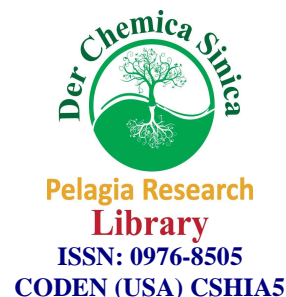




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Der Chemica Sinica, 2011, 2 (1): 38-42



### Study of the volatile compounds in *Malabaila Isfahanica* from Iran using HS/SPME/GC/MS

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#### ABSTRACT

The aerial parts of the plant *Malabaila Isfahanica* were collected in July 2010 from Binaloud mountain (Khorasan Razavi Province of Iran). It is air dried in a shadow place. A headspace solid-phase micro-extraction (HS-SPME) method followed by gas chromatography–mass spectrometry (GC/MS) was used for the analysis of volatile compounds in the leaves of *Malabaila Isfahanica*. The dried plant was powdered and the aroma compounds of a 0.05g were isolated by HS-SPME fiber in 15 min. The chemical compounds of the plant were investigated by gas chromatography mass spectrometry (GC/MS). A total of 13 constituents, representing more than 94% of the volatiles were identified. The main compounds, were limonene oxide [(16.80%), 3-buten-2-one, 4-[2,6,6-trimethyl-1-cyclohexen-1-yl] (16.44%),  $\beta$ -cyclocitral (12.56%) and  $\beta$ -pinene (12.41%). This herbal medicine traditionally uses as anti-inflammatory in Iran. Consequently, this fast and simple method can be used for the analysis of the volatile compounds emitted from *Malabaila Isfahanica*.

**Keywords:** *Malabaila Isfahanica*; GC/MS; SPME;  $\beta$ -pinene.

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#### INTRODUCTION

*Malabaila Isfahanica* belongs to the family Umbelliferae [1]. Chemical constituents found in the family include: volatile oils, coumarins, acetylenes and flavonoids, while terpenes, sesquiterpenes and alkaloids are rare [2]. Major volatile oil constituents reported in *Malabaila* species are: *p*-cymene and *a*-phellandrene [3], while, bergapten, isobergapten, imperatorin, pimpinellin, isopimpinellin, umbelliferone and sphondin are reported in *Malabaila dasycarpa* and *M. graveolens* fruits [4], in addition to marmesin and dihydroimperatorin. Nothing is reported on *Malabaila suaveolens*.

Different chemotypes were reported in literature [5-7] and the main components were found to differ in relation to the plants origin. Extraction methods such as Soxhlet extraction and liquid-liquid extraction are routinely being used in laboratories throughout the world. Unfortunately, these methods are generally time consuming and sometimes require large amounts of toxic and expensive organic solvents. Considering the limitations of these sampling techniques, headspace solid-phase micro-extraction (HS-SPME) emerges as an attractive alternative [8]. The technique has been reported to be relatively inexpensive, solventless, fast, reproducible, and simple procedure[8-13].

The aim of this research was to develop the HS/SPME method in combination with GC/MS, for the analysis of the volatile compounds from *Malabaila Isfahanica* plant. In our present work, the chemical composition of *Malabaila Isfahanica* identified by using aerial part of the dried plant. *Malabaila Isfahanica* were collected in July 2010 from Binaloud mountain (Khorasan Razavi Province of Iran ). After one week drying the plant in shadow place, we used the dried plant for our experiments.

## METHODS AND MATERIALS

### *Plant material and SPME fiber*

Aerial parts of wild growing *Malabaila Isfahanica* were collected in July 2010 from Binaloud mountain (Khorasan Razavi Province of Iran ).The plant was identified in Herbarium of Payame Noor University, Mashhad and a Voucher specimens (PNUMH31) was deposited. It is air dried in a shadow place. The SPME manual holder and a 50 $\mu$ m poly(dimethyl siloxane)-divinylbenzene (PDMS-DVB) fiber , were purchased from Supelco(USA) .The SPME fiber was conditioned as recommended at some degrees below the fiber maximum temperature before it was used for the first time . Before the first daily analysis , the fiber were conditioned for 5 min at 250°C in the GC injector.

