African Journal of Biotechnology Vol. 7 (9), pp. 1261-1264, 2 May, 2008
Available online at http://www.academicjournals.org/AJB
DOI: 10.5897/AJB08.033
ISSN 1684–5315 © 2008 Academic Journals

Full Length Research Paper

Chemical composition of essential oil from the peel of Satsuma mandarin

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Accepted 7 March, 2008

The chemical composition of the essential oil obtained from the peel of Satsuma mandarin was analyzed by GC/MS analysis. As a result, 28 components were isolated. Among the 25 components identified, the monoterpenes hydrocarbons group was predominant, accounting for 86.62% (w/w) of the total oil. Of which, limonene was the most abundant (67.44%), followed by β-myrcene (7.15%), 3-carene (4.4%), α-pinene (2.52%), *p*-cymene (2.43%), β-pinene (1.46%), sabinene (0.77%), terpinolene (0.47%) and α-thujene (0.45%). Oxygenated monoterpenes (6.33%) and sesquiterpene (3.43%) were also present in the oil.

Key words: Essential oil, peel, GC/MS, limonene, Satsuma mandarin.

INTRODUCTION

Citrus is one of the most important commercial fruit crops grown in all continents of the world (Tao et al., 2007). According to the FAO report in 2005, citrus in China covers a cultivating area of 17.1 million hm^2, with a production of almost 16 million tons. In current citrus industry, citrus fruits are marketed fresh or as processed juice and canned segments, while fruit peel is produced in great quantities and normally regarded mainly as waste. For this reason, researchers have focused on the utilization of citrus products and by-products (Kubo et al., 2005; Wu et al., 2007).

Essential oil was one of the citrus by-products attracting keen interests of people (Njoroge et al., 2005). In recent years, the citrus essential oil has been identified in different parts of fruits as well as in leaves (preferably present in fruit flavedo), showing that limonene, β-myrcene, 3-carene, α-pinene, *p*-cymene, β-pinene, sabinene, terpinolene and other elements are the major aromatic compounds of many citrus species (Stashenko et al., 1996; Caccioni et al., 1998; Lota et al., 2000, 2001; Minh et al., 2002; Vekiari et al., 2002; Buettner et al., 2003; Merle et al., 2004; Pultrini et al., 2006; Sharma and Tripathi, 2006; Hérent et al., 2007). These aromatic compounds have been illustrated to be relatively inexpensive and abundant raw materials with applications in the food and flavor industries (Reische et al., 1998). They can also serve as an excellent starting material in the synthesis of fine chemicals and of new fragrances for the cosmetics industry (Lis-Balchin and Hart, 1999).

Satsuma mandarin (*Citrus unshiu*) is one of the native citrus cultivars grown in China, constituting about 60 percent of total citrus yields and keeping a stable development (Shan, 2006). The peel of Satsuma mandarin is normally discarded which consequently generated some environmental problems and hampered the development of citrus industry. Exploring essential oil seemed to be an alternative way to evaluate the underlying economical values of citrus due to the special roles it played in food, flavor and cosmetics industries. With this mind, in this paper, the chemical composition of essential oil from the peel of Satsuma mandarin would be introduced, in an effort to enhance the economic value of this cultivar.

MATERIALS AND METHODS

MATERIALS

Fruits of Satsuma mandarin (*Citrus unshiu*) were purchased on January 3rd, 2007 from the supermarket of Xiangtan University, Xiangtan, Hunan province.

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Extraction of essential oils

Fresh flavedo of Satsuma mandarin was saturated in 1% Ca $(OH)_2$ for 8 h to remove the polysaccharides in it, and then dried in 45°C and ground into powder. About 80 g flavedo powder was put in a flask supplied with 500 ml ddH_2O plus 10 g NaCl and subjected to steam distillation (Chyaua et al., 2007) until there was no significant increase in the volume of the oil collected. The oil was dried by anhydrous Na_2SO_4 for 30 min and extracted by 10 ml CH_2Cl_2, then concentrated under vacuum in a rotary-evaporator at 40°C to remove the CH_2Cl_2.

