

Chemical Constituents of the Root Essential Oils of *Zingiber rubens* Roxb., and *Zingiber zerumbet* (L.) Smith

Do N. Dai¹, Tran D. Thang^{2*}, Le T. M. Chau¹, Isiaka A. Ogunwande^{3*}

¹Faculty of Biology, Vinh University, Vinh City, Vietnam; ²Faculty of Chemistry, Vinh University, Vinh City, Vietnam; ³Natural Products Research Unit, Department of Chemistry, Faculty of Science, Lagos State University, Lagos, Nigeria.
Email: *thangtd@vinhuni.edu.vn, *isiaka.ogunwande@lasun.edu.ng

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ABSTRACT

Zingiber rubens Roxb., and *Zingiber zerumbet* (L.) Smith were collected respectively from Nghe An, Province and Ha Tinh, Province, Vietnam. The root essential oils were obtained by water distillation and analyzed by Gas chromatography (GC) and Gas chromatography coupled with Mass spectrometry (GC-MS). The most abundant components of *Z. rubens* were (*Z*)-citral (30.1%), camphene (9.7%), β -phellandrene (7.5%) and 1,8-cineole (7.0%) and zingiberene (5.3%). The main oil constituents of *Z. zerumbet* were (*Z*)-citral (26.1%), camphene (16.3%), sabinene (14.6%), zingiberene (7.2%) and lavandulyl acetate (6.7%). This species has low zerumbone (1.2%) content.

Keywords: *Zingiber rubens*; *Zingiber zerumbet*; Root Essential Oil; (*Z*)-Citral; Camphene; Sabinene; Zerumbone

1. Introduction

In continuation of our research into the volatile oils of Vietnamese flora as they are made available [1], we report herein the constituents of the root oils of *Zingiber rubens* Roxb., and *Zingiber zerumbet* (L.) Smith. *Zingiber* Miller is a genus of the big family of plant, Zingiberaceae. It has about 150 species distributed in tropical rain forest and in much of the Southeast Asia, China, India and throughout the Islands in the Pacific [2]. In Vietnam, the genus is diverse with about 10 endemic species. They contained essential oils which are used as medicinal drugs, spices and raw materials for industry [3]. The plants are also used for ornamental purposes [4]. The chemistry of volatile compounds of *Zingiber* species have been studied by various authors. For example, the major content of *Z. zerumbet*, zerumbone, varied according to geographical location [5]. Several other terpenoid compounds have been isolated and described from these species.

2. Materials and Methods

2.1. Plant Materials

Mature roots from *Z. rubens* were collected from Nghe An Province while *Z. zerumbet* was obtained from Ha Tinh, Vietnam, in 2010. Voucher specimens DND 211 and DND 212 respectively were deposited at the Botany Museum, Vinh University, Vietnam.

2.2. Extraction of the Volatile Oils

Aliquots of air dried and pulverized samples (0.5 kg each) were subjected to water distillation for 3 h at normal pressure, according to the Vietnamese Pharmacopoeia [6]. The yields of the oils were 0.40% and 0.35% (v/w) respectively for *Z. rubens* and *Z. zerumbet*, on a dry weight basis. The chemical composition of the oils is summarized in **Table 1**.

2.3. Gas Chromatography (GC)

About 15 mg of each oil sample, which was dried with anhydrous sodium sulfate, was dissolved in 1 mL of hexane (for spectroscopy or chromatography). GC analysis was performed on Agilent Technologies HP 6890 Plus Gas chromatograph equipped with a FID and fitted with HP-Wax and HP-5MS columns (both 30 m \times 0.25 mm, film thickness 0.25 μ m, Agilent Technology). The analytical conditions were: carrier gas H₂ (10 mL/min), injector temperature (PTV) 250°C, detector temperature 260°C, column temperature programmed 60°C (2 min hold) to 220°C (10 min hold) at 4°C/min. Samples were injected by splitting and the split ratio was 10:1. The volume injected was 1.0 μ L. Inlet pressure was 6.1 kPa.

2.4. Gas Chromatography-Mass Spectrometry Analysis (GC-MS)

An Agilent Technologies HP 6890N Plus Chromatograph

*Corresponding authors.

Table 1. Essential oil composition of *Z. rubens* and *Z. zerumbets*.

