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Essential Oils: Quality Indicators of Spices in Supermarkets

Aceites esenciales: indicadores de calidad de especias en supermercados

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ABSTRACT

Chemical composition of oregano (*Origanum vulgare* L.), rosemary (*Rosmarinus officinalis* L.) and thyme (*Thymus vulgaris* L.) essential oils traded as spices at supermarkets was determined by Gas-Chromatography-Mass Spectrometry analysis. One hundred-five compounds accounting for 84-98 % of the total essential oils were identified. Significant differences were found in both yield and chemical composition of spice essential oils and the trademarks employed. Oxygenated monoterpenes (51.58-95.39 %) were the principal fraction in all analyzed essential oils. Thymol was the main compound in oregano (79.53 and 27.87 %) and thyme (30.70 and 18.74 %) essential oils followed by carvacrol (15.42 %) or terpinen-4-ol (9.97 %) in oregano trademarks and carvacrol (19.59 %) or borneol (18.00 %) in thyme trademarks. 1,8-cineole (36.74 and 47.39 %) and camphor (20.78 and 15.96 %) were the main compounds in commercial rosemary food items. Large differences in the amount of the main bioactive compounds that can affect both aroma and health benefits are found in the analyzed trademarks.

KEYWORDS: *oregano, rosemary, thyme, essential oils, GC-MS.*

RESUMEN

Se ha determinado la composición química de los aceites esenciales de orégano (*Origanum vulgare* L.), romero (*Rosmarinus officinalis* L.) y tomillo (*Thymus vulgaris* L.) comercializados como especias en supermercados de alimentación, mediante su análisis por Cromatografía de Gases-Espectrometría de Masas. Se identificaron ciento cinco compuestos que representaron entre el 84 y el 98 % de la composición total de los aceites esenciales. Se observaron diferencias significativas tanto en el rendimiento como en la composición química de los aceites esenciales de las especias y marcas comerciales empleadas. Los monoterpenos oxigenados (51,58-95,39 %) fueron la fracción principal en todos los aceites esenciales analizados. Timol fue el componente mayoritario en los aceites esenciales de orégano (79,53 y 27,87 %) y tomillo (30,70 y 18,74 %) seguido de carvacrol (15,42 %) o terpinen-4-ol (9,97 %) en las marcas comerciales de orégano y carvacrol (19,59 %) o borneol (18,00 %) en las de tomillo. 1,8-cineol (36,74 y 47,39 %) y alcanfor (20,78 y 15,96 %) fueron los componentes mayoritarios de los productos comerciales de romero. En las marcas comerciales analizadas se encontraron grandes diferencias cuantitativas en los principales compuestos bioactivos que pueden modificar tanto el aroma como sus efectos beneficiosos para la salud.

PALABRAS CLAVE: *orégano, romero, tomillo, aceites esenciales, CG-EM.*

INTRODUCTION

Aromatic plants have been extensively employed as ornamentals and/or culinary herbs, besides treatment in traditional and complementary medicine around the world. Herbs and spices are two food items that play an important role in diets, beverages, medicines and cosmetics [1] since they improve sensory attributes being useful in numerous culinary dishes, as food additives and preservatives; as well as because of their well-known curative properties as manufacture of pharmaceuticals [2]. A consequence of the flavour and health benefits of spices and herbs is the rapid growth in global trade every year: the value of produced spices worldwide in 2010 was 4709 tonnes; this value increased in three years reaching 5468 tonnes of produced spices [3]. The supply and demand of herbs and spices are fundamental economic steps which determine their price [4].

Despite this increasing trend in the use of herbs and spices, consumers should be cautious, as the adulteration or fraud of these products is more frequent than in other food ingredients: dried herbs and spices can be contaminated by a wide variety of pathogenic microorganisms, mycotoxins, pesticides, as well as by unintended substances coming from the technology employed; being in some cases the adulteration deliberated due to economic or other reasons [5]. In this sense, *Origanum vulgare* L., an endemic aromatic plant of the Mediterranean area commonly associated to pizza and other Mediterranean dishes, was subjected to a study of fraudulent adulteration in which over 24 % of 78 samples contained some form of adulterant [4]. In general, *Origanum* spp. are usually confused between them and also with other Mediterranean aromatic plant species, such as *Thymus* [6,7] and *Rosemary* spp., so the analysis of their chemical composition and other reliable test methods have been developed in order to authenticate the botanical origin and mixtures of herbs [8]commonly referred to as herbal teas are among the most widely consumed hot beverages. Herbal tea authenticity is an issue of food safety. Reliable test methods, which could identify the botanical origin of herbal tea products, are required in order to protect the consumer from fraud and authenticate genuine products considering also the potential medical use of the herbs. Herein, we present a method that enables the simultaneous and reliable identification of 9 herbal species of sage, Greek sage, chamomile, mountain-tea, oregano, Cretan oregano, yarrow, lemon balm and rosemary. A high resolution melting (HRM. Regarding this, many countries have released certain regulations in order to assess the quality and quantity of the potential contaminants, reduce and prevent their presence in these food items and save confusions between spices and herbs and so avoid potential hazard for consumers [9].