### *HS-SPME extraction*

The sample was ground to a fine powder and in each experiment 60 mg of it was used . The sample placed in a vial , which is sealed with a septum-type cap. The sample preparation ( HS-SPME) in the presence of water as a solvent was provided at 50°C temperatures. In the experiments after transfer of the sample to glass vial , 1ml of double distilled water was added to it . The vial was put in a aluminum block over a hot plate / magnetic stirrer device and samples were heated and stirred for 10 min at 50°C. Thermal desorption of analyte from the fiber in the GC injection port for 5min and GC/MS analysis were done simultaneously.

### *GC/MS analysis*

The GC/MS analysis was carried out on a Shimadzu GC/MS model QP5050 . The capillary column was DB-5(30x 0.2mm,film tickness 0.32 $\mu$ m). The operating conditions were as follows, carrier gas , helium with a flow rate at 1.7ml/min, column injector and detector temperatures , were 250°C and 285°C, respectively. The ionization potential was 70 ev. The initial temperature of column was 60°C( held 1min) and then heated to 140°C with a 3°C/min rate and then heated to 250°C with 50°C/min and kept constant for 3 min. Identification of components in the sample was based on the similarity Index ( SI) , National Institute of Standards and Technology (NIST107) MS spectral library and literature survey . The relative percentage of the oil

constituents was calculated from GC peak areas. Fig. 1, shows the chromatogram of *Malabaila Isfahanica* volatiles obtained by HS/SPME/GC/MS. The parameters of sample preparation and analysis like adsorption, desorption, sample amount and volume of water were used the amounts that reported in the literatures [12].

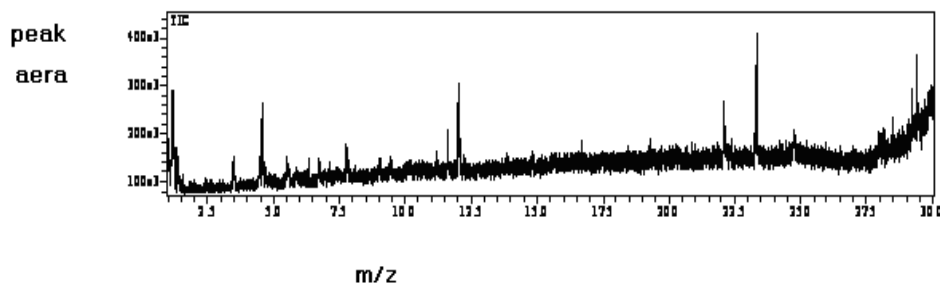


Fig. 1. The chromatogram of *Malabaila Isfahanica* from Binaloud obtained by HS-SPME/GC/MS

## RESULTS AND DISCUSSION

The sample preparation time was 15min (10 and 5min for adsorption and desorption, respectively). Also, the total analysis time including sample preparation and GC/MS run was less than 1h. The qualitative and quantitative analytical results are show in Table1. A total of 13 components were identified by GC/MS, representing 94.29% of the volatile components in the head space of the sample.

Table 1. The variation of essential oil compositions of *Malabaila Isfahanica* collected from Binaloud mountain, and identified by HS/SPMEGC/MS.