Analysis of essential oils

The oil was immediately analyzed by a Hewlett-Packard MSD system equipped with an HP-5MS cross-linked fused-silica capillary column (30 m × 0.25 mm, 0.25 mm film thickness). The analyses were carried out using helium as carrier at 1.4 ml/min in a split ratio of 50:1 and programmed: (a) 50°C for 1 min; (b) rate of 5°C/min from 50 to 180°C and hold for 10 min; (c) rate of 5°C/min from 180 to 220°C and hold for 10 min. The injector temperature was hold at 250°C. Injection volume was 1 µL.

GC/MS analyses were carried out on the same chromatograph equipped with a Hewlett-Packard MS computerized system, Model 5971A, ionization voltage 70 eV, electron multiplier 1300 V, ion source temperature 280°C, mass range *m/z* 35–450, scanning interval 0.5 s, scanning speed 1000 amu/sec. GC conditions were the same as above. Identification of components was based on computer matching with NIST107 and NIST21 library and comparison of the fragmentation patterns with those reported in the literatures (Stashenko et al., 1996; Caccioni et al., 1998; Lota et al., 2000, 2001; Minh et al., 2002; Vekiari et al., 2002; Buettner et al., 2003; Merle et al., 2004; Pultrini et al., 2006; Sharma and Tripathi, 2006; Hérent et al., 2007). Relative percentage amounts were calculated from total ion chromatogram (TIC) by the computer.

RESULTS AND DISCUSSION

Using the steam distillation method, the essential oil contents in Satsuma mandarin flavedo were reported with average of 3.08%. The gas chromatographic profiles and compositions of the essential oil are presented in Table 1. A total of 28 different compounds were isolated by steam distillation and among them, 25 compounds with 97.60% of total areas were identified using both chromatographic (retention indices) and spectroscopic (mass spectra) criteria. As revealed by Table 1, the principal components of the oil were monoterpenes hydrocarbons ($C_{10}H_{16}$), including limonene (67.44%), β-myrcene (7.15%), 3-carene (4.4%), α-pinene (2.52%), *p*-cymene (2.43%), β-pinene (1.46%), sabinene (0.77%), terpinolene (0.47%) and α-thujene (0.45%), which represented 86.62% of the total oil. Oxygenated monoterpenes represented 6.33% of the total oil, with *cis* limonene oxide (1.45%) and *tans* limonene oxide (0.81%) being the most abundant constituents of this group. The sesquiterpene ($C_{15}H_{24}$) contents were found to be only 3.43% of the total oil, mainly α-farnesene (1.11%) and β-elemene (1.04%). The 1-pentanol was also detected (0.75%).

The chemical compositions of essential oils were various from the citrus species. Generally, the citrus oils were characterized by high percentage of the limonene (more than 90.00%) (Stashenko et al., 1996; Caccioni et al., 1998; Lota et al., 2000, 2001; Merle et al., 2004; Pultrini et al., 2006; Hérent et al., 2007). Studies of other citrus species such as *Citrus limon*, *Citrus sphaerocarpa*, *C. sinensis* × *Poncirus trifoliata* and *Citrus reticulata* also showed that the oil have about 70% limonene as the major components in the oils (Caccioni et al., 1998; Buettner et al., 2003), similar to 67.44% in the Satsuma mandarin oil. β-myrcene is commonly found preferably in *C. sinensis* × *P. trifoliata,* with more than 7% of the total essential oil (Caccioni et al., 1998). Particularly, *C. sphaerocarp* is rich in β-myrcene (20.2%) (Minh et al., 2002). The contents of 3-carene (4.4%) were similar to those in *C. sinensis* epicarp (Sharma and Tripathi, 2006), while significant higher than those in *C. deliciosa*, *C. limon* and *C. reticulata*, where it only accounted for 1-2% of total essential oil (Stashenko et al., 1996; Lota et al., 2000, 2001; Merle et al., 2004; Hérent et al., 2007). α-pinene (2.52%) and β-pinene (1.46%) in the oil were similar to those in *C. deliciosa* and *C. sinensis* × *P. trifoliate* (Caccioni et al., 1998), while significantly higher than those in *C. sinensis* (Stashenko et al., 1996; Caccioni et al., 1998; Sharma and Tripathi, 2006), *C. paradise* (Caccioni et al., 1998) and *C. reticulate* (Merle et al., 2004), where they only constitute less than 1% of the total oil. It should be pointed that, however, essential oil content could differ greatly even in the same genus, as well as in different ripening stage and different organs (Stashenko et al., 1996; Caccioni et al., 1998; Lota et al., 2000, 2001; Vekiari et al., 2002).

