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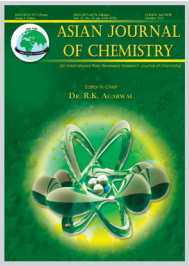

Solvent-Free Microwave Extraction of Essential oil of *Artemisia tschernieviana*

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Solvent-free microwave extraction is a combination of microwave heating and dry distillation is performed at atmospheric conditions without adding any solvent or water. Solvent-free microwave extraction has already been applied to extraction of essential oil from plant materials. In this paper, solvent-free microwave extraction has compared with a conventional hydrodistillation, for the isolation and identification of essential oils of leaf of *A. tschernieviana*. In hydrodistillation and solvent-free microwave extraction methods 28 and 37 components were identified, which represented 99.39 and 99.81 % of the total composition of the oil, respectively. In this methods, β-pinene, limonene, α-pinene and γ-terpinene were the main components. Experimental results show that more components were isolated and identified by solvent-free microwave extraction than those by hydrodistillation. Solvent-free microwave extraction is a good alternative for the extraction of essential oil from *A. tschernieviana*. Solvent-free microwave extraction is a green technology or green chemistry.

Key Words: *Artemisia tschernieviana*, Essential oils, Solvent-free microwave extraction, Hydrodistillation.

INTRODUCTION

The genus *Artemisia* (Commonly wormwood or sagebrush) is one of the largest and most widely distributed genera of the family *compositae*[1]. Over 250 species of *Artemisia* are distributed throughout the world and *A. tschernieviana* is one of the 40 species of *Artemisia* found in Iran[2]. It is an aromatic herbaceous annual plant that grows wild (up to 50 cm) in north Iran during the summer season. Since *Artemisia tschernieviana* oil has been widely used as pharmaceuticals, flowering, antifungal and antimicrobial agents in the food industry, it is necessary to find the most suitable method for the improvement of the quality of *A. tschernieviana* oil[3,4]. The main methods to obtain essential oils from the plant materials are hydrodistillation (HD), steam distillation, steam and water distillation, maceration, empyreumatic (or destructive) distillation and expression. Among these methods, hydrodistillation has been the most common approach to extract the essential oils from the medicinal herbs/plants[5]. The chemical composition, antimicrobial activity of the aerial part of *A. tschernieviana* oil from Iran, was investigated. The results showed *p*-cymene (21.3 %), β-pinene (17.8 %), α-pinene (9.4 %), γ-terpinene (9.1 %) and (z)-*cis*-ocimene (8/8 %) as the main components and the oil was active against six bacterial stains and one fungal strain[6]. However, in order to reduce the extraction time and possibly improve the extraction yield, to enhance the quality of the extracts and also to reduce the operation costs. The new approach of solvent-free microwave extraction (SFME), has also been sought[5,7]. Solvent- free microwave extraction is a new technique which combines microwave heating with dry distillation at atmospheric pressure for the isolation and concentration of the essential oils in plant materials. In solvent-free microwave extraction method, there is no need to add any solvent or water if fresh plant material is used. If dry plant material is used, the sample is rehydrated by soaking in water for some time and then draining off the excess water[8]. Solvent-free microwave extraction has been used to obtained essential oils from three different spices (ajowan, cumin and star anise)[9], three different aromatic herbs (basil, garden mint and thyme)[10] and cardamom seed[11]. Microwave heating has been recently used also, for the isolation and analysis of essential oils[9-11]. In other studies, solvent-free microwave extraction offered significantly higher essential oil yield (0.054 mL/g) as compared to hydrodistillation (0.048 mL/g)[8]. Although, literature of the essential oils of different species of *Artemisia*[12-19] is prevalent. So far no studies have been reported on the oil of *A. tschernieviana* by solvent-free microwave extraction method. In this study, the chemical composition of the essential oil of the leaf *A. tschernieviana* was obtained by solvent-free microwave extraction and then compared with a

conventional method, hydrodistillation. Appropriate comparisons in terms of extraction time, extraction yield and essential oil composition is also made.

EXPERIMENTAL

Leaves of *A.tschernieviana* were collected in September 2010 from the Joybar, Province of Mazandaran, northern Iran. Voucher specimens have been deposited at the herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Tehran University of Medical science, Tehran, Iran.

Essential oil extraction

Hydrodistillation: The dried leaves (100 g) were separately subjected to hydrodistillation using a Clevenger-type apparatus according to the European pharmacopeia[20] for 4 h. The essential oil was collected, dried under anhydrous sulphate and stored at 4 ºC until used. Essential oil yield was expressed in terms of the weight of the oil collected per gram of dry plant material. The yield was, 0.115 % (w/w).