Specifically, variations in spices and herbs caused by adulterations, addition of foreign materials and low quantity or poor-quality amounts of them, could be clearly identified through the study of the chemical composition of their resulting essential oils [10] that have been a key study for many years, mainly looking for the knowledge of chemotypes [11]. According to the European Pharmacopoeia, an essential oil is defined as a manufactured product from pure, identified raw materials of plant origin, obtained by hydrodistillation, steam distillation or "dry" distillation for some woods and mechanical processes in the case of *Citrus* fruits. In many cases, the chemical composition of essential oils varies naturally according to intrinsic factors (plant genotype) and numerous extrinsic factors, such as plant origin, geographic location, soil, climate, etc.; but in other cases, other materials, including non-volatile ingredients, synthetic and natural compounds or another essential oils are added due to olfactory or economic reasons [12]. Field experiments demonstrated that foliar nutrition (including N, P and K in combination with salicylic acid) in *T. vulgaris* plants can significantly increase the yield of the essential oils as well as the amount of the main compounds [13]. These induces qualitative and quantitative changes in the essential oil composition which could affect its medicinal and organoleptic properties.

Hence, the aims of this study included the analyses through Gas Chromatography-Mass Spectrometry of the essential oils of oregano, rosemary and thyme obtained by hydrodistillation from two trademarks sold in food supermarkets, in order to determine their chemical composition, to identify the qualitative and quantitative difference among trademarks and to compare quality-price relationship between these widely consumed food ingredients in the Mediterranean gastronomy.

MATERIALS AND METHODS

Plant Material

Two Spanish leading brands of dried oregano (*Origanum vulgare* L.), rosemary (*Rosmarinus officinalis* L.) and thyme (*Thymus vulgaris* L.) traded as spices at public food markets were purchased.

Obtention of Essential Oils

One hundred grams of each spice with three replicates by brand were subjected to hydrodistillation for 3 h in a Clevenger-type apparatus. Essential oils were dried over anhydrous sodium sulphate and stored at 4 ºC until GC-MS analysis.

Gas Chromatography-Mass Spectrometry Analysis

A GC-MS analysis was carried out with a 5973N Agilent equipment, with a capillary column (95 dimethylpolysiloxane-5 % diphenyl), Agilent HP-5MS UI (30 m long and 0.25 mm i. d. with 0.25 µm film thickness). The column temperature program was 60 ºC during 5 min, with 3 ºC/min increases to 180 ºC, then 20 ºC/min increases to 280 ºC, which was maintained for 10 min. The carrier gas was helium at a flow-rate of 1 mL/min. Split mode injection (ratio 1:30) was employed. Mass spectra were taken over the *m/z* 30-500 range with an ionizing voltage of 70 eV. Kovat's retention index was calculated using co-chromatographed standard hydrocarbons. The individual compounds were identified by Mass Spectrometry (MS) and their identity was confirmed by comparison of their Retention

Indexes (RIs), relative to C_8-C_{32} *n*-alkanes, and mass spectra with reference samples or with data already available in the NIST 2005 mass spectral library and in the literature [14].

RESULTS AND DISCUSSION

Eighteen samples of oregano, rosemary and thyme (including two commercial brands for each spice) available at food supermarkets were subjected to hydrodistillation yielding 1.07±0.12 and 0.20±0.09 %; 1.03±0.46 and 2.03±0.12 %; and 2.40±0.20 and 0.20±0.00%, respectively, of yellowish essential oils. No relationship was observed between yield and trademark used. Trademark 1 provided a higher yield than trademark 2 in oregano and thyme, whereas trademark 2 was higher in rosemary samples. This fact may be due to the characteristics of the rosemary leaves employed: trademark 2 leaves were greener than trademark 1, probably due to desiccation process; furthermore, differences among rosemary samples of the same trademark have been observed that may be probably due to the different time of harvest required to provide the market with a continuous new spices supply. Thus, 0.5 % yield was obtained from rosemary samples with an expiration date 7th April 2017, while the same yield (1.3 %) was observed in the six samples with the same expiration date 8th July 2017. Not only the characteristics of the samples can influence the properties of the resulting essential oils, but also the obtaining process that can affect both the chemical composition and aroma of essential oils. Previous studies showed that rosemary essential oil obtained by supercritical carbon dioxide extraction reproduced better the natural aroma of rosemary leaves than rosemary essential oil hydrodistilled, due to the higher content of oxygenated monoterpenes which strongly contribute to the fragrance [15].

