CHEMICAL CONSTITUENTS OF THE ESSENTIAL OIL FROM THE RHIZOMES OF ZINGIBER OFFICINALE COLLECTED IN CẢ PASS MOUNTAIN REGION, VIETNAM

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Title:

Thành phần hóa học từ thân rễ loài gừng (Zingiber officinale) được thu hái tại vùng núi đèo Cả, Việt Nam

Keywords:

Zingiber officinale, essential oil, limonene, α-pinene, β-caryophyllene.

Từ khóa:

Gừng, tinh dầu, limonene, α-pinene, β-caryophyllene.

TÓM TẮT: *Thành phần hóa học của dầu gừng từ thân rễ tươi của loài Zingiber officinale đã được phân tích bằng GC-MS. Tinh dầu chủ yếu chứa các hợp chất monoterpenoid và sesquiterpenoid, bao gồm α-pinene, limonene, δ-3-carene, γ-terpinene, α-phellandrene và β-caryophyllene.*

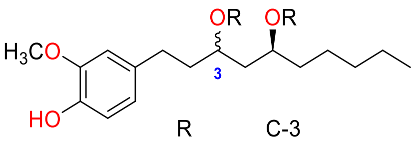
ABSTRACT: *The chemical composition of the ginger oil from fresh rhizomes of Zingiber officinale was analyzed by GC-MS. The essential oil consists predominantly of monoterpenoids and sesquiterpenoids, including α-pinene, limonene, δ-3-carene, γ-terpinene, α-phellandrene, and β-caryophyllene.*

1. Introduction

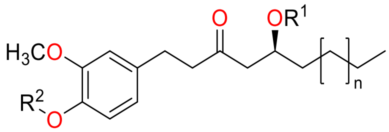
The genus *Zingiber* includes around 85 herb species mainly found in East Asia, Southeast Asia, and tropical Australia. These plants have garnered attention for their significant roles in both traditional medicine and culinary practices across various cultures [1]. Investigation into *Zingiber* rhizomes has unveiled bioactive constituents, including gingerols and shogaols, which are renowned for their potent antibacterial properties [2,3]. Additionally, a diverse array of compounds, comprising diarylheptanoids [4], phenylbutenoids [5], flavanoids [6], diterpenoids [7], and sesquiterpenoids [8], paradol, gingerdiols, dehydrogingerdione, phenylpropanoid, steroids [9] have been identified within this genus (Figure. 1).

Extensive research efforts have focused on elucidating the chemical profiles of essential oil derived from these plants and exploring their pharmacological effects [10-15].

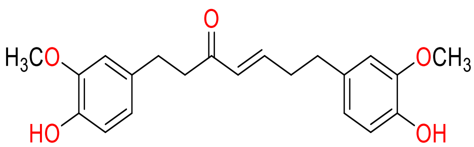
Among the *Zingiber* species, *Zingiber officinale* stands out as a globally recognized botanical with a rich history of utilization both as a culinary spice and a medicinal agent. It has been used to treat stomach ache, diarrhea, stroke, diabetes, asthma, toothache and arthritis [16, 17]. Notably, specific bioactive constituents within *Z. officinale*, such as sesquiterpenes, diarylheptanoids, and gingerol derivatives, have been the subject of extensive study due to their documented anti-inflammatory, anti-emetic, and analgesic properties [18-21]. This study provides initial qualitative insights into the organic compounds present in ginger rhizomes, focusing on assessing the essential oil content in freshly collected samples. The analytical approach involves the utilization of gas chromatography-mass spectrometry (GC-MS) to identify and quantify the various constituents constituting ginger essential oil.