Solvent-free microwave extraction (SFME): The microwave oven used for solvent-free microwave extraction was a Milestone srl operating at 2450 MHz and the dimensions of the interior cavity of the oven were 29 cm × 37 cm × 40 cm. A clevenger system outside the microwave cavity condensed the distillate continuously. Condensed water was refluxed to the extraction vessel in order to provide uniform condition of temperature and humidity for extraction. For solvent-free microwave extraction, 50 g dried leaf of *A. tschernieviana* was soaked in 800 mL distilled water at room temperature (25 ºC) for 1h in order to hydrate the external layers of the plant material performed at atmospheric pressure, the leaf of *A. tschernieviana* was heated using an optimize fixed power of 800 w for optimize time 0.5 h without added any solvent or water. The chemical composition of essential oil isolated was analyzed by GC/MS. The yield of this method was 0.160 % (w/w).

Gas chromatography: Gas chromatography analysis was performed on a Shimadzu 15A gas chromatograph equipped with a spilt/spiltless (ratio 1:30), injector (250 ºC) and a flame ionization detector (250 ºC). N_2 was used as carrier gas (1 mL/min) and the capillary column used was DB-5 (50 m × 0.2 mm, film thickness 0.32 pin). The column temperature was kept at 60 ºC for 3 min and then heated to 220 ºC with a 5 ºC/min rate and kept constant at 220 ºC for 5 min. Relative percentage amounts were calculated from peak area using a CR5 Shimadzu CR PACK without the use of correction factors.

Gas chromatography-mass spectrometry: GC/MS analysis was performed using a Hewlett-Packard 5973 with a HP-5MS column (30 m × 0.25 mm, film thickness 0.25 μm). The column temperature was kept at 60 ºC for 3 min and programmed to 220 ºC at a rate of 5 ºC/min and kept constant at 220 ºC for 5 min. The flow rate of Helium as carrier gas was 1 mL/min, final temperature 230 ºC and detector temperature 250 ºC; MS were taken at 70 eV (E1), electron multiplier voltage 1800 eV; mass range, 30 to 350 amu; scan time and 2 scan/sec.

Identification of components: The components of the oil were identified by comparison of their mass spectra with those of the MS library or with authentic compounds and confirmed by comparison of their retention indices either with those of authentic compounds or with data published in the literature[21]. The retention indices were calculated for all volatile constituents using a homologous series of C9 to C18 *n*-alkanes.

RESULTS AND DISCUSSION

The volatile components obtained from *A. tschernieviana* are listed in Table-1 in which the percentage and retention indices of the component are given. In hydrodistillation method, 28 components were identified in the leaf oil, which represented 99.39 % of the total composition of the oil. β-Pinene (21.68 %), limonene (13.65 %), γ-terpinene (13.23 %) and α-pinene (9.19 %) were the major constituents in the leaf oil. In solvent-free microwave extraction method 37 components were identified in the leaf oil, which represented 99.81 % of the total composition of the oil. β-Pinene (17.60 %), limonene (11.20 %), γ-terpinene (10.09 %), cubenol (6.83 %) and *o*-cymene (6.54 %) were the major constituents in the leaf oil. Previous studies showed that β-pinene (16.30 %), γ-cadinene (10.90 %), bornylacetate (8.80 %), limonene (8.30 %), *p*-cymene (7.50 %) and α-pinene (7.40 %) were the major constituents in *A. tschernieviana* in hydrodistillation method[22].

The chemical class distribution of the essential oils components of the plant is reported in Table-1. The compounds were separated into four classes, which were monoterpene hydrocarbons, oxygenated monoterpens, sesquiterpene hydrocarbons and oxygenated sesquiterpens. As it can be seen in Table-1, that in the hydrodistillation and solvent-free microwave extraction methods, in the leaf oils, monoterpens were higher than sesquiterpens and monoterpene hydrocarbons were the major constituents of the essential oils and in the amounts 73.67 and 60.27 %, respectively.