One hundred-five compounds accounting for 84.22-98.32 % of the essential oils were identified by capillary GC-MS, a powerful combination in quality control of volatiles [16]. Components are listed (Table 1) as homologous series of monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpenes, diterpene hydrocarbons, oxygenated diterpenes, aromatic compounds and others and listed according to Kovat's RI.

Table 1. Identified compounds in oregano, rosemary and thyme essential oils in commercial food items employed

Compound	RT	RI Cal	RI Ref	*Origanum vulgare* L.		*Rosmarinus officinalis* L.		*Thymus vulgaris* L.	
				Peak Area (%) Trademark 1	Peak Area (%) Trademark 2	Peak Area (%) Trademark 1	Peak Area (%) Trademark 2	Peak Area (%) Trademark 1	Peak Area (%) Trademark 2
Monoterpene Hydrocarbons				***0.22±0.13***	***3.19±4.14***	***11.79±4.21***	***20.39±1.78***	***35.25±2.30***	***11.05±1.96***
Tricyclene	6.421	926	926	-	-	0.04±0.04	0.12±0.03	0.02±0.01	0.06±0.04
α-Thujene	6.599	931	930	-	0.04±0.04*	0.02±0.02	-	0.78±0.13	0.05±0.03
α-Pinene	6.888	939	939	-	0.02±0.03*	5.72±2.61	10.60±0.70	1.08±0.14	1.59±0.59
Camphene	7.398	953	954	-	-	1.82±0.71	3.64±0.72	0.54±0.09	2.36±1.15
Sabinene	8.360	976	975	-	0.16±0.27*	-	-	-	-
β-Pinene	8.481	979	979	-	-	0.71±0.32	1.06±0.08	0.27±0.04	0.12±0.09
Myrcene	9.123	993	990	-	0.09±0.13	0.47±0.10	1.01±0.14	1.37±0.16	0.22±0.18
α-Phellandrene	9.647	1005	1002	-	0.02±0.04*	0.15±0.01	0.23±0.07	0.12±0.10	-
δ-3-Carene	9.902	1012	1011	-	-	0.03±0.02	0.04±0.00	0.06±0.04	-
α-Terpinene	10.200	1019	1017	0.02±0.01	0.56±0.67	0.41±0.05	0.51±0.11	1.37±0.59	0.17±0.14
p-Cymene	10.538	1027	1024	0.12±0.07	0.31±0.53*	1.83±0.37	2.86±0.09	19.87±5.15	5.13±2.83
Limonene	10.638	1030	1029	-	0.26±0.31	-	-	0.31±0.01	0.48±0.10
β-Phellandrene	10.707	1031	1029	-	0.26±0.31	-	-	-	-
cis-Ocimene	11.177	1042	1037	-	0.06±0.10*	-	-	-	-
trans-Ocimene	12.050	1050	1050	-	-	-	-	0.04±0.03	-
γ-Terpinene	12.102	1062	1059	0.08±0.06	1.20±1.47	0.32±0.03	0.07±0.11	9.57±2.67	0.76±0.18
Terpinolene	13.460	1089	1088	-	0.23±0.28*	0.27±0.02	0.27±0.05	0.20±0.02	0.11±0.10
Oxygenated monoterpenes				***95.39±0.50***	***51.58±25.30***	***79.58±1.93***	***76.19±2.37***	***59.51±2.43***	***61.84±7.66***
1,8-cineole	11.034	1039	1031	-	-	36.74±12.20	47.39±2.07	1.08±0.21	1.15±0.46
cis-Sabinene Hydrate	12.429	1069	1070	-	0.27±0.47*	-	-	0.18±0.07	-
Linalool Oxide	12.724	1075	1072	-	-	0.01±0.01	0.01±0.01	-	-
Linalool	14.030	1100	1096	0.05±0.020	0.56±0.41	1.33±0.30	1.11±0.16	6.69±2.21	2.29±0.11
trans-Sabinene Hydrate	14.073	1101	1098		1.72±2.74*				
α-Fenchol	14.626	1114	1116	-	-	0.12±0.02	0.09±0.01	-	-
cis-*p*-Menth-2-en-1-ol	15.002	1123	1121	-	0.76±0.49	0.06±0.02	0.04±0.00	-	-
α-Campholenal	15.205	1128	1126	-	-	0.07±0.01	0.06±0.01	-	-
trans-*p*-Menth-2-en-1-ol	15.824	1141	1140	-	0.65±0.40	-	-	-	-
Camphor	16.162	1149	1146	-	-	20.78±2.61	15.96±0.62	0.04±0.04	2.20±0.57
Isoborneol	16.598	1158	1160	-	-	0.10±0.02	0.07±0.02	-	-
trans-Pinocamphone	16.778	1162	1162	-	-	0.15±0.09	0.21±0.01	-	-
Pinocarvone	16.881	1164	1164	-	-	0.17±0.07	0.15±0.01	-	-
Borneol	17.096	1168	1169	0.20±0.03	0.10±0.09*	8.26±2.74	4.35±0.35	0.21±0.16	18.00±7.20
Terpinen-4-ol	17.615	1178	1177	-	9.97±6.52	1.54±0.44	0.91±0.03	0.30±0.14	1.01±0.18
p-Cymen-8-ol	17.927	1184	1182	0.05±0.04	-	-	-	-	-
α-Terpineol	18.322	1192	1188	0.09±0.01	2.54±1.61	7.38±2.22	4.05±0.28	0.09±0.08	7.08±3.00
cis-Piperitol	18.474	1195	1196	-	0.23±0.21*	-	-	-	-
Myrtenol	18.508	1196	1195	-	-	-	0.10±0.00	-	-
γ-Terpineol	18.591	1197	1199	-	-	-	-	-	-
trans-*p*-Menth-8-en-2-one	18.900	1203	1200	0.02±0.01	-	-	-	-	-
Verbenone	19.027	1207	1205	-	-	0.71±0.57	0.71±0.14	-	-
trans-Piperitol	19.053	1207	1208	-	0.47±0.27	-	-	-	-

