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Studying of optimization condition of rosemary essence extraction with microwave assisted hydro-distillation method

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Abstract
The most applicable method for extraction of essential oil is hydro-distillation. It is a traditional technique which is used in most industrious companies. Microwave-assisted hydro-distillation (MAHD) is an advanced hydro-distillation (HD) technique utilizing a microwave oven in the extraction process. MAHD of essential oils from the aerial parts (leaves) of rosemary (*Rosmarinus officinalis*) was studied and the results were compared with those of the conventional HD in terms of extraction time, extraction efficiency, chemical composition, quality of the essential oils and cost of the operation. Microwave hydro-distillation was superior in terms of saving energy and extraction time. Gas chromatography–mass spectrometry was used for analysis of quantity of the extracted essential oils. Also microwave hydro-distillation was found to be a green technology.

Keywords: Essential Oil, Rosemary, Microwave Distillation, Hydro Distillation

1. Introduction
Rosmarinus officinalis, commonly known as rosemary, is a woody, perennial herb with fragrant, evergreen, needle-like leaves native to the Mediterranean region. Rosemary's antioxidant properties are still used to extend the shelf life of prepared foods [1]. Rosemary is also known medicinally for its powerful antioxidant activity [2] antibacterial properties and as a chemopreventive agent [3]. Today, essential oil of rosemary is widely used in the cosmetic industry producing various bathing essences, hair lotions and shampoos [4]. Traditional methods used for extraction of essential oil were hydro-distillation (HD) or steam distillation. Essential oils are well known to be thermally sensitive and vulnerable to chemical changes [5-8]. Losses of some volatile compounds, low extraction efficiency, toxic solvent residue in the extract may be encountered using these extraction methods [9-11]. Microwave-assisted hydro-distillation combines rapid heating in the microwave field with the traditional solvent extraction. This enables significant time-saving, so the extraction can be completed in meter of minutes [12]. Microwave-assisted solvent extraction [13] appeared to be particularly attractive for isolation of essential oil from rosemary.
Tigrine-Kordjani *et al.*, [14] developed a microwave assisted distillation (MAD) with free solvent for laboratory scale applications in the extraction of essential oils from different kinds of aromatic plant. Sui *et al.*, [15] have worked on an efficient microwave pretreatment (MP) method to maintain quality of postharvest rosemary leaves and observed that MP could be a good method for extracting essential oil and maintaining quality in rosemary and other aromatic herbs.
In this paper, the essential oil from rosemary obtained by microwave hydro-distillation has been compared with those obtained by conventional hydro-distillation. Then the quality and quantity of essential oil, cost, energy consumption and safety environmental consideration of two methods was studied. Also different parameter on essential oil extraction quantity and quality was checked. The aim of this research is finding an optimum method for extraction of essential oil.

2. Material and Methods
2.1 Material
Leaves of the cultivated plants of rosemary were collected from Arak University. The leaves were dried under environmental condition.

2.2 Hydro-distillation (HD) apparatus and procedure
Rosemary leaves were submitted to hydro-distillation with a Clevenger-type apparatus with a maximum delivered power of 1000 W. The essential oil was extracted with 300 mL of water in a 2-L flask for 90 min (until no more essential oil was obtained). Then the essential oil was collected and stored at laboratory condition.

2.2.2. Addition of salt
Addition of salt increases the boiling point of water. It seems that higher temperature of water will lead to separation of low volatile components. Base on this approach, 30 g salt (NaCl) was solved into 300 mL water and added to rosemary. Addition of salt made the extraction operation faster but the extraction efficiency didn't improve as expected.

2.3 Microwave-assisted hydro-distillation (MAHD) apparatus and procedure
Microwave hydro-distillation has been performed using the Tecnokit Chen (Italy, Tek-2611) microwave oven illustrated in Figure 1. It is a 2450 MHz multimode microwave with a maximum delivered power of 900 W. In a typical MHG procedure performed at atmospheric pressure, 100 g of rosemary were heated for 15 min with addition of 300 mL water.

2.3.1 Effect of different Microwave power on efficiency
First experiment was done with 60% of microwave power (900 W). Extraction was very fast and done in 10 min. Because of high intensity of heating to the mixture and possibility of destroying of some component due to high temperature, this case was rejected. Again, experiment was repeated with 20% power again. In this time, the intensity of reached heat was so low that the extraction time lasted 60 to 90 min like hydro-distillation. So the 40% of maximum Microwave power was chosen as the best one. The time of extraction and the amount of extracted essential oil in this case was about 30 min and 1.5 cc.