In the essential oil herein, such constitutes as limonene, α-pinene, *p*-cymene, β-pinene, and Germacrene-D exhibited typical flavors (Chyaua et al., 2007). Limonene exhibited a fresh, light and sweet odor. *p*-Cymene displayed a typical gassy-kerosene-like odor. Germacrene-D possessed a warm-spicy-woody flavor. The odors of α-pinene and β-pinene were warm-resinous, refreshing pine-like. Therefore, the essential oil of Satsuma mandarin constitutes may be valuable for the flavouring of foods, where floral-fresh-fruity aromas are required, such as chewing gums, sweets, teas, soft and energy drinks as well as milk products. In cosmetics, the investigated essential Satsuma mandarin sample with characteristic floral-fresh-fruity odour impressions may be used in shampoos, soaps, shower gels, body lotions and tooth pastes, while an application of the oils in fine perfumery seems to be interesting as top-notes in perfumes and deodorants. It could also be used in the food preservation due to high percentage of well-known antimicrobial compounds with the α-pinene, β-pinene and limonene (Caccioni et al., 1998; Williams et al., 1998; Filipowicz et al., 2003; Cakir et al., 2004 ; Magwa et al., 2006; Bajpai et al., 2007).

ACKNOWLEDGEMENTS

This work was supported by the Scientific Research

Table 1. Chemical composition of essential oil of Satsuma mandarin peel.

Compounds	Molecular formula	Retention time (min)	%
α-thujene	$C_{10}H_{16}$	5.031	0.45
α-pinene	$C_{10}H_{16}$	5.155	2.52
Sabinene	$C_{10}H_{16}$	5.794	0.77
β-pinene	$C_{10}H_{16}$	5.863	1.46
β-myrcene	$C_{10}H_{16}$	6.048	7.15
p-cymene	$C_{10}H_{16}$	6.667	2.43
Limonene	$C_{10}H_{16}$	6.811	67.44
3-Carene	$C_{10}H_{16}$	7.222	4.4
Terpinolene	$C_{10}H_{16}$	7.693	0.47
Cis limonene oxide	$C_{10}H_{16}O$	8.438	1.45
Trans limonene oxide	$C_{10}H_{16}O$	8.506	0.81
3-Cyclohexene-1-acetaldehyde, alpha, 4-dimethyl-	$C_{10}H_{16}O$	9.45	0.28
1-Pentanol	$C_9H_{16}O$	9.507	0.75
Trans-carveol	$C_{10}H_{16}O$	9.779	0.56
Cis-carveol	$C_{10}H_{16}O$	9.962	0.41
Carvone	$C_{10}H_{14}O$	10.193	0.7
Limonene dioxide	$C_{10}H_{16}O_2$	10.925	0.41
Unidentified	-	11.102	0.79
Unidentified	-	11.302	0.61
Neraniol	$C_{10}H_{18}O$	11.48	0.35
β-Terpineol	$C_{10}H_{18}O$	11.596	0.42
(1S,5R)-2-Cyclohexen-1-ol-2-methyl-5- (1-methylethenyl)	$C_{10}H_{16}O$	11.892	0.94
Unidentified	-	12.124	1.00
Copaene	$C_{15}H_{24}$	12.2	0.23
β-elemene	$C_{15}H_{24}$	12.393	1.04
Decahydro-4a-methyl-1-methylene-7-(1-methylethylidene) naphthalene	$C_{15}H_{24}$	13.842	0.78
α-Farnesene	$C_{15}H_{24}$	13.873	1.11
Germacrene-D	$C_{15}H_{24}$	14.19	0.27

Foundation for Doctors of Xiang-tan University (No.06QDZ11), Scientific Research Foundation for Cross-Field research of Xiang-tan University (No. 06IND01) and Hunan Provincial Natural Science Foundation of China (No.08jj6020)..

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