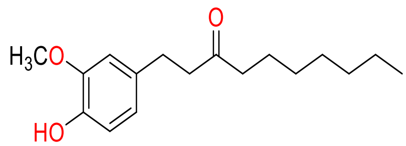


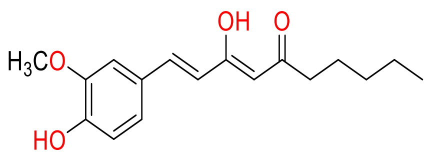
R	C-3
H	*S*
H	*R*
Ac	*R*

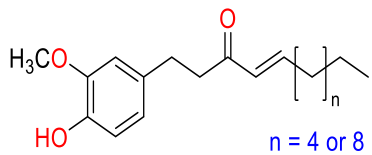


R^1	R^2	n	R^1	R^2	n
H	H	0	H	CH_3	2
H	H	2	H	H	4
Ac	H	2	H	H	6

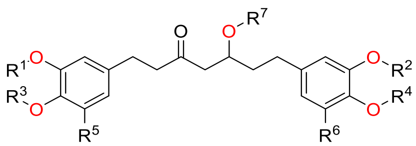




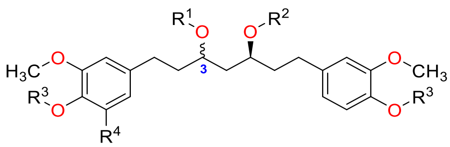




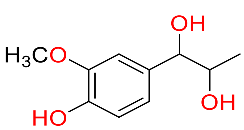
n = 4 or 8

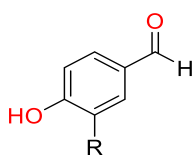


R^1	R^2	R^3	R^4	R^5	R^6	R^7
CH_3	CH_3	H	H	H	H	Ac
H	CH_3	H	H	OCH_3	H	H
CH_3	H	H	H	H	OCH_3	H
CH_3	H	H	H	H	H	H
CH_3	CH_3	H	H	H	H	H
CH_3	CH_3	Ac	Ac	H	H	Ac

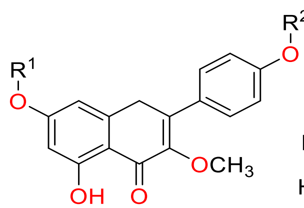


R^1	R^2	R^3	R^4	C-3
Ac	Ac	H	H	*S*
Ac	H	H	H	*R*
H	H	H	OCH_3	*R*
Ac	Ac	H	H	*R*
Ac	Ac	H	OCH_3	*R*
H	H	H	H	*S*
H	H	H	H	*R*
Ac	Ac	Ac	H	*R*
H	H	H	OCH_3	*S*





R: H
R: OCH_3



R^1	R^2
H	H
CH_3	CH_3
H	CH_3

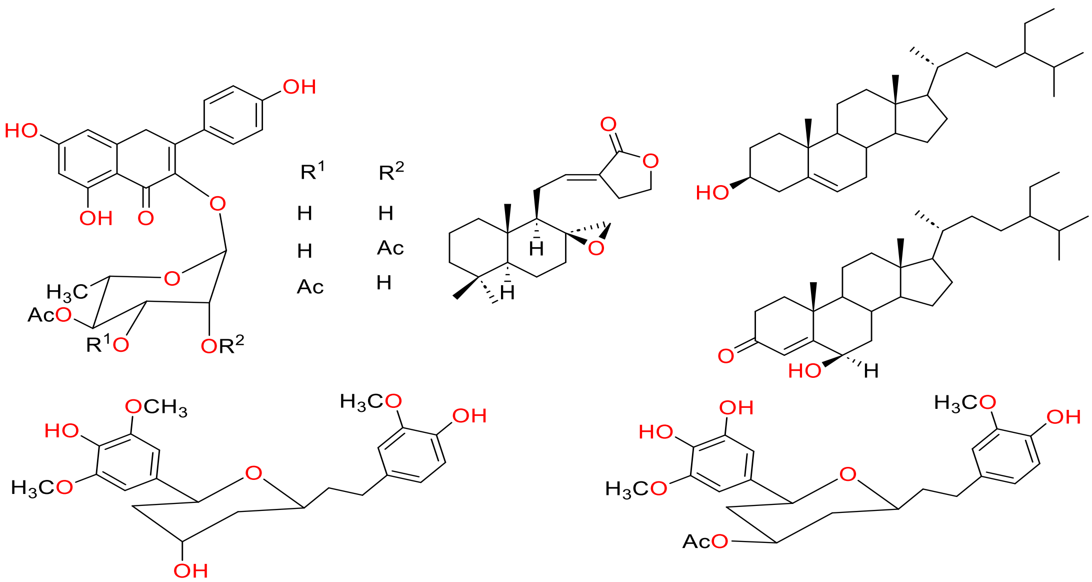


Figure 1. *The chemical structures of some compounds isolated from Zingiber sp.* [2-15]

2. Materials and methods

2.1. Herb materials

Rhizomes of *Zingiber officinale* were collected in September 2021 in the Cả Pass mountain region, Hoa Tam, Dong Hoa, Phu Yen province, and authenticated by Assoc. Prof. Do Huu Thu from the Institute of Ecology and Biological Resources, Vietnam Academy of Science and Technology (VAST). Voucher specimen (No. Zo.01) is deposited in the Laboratory of Drug Research and Discovery, Institute of Chemistry, VAST, Hanoi, Vietnam. The fresh rhizome sample was cleaned, pulverized, and used for analysis.

2.2. Essential oil extraction

The fresh ginger rhizomes (350 g) were steam distilled with 500 mL of water for 3 hours. The distillate was collected, extracted twice with 100 mL of diethyl ether, and then dried using anhydrous sodium sulfate. Upon evaporation of the solvent, 7.72g (2.21%) of essential oil was obtained, based on the initial weight of the rhizomes. For GC-MS spectral analysis, 1.5 mg of the oil was dissolved in 1.0 mL of dried pure *n*-hexane (over anhydrous sodium sulfate). The essential oil underwent GC-MS analysis.