Compound	RT	RI $_{Cal}$	RI $_{Ref}$	*Origanum vulgare* L. Peak Area (%) Trademark 1	*Origanum vulgare* L. Peak Area (%) Trademark 2	*Rosmarinus officinalis* L. Peak Area (%) Trademark 1	*Rosmarinus officinalis* L. Peak Area (%) Trademark 2	*Thymus vulgaris* L. Peak Area (%) Trademark 1	*Thymus vulgaris* L. Peak Area (%) Trademark 2
Citronellol	20.001	1230	1225	-	-	0.07±0.02	0.01±0.02	-	-
Nerol	20.050	1231	1229	-	0.09±0.05			-	-
Methyl Thymol	20.327	1237	1235	-	0.34±0.24	-	-	0.02±0.01	-
Pulegone	20.451	1240	1237	-	-	0.03±0.03	0.03±0.01	-	-
Cuminaldehyde	20.459	1240	1241	-	0.20±0.11	-	-	-	-
Carvone	20.654	1245	1243	-	-	-	0.01±0.01	-	-
Methyl Carvacrol	20.746	1246	1244	-	0.84±0.57	-	-	0.47±0.16	2.89±1.28
Linalyl Acetate	21.256	1247	1257	-	1.10±0.85	-	-	-	-
Isobornyl Acetate	22.880	1285	1285	-	-	-	-	-	0.69±0.22
Bornyl Acetate	22.599	1286	1288	-	-	1.52±0.80	0.58±0.37	-	0.93±0.22
Thymol	22.820	1290	1290	79.53±6.06	27.87±12.15	0.31±0.20	0.12±0.08	30.70±4.58	18.74±5.14
Carvacrol	23.213	1298	1299	15.42±6.38	2.87±1.06	0.23±0.16	0.24±0.04	19.59±1.75	6.85±1.81
Thymyl Acetate	26.030	1352	1352	-	-	-	-	0.02±0.01	-
Neryl Acetate	26.158	1367	1361	-	0.32±0.12	-	-	-	-
Piperitone Oxide	26.178	1368	1368	0.04±0.01	-	-	-	-	-
Carvacryl Acetate	27.060	1372	1372	-	-	-	-	0.05±0.04	-
Geranyl Acetate	27.000	1386	1381	-	0.69±0.21	-	-	-	-
Geranyl Butyrate	34.500	1564	1564	-	-	-	-	0.04±0.02	-
Sesquiterpene Hydrocarbons				***1.16±0.31***	***10.82±1.35***	***2.18±1.62***	***0.71±0.16***	***2.12±0.41***	***4.94±1.44***
δ- Elemene	24.883	1339	1338	-	0.22±0.02	-	-	-	-
α-Ylangene	26.299	1371	1375	-	-	-	-	-	-
α-Copaene	26.498	1375	1376	-	-	0.11±0.08	-	-	0.14±0.11
β-Bourbonene	27.380	1388	1388	-	-	-	-	0.01±0.01	-
β-Caryophyllene	28.324	1418	1419	0.57±0.16	5.35±0.60	1.77±1.26	0.49±0.14	1.73±0.40	3.51±1.32
Aromadendrene	29.154	1438	1441	0.09±0.02	0.16±0.03	-	-	-	-
α-Humulene	29.727	1453	1454	0.14±0.01	0.74±0.08	-	0.13±0.01	0.06±0.01	0.22±0.19
trans-β-Farnesene	29.999	1459	1456	0.09±0.06	-	-	-	0.05±0.01	-
γ-Muurolene	30.713	1476	1479	-	-	-	0.01±0.01	-	-
α-Curcumene	31.011	1483	1480	0.03±0.03	-	-	-	-	-
Bicyclogermacrene	31.564	1496	1500	-	4.11±0.66	-	-	-	-
α-Muurolene	31.595	1496	1500	-	-	-	-	-	-
β-Bisabolene	31.959	1506	1505	0.25±0.05	0.04±0.04*	-	-	-	-
γ-Cadinene	32.510	1513	1513	-	-	-	-	0.05±0.02	0.41±0.11
Calamenene	32.560	1522	1522	-	-	-	0.04±0.01	-	-
δ-Cadinene	32.587	1523	1523	-	0.21±0.05	0.24±0.22	0.04±0.01	0.14±0.02	0.65±0.17
α-calacorene	33.334	1543	1545	-	-	0.06±0.06	0.02±0.01	-	-
Cadalene	38.293	1674	1676	-	-	-	0.01±0.00	-	-
Oxygenated Sesquiterpenes				***1.28±0.10***	***19.60±13.56***	***1.30±0.90***	***0.40±0.03***	***0.69±0.13***	***4.52±1.42***
E-Nerolidol	34.217	1565	1563	-	0.59±0.35	-	-	-	-
Caryophyllenol	34.330	1568	1572	-	-	-	0.02±0.01	-	-
Spathulenol	34.681	1579	1578	0.58±0.06	8.95±4.81	-	-	0.04±0.01	-
Caryophyllene Oxide	34.838	1581	1583	0.60±0.12	4.86±2.54	1.14±0.81	0.29±0.02	0.60±0.11	2.02±0.64
Globulol	35.199	1590	1590	-	0.65±0.48	-	-	-	-

