Chemical Composition of the Essential Oils of Two Alpinia Species from Hainan Island, China

Peng Nan^{a,b}, Yaoming Hu^c, Jiayuan Zhao^a, Ying Feng^b, and Yang Zhong^{a,*}

- ^a Ministry of Education Key Laboratory for Biodiversity Science and Ecological Engineering, School of Life Sciences, Fudan University, Shanghai 200433, China. Fax: 86-21-65642468. E-mail: yangzhong@fudan.edu.cn
- ^b Shanghai Center for Bioinformation Technology, Shanghai 201203, China
- ^c Center for Analysis and Measurement, Fudan University, Shanghai 200433, China
- * Author for correspondence and reprint requests
- Z. Naturforsch. **59 c**, 157–160 (2004); received July 24/August 29, 2003

The essential oils of two *Alpinia* species, *i.e. A. hainanensis* and *A. katsumadai*, from Hainan Island, China were analyzed by using GC-MS. The major constituents in the leaf oil of *A. hainanensis* were ocimene (27.4%), β -pinene (10.1%), 9-octadecenoic acid (6.5%), n-hexadecanoic acid (5.8%), 9,12-octadecadienoic acid (5.4%), and terpinen (4.3%). The oil constituents obtained from the flowers of *A. hainanensis* were ocimene (39.8%), β -pinene (17.7%), terpinene (5.5%), p-menth-1-en-ol (4.9%), caryophyllene (4.9%), and phellandrene (4.4%). In *A. katsumadai*, the major constituents in the leaf oil were p-menth-1-en-ol (22.0%), terpinen (19.0%), 4-carene (9.1%), 1,8-cineole (8.3%), and camphor (5.6%). The major constituents in the flower oil were p-menth-1-en-ol (21.3%), 1,8-cineole (20.2%), terpinen (12.6%), phellandrene (7.0%), 4-carene (6.4%), and β -pinene (5.2%).

Key words: Alpinia hainanensis and katsumadai, Essential Oil, GC-MS

Introduction

The galangal genus of *Alpinia* with about 250 species in the ginger family Zingiberaceae is distributed mainly in China, India, East Indies, and Polynesia (Lemmon and Sherman, 1964; Lötschert and Beese, 1983). The Alpinia plants have thick fragrant rootstocks, resembling the scent of ginger, from which the new shoots sprout in the spring, and their leaves are lance-shaped with fringed borders and they are produced on reedy stems. They can grow up to 10 feet high with a 3-foot spread. Many Alpinia species are appreciated for their medicinal properties; they have a long history of use in traditional medicine as a spasmolytic, hypotensive or diuretic due to their strong cardiovascular, anti-emetic, anti-oxidant, anti-inflammatory, bacteriostatic, or fungistatic effects in China, India and other regions (Jitoe et al., 1992; Habsah et al., 2000; Shin et al., 2002; Miyazawa and Hashimoto, 2002; Ficker et al., 2003). Currently, the compositions of essential oils from A. galanga including 1,8-cineole, β -pinene, and camphor (Raina *et al.*, 2002; Mallavarapu et al., 2002), A. speciosa including limonene, 1,8-cineole, and terpinen-4-ol (Zoghbi et al., 1999), A. purpurata including β -pinene, 1,8-cineole, and α -pinene (Zoghbi et al., 1999), A. smithiae including β -caryophyllene, sabinene, myrcene, and 1,8-cineole (Joseph *et al.*, 2001), and *A. zerumbet* including terpinen-4-ol, 1,8-cineole, and β -pinene (Ali et al., 2002) are investigated in detail.

Hainan Island (Hainan Province) is one of the major distribution regions of *Alpinia* plants in China. For example, the type specimens of *A. katsumadai* and *A. hainanensis* were collected from the island. In recent years, about 80% of annual production of Chinese *A. katsumadai* used as a famous Chinese traditional medicine were also from Hainan Island. However, the chemical composition of essential oils of *Alpinia* plants in this region has not been reported yet. Therefore, the chemical constituents of essential oils from leaves and flowers of *A. hainanensis* and *A. katsumadai* in Hainan Island were analyzed using GC-MS.

Materials and Methods

Plant materials

The leaves and flowers of *A. hainanensis* and *A. katsumadai* used in this study were collected from Bawangling National Nature Reserve for Black-crested Gibbon (18° 53′ ~ 19° 30′ N, 109° 0′ ~ 109° 17′ E), Changjiang County in Hainan Island in January 2003. The voucher specimens were

deposited at the MOE Lab for Biodiversity Science and Ecological Engineering, School of Life Sciences, Fudan University.