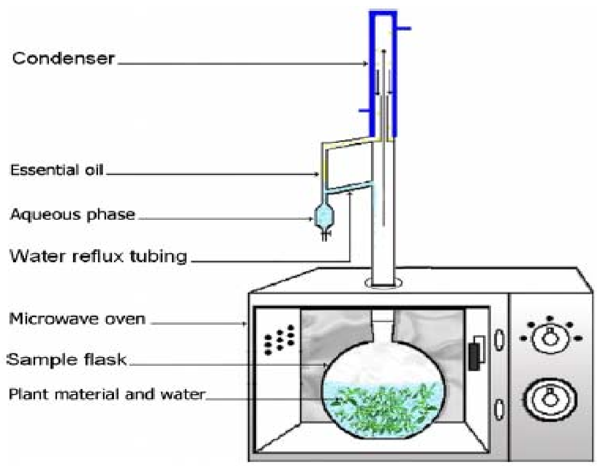

Fig 1: Microwave-assisted hydro-distillation apparatus

2.4 Gas chromatography mass spectrometry (GC–MS)
The essential oils obtained at different conditions were analysed by gas chromatography coupled to mass spectrometry. In order to perform quantitative analysis with FID at the same time with the component characterization of MSD, a two holes ferrule was used in which two columns were placed. The capillary columns used for both of the analysis were HP-5MS (30m×0.25mm×0.25μm) with a 5% phenyl methyl siloxane stationary phase. GC-MS conditions were as follows: carrier gas: He, flow rate: 0.8 mL/min, splitless, injection volume: 1μL, injection temperature: 250 °C, oven temperature program, holding at 50 °C for 2 min, rising to 22 5°C with 3 °C/min; electronic impact at 70 eV. Solvent delay was for 4.5 min.
The GC analysis was performed with the following conditions: flow rate, 0.4 mL/min; FID temperature, 275 °C; make-up gas type, He with a make-up flow rate of 45 mL/min.
Identification of the components of the essential oils were done by comparing data with those of literatures [16-18] which is based on comparison of retention times of compounds with those of available standards and with library matching of their mass spectra.

3. Results and discussion

3.1 Essential oil Efficiency
As mentioned previously, the extracted amount of essential oil obtained by both methods was 1.5 mL for 100 g rosemary leaves. Therefore a similar extraction yield was achieved at significantly shorter extraction time when using MAHD instead of HD.

3.2 Cost, cleanliness and safety considerations
The reduced cost of extraction is clearly advantageous for microwave method in terms of time and energy. Hydro-distillation required an extraction time of 90 min for heating to the extraction temperature. But MAHD only takes 30 min. The extraction time was reduced by about 67% by using microwave. Furthermore, the energy requirements to perform the extraction based on the maximum power consumption of the electro mantle for HD was more than for microwave oven for MAHD. This indicates a substantial saving in the extraction cost when using MAHD instead of HD.
With regard to environmental impact, the calculated quantity of carbon dioxide emitted to the atmosphere is higher in the case of HD (2400 g CO_2) than for MAHD (160 g CO_2) [19]. MAHD is proposed as an ‘‘environmentally friendly” extraction method suitable for sample preparation before essential oil analysis.

3.3 Essential oil composition
The total mass chromatography of the rosemary essential oil by MAHD is given in Figure 2 and the composition of the essential oil of rosemary obtained by both methods is given in

Table 1. The compositions of the essential oils obtained by both of the methods were found to be almost the same qualitatively, whereas some quantitative differences were observed.