Compound	RT	RI $_{Cal}$	RI $_{Ref}$	*Origanum vulgare* L. Peak Area (%) Trademark 1	*Origanum vulgare* L. Peak Area (%) Trademark 2	*Rosmarinus officinalis* L. Peak Area (%) Trademark 1	*Rosmarinus officinalis* L. Peak Area (%) Trademark 2	*Thymus vulgaris* L. Peak Area (%) Trademark 1	*Thymus vulgaris* L. Peak Area (%) Trademark 2
Oxygenated Sesquiterpene MW 220	35.538	1600	-	-	0.41±0.71*	-	-	-	-
Oxygenated Sesquiterpene MW 220	35.861	1607	-	-	0.32±0.56*	-	-	-	-
Humulene Epoxide II	36.160	1608	1608	-	-	0.15±0.10	0.05±0.01	-	0.59±0.17
10-*epi*-γ-Eudesmol	36.640	1623	1626	-	-	-	-	0.05±0.01	-
Oxygenated Sesquiterpene MW 220	36.858	1635	-	-	0.38±0.66*	-	-	-	-
Isospathulenol	36.947	1638	-	0.06±0.01	1.66±1.45	-	-	-	-
epi-α-Cadinol	37.050	1640	1640	0.04±0.01	-	-	-	-	0.88±0.24
α-Cadinol	37.554	1654	1654	-	0.93±0.65	-	0.01±0.00	-	-
Oxygenated Sesquiterpene MW 220	38.150	1670	-	-	0.84±1.45*	-	-	-	-
α-Bisabolol	38.640	1683	1685	-	-	-	0.03±0.01	-	-
Eremophilone	40.850	1736	1736	-	-	-	-	-	0.53±0.21
8-Hydroxy-Eremophilone	44.650	1847	1847	-	-	-	-	-	0.51±0.35
Diterpene Hydrocarbons				***-***	***0.33±0.34***	***-***	***-***	***-***	***0.62±0.13***
Abietatriene	48.014	2064	2056	-	0.33±0.34	-	-	-	0.62±0.13
Oxygenated Diterpenes				***0.08±0.03***	***2.99±3.97***	***-***	***-***	***-***	***-***
trans-Phytol	48.487	2116		0.08±0.03	1.35±1.34	-	-	-	-
Oxygenated Diterpene	48.713	2146	-	-	0.41±0.71*	-	-	-	-
Oxygenated Diterpene	49.309	2231	-	-	0.39±0.68*	-	-	-	-
Oxygenated Diterpene	49.601	2279	-	-	0.43±0.75*	-	-	-	-
Dehydroabietol	50.130	2371	2368	-	0.41±0.52	-	-	-	-
cis-Ferruginol	50.203	2386	2371	-	-	-	-	-	1.25±0.72
Aromatics (C_6-C_3 y C_6-C_1)				***0.04±0.01***	***0.36±0.14***	***0.09±0.04***	***0.13±0.02***	***0.03±0.01***	***-***
Eugenol	26.47	1359	1359	-	-	0.09±0.04	0.05±0.01	0.03±0.01	-
Methyl Eugenol	27.845	1406	1403	0.04±0.01	-	-	0.08±0.01	-	-
Myristicin	32.523	1521	1518	-	0.27±0.06	-	-	-	-
Benzyl Benzoate	41.430	1762	1760	-	0.10±0.09	-	-	-	-
Others				***0.09±0.03***	***2.22±2.35***	***0.29±0.07***	***0.18±0.03***	***0.72±0.30***	***-***
1-Octen-3-ol	8.644	983	979	0.06±0.03	-	0.13±0.01	-	0.72±0.30	-
3-Octanone	8.900	988	983	-	-	0.03±0.03	0.14±0.03	-	-
trans-β-Ionone	31.140	1486	1488	-	0.09±0.08	-	-	-	-
Methyl Jasmonate	37.351	1648	1649	-	-	0.13±0.10	0.04±0.01	-	-
6,10,14-Trimethyl-2-Pentadecanone	44.298	1850		0.03±0.01	0.36±0.29	-	-	-	-
Octadecanol	48.229	2086	2077	-	1.17±1.32*	-	-	-	-
Methyl Linoleate	48.389	2103	2085	-	0.25±0.25	-	-	-	-
Pentacosane	50.827	2499	2500	-	0.35±0.49	-	-	-	-
TOTAL				**98.26±0.84**	**91.10±7.25**	**95.21±1.56**	**98.00±1.06**	**98.32±1.12**	**84.22±2.74**