Extraction of essential oils

The fresh flowers (250 g) and dry leaves (100 g) of *A. hainanensis* and *A. katsumadai* were subjected to steam distillation for 3 h using a Clevenger-type apparatus. The essential oils were collected in a lighter than water oil graduated trap and dried over anhydrous sodium sulfate.

GC-MS analysis

The GC-MS analysis was performed on a combined GC-MS instrument (Finnigan Voyager, San Jose, CA, USA) using a HP-5 fused silica gel capillary column (30 m length, 0.25 mm diameter, $0.25 \,\mu \text{m}$ film thickness). A $1 \,\mu \text{l}$ aliquot of oil was injected into the column using a 10:1 split injection, which temperature was set up at 250 °C. The GC program was initiated by a column temperature set at 60 °C for 2 min, increased to 250 °C at a rate of 10 °C/min, held for 10 min. Helium was used as the carrier gas (1.0 ml/min). The mass spectrometer was operated in the 70 eV EI mode with scanning from 41 to 450 amu at 0.5 s, and mass source was set at 200 °C. The compounds were identified by matching their mass spectral fragmentation patterns with those stored in the spectrometer database using the National Institute of Standards and Technology Mass Spectral database (NIST-MS, 1998).

Results and Discussion

The steam distillation of the flowers and leaves of *A. hainanensis* and *A. katsumadai* yielded clear and yellowish essential oils. They were about 0.08% v/w and 0.1% v/w in the flowers of *A. hainanensis* and *A. katsumadai*, and about 0.14% v/w and 0.11% v/w in the leaves of *A. hainanensis* and *A. katsumadai*, respectively. The chemical constituents identified by GC-MS in the essential oils of leaves and flowers of *A. hainanensis* and *A. katsumadai* are listed in Table I.

In *A. hainanensis*, a total of 34 and 36 compounds (about 93.6% and 98.7% of the oils) were identified from leaves and flowers, respectively. The major constituents identified in the leaf oil of *A. hainanensis* were ocimene (27.4%), β -pinene (10.1%), 9-octadecenoic acid (6.5%), *n*-hexadecanoic acid (5.8%), 9.12-octadecadienoic acid (5.4%),

Table I. Chemical constituents of the essential oils from *A. hainanensis* and *A. katsumadai* in Hainan Island, China.

Compound	A. hainanensis Leaf Flower		A. katsumadai Leaf Flower	
3-Hexenol		0.2		
Hexanol		0.1		
2-Heptanol	tr	0.1	0.7	0.2
Thujene		0.1		
Cyclofenchene	tr	2.1		
Camphene	tr	1.4	1.2	0.7
Phellandrene	2.1	4.4	0.7	7.0
β-Pinene	10.1	17.7	2.7	5.2
Myrcene		0.7	1.3	1.3
4-Carene	tr	0.7	9.1	6.4
<i>m</i> -Cymene	1.0	1.8	2.0	1.0
Limonene	,	1.9	2.0	1.8
1,8-Cineole	<i>tr</i>	0.5	8.3	20.2
Ocimene	27.4	39.8	10.0	10.6
Terpinen	4.3	5.5	19.0	12.6
Terpineol	0.2	0.4	2.7	1.1
<i>p</i> -Mentha-1,4-diene	tr	0.6	4.2	3.4
Unidentified	<i>tr</i> 0.3	$0.1 \\ 0.1$		
Linalool 1 Menthyl 4 isopropyl	0.5	0.1		
1-Menthyl-4-isopropyl- 2-cyclohexenol			1.2	1.8
	+4	0.1	1.2	1.0
Dimethyl octatetraene Camphor	<i>tr</i> 2.8	3.4	5.6	3.5
Trimethyl norbornanol	tr	0.1	0.1	0.1
Borneol	tr	0.1	0.1	0.1
p-Menth-1-en-ol	3.0	4.9	22.0	21.3
Benzylacetone	5.0	٦.۶	0.7	21.3 tr
2-Isopropyl-5-methyl-			0.7	u
3-cyclohexenone	0.1	0.2	0.4	0.1
Nonenal	0.1	0 .2	tr	0.2
Unidentified			0.3	0.1
Unidentified			0.1	tr
Dodecane	0.4	tr		
Copaene		0.1		
Santalene	tr	0.2	0.1	0.9
Caryophyllene	3.0	4.9	2.3	1.7
Dimethyl-6-				
methylpentenyl-2-				
norpinene			1.1	0.5
Unidentified	tr	0.1		
(Z)- β -Farnesene			0.3	0.2
β -Caryophyllene	2.1	1.9	0.6	0.6
Cubebene	0.1	tr		
Tetramethyl hexahydro-	-			
benzocycloheptene			0.2	0.1
Germacrene D	1.5	2.1	1.5	1.8
Eudesma-4,11-diene			0.7	0.1
Chamgrene			0.8	0.2
α -Farnesene	0.4	0.7		
Longipinene			0.8	0.6
Eudesma-3,7-diene			0.1	0.2
Cadina-1,4-diene	tr	0.1		
Ledol			0.7	
<i>n-trans-</i> Nerolidol			1.5	1.1
Denderalasin			0.1	tr
Spathulenol		0.4	0.1	tr

