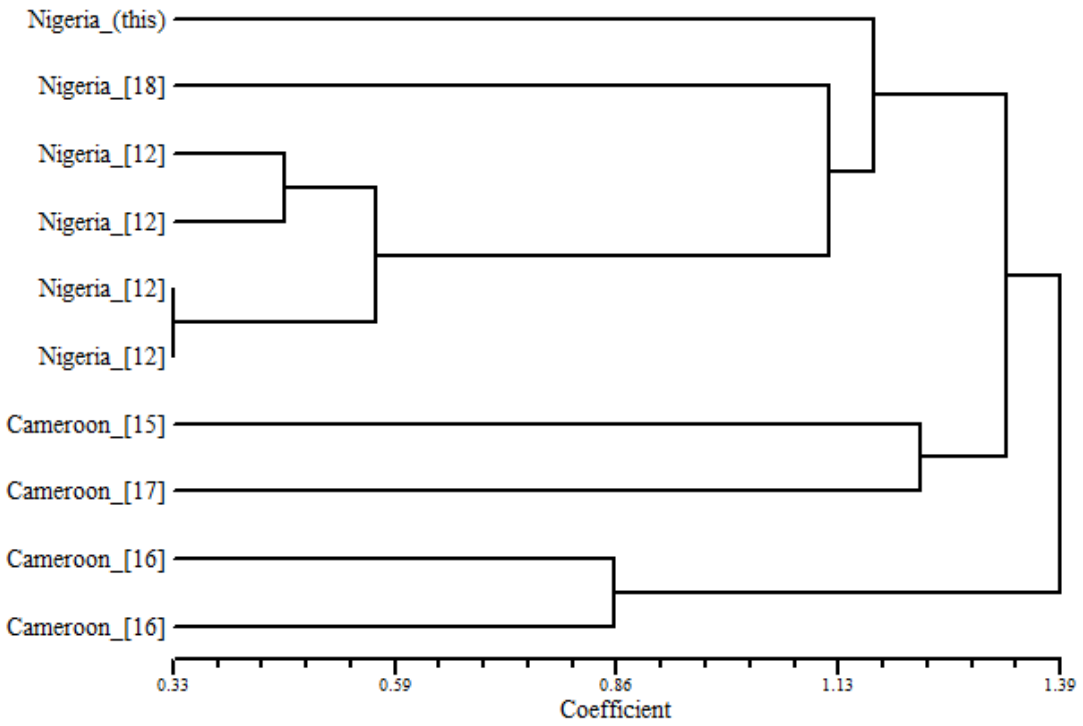


**Fig 1:** Dendrogram obtained by cluster analysis of the percentage composition of essential oils from *Piper guineense* samples, based on correlation and using the unweighted pair-group method with arithmetic average (UPGMA).

## 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.

## 5. Acknowledgments

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