Compounds listed in order of elution in the HP-5MS column. RI: retention index relative to C_8-C_{32} n-alkanes on the HP-5MS column. Peak area values are means ± standard deviation of three samples. *: identified compound only in one or two samples.

Monotepene fraction was the major phytochemical group in all analysed essential oils (O1: 95.61 %, O2: 54.77 %; R1: 91.37 %, R2: 96.58 %; T1: 94.76 %, T2: 72.89 %), being qualitatively and quantitatively the oxygenated monoterpenes the main fraction (O1: 95.39±0.50 %, O2: 51.58±25.30 %; R1: 79.58±1.93 %, R2: 76.19±2.37 %, T1: 59.51±2.43 %, T2: 61.84±7.66 %). Thymol was the principal oxygenated monoterpene in oregano (79.53±6.06 %, 27.87±12.15 %) as well as thyme (30.70±4.58 %, 18.74±5.14 %) essential oils, followed by carvacrol in trademark 1 (O1: 15.42±6.38 % T1: 19.59±1.75 %) (Figure 1) and terpinen-4-ol (9.97±6.52 %) in oregano essential oils and borneol (18.00±7.20 %) in thyme essential oils obtained from trademarks 2. Both alcohols were absent or in lesser amounts in the first analysed trademark (Figure 2).

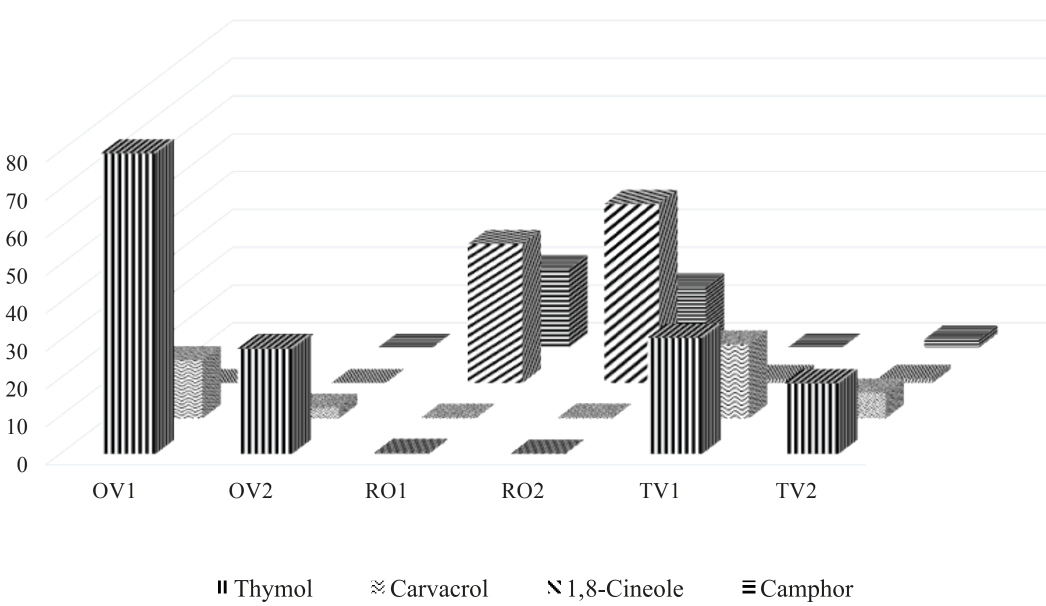

Figure 1. Main compounds in oregano, rosemary and thyme essential oils. (OV1: O. vulgare trademark 1; OV2: O. vulgare trademark 2; RO1: R. officinalis trademark 1; RO2: R. officinalis trademark 2; TV1: T. vulgaris trademark 1; TV2: T. vulgaris trademark 2).

