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Volatile composition of the peel and leaf essential oils of *Citrus nobilis* Lour. var *deliciosa* Swingle

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The fruits and leaves of Citrus nobilis Lour. var deliciosa Swingle were collected from south of Iran and their essential oils were analysed by gas chromatography-mass spectrophotometry (GC-MS). The oil yields of the fresh peel and leaves obtained separately by hydrodistillation were 1.2 and 0.2% (V/W), respectively. 17 components accounting for 99.2% of the peel oil and 34 components accounting for 98.5% of the leaf oil were identified. The main classes of compounds were found to be monoterpenes [monoterpene hydrocarbons (96.0%) and monoterpene alcohols (1.8%)] in the peel oil and monoterpenes [monoterpene hydrocarbons (47.6%), monoterpene alcohols (36.9%)] and sesquiterpenes [sesquiterpene hydrocarbons (2.9%) and sesquiterpene alcohols (3.7%)] in the leaf oil. The major constituent of the peel oil were limonene (87.8%) and γ-terpinene (6.1%), while the major constituents of the leaf oil were linalool (32.8%), sabinene (28.8), (E)-β-ocimene (6.2%) and limonene (5.2%).

Key words: Citrus nobilis Lour., chemical composition, essential oils, class composition.

INTRODUCTION

The genus *Citrus* belongs to Rutaceae family which includes approximately 160 genera and 1700 species (Hadjiakhundi and Baligh, 2005). Many *Citrus* species and/or their essential oils are commonly used in the foods, drugs, cosmetics, perfumery industries and soap products (Monajemi et al., 2005). Limonene is what gives *Citrus* oils their familiar aroma, and is therefore used in perfume and household cleaners for its fragrance. Recently, interest has shifted from volatile oil of the fruit to that of the *Citrus* leaves that are rich in limonene, and leaf oil has become a new source of *Citrus* essential oil because the leaves grow much faster than the fruits and are available all year long (Cheng and Lee, 2007).

Citrus nobilis Lour. Var *deliciosa* Swingle (Bam mandarin) is one of about 10 species of Iranian *Citrus* which is found in Bam, a city in southern part of Iran. The commercial cultivation of mandarin in Iran has developed mostly in Kerman (Bam), Gilan and Mazandaran. The average amount of crop is 90,000 T, of which about

50,000 T are exported. The infusion of the peel have been widely used as tonic, diuretic, antipyretic, laxative and anti-inflammatory in Iranian traditional medicine (Zargari, 1990). However, the essential oils of peel and leaves of *C. nobilis* Lour. var *deliciosa* Swingle which grows in Bam, Iran has not been investigated before. Therefore, due to the widespread use of *Citrus* oil, it was worthwhile to identify the chemical composition of samples of *C. nobilis* Lour. var *deliciosa* Swingle oil from Bam, Iran.

MATERIALS AND METHODS

Fresh fruits and leaves of *C. nobilis* Lour. var *deliciosa* Swingle were collected from Bam, south of Iran, in January 2009. The plant was identified by Dr. G. H. Amin. A voucher specimen has been deposited at the herbarium of Pharmacy Faculty, Tehran University of Medical Sciences, Tehran, Iran, under code number 1922.

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The fresh peel (100 g) and dried leaves (100 g) were separately submitted for hydrodistillation in a Clevenger-type apparatus for 3 h. At the end of each distillation, the oils were collected, dried with anhydrous Sodium sulfate (Na_2SO_4), measured, and then transferred to glass flasks that were filled to the top and kept at a temperature of -18°C for further analysis (Morteza-Semnani and Akbarzadeh, 2009).

Compoundª	RI ^b	RI°	Percentage
α-Thujene	925	931	0.4
α-Pinene	932	939	2.1
Sabinene	976	976	1.2
Myrcene	983	991	4
Limonene	1022	1031	81.8
γ-Terpinene	1053	1062	6.1
Terpinolene	1083	1088	0.4
Linalool	1086	1098	0.9
trans-Limonene oxide	1139	1139	0.3
Terpinene-4-ol	1177	1177	0.5
α-Terpineol	1189	1189	0.2
Carvone	1242	1242	0.3
Geranyl acetate	1383	1383	0.2
β-Elemene	1391	1391	0.3
Germacrene-D	1480	1480	0.1
α-Farnesene	1508	1508	0.3
δ-Cadinene	1524	1524	0.1
Total			99.2

 Table 1. Chemical composition of the essential oil of C. nobilis Lour. var deliciosa Swingle peel.

^aCompounds listed in order of elution. ^bRI measured relative to n-alkanes (C9-C18) on the nonpolar DB-5 column under condition listed earlier. ^cRI, from literature. RI, Retention index.

 Table 2. Class composition of C. nobilis Lour. var deliciosa Swingle

 peel essential oil.

Class of compound	Percentage		
Monoterpene hydrocarbons	96		
Monoterpene alcohols	1.8		
Others	1.4		
Total	99.2		

Analysis of the essential oils

Oil sample analyses were performed on an Hp-6890 gas chromatograph equipped with a flame ionization detector (FID) and a DB-5 capillary column, 30 m × 0.25 mm, 0.25 μ M film thickness and temperature programmed as follows: 60 to 240 °C at 4 °C/min. The carrier gas was nitrogen (N₂) at a flow of 2.0 ml/min; injector port and detector temperature were 250 and 300 °C, respectively. Samples (1 μ L) were injected by splitting and the split ratio was 1:10.