Table I. (cont.)

Compound	A. hainanensis		A. katsumadai	
•	Leaf	Flower	Leaf	Flower
Caryophyllene oxide	0.6	0.5	0.2	0.1
Unidentified	tr	0.2		
Dodecadienol acetate			0.1	tr
Cadinol	0.8			
Bisabolol			0.2	0.1
Unidentified			1.2	0.9
Tetradecanioc acid	0.4			
Benzyl benzoate	0.3	tr		
Sinensal			0.5	
Hexahydrofarnesyl				
acetone	0.5	0.2		
Unidentified	0.4	0.7		
trans-Bergamotol			0.1	tr
9-Hexadecenoic acid	1.0			
<i>n</i> -Hexadecanoic acid	5.8	0.5	0.4	1.0
Myristamide	0.8		0.1	
Isopropyl palmitate	0.9			
trans-Farnesyl actate	0.2	tr		
<i>n</i> -Heptadecanoic acid	0.4			
Unidentified	0.6		0.2	
Phytol			0.5	0.1
9,12-Octadecadienoic				
acid	5.4			
9-Octadecenoic acid	6.5			
Unidentified	3.4			
Hexadecanamide	4.0	tr	0.5	0.3
<i>n</i> -Tricosane	1.3			
9-Octadecenamide	2.0	0.9	1.1	2.2
Octadecanamide	1.8			
<i>n</i> -Pentacosane	2.1		0.1	

Numbers represent the percentage of each constituent in total essential oil.

and terpinen (4.3%). The major constituents identified in the flower oil were ocimene (39.8%), β -pinene (17.7%), terpinene (5.5%), p-menth-1-en-ol (4.9%), caryophyllene (4.9%), and phellandrene (4.4%).

In another species, *A. katsumadai*, a total of 44 and 36 compounds (about 96.8% and 98.5%) were identified from leaves and flowers, respectively.

The major constituents identified in the leaf oil of *A. katsumadai* were *p*-menth-1-en-ol (22.0%), terpinen (19.0%), 4-carene (9.1%), 1,8-cineole (8.3%), camphor (5.6%). The major constituents in the flower oil were *p*-menth-1-en-ol (21.3%), 1,8-cineole (20.2%), terpinen (12.6%), phellandrene (7.0%), 4-carene (6.4%), and β -pinene (5.2%).

Of the major constituents of essential oils in A. hainanensis and A. katsumadai, four constituents, *i.e.* β -pinene, 1,8-cineole, p-menth-1-en-ol, and ocimene, have strong antimicrobial activities (Juliani et al., 2002; Faleiro et al., 2003; Kim et al., 2003) and 1,8-cineole has also cardiovascular effects (Lahlou et al., 2002). However, the main components were diversified, which led to different effects in some Alpinia species (Zoghbi et al., 1999; Raina et al., 2002). On the other hand, the composition variations of essential oils in Alpinia species have chemotaxonomic implications. Although some authors suggested that the four Alpinia species, i.e. A. hainanensis, A. katsumadai, A. henryi, and A. kainantensis, should be merged into one species A. hainanensis based on morphological characters (Wu, 1997). Our study shows that there are significant differences between the chemical constituents from essential oils of A. hainanensis and A. katsumadai. It is obvious that further comparative studies of chemical constituents of essential oils in *Alpinia* are necessary.

