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The composition of the essential oil of dried Nigerian ginger (*Zingiber officinale* Roscoe)

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Abstract The essential oil composition of dried Nigerian ginger (*Zingiber officinale* Roscoe) was determined by means of gas chromatography and gas chromatography-mass spectrometry techniques. The ginger was hydrodistilled; the oil yield was 2.4% and consisted of 64.4% sesquiterpene hydrocarbons, 6.6% carbonyl compounds, 5.6% alcohols, 2.4% monoterpene hydrocarbons and 1.6% esters. The main compounds were zingiberene (29.5%) and sesquiphellandrene (18.4%). A number of constituents not previously reported in ginger oil were identified. These include 2,6-dimethyl hepten-1-ol, α -gurjunene, linalool oxide, isovaler-aldehyde, 2-pentanone, cadinol, α - and γ -calacorene, eremophyllene, *t*-muurolol, α -himachallene, α -cubebene acetic acid, pinanol, α -santalene, geranyl propionate, geranoic acid, (*E,E*)- α -farnesene, *n*-methyl pyrrole and geranic acid.

Key words Essential oil · Nigerian ginger · Zingiberene · Sesquiphellandrene · Gas chromatography-mass spectrometry

Introduction

Ginger, one of the most important spices in the world, is known for its medicinal and flavoring potentials. The medicinal properties are attributed to its spicy, pungent constituents, mainly gingerols, which stimulate the ther-

moregulatory receptors [1]. This stimulation influences stomach and bile secretions by reflex action [2]. The volatile components give ginger its peculiar aromatic smell. Wide application of the oil in the food and cosmetics industries and the existence of many varieties has led to many studies of the oil. Although the variety and the age of the rhizome at harvest and distillation affect the yield and composition of the essential oil and hence its flavor, the major factor that determines its value in the international market is its origin [3].

Lawrence [4], using a combination of separation techniques, identified a total of 115 isolates, of which 72 were identified for the first time and 4 years later Van Beek et al. [5] identified 11 new components of ginger oil. The significance of this is that there may still be some constituents of the oil which have not have been identified. West African gingers, known for their stronger, more pungent and coarser flavors [3], of which Nigerian ginger is one, are the least studied of the varieties. The only report on Nigerian ginger was one published by Connell and Jordon [6].

In view of the applications of ginger oil in the medicine and food industries and the compositional differences due to origin, there is the need for better understanding of the composition of West African ginger which is the least studied so far. We present a more detailed report on the composition of Nigerian ginger oil and compare the results with oils previously reported on from other areas.

Materials and methods

Freshly harvested ginger rhizomes, from the Institute for Agricultural Research horticulture farm Zaria, were sliced into two halves and sun-dried for 29 h. The dried rhizomes with residual moisture of 9.5% were ground into powder and hydrodistilled according to AOAC [7] using the Clevenger apparatus. The distilled water was extracted with 10 ml of pentane twice and the pentane was evaporated in vacuo under reduced pressure. The hydrodistilled oil and pentane extract were pooled and used for the gas chromatography (GC) and GC-mass spectrometry (MS) analysis.

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QL-Gas chromatography. A chromatograph (Hitachi GC 663-30) fitted with a Flame Ionization Detector (FID) at 250 °C and a Fused Silica (FS) bonded Polyethylene Glycol (PEG) 20M column (50 m × 0.2 mm i.d) with 0.3 μm film thickness was used. Helium was the carrier gas and the column temperature was programmed for 80 °C held for 3 min followed by a 3 °C/min increase to a final temperature of 240 °C. The injection temperature was 250 °C.

Gas chromatography-mass spectrometry. For the combined GC-MS, a Hitachi GC-MS MB-80B was used. The gas chromatograph using the FFS bonded PEG 20M column was programmed to increase the temperature from 70 °C to 210 °C at a rate of 3 °C/min with the mass spectrometer operating at 70 eV and an ion source temperature of 180 °C.

Identification. The constituents of the volatile oil were identified by comparing their GC retention times with those of other essential oils of known composition. Confirmation was obtained by comparing the MS fragmentation pattern of each component with those of the authentic compounds.

Results and discussion

After 6 h of hydrodistillation, the essential oil yield was 2.4% and the yield from pentane extraction was 0.12%, giving a total of 2.52%. The GC analysis showed that the oil was composed of many compounds and a total of 266 peaks were resolved. However, only 89 constituents were identified and confirmed by comparing their retention times, similarity indices and mass spectra with those of reference samples and data. The identified constituents, their percentage compositions, and methods of identification are shown in Tables 1 and 2. Compounds constituting less than 0.01% of the oil are regarded as trace. The concentrations of compounds that were identified by their mass spectra alone are not shown.

