CHEMICAL COMPOSITION OF SOME ESSENTIAL OILS OF *LAMIACEAE* FAMILY

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Abstract

Aim. *In this paper we present the chemical composition of two commercial samples of essential oils extracted from herbs belonging to Lamiaceae family, determined by gas – chromatography – mass spectrometry and two different techniques of sample injection.*

Methods. *The essential oils of Lavender and Rosemary were analyzed by gas chromatography – mass spectrometry (GC-MS), using two different techniques of injection: split-splitless (solvent diluted sample) and headspace (gas phase).*

Results. *The chemical composition resulted for each essential oil was compared with literature data and previous practical experience of authors. Qualitative and quantitative differences were obtained between the two injection techniques used.*

Conclusions. *Both type of sample injection (split-splitless and headspace) show high applicability for the evaluation of essential oils composition.*

Keywords: essential oils, rosemary, lavender, GC-MS, HS/GC-MS.

COMPOZIŢIA CHIMICĂ A UNOR ULEIURI VOLATILE APARŢINÂND FAMILIEI *LAMIACEAE*

Rezumat

Scop. *În această lucrare este prezentată compoziţia chimică a două mostre comerciale de uleiuri volatile provenite de la plante din familia Lamiaceae, analizate prin gaz-cromatografie cuplată cu spectrometrie de masă, utilizând două modalităţi de injectare a probei.*

Metode. *Uleiurile volatile de lavandă şi rozmarin au fost analizate prin gaz cromatografie cuplată cu spectrometrie de masă (GC-MS), utilizând două tehnici diferite de injectare a probei: split-splitless (diluate în solvent) şi headspace (fază gazoasă).*

Rezultate. *Compoziţia chimică determinată pentru fiecare ulei volatil a fost comparată cu datele din literatură şi rezultatele obţinute anterior de către autori. S-au observat atât diferenţe calitative, cât şi cantitative între cele două tehnici de injectare folosite.*

Concluzii. *Ambele metode de injectare a probei utilizate (split-splitless şi headspace) au dovedit o largă aplicabilitate în sprijinul evaluării compoziţiei chimice a uleiurilor volatile.*

Cuvinte cheie: uleiuri volatile, rozmarin, lavandă, GC-MS, HS/GC-MS.

INTRODUCTION

Lavender essential oils are obtained from the flowering tips of the herbs *Lavandula angustifolia Mill*. (lavender), *L. hybrida R*. (lavandin), *L. latifolia Med.* (spike lavender). Lavender oil has sedative, anti-flatulence, anti-

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colic, antifungal, antibacterial, and flavouring properties [1,2].

Rosmarinus officinalis L. is native of the Mediterranean countries, and now cultivated also in North America. Rosemary is one of the classic culinary herbs. Rosemary essential oils increase the circulation of blood and improve memory, concentration and mental alertness. Moreover rosemary oils have digestive, antiseptic, antispasmodic and anti-inflammatory properties [1-3].

MATERIALS AND METHODS

Essential oils

The essential oils used in this study were commercial samples of lavender and rosemary essential oils.

EXPERIMENTAL METHOD

The analysis of the essential oils was performed using a gas chromatography method (GC-MS) [4]. The analysis method was developed on a Shimadzu GC-MS QP-2010 model gas chromatograph – mass spectrometer equipped with an AOC-5000 autosampler (CombiPAL). Alltech, USA, AT-5 capillary column of 30m x 0.25mm i.d. and 0.25µm film thickness was used. The parameters for the method were: injector temperature 250°C; pressure 37.1 kPa; column flow 1,5 ml/min; linear velocity 44,7 cm/s; split ratio 1:200 (lavender oil) and 1:300 (rosemary oil), sample volume 3 µl (lavender oil) and 2.5 µl (rosemary oil). Carrier gas helium; detector: MS, ion source temperature 250°C; interface temperature 250°C; MS mode: EI; mass range: 40-400u (rosemary oil), 40-650u (lavender oil); scan speed: 769u/s. The temperature program for column oven is presented in Table I for both essential oils analyzed. In the case of headspace injection (HS/GC-MS) the samples were incubated at 85°C for 15 minutes prior the injection.

The identification of the components separated by GC-MS was made by comparing the obtained mass spectra for each component with the values stored in mass spectra libraries, NIST27 and NIST147. The percentage composition of the oils was calculated in peak areas using normalization method.

RESULTS AND DISCUSSION

Lavender oil

The main constituents of Lavender oil are linalool and linalyl acetate. The results from GC-MS analysis revealed 32 components in the oil, and 20 of them were identified, representing 97.77% of total oil composition.

Table I. Column oven temperature program.

Entry	Step 1			Step 2			Step 3			Step 4		
	T	t	r	T	t	r	T	t	r	T	t	r
Rosemary oil	60	5	-	160	-	4	240	-	15	240	1	-
Lavender oil	40	3	-	180	-	7	240	-	30	240	5	-

T - temperature (°C); t – time (min); r – rate (°C/min)

Table II. Composition of Lavender essential oil. The components identified in the highest yields are in bold.

