Essential oil constituents of *Chimonanthus fragrans* flowers population of Tehran

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ABSTRACT

Chimonanthus fragrans Lindle (Calycanthaceae) is an aromatic plant which little information has been reported so far on the composition of its essential oil. In this study the essential oil of flower of this plant was obtained by hydrodistillation and analyzed by GC and GC-MS. Forty nine components were identified corresponding to *ca*. 98.12 % of the total components of the essential oil with 0.12 % yield. The major components were elemol (20.06%), β–caryophyllene (9.51%), β–elemene (8.65%), bicyclogermacrene (8.15%), γ–elemene (7.2%), germacrene–D (5.65%), trans–β–ocimene (5.5%), sabinene (3.65%), linalool (2.6%), caryophyllene oxide (2.3%), and δ–cadinene (1.95%). Comparison of the data of this study with other data including recent report by HS-SPME-GC-MS showed quantitative and qualitative differences due to geographical, agricultural, and technical factors.

Keywords: *Chimonanthus fragrans*, Calycanthaceae, Essential oil, Elemol

INTRODUCTION

The Family, Calycanthaceae is native to China and North America and has only two genera of Chimonanthus (Chinese or Asian origin) and Calycanthus (American origin) and 6 species (1, 2). *Chimonanthus fragrans* Lindle (Gol-e Yakh in Iran, La Mei in China, Roubai in Japan and winter sweet in England; Fig. 1) is an aromatic, perennial shrub or small tree which has been called by various synonyms such as *Calycanthus praecox* L.; *Meratia praeox* Rehd. & Wils.; *Chimonanthus praecox* (L.) Link (3). The plant is native to China, Japan and cultivated in Iran and other countries. The infusion of the flower has been traditionally used for treatment of mouth and throat wounds and as diuretics in China (3). Its root is also used as an analgesic for rheumatoid pains (4). Reviewing literature showed only few reports on the constituents of essential oil of the flower of this plant have been published and the main aromatic compounds present in the flower of this plant deserves further investigation. The aim of this study was to compare volatile components of flowers of this population with those reported for the same flower from other locations.

MATERIAL AND METHODS

Plant material and essential oil

The fresh flowers were collected from Amirabad district of Tehran province (Capital of Iran) in February 2005 during the flowering stage. Voucher specimen (No. 4438-TEH) was deposited in the Herbarium of Faculty of Pharmacy, Tehran University of Medical Sciences. The essential oil was obtained from fresh flowers of the plant by hydrodistillation for 3 hrs using a Clevenger-type apparatus. The pale yellow isolated oil (0.12 % v/w) was dried over anhydrous sodium sulfate and preserved in a sealed flask at 4-10 °C until analysis.

Analysis of the volatile oil by GC

The essential oil of *C. fragrans* was analyzed by GC-FID using a Hewlett-Packard 6890 gas chromatograph equipped with fused silica capillary column coated with methyl silicone (HP-5), 30 m x 0.25 mm i.d. (film thickness 0.25 µm). Analytical conditions were; carrier gas: He (5 ml/min); split ratio 1:60; injector temperature: 250 °C; detector temperature: 270 °C. The column temperature was programmed from 60 °C (2 min) to 240 °C at a rate of 4 °C/min and then kept at 240 °C for 20 min.

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Figure 1. *Chimonanthus fragrans* L. flower

Analysis of the volatile oil by GC/MS

GC/MS analysis was performed on a Hewlett-Packard (HP-5973) instrument equipped with Wiley library search spectral data system. The data were obtained on a 5% methyl silicone fused silica capillary column (HP-5), 30 m x 0.25 mm i.d. (film thickness 0.25 µm) installed in a Hewlett-Packard 6890 gas chromatograph. Operation conditions were: carrier gas: He (1.5 ml/min); column oven temperature program: 60°C (2 min), 60-240°C at 4°C/min; injection port and jet separator temperature: 250°C; ionization voltage: 70 eV; ionization current: 60 µA; scanning speed: 1s over 30-400 amu range; split ratio; 1:100. Identification of the components was based on comparison of their mass spectra with those reported in the literatures (6-8) and by computer search of their 70 eV mass spectra with those stored in the Wiley library of the GC/MS data system (7), as well as by retention indices (RRI, HP-5). Retention indices were calculated using retention times of *n*-alkanes that were injected after the oil under the same chromatographic conditions.