no.	compound	formula	SI% <sup>a</sup>	cont. %
1	$\gamma$ -terpinene	C <sub>10</sub> H <sub>16</sub>	91	3.82
2	4-hexene-2-one, methyloxime	O- C <sub>7</sub> H <sub>13</sub> NO	85	4.15
3	$\beta$ -pinene	C <sub>10</sub> H <sub>16</sub>	95	12.41
4	2,5,5-trimethylcyclohex-2- enone	C <sub>9</sub> H <sub>14</sub> O	85	5.76
5	Bicyclo[2.2.1]heptan-3- one,6,6-dimethyl-2- methylene	C <sub>10</sub> H <sub>14</sub> O	87	0.22
6	Glavcic acid	C <sub>15</sub> H <sub>22</sub> O <sub>2</sub>	90	0.42
7	Hexahydro-5-methyl- phenyl-1,3,5-triazine-2- thione	C <sub>15</sub> H <sub>22</sub> O <sub>2</sub>	90	0.54
8	$\beta$ -cyclocitral	C <sub>11</sub> H <sub>20</sub>	93	12.56
9	Geranyl vinyl ether	C <sub>12</sub> H <sub>20</sub> O	95	8.37
10	3-buten-2-one,4-[2,6,6- trimethyl-1-cyclohexen-1- yl] (16.44%)	C <sub>13</sub> H <sub>20</sub> O	90	16.44
11	methoprene	C <sub>19</sub> H <sub>34</sub> O <sub>3</sub>	89	6.10
12	limonene oxide	C <sub>10</sub> H <sub>16</sub> O	95	16.80
13	suberol	C <sub>7</sub> H <sub>14</sub> O	92	6.70
<b>total</b>				<b>94.29</b>

<sup>a</sup> a similarity index%

The major components were ( Table 1) of limonene oxide [(16.80%) , 3-buten-2-one,4-[2,6,6-trimethyl-1-cyclohexen-1-yl] (16.44%),  $\beta$ -cyclocitral (12.56%),  $\beta$ - pinene (12.41%), geranyl vinyl ether ( 8.37%) and suberol ( 6.70%). These results are in the most cases agreement with the components that obtained for aerial parts of the plant in studies with hydrodistillation methods of the *Malabaila* specis [1-2].

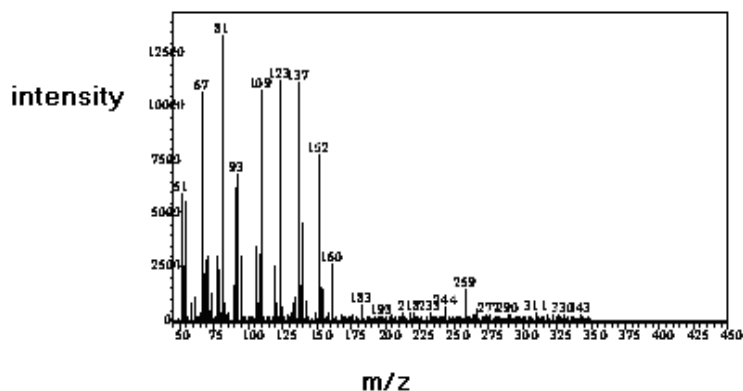


Fig.2. The mass spectrogram of limonene oxide obtained from *Malabaila Isfahanica* by HS/SPME/MC/MS.

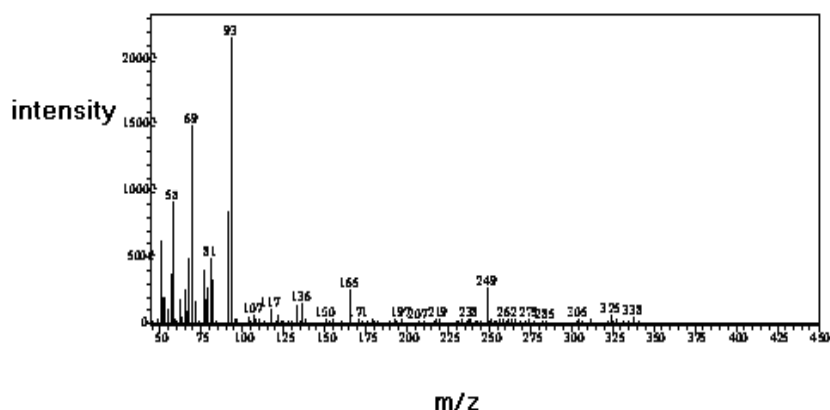


Fig.3. The mass spectrogram of  $\beta$ - pinene obtained from *Malabaila Isfahanica* by HS/SPME/MC/MS.

