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Gas Chromatography-Mass Spectrometry Profile of Essential Oils Derived from *Zingiber officinale* Rosc. Rhizome

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ABSTRACT

White ginger which is also called Jahe Putih (*Zingiber officinale*) in Indonesia, is widely used in local Indonesian communities. It is a popular ingredient in beverages for stamina and also a bioactive ingredient for many traditional Indonesian food recipes. It is a popular ingredient in beverages for stamina and also a bioactive ingredient for many traditional food recipes. However, with the increase in demand for ginger related products, fake ginger formulated products are widespread in the market. This paper is disclosed the chemical profile of essential oil obtained from steam distillation of the local ginger. The results of this study can be used as a standard to detect original ginger. It was found that the chemical composition of the essential oil obtained from the white ginger contained 0.19% of a dried weight after 3 h of steam distillation. A total of 40 monoterpenoids (C10) and sesquiterpenoids (C15) secondary metabolite compounds were respectively detected in the oil.

Keywords: ginger; Zingiber officinale; secondary metabolite; essential oils

INTRODUCTION

Ginger is commonly used as herbal medicine and also to enhance flavor in cuisine. It has the ability to relieve pain, rheumatism, stimulate the immune system and improve stamina [1,2]. Molecules such as 6-gingerol, 8-gingerol, 10-gingerol [3], 6-shogaol, 8-shogaol, 10-shogaol [4,5], paradols, gingerone, (-)-zingiberene, curcumene, β-sesquiphellandrene, and β-bisabolene have previously been isolated from white ginger. These molecules are classified as phenolic and terpenoid groups of secondary metabolites (Figure 1). They have antibacterial, antioxidant [1,6,7], anticancer [8,9] and anti-inflammatory activities [5,10] with a potential to prevent obesity [11,12] and diabetes [13]. The family of Zingiberaceae and genus zingiber is reported to consist of 125 plants species [14]. This wide species distribution can cause common physical feature identification and differentiation challenging. Supercritical extraction method using carbon dioxide for chemical compound isolation from ginger has been previously reported [7,15–17]. A hydro-distillation process which involved the mixing of the sample with water and steam distillation for compound isolation from ginger has also been reported [18,19]. The supercritical process using carbon dioxide is a green and more efficient process, however, the procedure requires sophisticated tools and high-pressure tanks to conduct. Meanwhile, the hydro-distillation process in some stages affords oleoresin precipitate in the flash reactor and oxidized or hydrated products are

also observed after identification. Therefore, steam distillation is more favorable and ease to handle. However, in a previous paper [20], incomplete chemicals were detected during analysis. In this paper, we report 40 compounds isolated from a local ginger species by a steam distillation process. The compounds were analysed by a gas chromatography-mass spectrometric method.

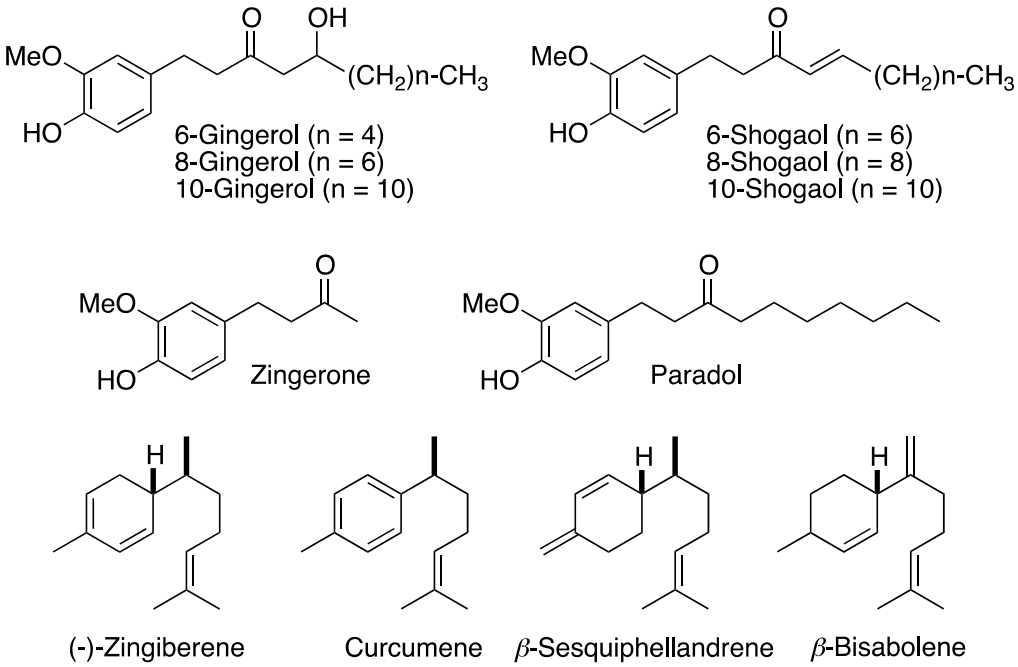

Figure 1. Common molecules previously isolated from *Zingiber officinale* Rosc rhizome