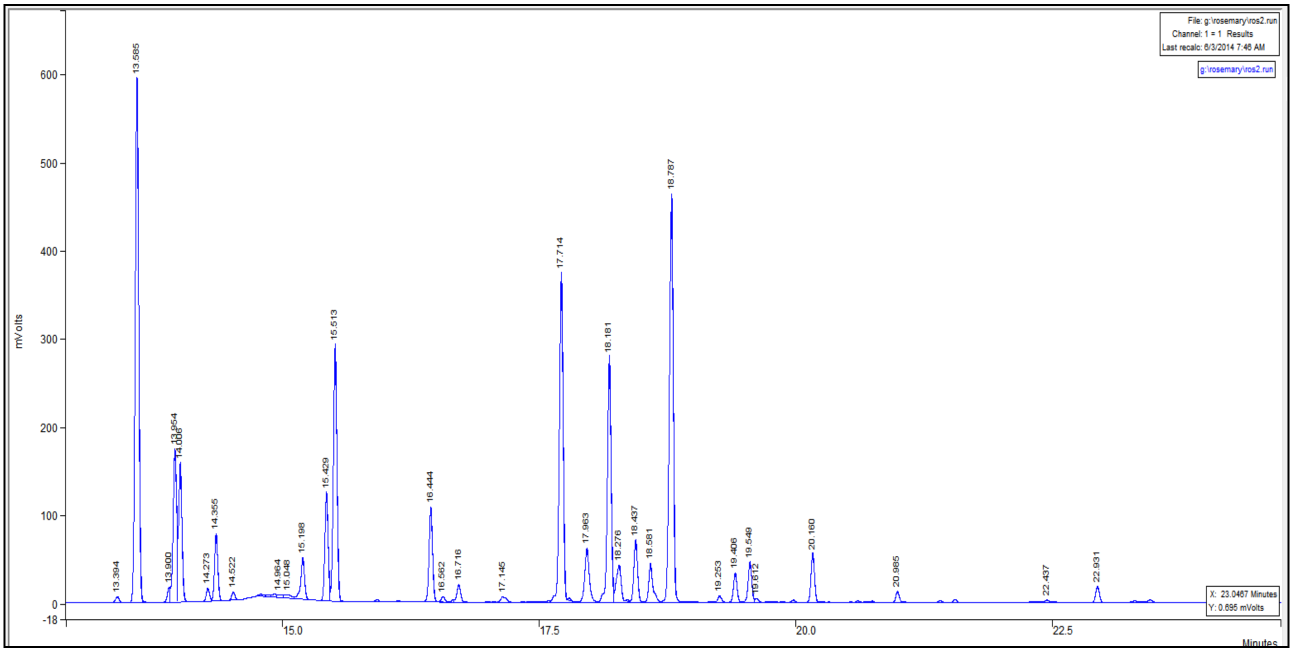

Fig 2: Mass chromatography of Rosemary essential oil by MAHD

The main components of the rosemary essential oil were obtained a-Pinene, Camphene, 1,8-Cineole, Linalool, Camphor and Borneol. It was also found that the essential oil mainly composed of oxygenated compounds (51.35–59.74%) while monoterpene hydrocarbons and sesquiterpenes constituted 38.86–47.43% and 0.36–0.6% of it, respectively. The main component of oxygenated compounds and monoterpene hydrocarbons detected were Borneol (10.39-15.38 mg/mL) and a-Pinene (17.95-24.24 mg/mL) in the case of MAHD.

The concentration of oxygenated and sesquiterpenes compounds increased in MAHD method. Beside the concentration of monoterpene hydrocarbons decreased in comparison to HD (Table 1). Ferhat *et al.* [20], Lucchesi *et al.* [21], Okoh *et al.* [22], and Bendahou *et al.* [23] showed that the content of oxygenated compounds in the oil obtained by microwave distillation (MD) was higher than in the oil obtained by HD. But Wang *et al.* [24] reported that the content of oxygenated compounds of the oil obtained by MD was lower than that by HD for *Cuminum cyminum L.*, and *Zanthoxylum bungeanum Maxim*. Therefore, the possible reason for this contradictory fact is that the content of oxygenated compounds of the oil was dependent on the species instead of the extraction method. During the procedure of MD, microwave irradiation highly accelerated the extraction process without causing considerable changes in the essential oil composition, although the percentages of some components depended on the technique applied.

Concentration of oxygenated compounds and monoterpene hydrocarbons were 17% increased and 17.7% decreased with the increasing of 50% microwave power comparing to HD method. This is due to the diminution of thermal and hydrolytic effects compared with hydro distillation which uses a large quantity of water and is time and energy consuming. Besides, the concentrations of these compounds were 5.8% decreased and 8.3% increased in the presence of salt in MAHD method, respectively.

Because of aroma, flavor and therapeutic properties; oxygenated compounds can be used as measurements of essential oil quality. Monoterpene hydrocarbons are less valuable than oxygenated compounds in terms of their contribution to the fragrance of the essential oil. So, the higher amount of oxygenated compounds in MAHD indicates the higher quality of essential oil.