The oil was rich in sesquiterpene hydrocarbons (Table 1) which constituted about 64.4% of the total oil. This result is in agreement with the report of Connell and Jordan [6], who noted that sesquiterpenes are the main constituents of West African ginger. Zingiberene, reported earlier as the major constituent of ginger oil from Nigeria [6], Australia [6, 8], and India [4, 9], was found to be the major constituent in the present study. Arcurcumene was not detected in the present study, contrary to earlier studies. Instead, a higher concentration of β -sesquiphellandrene (18.42%) was recorded. Sesquiphellandrene was noted by Smith and Robinson [10] to undergo rearrangement to arcurcumene, although it had earlier been suggested that arcurcumene may not be an original component of ginger but formed during storage. Onyenekwe and Ogbadu [11] observed that gamma radiation of ginger prevents this rearrangement of sesquiphellandrene to arcurcumene for up to 1 month of storage. Two other constituents, reported in the work of Connell and Jordan [6] on Nigerian ginger, neral and geranial (Table 2) were found to be above the ranges given by them (trace-2% and trace-3% respectively). Excepting 2,6-dimethyl hepten-1-ol, linalool oxide, isovaleraldehyde, 2-pentanone, cadinol, *t*-muu-

Table 1 Hydrocarbons identified in the volatile oil of ginger. Compounds identified only by MS had no concentration values

S/No	Compounds	Concentration (%)	Method of identification
Aromatic			
1.	Toluene	0.03	GC-MS
2.	ρ -Cymene	0.03	GC-MS
Monoterpenes			
1.	α -Pinene	0.21	GC-MS
2.	Camphene	0.61	GC-MS
3.	β -Pinene	0.61	GC-MS
4.	Myrene	0.11	GC-MS
5.	α -Phellandrene	0.03	GC-MS
6.	δ -Terpinene	0.01	GC-MS
7.	Terpinolene	0.09	GC-MS
8.	Sabinene	Trace	GC-MS
9.	Limonene	0.34	GC-MS
10.	β -Phellandrene	0.95	GC-MS
Sesquiterpenes			
1.	α -Ylangene	0.55	GC-MS
2.	Camphor	0.06	GC-MS
3.	α -Gurjumene	0.01 ^a	GC-MS
4.	Bergameten	0.23	GC-MS
5.	δ -Elemene	0.01	GC-MS
6.	α -Calacorene	trace	GC-MS
7.	γ -Calalorene	trace	GC-MS
8.	β -Elemene	1.14	GC-MS
9.	Eremophyllene	0.09 ^a	GC-MS
10.	β -Caryophyllene	0.35	GC-MS
11.	γ -Elemene	0.12	GC-MS
12.	(<i>E</i>)-farnesene	0.73	GC-MS
13.	α -Humulene	0.22	GC-MS
14.	Germacrene D	3.58	GC-MS
15.	Zingiberene	29.54	GC-MS
16.	Farnesene	6.46	GC-MS
17.	β -Sesquiphellandrene	18.42	GC-MS
18.	α -Himachallene	^a	GC-MS
19.	α -Cubebene	0.11 ^a	MS
20.	α -Copaene		MS
21.	<i>t</i> -Muuroleone	^a	MS
22.	Vetivinen	0.57	GC-MS
23.	Allaromadendrene	Trace	GC-MS
24.	Perillene	^a	MS
25.	Santalene	Trace	GC-MS
26.	(<i>Z</i>)- β -Farnesene	^a	MS
27.	(<i>E,E</i>)- α -Farnesene	1.92	GC-MS
28.	β -Selinene	0.16	GC-MS
29.	Calamenene		

^a Newly identified compounds

rolol, acetic acid, pinanol, geranyl propionate, geranoic acid, *n*-methyl pyrrole and geranic acid (Table 2) and α -gurjunene, α - and γ -calacorene, eremophyllene, α -himachallene, α -cubebene, α -santalene, and (*E,E*)- α -farnesene (Table 1), all components had been identified in earlier works on ginger oils. α -Santalene was reported as a constituent of carrot oil, whereas linalool oxide, α -gurjunene, cadinol, and α -cubebene were identified as components of *Piper guineense* [12].