RI ^a	Compound ^a	<i>Z. rubens</i>	<i>Z. zerumbets</i>
926	Tricylene	-	0.2
939	α -Pinene	2.6	3.3
953	Camphene	9.7	16.3
976	Sabinene	-	14.6
980	β -Pinene	0.4	0.5
999	<i>n</i> -Octanal	0.4	0.1
1006	α -Phellandrene	0.4	0.7
1026	ρ -Cymene	-	0.1
1028	β -Phellandrene	7.5	-
1034	1, 8-Cineole	7	0.5
1043	2-Heptanol acetate	0.6	0.4
1061	g-Terpinene	-	0.1
1090	α -Terpinolene	-	0.4
1100	Linalool	1.6	-
-	1,5-Heptadiene [#]	-	0.3
1153	Citronellal	1.3	1.4
1167	Borneol	1.3	2
-	1,6-Octadien-3-ol [#]	-	0.7
1189	α -Terpineol	1.1	-
1090	2-Nonanone	-	0.1
1253	Geraniol	6.6	0.8
1267	Geranial	3	-
1287	Bornyl acetate	1.6	-
1289	α -Thujenal	-	0.3
1290	Lavandulyl acetate	-	6.7
1318	Z-Citral	30.1	26.1
1353	Citronelly acetate	0.4	0.1
1359	Eugenol	-	0.4
1381	Geranyl acetate	0.7	1.6
1391	β -Elemene	-	0.2
1410	α -Gurjunene	-	0.3
1412	α -Cedrene	-	0.9
1435	<i>trans</i> - α -Bergamotene	-	0.1
1437	g-Elemene	-	0.2
1443	(<i>Z</i>)- β -Farnesene	-	0.1
1456	(<i>E</i>)- β -Farnesene	-	0.7
1463	Dehydro-Aromadendrene	-	0.2
1481	<i>ar</i> -Curcumene	0.8	1.1
1483	g-Curcumene	-	0.1

Continued

1485	Germacrene D	-	0.3
1489	<i>epi</i> -Bicyclosesquiphellandrene	-	2.6
1490	β -Selinene	-	0.6
1494	Zingiberene	5.3	7.2
1506	(<i>E,E</i>)- α -Farnesene	1.8	1.5
1508	β -Bisabolene	1.6	1.9
1515	(<i>Z</i>)-g-Bisabolene	-	0.2
1523	β -Sequiphellandrene	1.9	-
1525	Selina-4(14), 11-diene	-	0.3
-	Cyclohexanemethanol [#]	-	1.1
1533	(<i>Z</i>)-Nerolidol	-	0.4
1550	Elemol	0.9	-
1563	(<i>E</i>)-Nerolidol	0.2	-
1651	β -Eudesmol	1.2	0.7
1742	Zerumbone	-	1.2
	Total identified	90.1	99.6
	Monoterpene hydrocarbon	20.6	32.6
	Oxygenated monoterpenoids	54.7	39.9
	Sesquiterpene hydrocarbons	11.4	18.5
	Oxygentaed Sesquiterpene	2.3	1.1
	Others	1	2.7

^aIdentification by RI, MS and co-injection; ^bRetention indices on HP-5MS capillary column; - not identified; [#]identification by MS fragmentation pattern only.

fitted with a fused silica capillary HP-5 MS column (30 m \times 0.25 mm, film thickness 0.25 μ m) and interface with a mass spectrometer HP 5973 MSD was used for the GC/MS analysis, under the same conditions used for GC analysis, with He (10 mL/min) as carrier gas. The MS conditions were as follows: ionization voltage 70 eV; emission current 40 mA; acquisitions scan mass range of 35 - 350 amu at a sampling rate of 1.0 scan/s.

2.5. Identification of Constituents

The identification of constituents was performed on the basis of retention indices (RI) determined with reference to a homologous series of *n*-alkanes, under identical experimental conditions, co-injection with either standards (Sigma-Aldrich, St. Louis, MO, USA) or known essential oil constituents, MS library search (NIST 08 and Wiley 9th Version), and by comparing with MS literature data [7,8]. The relative amounts of individual components were calculated based on the GC peak area (FID response)

Table 2. Major compounds of previously studied *Z. zerumbet* oils from different regions.