RESULTS AND DISCUSSION

The hydrodistillation of the fresh flowers of *C. fragrans* gave pale yellow oil with a yield of 0.12 % (v/v), based on the dry weight. The general chemical profiles of the identified compounds, the percentage of the individual components and their retention indices are summarized in Table 1.

Gas chromatogram showed the presence of more than fifty compounds. Forty-nine compounds (representing *ca*. 98.12 % of the total detected constituents) were identified and the oil is characterized by the presence of large amounts of sesquiterpenic hydrocarbons (79.2%) and monoterpenes (12.92%). The main components were elemol (20.06%), β–caryophyllene (9.51%), β–elemene (8.65%), bicyclogermacrene (8.15%), γ–elemene (7.2%), germacrene–D (5.65%), trans–β–ocimene (5.5%), sabinene (3.65%), linalool (2.6%), caryophyllene oxide (2.3%), and δ–cadinene (2.20%). Some unidentified compounds were observed within mass spectra similar to those of certain sesquiterpenoids, but did not match with any known structures in the data banks, which was employed.

Although comparison of the compounds obtained in this study with two other reports, that is Shiraz (9) and China (2) populations show some similarities, but there are considerable quantitative and qualitative differences between these three samples. This comparison also revealed that there are considerable differences even within the two samples from two different locations of Iran. For example, ten out of 23 compounds reported for Tehran sample and 5 out of 18 compounds reported for Shiraz sample were not found respectively in each other's. Furthermore, while the oils of two samples are rich in sesquiterpene, elemol one of the major compounds of Tehran sample, with a fresh long lasting fragrance, is not reported in Shiraz sample (9). The differences may be attributed to the environmental and agricultural factors.

Recently the essential oil of the same flower is analyzed (10) by a new reported extraction technique, which is called Headspace Solid-Phase Microextraction (HS-SPME), and GC-MS technique (11). This technique is used to compare the volatile constituents of *C. praecox* flower (population Shanghai) emitted from living flowers with those from the excised flowers (10). It is claimed that from thirty-one compounds emitted from living flowers all except three compounds were found in excised flowers. There are large quantitative and qualitative differences between compounds detected by new HS-SPME technique with those obtained by classical hydrodistillation method. Among the 32 compounds detected by this new technique, only 4 compounds were identified by the hydrodistillation method. Linalool (35.95 %), which was the highest constituent by SPME technique, was found in very low amount in this study (2.6 %) and in a report from China (10).

Table 1. Chemical composition of the essential oil of flower of *Chimonanthus fragrans* flowers population of Tehran (Iran)