Acknowledgements

We would like to thank Professor Suhua Shi of Zhongshan University and Mr. Shaowei Chen of Bawangling National Nature Reserve for Black-crested Gibbon for their help in fieldwork. This study was partially supported by Chinese National Key Project for Basic Research (973) (2002 CB 512801) and Chinese PostDoc Foundation (2003033270).

tr: Trace quantities (< 0.1%).

- Ali S., Sotheeswaran S., Tuiwawa M., and Smith R.-M. (2002), Comparison of the composition of essential oils of *Alpinia* and *Hedychium* species essential oils of Fijian plants, part 1. J. Essent. Oil Res. **14**, 409–411.
- Faleiro M.-L., Miguel M.-G., Ladeiro F., Venancio F., Tavares R., Brito J.-C., Figueiredo A.-C., Barroso J.-G., and Pedro L.-G. (2003), Antimicrobial activity of essential oils isolated from Portuguese endemic species of *Thymus*. Lett. Appl. Microbiol. 36, 35–40.
- Ficker C.-E., Smith M.-L., Susiarti S., Leaman D.-J., Irawati C., and Arnason J.-T. (2003), Inhibition of human pathogenic fungi by members of Zingiberaceae used by the Kenyah (Indonesian Borneo). J. Ethnopharmacol. 85, 289–293.
- Habsah M., Amran M., Mackeen M.-M., Lajis N.-H., Kikuzaki H., Nakatani N., Rahman A.-A., Ghafar, and Ali A.-M. (2000), Screening of Zingiberaceae extracts for antimicrobial and antioxidant activities. J. Ethnopharmacol. 72, 403–410.
- Jitoe A., Masuda T., Tengah I.-G.-P., Suprapta D.-N., Gara I.-W., and Nakatani N. (1992), Antioxidant activity of tropical ginger extracts and analysis of the contained curcuminoids. J. Agric. Food Chem. 40, 1337-1340.
- Joseph R., Joseph T., and Joseph J. (2001), Volatile essential oil constituents of *Alpinia smithiae* (Zingiberaceae). Rev. Biol. Trop. **49**, 509–512.
- Juliani H.-R., Biurrun F., Koroch A.-R., Oliva M.-M., Demo M.-M., Trippi V.-S., and Zygadlo J.-A. (2002), Chemical constituents and antimicrobial activity of the essential oil of *Lantana xenica*. Planta Med. 68, 762–764.
- Kim K.-J., Kim Y.-H., Jeong S.-I., Cha J.-D., Kil B.-S., and You Y.-O. (2003), Antibacterial activity and

- chemical composition of essential oil of *Chrysanthe-mum boreale*. Planta Med. **69**, 274–277.
- Lahlou S., Figueiredo A.-F., Magalhaes P.-J.-C., and Leal-Cardoso J.-H. (2002), Cardiovascular effects of 1,8-cineole, a terpenoid oxide present in many plant essential oils, on normtensive rats. Can. J. Physiol. Pharm. **80**, 1125–1131.
- Lemmon R.-S. and Sherman C.-L. (1964), Flowers of the World. Doubleday, New York.
- Lötschert W. and Beese G. (1983), Guia de plantas tropicales. Ed. Omega, Barcelona.
- Mallavarapu G.-P., Pao L.-M., Ramesh S., Dimri B.-P., Rao B.-R.-R., Kaul P.-N., and Bhattacharya A.-K. (2002), Composition of the volatile oils of *Alpinia galangal* rhizomes and leaves from India. J. Essent. Oil Res. **14**, 397–399.
- Miyazawa M. and Hashimoto Y. (2002), Antimicrobial and bactericidal activities of esters of 2-endo-hydroxy-1,8-cineole as new aroma chemicals. J. Agric. Food Chem. **50**, 3522–3526.
- Raina V.-K., Srivastava S.-K., and Syamasunder K.-V. (2002), The essential oil of 'greater galangal' [*Alpinia galangal* (L.) willd] from the lower Himalayan region of India. Flavour Fragr. J. **17**, 358–360.
- Shin D., Kinoshita K., Koyama K., and Takahashi K. (2002), Antiemetic principles of *Alpinia officinarum*. J. Nat. Prod. **65**,1315–1318.
- Wu T. -L. (1997), Notes on the Lowiaceae, Musaceae, and Zingiberaceae for the Flora of China. Novon 7, 440–442.
- Zoghbi M., Andrade E., and Maia J. (1999), Volatile constituents from leaves and flowers of *Alpinia speciosa* K. Schum., and *A. purpurata* (Viell.) Schum. Flavour Fragr. J. **14**, 411–414.