The significance of the constituents to the aromatic properties has been a subject of debate. Using a test panel, Bednarczyk and Krammer [13] attributed ginger

Table 2 Oxygenated constituents of the volatile oil of ginger. Compounds identified by MS only had no concentration values

S/No	Compounds	Concentration (%)	Method of identification
Alcohols			
Aliphatics			
1.	<i>n</i> -Heptanol-2-ol	0.02	GC-MS
2.	2,6-Dimethylhepten-1-ol	0.01 ^a	GC-MS
3.	2-Ethyl hexanol	^a	MS
Monoterpenes			
1.	Linalool	0.40	GC-MS
2.	α -Terpineol	0.61	GC-MS
3.	Borneol	1.27	GC-MS
4.	Geraniol	0.77	GC-MS
5.	Limonen-10-ol	0.02	GC-MS
6.	Citronellol	0.60	GC-MS
Sesquiterpenes			
1.	Cadinol		
2.	Nerolidol	0.54	GC-MS
3.	Elemol	0.36	GC-MS
4.	α -Eudesmol	0.11	GC-MS
5.	Eudesmol	0.36	GC-MS
6.	β -Sesquiphellandrol	0.34	GC-MS
7.	<i>t</i> -Muurolol	0.14	GC-MS
8.	Pinanol	^a	MS
9.	α -Bisabolol	^a	MS
Phenols			
1.	<i>trans</i> -Isoeugenol	0.60	GC-MS
2.	α -Eugenol	Trace	GC-MS
Aldehydes			
Aliphatics			
1.	Hexanal	0.02	GC-MS
2.	<i>trans</i> -2-Octanal	Trace	GC-MS
3.	<i>n</i> -Butylaldehyde	Trace	GC-MS
4.	Isovaleraldehyde	^a	MS
5.	2-Methyl butanal	^a	MS
Monoterpenes			
1.	Citronellal	0.14	GC-MS
2.	Neral	2.50	GC-MS
3.	Geranial	3.46	GC-MS
Ketones			
Aliphatics			
1.	2-Methyl-2-hepten-6-one	0.09	GC-MS
2.	Methyl- <i>n</i> -heptylketone	0.03 ^a	GC-MS
3.	Acetone	0.02	GC-MS
4.	2-Pentanone	^a	MS
5.	Methyl nonyl ketone	0.23	GC-MS
6.	Methyl- <i>n</i> -undecylketone	0.09	GC-MS
Monoterpenes			
1.	Geranylacetone	^a	MS
Sesquiterpene			
1.	Ionone		MS
Acids			
Aliphatics			
1.	Lauric acid		MS
2.	Acetic acid	0.03 ^a	GC-MS
Monoterpenes			
1.	Geranoic acid	0.24 ^a	GC-MS
2.	Geranic acid	^a	MS

Table 2 Continued

S/No	Compounds	Concentration (%)	Method of identification
Esters			
Monoterpene			
1.	Isobornyl acetate	0.03	GC-MS
2.	Citronelly acetate	0.39	GC-MS
3.	Geranyl acetate		MS
4.	Geranyl propionate	^a	MS
5.	Neryl acetate	1.22	GC-MS
Oxides			
Monoterpenes			
1.	1,8-Cineole	0.41	GC-MS
2.	Linalool oxide	^a	MS
Sesquiterpene			
1.	Caryophyllene oxide	0.18	GC-MS
Other compounds			
1.	Acetyl furan		MS
2.	Methyl pyrrole	^a	MS

^a Newly identified compounds

aroma to terpineol, neral, geranial, β -sesquiphellandrene, arcurcumene, nerolidol and *cis*- β -sesquiphellandrol, which accounted for 85% of the flavor. Seven years later Govindarajan's work showed that hydrocarbons do not contribute significantly to the aroma of ginger [14]. Neral, geranial, bornyl acetate, β -zingiberene, β -eudesmol and *trans*- β -sesquiphellandrol are important known contributors to the aroma of ginger. Based on these reports and others it seems that there is consensus on the contribution of neral and geranial to the ginger aroma. Neral and geranial are known to be responsible for the lemon flavor of ginger. Using GC-sniff evaluation, Chung et al. [15] observed that the fruity aroma of edible Korean chamchwi (*Aster scaber* Thunb) was due to heptanal, α -phellandrene, α -terpinene, ρ -cymene, limonene, β -phellandrene, γ -terpinene, benzyl alcohol, terpinen-4-ol, neral, geranial and 2-hexadecanone. Most of these compounds have been identified as constituents of ginger and could therefore contribute to the fruity aroma of ginger, while the camphoraceous aroma/flavor could be attributed to camphene, 1,8-cineole and borneol components. The organoleptic characteristics of other essential oil components have been described by several others using different techniques including GC-sniffing [15–18]. The reconstruction of ginger oil in vitro may mean more than the mixing of some of these known components because some of the unidentified volatile components probably contribute and may play a significant role in the aroma of ginger's essential oil. Again because of the differences in composition due to variety and origin it may not be possible for a particular mixture to serve as an imitation of ginger oil in general.

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