American Journal of Essential Oils and Natural Products
Available online at www.essencejournal.com
AJEONP American Journal of Essential Oils and Natural Products
AkiNik

ISSN: 2321 9114
AJEONP 2016; 4(4): 09-11

Received: 04-08-2016
Accepted: 05-09-2016

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GC and GC-MS analysis of the fresh flower essential oil of *Cananga odorata* (Lam.) Hook. f. et Th. var. *fruticosa* (Craib) J. Sincl.

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Abstract
C*ananga odorata* (Lam.) Hook. f. et Th. var. *fruticosa* (Craib) J. Sincl. is a less well-known ylang-ylang species. The flower essential oil of the plant growing in northern Vietnam was analyzed for the first time in this study using GC and GC-MS analysis. The identification of the main constituents α-humulene (7.1%), germacrene D (8.1%), (*E*, *E*)-α-farnesene (12.6%), (*E*, *E*)-farnesol (5.6%) and benzyl benzoate (3.8%) agrees well with the results previously reported for ylang-ylang (*C. odorata*) oils. The major aroma constituents of the oil were identified as linalool (8.7%) and β-caryophyllene (26.8%).

Keywords: Linalool, β-caryophyllene, α-humulene, (*E*, *E*)-α-farnesene, germacrene D, *Cananga odorata* var. *fruticosa*

1. Introduction
Ylang-ylang (cananga) oil is an important ingredient in fragrance products such as perfumes, creams, lotions, soap and detergent. The oil is primarily extracted from the fresh flowers of *Cananga odorata* (Lam.) Hook. f. & Thomson (syn. *Canangium odoratum* Baill. *forma macrophylla*) (family Annonaceae) by hydrodistillation and the quality of the oils is differentiated on the basis of their chemical constituents [1, 2]. Obviously, a number of studies have been performed in terms of extraction methods, conditions of the flowers, and origins of the flowers to find out the compositional variation of the oils [3-6]. Several characteristic compounds for the oil aroma such as *p*-cresyl methyl ether and methyl salicylate (medicinal odor of the oil), linalool, α-terpineol, and geraniol (floral odor), methyl benzoate and eugenol (spicy/balsamic odor), benzyl acetate (fruity odor), cadinene and β-caryophyllene (woody odor) were determined [2]. The quality of the oil increases with the content of light-oxygenated compounds [4] (alcohols, esters and phenol derivatives) such as *p*-methylanisole, linalool, methyl benzoate, methyl salicylate and benzyl acetate. Benzyl benzoate and some sesquiterpenoids, (*E*, *E*)-farnesene, α-humulene, germacrene D and (*E*, *E*)-farnesol were found as main components in ylang-ylang oils [1-6]; they are not important odor contributors to the oil but can be used in addition to the main aroma compounds to characterize ylang-ylang oils. The less well-known ylang-ylang species, *C. odorata* (Lam.) Hook. f. et Th. var. *fruticosa* (Craib) J. Sincl., was taxonomically identified in northern Vietnam. To examine the possibility of the flower oil of this plant as a substitute for the ylang-ylang oil, the oil was analyzed by GC and GC-MS and the chromatographic and mass data obtained were compared with the library data generated under identical conditions.

2. Materials and Methods
2.1 Plant material
The fresh yellow flowers of *C. odorata* (Lam.) Hook. f. et Th. var. *fruticosa* (Craib) J. Sincl. (Annonacae) were collected in Hanoi, Vietnam. The plant was identified by Professor Vu Van Chuyen of Hanoi College of Pharmacy (Hanoi, Vietnam). A voucher specimen (No. HCTC 701) was deposited in the Laboratory of Chemistry of Natural Products, College of Natural Science, Vietnam National University, Hanoi.

2.2 Oil preparation
The fresh flowers were subjected to hydrodistillation using a Clevenger-type apparatus for 6 h to produce a pleasant-smelling oil of 1.1% yield (w/w). The oil was stored at 4 ºC for gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analysis.

2.3 GC and GC-MS analysis
An Orion Micromat 412 gas chromatograph equipped with two fused silica capillary columns (25 m × 0.25 mm i.d., 0.15 µm film thickness) coated with CP-Sil-5-CB and CP-Sil-19-CB, respectively, was used. Split injection and flame ionization detection (FID) were used for GC analysis. The injector and detector temperatures were maintained at 200 and 250 ºC, respectively. The oven temperature was programmed from 50 to 250 ºC at 3 ºC/min. The carrier gas was H_2 at 1.2 mL/min. A Hewlett-Packard HP 5890 gas chromatograph coupled to a VG Analytical 70-250S mass spectrometer was used for GC-MS analysis. The GC was fitted with a fused silica capillary column coated with CP-Sil5-CB (25 m × 0.25 mm i.d., 0.15 µm film thickness). The GC operating conditions were identical with those described above for GC analysis except that helium was used as carrier gas. As EI-MS operating parameters the ionization voltage was 70 eV and the ion source temperature was 230 ºC.