EXPERIMENT

Sample

The *Zingiber officinale* Rosc sample was bought from a traditional market in Malang, Indonesia. The species name was confirmed from a reference by previous reports. The fresh sample was cut into small pieces of 1-2 cm and then air-dried between 29-30 ^{o}C for two days.

Steam distillation

The dried sample (83.2 g) was placed in a round-bottom flask connected to the steam distillation apparatus. The water container was boiled and the steam allowed to enter the flask. The vapor condensed to liquid and afforded a mixture of ginger essential oil and water. This process was allowed to run for 3 h and the floating oil was subsequently separated from the liquid by using separating funnel. A clean-yellowish oil was collected for GC-MS analysis. The liquid product yield was determined using the equation below.

$$\text{Product Yield (\%)} = (\text{ginger oil weight (g)}/\text{dried sample weight (g)}) \text{ x } 100$$

Gas chromatography-mass spectrometry analysis

The GC-MS (Shimadzu QP2010S) condition of analysis was a column Restex of 30 m, an injection temperature of 310 ^{o}C, a column flow of 0.55 mL/min and an initial temperature of 70 ^{o}C (2 mins). The temperature was increased to 10.0 ^{o}C/min to a maximum of 310 ^{o}C. An MS ion source of 70 eV, a temperature of 250 ^{o}C, and a scan speed of 1250 from 40 m/z

to 600 m/z were also applied. The identification of the compounds in the product was based on the similarity index (SI) of the analyzed spectra with the library database of Wiley and the National Institute of Standards and Technology (NIST) of Indonesia.

Figure 2. *Zingiber officinale* Rosc. produced and marketed by locals

RESULT AND DISCUSSION

A recent report on supercritical carbon dioxide ($scCO_2$) for solvent extraction [21] of dried ginger afforded 2.77% ginger oil. A total of 12 compounds [21] which belongs to the family of monoterpenes (10 carbon atoms or C10) and sesquiterpenes (15 carbons atom or C15) of the secondary metabolite group were isolated. The isolated compounds were α-pinene, camphene, limonene, β-phellandrene, borneol, neral, geranial, ar-curcumene, α-gingeberene, α-farnesene, β-bisabolene, and β-sesquiphelandrene. The major components in the product were α-gingeberene (37.04%) and β-sesquiphelandrene (13.59%), both of which are sesquiterpenes. On the other hand, our study identifies 40 different molecules isolated from the essential oil of a local ginger species by steam distillation. The molecules are detected based on the GCMS analysis similar to reports by [20,21] but with a different condition of analysis. However, a lower essential oil yield oil (0.19%) is afforded by the distillation process.

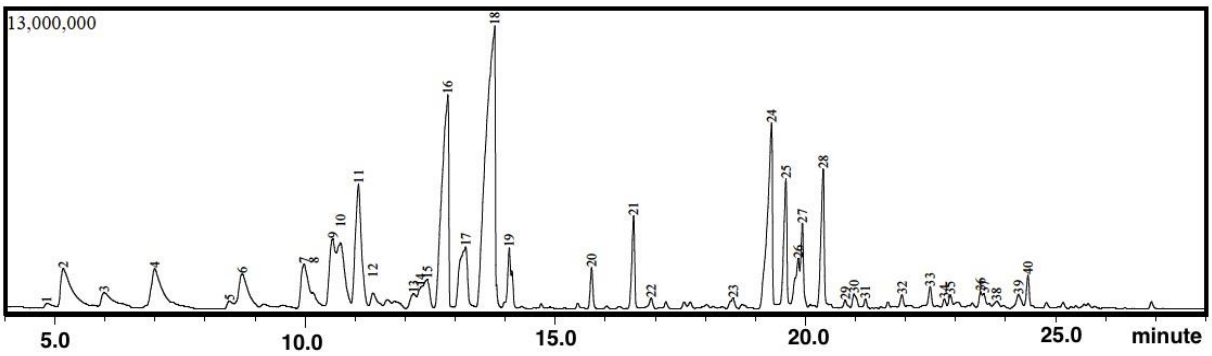

Figure 3. Chromatogram of the ginger essential oil isolated from *Zingiber officinale* Rosc by steam distillation