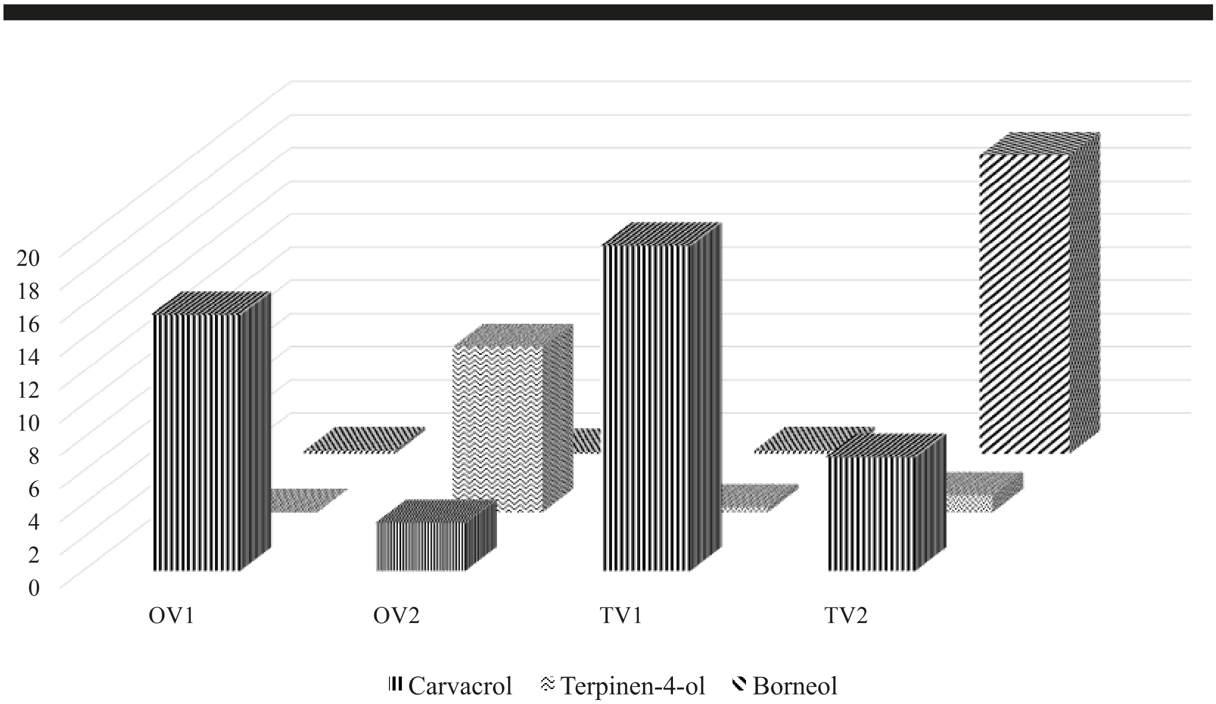

Figure 2. Differences in the percentage of secondary oxygenated monoterpenes in oregano and thyme essential oils between both trademarks (OV1: *O. vulgare* trademark 1; OV2: *O. vulgare* trademark 2; TV1: *T. vulgaris* trademark 1; TV2: *T. vulgaris* trademark 2).

The variations in the chemical composition of these essentials, especially *O. vulgare*, which is the most variable species of the genus *Origanum* [17] it is well known. Previous studies showed differences in the main compounds in oregano and thyme essential oils with respect to ours results, being more significant in oregano essential oil with carvacrol (64.50 %), followed by *p*-cymene (10-90 %) and γ-terpinene (10.80 %) as the main compounds [18]

Also, qualitative and quantitative differences were observed in monoterpene hydrocarbons (35.25±2.20 %, 11.05±1.96 %) of thyme essential oil, with *p*-cymene (19.87 %) and γ-terpinene (9.57 %) as the main compounds of this fraction in trademark 1, biogenetic precursors of thymol and carvacrol, that only reached 5.13 % and 0.76 % respectively in trademark 2 (Table 1, Figure 3). This variability in the composition of *T. vulgaris* essential oil could be due by genetic or climatic and growing conditions [19] as well as a way of drying.