RT	Component	A1	A2	MW	S%	BP
9.47	**α-pinene**	**2.876**	**8.752**	136	97	93
9.88	Camphene	0.056	0.210	136	95	93
10.64	β-pinene	0.729	2.788	136	96	93
11.00	β-myrcene	0.689	0.853	136	96	93
11.36	α-phellandrene	Not found	0.093	136	85	93
11.52	**3-Carene**	**1.942**	**6.008**	136	96	93
11.64	1,4-Cineole	0.200	0.370	154	90	43
11.87	o/m-cymene	0.074	0.324	134	91	119
12.00	Limonene	0.292	0.872	136	93	68
12.07	**1,8-Cineole**	**1.926**	**3.236**	154	97	43
12.20	β-trans-ocimene	0.095	0.209	136	94	93
12.47	β-cis-ocimene	0.118	0.277	136	95	93
12.76	γ-terpinen	0.075	0.327	136	93	93
13.51	Terpinolen	0.400	1.782	136	96	93
13.75	**β-linalool**	**28.139**	**32.394**	154	90	93
14.14	Fenchol	0.052	0.122	154	89	81
14.55	Unknown $C_{11}H_{20}O_2$	0.479	0.746	184	84	69
14.91	**Camphor**	**2.931**	**5.529**	152	96	95
15.20	Borneol	0.481	1.228	154	89	95
15.95	α-terpineol	0.339	0.534	154	89	93
16.90	α-linalool	0.145	0.230	154	89	79
17.34	**Linalyl acetate**	**56.211**	**31.033**	196	91	93
	Component groups					
	Monoterpenes hydrocarbons	**7.272**	**22.171**			
	Oxygenated monoterpenes	**90.424**	**74.676**			
	Among them linalool and linalyl acetate	**84.495**	**63.657**			
	Aromatic terpenes	**0.074**	**0.324**			
	Total	**97.77**	**97.171**			
	Linalool/acetate de linalyl	**0.5**	**1.04**			

RT - Retention time (min); A1 – Area GC-MS (%); A2 – Area HS/GC-MS (%); MW – molecular weight; S – Similarity with mass spectra libraries, NIST27 and NIST147 (%); BP - Base Peak.

Using HS/GC-MS, 36 components were separed using the same working conditions, from which 21 components were identified, representing 97.17% of total composition of the oil (Table II). The components identified were reported previously in the literature data available for lavender and lavandin oils [5-9].

The Headspace preparation of the samples improved the extraction of monoterpenes hydrocarbons, such as α- and β-pinene and 3-carene and of oxignated monoterpenes, such as 1,8-cineole and β-linalool. The content of linalyl acetate detected decreased considerably from 56.211% (GC-MS) to 31.033% (HS/GC-MS) (Table II).

As per literature data, both commercial oils, lavender *(L. angustifolia Mill.)* and lavandin (L. *hybrida R.),* contain lavandulol and lavandulyl acetate as key constituents. *L. latifolia Med.* oil (other species of Lavandula genus) contains these compounds only as traces. Lavandulol was not identified in our sample (Table II). Low content of lavandulol or even the absence of this component was reported previously for Lavender oils originating from India and Bulgaria [8].

The molecular weight, base peak and similarity were obtained following HS/GC-MS analysis.

Rosemary oil

There are three types of rosemary essential oils: Spanish type, rich in α-pinene, 1,8-cineol and camphor; French type, rich in α-pinene, 1,8-cineole and bornyl acetate and African oils (Morocco, Tunisia) with high content of 1,8-cineole [3,5].

A total of 21 components from a total of 27 were identified in rosemary oil by GC-MS which represents 99.11% of total amount. Using HS/GC-MS 23 compounds were identified and evaluated from a total of 32, representing 98.77% from total amount (Table III). The main components were 1,8-cineole, α-pinene, camphor, β-pinene (Table III). All these compounds were reported before as components of rosemary oils [5,10,11]. The high content of 1,8-cineole may suggest an African type of Rosemary oil. We did not identify verbenone in our sample of Rosemary oil. Verbenone is an important constituent of European rosemary oils, although is found only in traces in African type of Rosemary oil [5].

The molecular weight, base peak and similarity were obtained following HS/GC-MS analysis.

In the case of rosemary oil few differences were detected in analysis using liquid and respectively headspace sample preparation (Figure 1).

The proportion of detection of monoterpenes hydrocarbons and 1,8-cineole decreased for rosemary oil when headspace injection (Figure 2). This is due to the increase in concentration of the minor components by HS/GC-MS technique. By the GC-MS technique the dilution of the essential oil in the injection solvent takes place that causes the detection of less minor components during analysis.

Table III. Composition of Rosemary essential oil. The components identified in the highest yields are in bold.