3. Results and Discussion
The essential oil of the fresh flowers of *C. odorata* (Lam.) Hook. f. et Th. var. *fruticosa* (Craib) J. Sincl. was analyzed by dual GC on a non-polar CP-Sil-5-CB and a more polar CP-Sil-19-CB capillary column of identical dimensions. GC-MS analysis was performed with a CP-Sil-5-CB column using the same operating conditions of the GC analysis. The identification of the oil constituents was carried out by using a computer-supported spectral library MassFinder 2.3 which allowed simultaneous comparison of retention indices and EI mass spectra [7, 8] obtained under identical experimental conditions. The relative percentages of the oil components were calculated by peak normalization using the GC CP-Sil-5-CB capillary column. Forty-three components (Table 1) were identified, constituting 90% of the oil. Thirteen monoterpenoids including monoterpene hydrocarbons (4%) and oxygenated monoterpenoids (9.2%), twenty-seven sesquiterpenoids including sesquiterpene hydrocarbons (60.7%) and oxygenated sesquiterpenoids (11.3%), and three aromatic compounds (4.8%) were identified. The major aroma compounds, *p*-methylanisole (0.6%), linalool (8.7%), and β-caryophyllene (26.8%) were identified in the oil. In comparison with the reported values for the Extra Grade ylang-ylang oil [1, 2], this oil is characterized by low concentration of *p*-methylanisole and almost four-fold concentration of β-caryophyllene. α-Terpineol (0.2%) and cadinenes (α-, δ-, and γ-: 2%) were also detected, however, the chemical composition of this oil differs from that of the reported ylang-ylang oils by the absence of a number of the light-oxygenated compounds [2]. High contents of the common constituents of ylang-ylang oils such as (*E*, *E*)-α-farnesene (12.6%), α-humulene (7.1%), germacrene D (8.1%), (*E*,*E*)-farnesol (5.6%), together with benzyl benzoate (3.8%) were noticeable.

Table 1: Chemical constituents of the fresh flower oil *C. odorata* var. *fruticosa*

No.	RI	Compound	Content (%)
1	926	α-Thujene	0.1
2	935	α-Pinene	0.3
3	970	Sabinene	0.2
4	974	β-Pinene	0.1
5	983	Myrcene	0.5
6	1004	*p*-Methylanisole	0.6
7	1013	α-Terpinene	0.3
8	1016	*p*-Cymene	1.0
9	1041	(*E*)-β-Ocimene	1.2
10	1055	γ-Terpinene	0.1
11	1083	Terpinolene	0.2
12	1087	Linalool	8.7
13	1168	Terpinen-4-ol	0.3
14	1178	α-Terpineol	0.2
15	1354	α-Cubebene	*tr*
16	1375	Methyl eugenol	0.4
17	1379	α-Copaene	1.1
18	1390	β-Elemene	0.5
19	1420	β-Caryophyllene	26.8
20	1430	β-Copaene	0.1
21	1446	Sesquisabinene B	0.1
22	1453	α-Humulene	7.1
23	1455	ε-Muurolene	0.6
24	1462	Allo-aromadendrene	0.1
25	1474	γ-Muurolene	0.6
26	1479	Germacrene D	8.1
27	1488	Eremophyla-1(10),7-diene	0.2
28	1498	(*E*,*E*)-α-Farnesene	12.6
29	1512	γ-Cadinene	0.2
30	1517	*cis*-Calamenene	0.3
31	1520	δ-Cadinene	1.6
32	1521	(*E*)-γ-Bisabolene	0.4
33	1523	Cadina-1,4-diene	0.1
34	1534	α-Cadinene	0.2
35	1568	Spathulenol	0.4
36	1573	Caryophyllene epoxide	1.9
37	- [b)]	Humulene epoxide [c)]	0.5
38	1630	T-Cadinol	0.7
39	1632	T-Muurolol	0.4
40	1642	α-Cadinol	1.1
41	1706	(*E*,*E*)-Farnesol	5.6
42	1731	Benzyl benzoate	3.8
43	1818	(*E*,*E*)-Farnesyl acetate	0.7

[a)] *tr* < 0.05%
[b)] Compound was identified by EI-MS
[c)] correct isomer was not identified

4. Conclusions
The essential oil of the fresh flowers of *C. odorata* (Lam.) Hook.f. et Th. var. *fruticosa* (Craib) J. Sincl. was determined for the first time. The identification of the main constituents α-humulene (7.1%), germacrene D (8.1%), (*E*, *E*)-α-farnesene (12.6%), (*E*, *E*)-farnesol (5.6%), and benzyl benzoate (3.8%) agrees well with the reported constituents of ylang-ylang oil. The oil differs from ylang-ylang oil by high content of β-caryophyllene (26.8%) and the absence of a number of the light-oxygenated compounds.

5. Acknowledgments
We thank the late Professor Wilfried A. König (Institut für Organische Chemie, Universität Hamburg, Hamburg, Germany) for the provision of GC and GC-MS facilities.

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