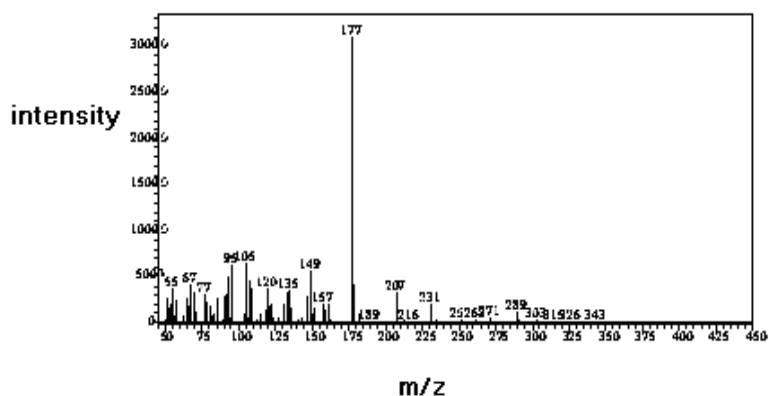


Fig.4. The mass spectrogram of 3-buten-2-one,4-[2,6,6-trimethyl-1-cyclohexen-1-yl] obtained from *Malabaila Isfahanica* by HS/SPME/MC/MS.

On the other hand the percent of the chemical compounds are not the same. These behaviors can be related to the type of the plant, aerial or flower parts and also the geographical regions of the plant growing places. Campho, *p*-cymene and isoeledon make about 34% of the volatile compounds in the herbal plant. Figs. 2-4 show the peaks of limonene oxide, 3-buten-2-one, 4-[2,6,6-trimethyl-1-cyclohexen-1-yl],  $\beta$ -cyclocitral and  $\beta$ -pinene, from mass spectrometer. A comparison between the percentages of some main components in the head space of the sample is shown in Fig.5.

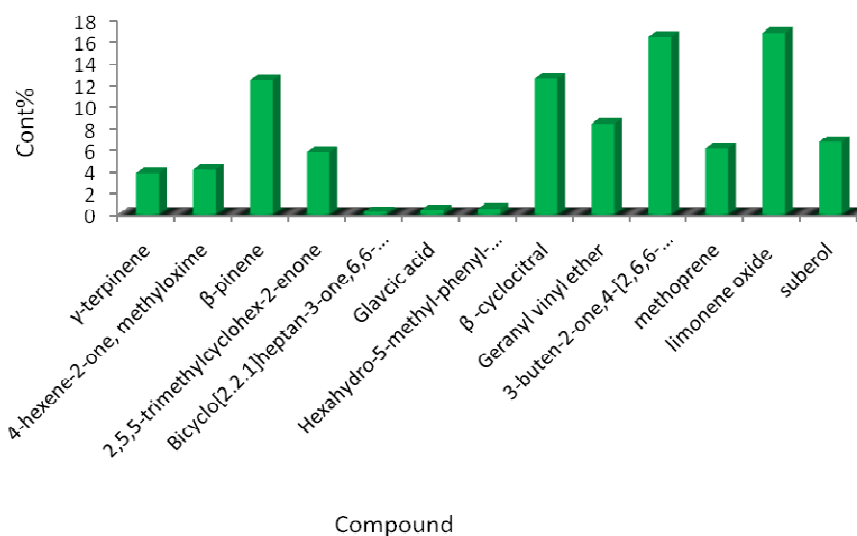


Fig.5. The variation of main constituents of *Malabala Isfahanica volatiles* from Binaloud mountain, Iran

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