2.3. GC-MS analysis

GC-MS was carried out on the Agilent Technologies USA HP 6890N Plus equipment, with a Mass selective detector: HP5973 MSD. Compounds were separated on HP-5MS capillary column (0.25 µm × 30 m × 0.25 mm) and HP1 (0.25 µm × 30m × 0.32 mm). Samples were injected with a split ratio of 10:1 and a helium flow rate of 1.0 mL/min (carrier gas). Other conditions included an oven temperature up to 60°C/2 min. hold, and up to 220°C at a rate of 5 deg/min. hold. The injector temperature was maintained at 220°C. The column was connected directly to the Mass Spectrometer operated in the electron ionization mode at 70 eV, with ion source temperature at 230°C, MS transfer line at 280°C, and a scan rate of 1.94/second.. The constituents were identified by comparing them with those available in the Willey/Chemstation HP Library attached to the GC-MS instrument and reported data [22-25].

3. Results and discussion

The rhizomes' essential oil compositions, obtained through steam distillation, were analyzed using GC-MS method. 51 components, representing > 93% of the total peak area, were identified in the essential oil.

These components are detailed in Table 1. The analysis revealed that key components like *α*-pinene (6.55%), limonene (6.83%), *δ*-3-carene (5.74%), *γ*-terpinene (5.75%), *α*-phellandrene (5.57%), and *β*-caryophyllene (11.72%) exist in varying quantities within the essential oil.

Table 1. Chemical components detected in GC-MS spectra of the rhizomes of *Zingiber officinale* essential oil.

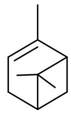
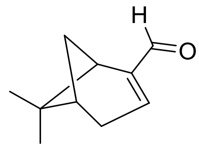
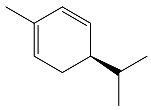
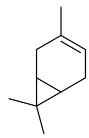
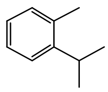
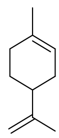
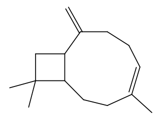
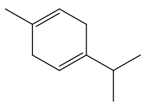
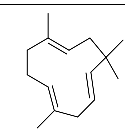
No	Compound	Molecular formula	M.W. (g/mol)	RT (min)	Peak area (percentage, %)
	α-thujene	$C_{10}H_{16}$	136	6.24	0.85
	***α*-pinene**	$C_{10}H_{16}$	136	6.42	**6.55**
	sabinene	$C_{10}H_{16}$	136	7.12	1.08
	camphene	$C_{10}H_{16}$	136	7.24	3.83
	verbenene	$C_{10}H_{16}$	136	7.56	0.28
	β-myrcene	$C_{10}H_{16}$	136	7.96	3.01
	***α*-phellandrene**	$C_{10}H_{16}$	136	8.23	**5.57**
	***δ*-3-carene**	$C_{10}H_{16}$	136	8.38	**5.74**
	α-terpinene	$C_{10}H_{16}$	136	8.54	0.77
	o-cymene	$C_{10}H_{14}$	134	8.77	4.42
	(*E*)-*β*-ocimene	$C_{10}H_{16}$	136	9.37	1.33
	limonene	$C_{10}H_{16}$	136	10.31	**6.83**
	γ-terpinene	$C_{10}H_{16}$	136	10.62	**5.75**
	α-terpinolene	$C_{10}H_{16}$	136	10.90	0.79
	linalool	$C_{10}H_{18}O$	154	11.00	0.31
	lyrtenol	$C_{10}H_{16}O$	152	12.12	0.19
	trans-alloocimene	$C_{10}H_{16}$	136	11.20	0.27
	camphor	$C_{10}H_{16}O$	152	11.45	0.14
	borneol	$C_{10}H_{18}O$	154	11.67	0.37
	α-thujenal	$C_{10}H_{14}O$	150	11.62	0.48
	α-terpineol	$C_{10}H_{18}O$	154	11.89	0.98
	myrtenal	$C_{10}H_{14}O$	150	12.09	4.18
	geranyl acetate	$C_{12}H_{20}O_2$	196	12.23	4.58
	thymol methyl ether	$C_{11}H_{16}O$	164	12.34	0.15
	(*E*)-citral	$C_{10}H_{16}O$	152	12.67	0.35
	4-(1-methylethyl)-benzaldehyde	$C_{10}H_{12}O$	148	12.79	0.32
	bornyl acetate	$C_{12}H_{20}O_2$	196	12.89	1.21
	bicycloelemene	$C_{15}H_{24}$	204	13.27	0.12
	myrtenyl acetate	$C_{12}H_{18}O_2$	194	13.36	0.59
	β-panasinsene	$C_{15}H_{24}$	204	13.58	0.42
	α-copaene	$C_{15}H_{24}$	204	13.77	2.30