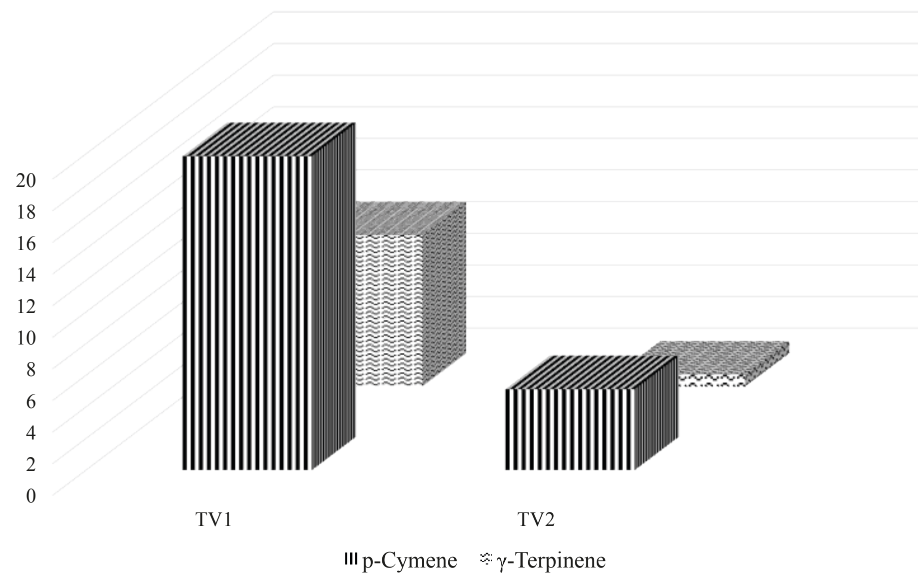

Figure 3. Differences in the percentage of the monoterpene hydrocarbons *p*-cymene and γ-terpinene between both trademarks of thyme essential oils (TV1: *T. vulgaris* trademark 1; TV2: *T. vulgaris* trademark 2).

On the other hand, 1,8-cineole (36.74±12.20 %, 47.39±2.07 %) was the main compound in all analysed rosemary samples (Figure 1), matching with *Rosmarinus officinalis* essential oil coming from Lebanon [20] and followed by camphor (20.78 %, 15.96 %) (Figure 1), which is a responsible compound of the antimicrobial [21], antifungal [22] and antiproliferative [23] properties of rosemary essential oil.

However, differences in the monoterpene fraction, mainly in monoterpene hydrocarbons (11.79±4.21 %, 20.39±1.78 %) were also found between trademarks. In this sense, relative large amounts of α-pinene (10.60 % *vs* 5.72 %), camphene (3.64 % *vs* 1.82 %) and *p*-cymene (2.86 % *vs* 1.83 %) were found in trademark 2 regarding trademark 1 (Table 1).

Although the sesquiterpene fraction (O1: 2.44 %, O2: 30.42 %; R1: 3.48 %, R2: 1.11 %; T1: 2.81 %, T2: 9.46 %) was not as abundant, with the exception of oregano essential oil samples obtained from trademark 2, qualitative and quantitative variations between both trademarks were also observed (Table 1). The largest differences were found in oregano and thyme samples obtained from trademark 2. Between sesquiterpene hydrocarbons, β-caryophyllene reached 5.35±0.60 % and 3.51±1.32 % in oregano and thyme trademark 2, whereas in trademark 1 it only added up to 0.57 % and 1.73 %, respectively. The sesquiterpene hydrocarbon bicyclogermacrene with a percentage of 4.11 % in oregano trademark 2 was not detected in the other analyzed essential oils. Among the oxygenated sesquiterpenes, caryophyllene oxide was found in all essential oils, while spathulenol and isospathulenol were identified only in oregano. The rest of oxygenated sesquiterpenes only were detected in a trademark of the analyzed spices (Table 1).

Regarding the diterpene fraction, it is interesting to note the presence of abietatriene in oregano (0.33±0.34 %) and thyme (0.62±0.13 %) in trademark 2 as well as the oxygenated diterpenes *trans*-phytol in both oregano trademarks, and dehydroabietol (0.41±0.52 %) or *cis*-ferruginol (1.25±0.72 %) only again in trademark 2 in oregano and thyme, respectively.

Finally, no homogeneity was found between compounds derived from shikimic acid pathway. The phenylpropanoid eugenol was detected in both trademarks of rosemary and thyme in trademark 1, whereas methyl eugenol was the only one detected in oregano essential oil trademark 1 (0.04±0.01 %) and rosemary essential oil trademark 2 (0.08±0.01 %).

CONCLUSION

Aroma, taste and preservative properties of spices are the most appreciated attributes by consumers. Many factors such as provenance of the plant, harvest time dry and preservation processes represent important variables affecting yield and chemical composition. Our study showed that no relationships between percentages of the main bioactive compounds, price and trademark can be established. The higher price of oregano in trademark 1 regarding trademark 2 could be justified by its high content of thymol (79.53 *vs* 27.87 %) and carvacrol (15.42 *vs* 2.87 %); however, the most expensive brand (trademark 1) of rosemary essential oils showed both less yield and lower percentage of the main bioactive compound, 1,8-cineole. Further studies are necessary with the same and/or other essential oils and trademarks in order to establish a good relation quality-price in a trademark.

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