No.	Components	RRI [a]	%	No.	Components	RRI [a]	%
1	α-pinene	931	0.05	26	α-humulene	1456	1.72
2	sabinene	972	3.65	27	allo-aromadendrene	1460	0.07
3	myrcene	989	0.07	28	germacrene-D	1484	5.65
4	α-phellandrene	1003	0.30	29	β-selinene	1488	0.20
5	p-cymene	1023	0.10	30	cis-β-guaiene	1493	0.24
6	limonene	1027	0.25	31	bicyclogermacrene	1500	8.15
7	cis-β-ocimene	1036	0.07	32	β-bisabolene	1507	0.60
8	trans-β-ocimene	1049	5.50	33	α-farnesene	1510	0.85
9	γ-terpinene	1058	0.12	34	γ-cadinene	1519	1.95
10	linalool	1103	2.60	35	δ-cadinene	1526	2.20
11	nonanal	1106	2.05	36	α-calacorene	1546	0.40
12	benzyl acetate	1165	0.72	37	elemol	1560	20.06
13	nonanol	1173	0.31	38	germacrene-B	1563	1.75
14	terpinene-4-ol	1178	0.16	39	trans-nerodiol	1568	0.85
15	Unidentified	1338	2.50	40	germacradien-4-ol	1579	0.45
16	α-cubebene	1350	0.18	41	spathulenol	1583	0.43
17	eugenol	1360	0.22	42	caryophyllen oxide	1588	2.30
18	α-copaene	1376	0.75	43	eudesmol (10-epi gamma)	1623	0.50
19	α-elemene	1386	0.50	44	γ-eudesmol	1635	0.65
20	β-elemene	1396	8.65	45	torreyol	1645	0.70
21	β-caryophyllene	1424	9.51	46	β-eudesmol	1654	0.65
22	epi-bicyclosesqui phellandrene	1430	0.12	47	α-eudesmol	1657	1.20
23	γ-elemene	1438	7.20	48	14-OH-9-epi-β-caryophyllene	1662	0.60
24	α-guaiene	1441	0.12	49	n-nonadecane	1898	0.05
25	*trans*-cinnamyl acetate	1448	0.20				

[a] RRI: relative retention indices on HP-5 capillary column.

Furthermore, 3 compounds which were absent in excised flower by HS-SPME technique were considered as biomarkers for living flowers of *C. praecox* (10). From the result of this study it appears that other than geographical and agricultural factors, the harvesting time, the technique of oil separation and the existence of different chemotypes must be considered as important parameters. Also it may concluded that some volatile compounds might be lost in the usual hydrodistillation method. Further studies are required to elucidate the advantages of HS-SPME technique in comparison with classical method of hydrodistillation.

REFERENCES

1. Ghahreman A. Flora of Iran. Research Institute of Forests and Rangelands Publication. Tehran, 1997. Vol: 16. No. 1908, Code 001, 002, 04.
2. Beijing D, Xuebao Z. Fragrance of *Chimonathus praecox* L. flowers. Keuxeban 1990; 26: 667–673 (through C. A. 1991, 115: 46026j).
3. Ueyama Y, Hashimoto S, Nii H, Furukawa K. The volatile constituents of the flower concrete of *Chimonanthus praecox* Link. from China. Flavour Fragr J 1990; 5: 85-88.
4. Zheng Y, Zhu Y, Zhang R, Sun Y, Wu Z, Liu M. Studies on the natural flavour components of *Chimonanthus praecox* L. Acta Sci Nat Univ Pekin 1990; 26: 667-673.
5. Duke JA, Ayensu ES. Medicinal Plants of China, Reference Publications, Inc. Michigan. 1985.
6. Ryhage R, Sydow EV. Mass spectrometry of terpenes I: Monoterpene Hydrocarbons. Acta Chem Scand 1963; 17: 2025–2035.
7. Massada Y. Analysis of Essential Oil by Chromatography and Spectrometry. John Wiley and Sons Inc., New York. 1976. p. 65-145.
8. Adams RP. Identification of Essential Oil Components by Gas Chromatography-Mass Spectroscopy. Allured, Publ. Corp., Illinois; 2001. p. 69-351.
9. Javidnia K, Miri R, Cheriki M, Shafiee A. Constituents of the essential oil of *Chimonanthus fragrance*. Daru 1999; 7: 25-26.
10. Deng C, Song G, Hu Y. Rapid determination of volatile compounds emitted from *Chimonanthus praecox* flowers by HS-SPME-GC-MS. Z Naturforsch 2004; 59c: 636-640.
11. Pawliszyn J. (Ed.), Applications of Solid Phase Microextraction, Royal Society of Chemistry, Cambridge, 1999. p. 3.