No	Compound	Molecular formula	M.W. (g/mol)	RT (min)	Peak area (percentage, %)
	β-elemene	$C_{15}H_{24}$	204	13.91	0.51
	***β*-caryophyllene**	$C_{15}H_{24}$	204	14.19	**11.72**
	calarene	$C_{15}H_{24}$	204	14.31	0.12
	α-guaiene	$C_{15}H_{24}$	204	14.33	0.18
	γ-elemene	$C_{15}H_{24}$	204	14.37	0.40
	aromdendrene	$C_{15}H_{24}$	204	14.41	0.29
	α-humulene	$C_{15}H_{24}$	204	14.54	3.52
	2-dodecenal	$C_{12}H_{22}O$	182	14.66	3.36
	α-amorphene	$C_{15}H_{24}$	204	14.85	0.59
	germacrene D	$C_{15}H_{24}$	204	14.85	1.17
	(*E,E)*-*α*-farnesene	$C_{15}H_{24}$	204	1508	1.36
	δ-cadiene	$C_{15}H_{24}$	204	15.25	0.76
	trans-*γ*-bisabolene	$C_{15}H_{24}$	204	15.35	0.42
	elemol	$C_{15}H_{26}O$	222	15.50	0.17
	nerolidol	$C_{15}H_{26}O$	222	15.63	0.41
	valencene	$C_{15}H_{24}$	204	15.81	1.07
	caryophyllene oxide	$C_{15}H_{24}O$	220	15.83	1.91
	α-cadinol	$C_{15}H_{26}O$	222	16.54	0.47
	caryophylla-4(12),8(13)-dien-5-*β*-ol	$C_{15}H_{24}O$	220	16.68	0.95
	α-bisabolol	$C_{15}H_{26}O$	222	17.53	0.15
		Total			93.29 51 compounds

[*] *Compounds with high concentrations are displayed in bold*

The chemical formulas of some main compounds are listed in Table 2. Compound (*E*) 2-dodecenal in oil form is a flavor with a citrus-like aroma commonly found in ginger, citrus peel, and eggplant, as well as in carrots and milk [26]. This compound exhibited the highest activity against *Salmonella choleraesuis* ssp. in food [27]. *α*-pinene is an anti-inflammatory and antimicrobial compound with a broad antibiotic spectrum. Compound *δ*-3-carene, at high concentrations, can act as a skin irritant or an analgesic for the central nervous system. Limonene is frequently used as a lemon flavoring agent in cosmetics, foods, and pharmaceuticals. It is also utilized in cleaning products due to its oil-dissolving properties and has insecticidal effects, stress-reducing, and depression-fighting abilities [26]. *β*-caryophyllene, a sesquiterpene found in the essential oil of various plants, possesses multiple biological activities including anti-inflammatory, antibiotic, antioxidant, anti-cancer, and local anesthetic properties [28]. Humulene, also known as *α*-humulene, is a monocyclic sesquiterpene. It derives its name from being present in the essential oil of the *Humulus lupulus* plant. Humulene is an isomer of *β*-caryophyllene and both are commonly found together in natural mixtures. Research has shown that humulene exhibits anti-inflammatory effects and holds promise as a treatment for inflammatory diseases [29].

Table 2. Molecular formula and chemical structure of key compounds in ginger essential oil

No	Compound	Structure	No	Compound	Structure
1	*α*-pinene ($C_{10}H_{16}$)		6	myrtenal ($C_{10}H_{14}O$)	
2	*α*-phellandrene ($C_{10}H_{16}$)		7	*δ*-3-carene ($C_{10}H_{16}$)	
3	*o*-cymene ($C_{10}H_{14}$)		8	2-dodecenal ($C_{12}H_{22}O$)	$CH_3(CH_2)_8CH=CHCH=O$
4	Limonene ($C_{10}H_{16}$)		9	*β*-caryophyllene ($C_{15}H_{24}$)	
5	γ-terpinene ($C_{10}H_{16}$)		10	*α*-humulene ($C_{15}H_{24}$)	

4. Conclusions

Steam distillation extraction coupled with GC-MS has proven to be a valuable method for analyzing ginger components, offering a helpful insight into variations in its constituents. The essential oil sample contains mainly sesquiterpenoids and monoterpenoids in approximately a 1:2 ratio. Major constituents in the rhizomes' essential oil include *β*-caryophyllene, limonene, γ-terpinene, *δ*-3-carene, *α*-phellandrene, and *α*-pinene.

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