Among the two samples, the leaf oil in the hydrodistillation method was shown the highest monoterpene hydrocarbons (73.67 %). But the leaf oil in the solvent-free microwave extraction method had the highest oxygenated monoterpens (20.68 %), sesquiterpene hydrocarbons (2.21 %) and oxygenated sesquiterpens (16.65 %). In the solvent-free microwave extraction method, the maximum yields obtained was found 0.160 % (w/w – dry basis), while in hydrodistillation method was found 0.115 % (w/w – dry basis). The lower yield in conventional hydrodistillation process can be attributed to the loss of some of the volatile compounds due to longer processing time. Compared to the extraction time (4 h) for hydrodistillation, the extraction time for solvent-free microwave extraction (0.5 h) was shorter because of the use of microwave. Additionally, the solvent-free microwave extraction method offers important advantages over traditional alternatives, namely: substantial savings of energy and a reduced environmental burden (less CO_2 rejected in the atmosphere). A review of the literature revealed that there is no report on the volatile constituents of leaves of *A. tschernieviana*. Therefore, we were unable to investigate variations of oil components due to differences in climate and geographic areas.

Conclusion

This research showed that, in comparison with the hydrodistillation which is time consuming and needs large

TABLE-1
YIELD, EXTRACTION TIME AND CHEMICAL COMPOSITION OF ESSENTIAL OIL OF THE LEAF OF *A. tshernieviana*

No.	Compounds[a]	Rt[b]	Content (%)	
			HD	SFME
1	α-Thujene	930	0.66	0.31
2	**α-Pinene**	939	**9.19**	**6.30**
3	Camphene	954	1.86	1.39
4	Sabinene	975	3.05	4.26
5	**β-Pinene**	979	**21.68**	**17.60**
6	Dehydro-1,8-cineol	991	0.23	N.D
7	α-Terpinene	1017	1.14	0.38
8	*o*-Cymene	1026	5.81	6.54
9	**Limonene**	1029	**13.65**	**11.20**
10	1,8-Cineole	1031	3.02	3.84
11	(Z)-β-Ocymene	1037	2.78	2.02
12	**γ-Terpinene**	1060	**13.23**	**10.09**
13	*cis*-Sabinene hydrate	1070	N.D	0.30
14	Terpinolene	1089	0.62	0.18
15	Linalool	1097	2.82	3.66
16	*trans*-Sabinene hydrate	1098	N.D	0.26
17	*cis-p*-Menth-2-en-1-ol	1122	N.D	0.19
18	Camphor	1146	N.D	0.50
19	Borneol	1169	N.D	1.30
20	4-Terpineol	1177	2.00	1.09
21	α-Terpineol	1189	0.99	0.32
22	*trans*-Piperitol	1208	N.D	0.16
23	Citronellol	1226	N.D	0.44
24	Geraniol	1253	N.D	0.54
25	Bornyl acetate	1289	3.96	5.84
26	Citronellyl acetate	1353	0.33	0.30
27	Neryl acetate	1362	0.25	0.37
28	Geranyl acetate	1381	1.33	1.57
29	β-Caryophyllene	1419	0.49	0.17
30	γ-Gurjunene	1477	0.42	N.D
31	β-Cadinene	1477	N.D	0.27
32	γ-Muurolene	1480	N.D	0.51
33	β-Selinene	1490	N.D	0.31
34	Bicyclogermacrene	1500	1.09	0.95
35	(Z)-Nerolidol	1533	1.98	3.15
36	Spathulenol	1578	0.65	2.23
37	Viridiflorol	1593	0.31	N.D
38	α-Muurolol	1646	N.D	0.29
39	Cubenol	1647	3.50	6.83
40	α-Bisabolol	1686	2.35	4.12
41	Total		**99.39**	**99.81**
42	Group components			
43	Monoterpene hydrocarbons		73.67	60.27
44	Oxygen-containing monoterpens		13.60	20.68
45	Sesquiterpene hydrocarbons		2.24	2.21
46	Oxygen-containing sesquiterpens		9.88	16.65
47	Extraction time (min)		240	30
48	Yield (w/w – dry basis)		0.115	0.160

[a]Compounds presented in order of elution from the HP-5MS capillary column; [b]Kovat's retention index to *n*-alkanes on the HP-5MS capillary column; N.D: Not detected; HD = Hydrodistillation; SFME = Solvent-free microwave extraction.

amounts of botanical material, the solvent-free microwave extraction (SFME) method offers advantages such as:

• Short extraction time, 0.5 h against 4 h for hydrodistillation.

• High extraction efficiency, 0.160 (w/w) against 0.115 (w/w) for hydrodistillation.

• More compounds isolated and identified, 37 compounds against 27 compounds for hydrodistillation.

• Does not needs large amount of plant material, 50 g against 100 g for hydrodistillation.

• Simplicity. All these advantages make solvent-free microwave extraction a good alternative for the extraction of essential oil from *Artemisia tschernieviana*. Solvent-free microwave extraction is a green technology or green chemistry.

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