Table 1. The identified compounds in the *Zingiber officinale* Rosc's oil isolated by steam distillation

Peak number	Retention time (min.)	Similarity index (SI) value	This study	Percentage (%)	Compound Class	Ref. [20]	Ref. [21]
1	4.83	97	α-Pinene	0.19	mono.	ND	+
2	5.16	98	Camphene	3.27	mono.	ND	+
3	5.98	96	β-Myrcene	0.66	mono.	ND	ND
4	6.99	86	1,8-Cineole	2.69	mono.	+	ND
5	8.48	74	2-Nonanone	0.42	-	ND	ND
6	8.74	94	Linalool	2.65	mono.	ND	ND
7	9.98	90	2-Methyl-6-methylene-2-octene	2.70	mono.	ND	ND
8	10.18	73	Isopulegol	0.66	mono.	ND	ND
9	10.55	83	Pulegone	3.72	mono.	ND	ND
10	10.70	91	Borneol	4.10	mono.	+	+
11	11.07	88	4,5-Epoxy-carane	6.43	mono.	ND	ND
12	11.36	96	Linalyl propionate	0.59	mono.	ND	ND
13	12.17	80	3,3,6,6-Tetra-methylcyclohex-1-enol	0.73	mono.	ND	ND
14	12.31	94	β-Citronellol	0.88	mono.	ND	ND
15	12.45	98	β-Citronellol	1.35	mono.	ND	ND
16	12.85	96	β-Citrale / Neral	12.39	mono.	ND	+
17	13.21	97	trans-Geraniol	4.25	mono.	ND	ND
18	13.79	96	trans-Citrale / Geranial	22.45	mono.	+	+
19	14.08	97	α-Fencyl acetate	2.13	mono.	ND	ND
20	15.72	95	Citronellyl acetate	0.92	mono.	ND	ND
21	16.56	97	Geranyl acetate	2.27	mono.	ND	ND
22	16.92	95	β-Elemene	0.23	mono.	ND	ND
23	18.55	92	β-sesqui-phellandrene	0.41	sesqui.	+	+
24	19.32	97	Ar-Curcumene	7.98	sesqui.	+	+
25	19.61	92	α-Zingiberene	3.67	sesqui.	+	+
26	19.85	84	Farnesene	1.91	sesqui.	ND	+
27	19.94	96	β-Bisabolene	2.00	sesqui.	+	+
28	20.35	95	β-Sesqui-phellandrene	3.94	sesqui.	+	+
29	20.79	80	(-)-Spathulenol	0.20	sesqui.	ND	ND
30	20.97	94	Elemol	0.50	sesqui.	+	ND
31	21.20	94	Nerolidol	0.24	sesqui.	ND	ND

32	21.93	85	Sesquisabinene hydrate	0.30	sesqui.	ND	ND
33	22.49	84	Zingiberenol	0.47	sesqui.	ND	ND
34	22.76	72	α-Copaene	0.19	sesqui.	ND	ND
35	22.89	85	Zingiberenol	0.34	sesqui.	ND	ND
36	23.50	89	β-Eudesmol	0.39	sesqui.	+	ND
37	23.57	71	Juniper camphor	0.34	sesqui.	ND	ND
38	23.82	79	β-Bisabolol	0.27	sesqui.	ND	ND
39	24.26	82	Longiborneol	0.48	sesqui.	ND	ND
40	24.45	79	Farnesol	0.70	sesqui.	ND	ND

Note: Mono is an abbreviation for monoterpene (C10), meanwhile sesqui is an abbreviation for sesquiterpene (C15), ND means the molecule is not reported or detected in the given reference and (+) means the molecule is reported.

Figure 3 shows the chromatogram of the detected molecules in the essential oil of *Zingiber officinale* Rosc isolated by steam distillation while the compounds determined are tabulated in Table 1. The important finding of our study is that the major components contained in the local ginger are trans-citrale and β-citrale (both structures are depicted in Figure 4) with a percentage of 12.39% and 22.45%, respectively. However, in contrast to the report by [21], limonene is not detected in the isolated oil. Shukla et al also reported a higher product yield (0.42%) with $scCO_2$ extraction method [21].