RT	Component	A1	A2	MW	S%	BP
8.09	**α-pinene**	**15.997**	**15.338**	**136**	**97**	**93**
8.65	**Camphene**	**5.479**	**5.343**	**136**	**97**	**93**
9.75	**β-pinene**	**10.280**	**10.963**	**136**	**96**	**93**
10.32	β-myrcene	1.426	1.329	136	96	93
10.85	α-phellandrene	0.319	0.432	136	94	93
11.10	3-carene	0.119	0.162	136	94	93
11.36	2-Carene	0.079	0.186	136	92	121
11.67	**p-cymene**	**2.599**	**3.287**	**134**	**96**	**119**
11.86	**Limonene**	**2.138**	**2.481**	**136**	**92**	**68**
11.97	**1,8-Cineole**	**42.386**	**36.301**	**154**	**97**	**43**
12.25	β-trans-ocimene	0.050	0.073	136	90	93
12.67	β-cis-ocimene	Not found	0.038	136	85	93
13.10	Gamma-terpinene	1.141	1.566	136	94	94
14.32	Terpinolen	0.092	0.135	136	94	93
14.78	β-Linalool	0.313	0.423	196	89	93
16.58	**Camphor**	**10.093**	**12.518**	**152**	**97**	**95**
17.10	Isobornyl formate	0.373	0.482	182	92	95
17.45	**Borneol**	**3.794**	**4.889**	**154**	**95**	**95**
18.42	α-terpineol	0.748	0.890	154	89	93
22.09	Bornyl acetate	0.467	0.950	196	94	95
25.38	α-cubebene	Not found	0.057	204	86	119
26.91	Caryophyllene	1.114	0.773	204	96	41
28.05	α-caryophyllene	0.105	0.151	204	92	93
	Component groups					
	Monoterpenes hydrocarbons	**37.12**	**38.046**			
	Oxygenated monoterpenes	**58.174**	**56.453**			
	Aromatic terpenes	**2.599**	**3.287**			
	Sesquiterpenes	**1.219**	**0.981**			
	Total	**99.112**	**98.767**			
	α-Pinene/β-Pinene	**1.56**	**1.37**			
	1,8-Cineole/Limonene	**19.83**	**14.63**			
	Camphor/Borneol	**2.66**	**2.56**			

RT - Retention time (min); A1 – Area GC-MS (%); A2 – Area HS/GC-MS (%); MW – molecular weight; S – Similarity with mass spectra libraries, NIST27 and NIST147 (%); BP - Base Peak.

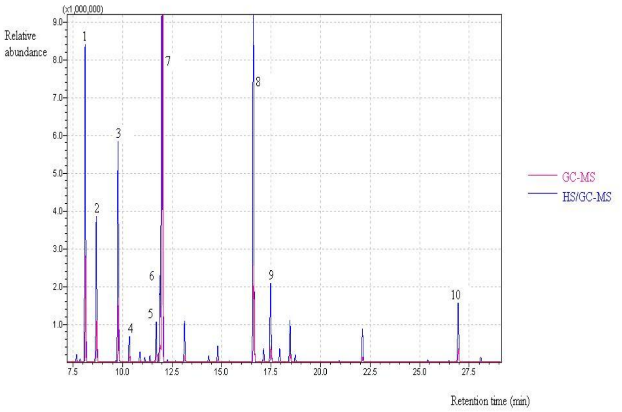

Figure 1. GC-MS versus HS/GC-MS profiles of Rosemary essential oil (1 - α-pinene, 2 – Camphene, 3 – β-pinene, 4 – β-myrcene, 5 – *p*-cymene, 6 - Limonene, 7 – 1,8-cineole, 8 – Camphor, 9 – Borneol, 10 - Caryophyllene).

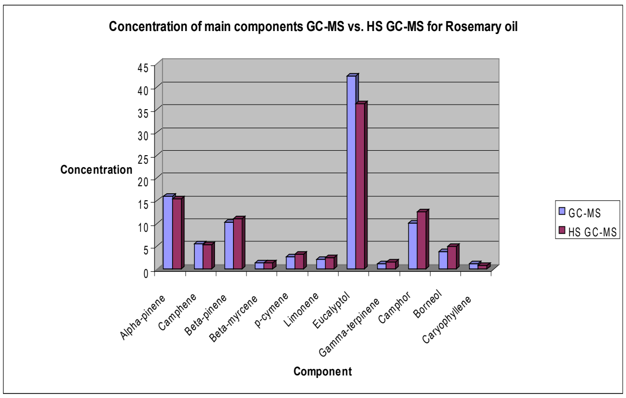

Figure 2. Concentration of main components in Rosemary essential oil.

CONCLUSIONS

The composition of tested samples of lavender and rosemary oils is in agreement with data reported in the literature. However, lavandulol from lavender oil and verbenone from rosemary oil were not detected in these samples.

Both type of sample injection (split-splitless and headspace) show high applicability for the evaluation of essential oils composition. Headspace injection offers a reliable and fast method for evaluation of different samples of essential oils. Further development of the method may be of interest.

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