Gas chromatography-mass spectrophotometry (GC-MS) analysis was performed on a Hewlett-Packard 6890/5972 system with a HP-5MS capillary column (30 m × 0.25 mm; 0.25 μ M film thickness). The operating conditions were the same conditions as described above but the carrier gas was helium (He). Mass spectra were taken at 70 eV. Scan mass range was from 40 to 400 m/z at a sampling rate of 1.0 scan/s. Quantitative data were obtained from the electronic integration of the FID peak areas. The components of the oils were identified by comparison of their mass spectra and retention indices with those published in the literature (Adams, 2007) and presented in the MS computer library (WILEY275.L).

RESULTS AND DISCUSSION

The hydrodistillation of the peel of *C. nobilis* Lour. var *deliciosa* Swingle gave yellowish oil with a yield of 1.2% (V/W), on fresh weight basis. The oil was analyzed by GC-MS. 17 components were identified in the oil, which represented about 99.2% of the total detected constituents. The general chemical profiles of the tested oil, the percentage content of the individual components, retention indices and retention times are summarized in Table 1. The chemical class distribution of the oil components was also reported in Table 2.

From Table 2, it is evident that the main class of components was monoterpenes which was a form of monoterpene hydrocarbons (RI range: 925 to 1083) and monoterpene alcohols (RI range: 1177 to 1383). As indicated in Table 2, monoterpenes [monoterpene hydrocarbons (96.0%) and monoterpene alcohols (1.8%)] were

Compound ^a	RI⁵	RI ^c	Percentage
α-Thujene	925	931	0.3
α-Pinene	932	939	1.7
Sabinene	976	976	28.8
Myrcene	983	991	3.1
Limonene	1022	1031	5.2
cis-Ocimene	1027	1040	0.5
trans-Ocimene	1050	1050	6.2
γ-Terpinene	1053	1062	1.1
cis-Menthenol	1072	1086	0.4
p-Cymenene	1082	1089	0.7
Linalool	1086	1098	32.8
trans-Menthenol	1140	1140	0.1
β-Terpineol	1144	1144	0.1
Terpinene-4-ol	1177	1177	3.5
α-Terpineol	1189	1189	0.5
Thymol methyl ether	1235	1235	3.6
Thymol	1290	1290	0.4
δ-Elemene	1319	1339	0.2
β-Elemene	1391	1391	0.4
β-Caryophyllene	1418	1418	0.6
γ-Elemene	1433	1433	0.4
β-Farnesene	1458	1458	0.4
Germacrene-D	1480	1480	0.2
Germacrene-A	1494	1503	0.4
α-Farnesene	1508	1508	0.1
δ-Cadinene	1524	1524	0.2
Nerolidol	1534	1534	0.3
Elemol	1549	1549	0.2
Spathulenol	1576	1576	2
Cadinol	1640	1640	0.6
Muurolol	1645	1645	0.6
β-Sinensal	1695	1695	1.7
α-Sinensal	1752	1752	1
Phytol	1949	1949	0.2
Total			98.5

 Table 3.
 Chemical composition of the essential oil of *C. nobilis* Lour. var *deliciosa* Swingle leaf.

^aCompounds listed in order of elution. ^bRI measured relative to n-alkanes (C9-C18) on the nonpolar DB-5 column under condition listed earlier. ^cRI, from literature. RI, Retention index.

the main constituents of the peel oil. The major constituents of the peel oil were limonene (87.8%) and γ -terpinene (6.1%). Other components were present in amount less than 5% (Table 1). The hydrodistillation of the leaves of *C. nobilis* Lour. var *deliciosa* Swingle gave yellowish oil with a yield of 0.2% (V/W), on dry weight basis. The oil was analyzed by GC/MS. Thirty-four components were identified in the oil, which represented about 98.5% of the total detected constituents. The general chemical profiles of the tested oil, the percentage content of the individual components, retention indices and retention times are summarized in Table 3. The

chemical class distribution of the oil components is also reported in Table 4.

From Table 4, it is evident that the components could be divided into two major groups. The first one composed of monoterpene hydrocarbons (RI range: 925 to 1053) and monoterpene alcohols (RI range: 1086 to 1189) and the second one formed sesquiterpene hydrocarbons (RI range: 1319 to 1524) and sesquiterpene alcohols (RI range: 1534 to 1645). In addition, as indicated in Table 4, monoterpenoides [monoterpene hydrocarbons (47.6%) and monoterpene alcohols (36.9%)] and sesquiterpenoids [sesquiterpene hydrocarbons (2.9%) and

Class of compound	Percentage
Monoterpene hydrocarbons	47.6
Monoterpene alcohols	36.9
Sesquiterpene hydrocarbons	2.9
Sesquiterpene alcohol	3.7
Others	7.4

 Table 4. Class composition of C. nobilis Lour. var deliciosa Swingle

 leaf essential oil.

sesquiterpene alcohols (3.7%)] were the main constituents of the leaf oil. The major constituents of the leaf oil were linalool (32.8%), sabinene (28.8), transocimene (6.2%) and limonene (5.2%). Other components were present in amount less than 5% (Table 3).

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