LC	P	Major Compounds	Ref
India	Rh	zerumbone (76.3% - 84.8%)	[5]
Malaysia	Rh	zerumbone (68.9%)	[5]
Vietnam	St	(<i>Z</i>)-nerolidol (16.8% - 22.3%)	[9]
	Lv	zerumbone (21.3% - 2.4%), trans-phytol (7.0% - 12.6%), β -caryophyllene (10.4% - 11.2%)	[9]
	Fl	(<i>Z</i>)-nerolidol (36.3%), β -caryophyllene (13.2%)	[9]
Vietnam	-	zerumbone (72.3%)	[10]
India	-	curzerenone (14.4%), zerumbone (12.6%), camphor (12.8%), isoborneol (8.9%), 1,8-cineole (7.1%)	[11]
French Polynesia	Rh	zerumbone (63.0%)	[12]
Reunion Island	Rh	zerumbone (37%), α -humulene (14.4%), camphene (13.8%)	[13]
	Lv	(<i>E</i>)-nerolidol (21.4%), β -caryophyllene (6.9%), linalool (7.7%), α -pinene, (10.3%), β -pinene (31.4%)	[13]
	Fl	(<i>E</i>)-nerolidol (34.9%), β -caryophyllene (10.2%), linalool (17.1%)	[13]
Bangladesh	Rh	zerumbone (46.8%), β -caryophyllene (19.0%), 1,5,5,8-tetramethyl-12-oxabicyclo[9.1.0]-dodeca-3,7-dien (4.3%)	[14]

LC = Location; P = Plant part; Rh = Rhizomes; Lv = Leaves; St = Stem; Fl = Flowers; -, part unknown.

without using correction factors.

3. Results and Discussion

The identities of compounds identified in the oil samples could be seen in **Table 1**. A total of 24 compounds were identified in the *Z. rubens* root oil, representing 90.1% of the oil content. The oil composed largely of monoterpenes (75.3%) dominated by (*Z*)-citral (30.1%), camphene (9.7%), β -phellandrene (7.5%) and 1,8-cineole (7.0%). Zingiberene (5.3%) was significant among the sesquiterpenoids. Literature information is scanty on the volatile oil of *Z. rubens* and as such this may represent the first of its kind.

A total of 46 compounds could be identified from the root oil of *Z. zerumbet*, representing 99.6% of the oil content. Also, monoterpenoids (76.1%) were in abundance in the oil. The major constituents were (*Z*)-citral (26.1%), camphene (16.3%), sabinene (14.6%), zingiberene (7.2%) and lavandulyl acetate (6.7%). This oil has low content of zerumbone (1.2%). Essential oils from various parts of *Z. zerumbet* have been analysed. The investigations revealed that the content of its predominant compound, zerumbone, varied from one geographical location to another [5,9-14]. For example, its contents from sample of India origin varied from 76.3% - 84.8% while the oil from Malaysia had a content of 68.9% [5]. Another sample from India has zerumbone content of 12.6% [11] while the rhizomes oils from Reunion Island [13] and French Polynesia [12] contained 37.0% and 63.0% of zerumbone respectively. However, there are reports in which other terpenoid compounds have predominated in the oils (**Table 2**). For example,

(*Z*)-nerolidol (36.3%) and β -caryophyllene (13.2%) were prominent in the flower oil from Vietnam [9]; (*E*)-nerolidol (34.9%), β -caryophyllene (10.2%) and linalool (17.1%) occurred in higher quantities in the flower oil from Reunion Island; (*E*)-nerolidol (21.4%), β -caryophyllene (6.9%), linalool (7.7%), α -pinene, (10.3%), β -pinene 31.4% constituted the bulk of the leaf oil from Reunion Island [13].

It is well known that the root oil from a plant could be different in chemical analysis of oils from other parts of the same plant [1]. This may have been responsible for the observed compositional variations within the oils of *Z. zerumbet*. (*Z*)-Citral, camphene and sabinene were not previously described to be of significant compound of the oils from the leaves and rhizomes of *Z. zerumbet*. While, (*Z*)-citral was known to be a significant compound of *Z. officinale* from Central African Republic [15], camphene occurred in high proportion in the oil of *Z. officinale* of Vietnam origin [16].

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