Table 1: Concentrations of the essential oil of rosemary compounds obtained by different methods

No.	Component	RI (DIMS5P)	Concentration			
			HD	MAHD (40%)	MAHD (60%)	MAHD (40%)+NaCl
1	Tricyclene	923.2	0.07	0.05	-	-
2	a-Thujene	927.8	0.31	0.25	0.21	0.28
3	a-Pinene	936.1	24.24	20.02	17.95	22.74
4	Camphene	950.3	7.51	6.40	5.35	6.95
5	β-Pinene	977.7	4.27	4.79	4.32	5.59
6	1-Octen-3-ol	980	0.34	0.49	0.41	0.50
7	β-Myrcene	989.2	2.48	2.30	2.14	2.37
8	α-Phellandrene	1004.1	0.33	0.30	0.26	0.30
9	3-Carene	1011.3	0.05	0.15	0.13	-
10	α-Terpinene	1017.1	1.64	1.59	1.52	1.38
11	p-Cymene	1024.3	3.74	3.50	3.46	3.52

12	1,8-Cineole	1031.8	8.79	9.35	8.84	9.34
13	Cis-Ocimene	1037.8	0.09	0.08	-	0.09
14	β-Ocimene	1047	0.05	0.06	-	-
15	ɣ-Terpinene	1059.7	2.36	3.49	3.33	3.28
16	cis-Sabinene hydrate	1066.5	0.69	0.74	0.66	0.74
17	Terpinolene	1086.9	0.32	0.38	0.30	0.22
18	Linalool	1099	10.98	11.99	12.19	12.13
19	Fenchol	1115.1	0.06	0.07	-	-
20	Campholaldehyde *[17]	1124	2.13	2.35	2.39	2.23
21	Camphor	1143.4	7.56	8.75	8.86	8.06
22	Isopulegol [17]	1145	1.49	1.71	1.80	1.62
23	Pinocamphone/Isopinocamphone	1160	1.83	2.15	2.24	1.91
24	Pinocarvone/trans-Pinocarvone	1160	1.25	1.48	1.56	1.32
25	Borneol	1166.2	11.28	11.53	15.38	10.39
26	Terpinen-4-ol	1177.1	0.19	0.21	0.23	0.20
27	p-Cymene-8-ol [17]	1183	0.77	0.95	1.01	0.82
28	α-Terpineol	1189.7	1.17	1.39	1.43	1.25
29	Myrtenol	1194.1	0.04	0.05	0.13	-
30	Verbenone	1206.2	1.49	1.66	1.72	1.33
31	Citronellol	1228.1	0.04	0.05	-	-
32	Bornyl acetate	1283.5	0.33	0.29	0.42	0.27
33	Carvacrol	1300.4	0.27	0.05	-	-
34	Methyl eugenol	1401.8	0.13	0.10	-	0.08
35	β-Caryophyllene [17]	1418	0.30	0.50	0.59	0.49
36	α-Humulene	1453.1	0.06	0.08	-	0.11
37	NI	1570.45	-	0.06	-	-
38	Methyl jasmonate [17]	1647	0.10	0.13	0.19	0.14
39	Others		0.35	0.35	0.51	0.29
40	Total		99.09	99.84	99.52	99.91
	Monoterpene hydrocarbon		47.00	42.84	38.67	46.39
	Oxygenated compounds		50.88	55.44	59.46	52.33
	Sesquiterpenes		0.36	0.58	0.59	0.60
	NI : Not identified					
	Monoterpene hydrocarbon	%	47.43	42.91	38.86	46.43
	Oxygenated compounds	%	51.35	55.53	59.74	52.37
	Sesquiterpenes	%	0.36	0.58	0.59	0.60

DIMS: di-Methyl silicone with 5% phenyl groups [18]

*Compounds determined using mass spectrum consistent with spectra found in the literature, but not using the retention time of standard compounds (Retention time: 17.96)

Conclusion

A similar extraction yield was achieved at significantly shorter extraction time when using MAHD instead of HD. In addition, MAHD method offers important advantages over traditional alternatives, namely: shorter extraction times, substantial savings of energy and a reduced environmental hazard (less CO_2 rejected in the atmosphere). So MAHD can be considered as a green technology. The GC-Mass results showed that the amount of oxygenated compounds and monoterpene hydrocarbons were increased and decreased respectively by MAHD method. Also increasing of 50% microwave input power increased and decreased the concentration of oxygenated compounds and monoterpene hydrocarbons. This results leads to the fact that the quality of essential oil increased by MAHD. Therefore MAHD is a good alternative for the extraction of essential oils from rosemary since it provides essential oils of similar quality compared to conventional HD while reducing the time and cost of the process drastically.

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