A previous report by [20] which applied a similar extraction method to ours identified 18 molecules based on GC-MS analysis. Considering the 40 molecules identified by our methods, this finding gives more detail information on the composition of the isolated ginger essential oil. Ali et al. [20] reported 3 similar monoterpene groups such as 1,8-cineole, borneol, and trans-citral or geranial and 7 similar sesquiterpene molecules such as β-sesquiphellandrene, ar-curcumene, α-zingiberene, β-bisabolene, β-sesquiphellandrene, elemol, and β-eudesmol. Decanal, α-terpineol, nerol or cis-citral, germacrene D, α-cedrene, and phenolic compounds such as zingerone and ethyl p-methoxycinnamate were also reported. In addition, 1*H*-cyclopropa[a]naphthalene and naphthalene were detected as well. However, it is rare to find 1*H*-cyclopropa[a]naphthalene and naphthalene [20] in ginger species.

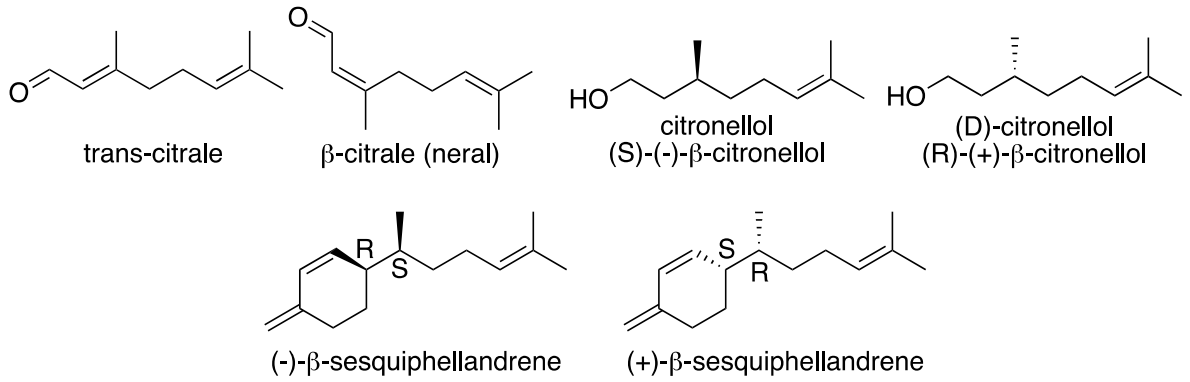

Figure 4. The structural isomers of citral, β-citronellol, and β-sesquiphellandrene

In this paper, citronellol and β-sesquiphellandrene are detected in two different retention times. Citronellol is detected at peak number 14 (12.31 min) and 15 (12.45 min)

respectively with similarity index (SI) values of 94 and 98 to the reference compounds. Interestingly, both compounds have the same molecular weight and formula. However, it is suggested that their structures possibly differ in the configuration as shown in Figure 4. Similarly, molecular structures of (R)-(+)-β-citronellol were previously isolated and detected in common herbs [22]. They are 1-citronellol and the natural occurring (-)-rhodinol [23] which is also reported to exist in opposite configurations.

In addition, β-sesquiphellandrene is detected at peak number 23 (retention time 18.55 min) and peak number 28 (retention time 20.35 min). The similarity index (SI) analysis gives a high value (SI 95%) for peak number 28 and SI 92% for peak number 23. Similar to β-citronellol, the chemical structure of β-sesquiphellandrene exist in a different configuration in nature. The difference in configuration is correlated with the physical and chemical properties including boiling point. β-sesquiphellandrene known as (-)-β-sesquiphellandrene [24,25] has configuration (6R,7S) at carbon atom number 6 and 7. Meanwhile, the other structure known as (+)-β-sesquiphellandrene [26] has a (6S,7R) configuration (Figure 4). In addition to the monoterpene and the sesquiterpene groups, we also detected a new compound identified as 2-nonanone with a molecular formula of $C_9H_{18}O$ and a molecular weight of 142 atomic mass unit.

CONCLUSION

The steam distillation of local white ginger (*Zingiber officinale* Rosc.) afforded an essential oil yield of 0.19% and 40 identified compounds consisting of monoterpene and sesquiterpene groups of secondary metabolites. GC-MS analysis showed a major composition of sesquiterpenes in the form of b-citrale or neral (12.39%) and trans-citral or geranial (22.45%).

CONFLICT OF INTEREST

Authors declares that no competing interest.

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