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Comparison of the chemical composition of commercial products containing Matricaria chamomilla L. essential oil

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ABSTRACT: Matricaria chamomilla L. (German chamomile) is an annual aromatic plant commonly used for its medicinal properties in herbal teas and as a source of essential oil (EO) as well. The aim of the present study is to evaluate the chemical composition of EO from wild Bulgarian M. chamomilla and to compared it to the chemical composition of commercial Matricaria chamomilla L. EOs using gas chromatography with mass spectrometry. All examined samples were characterized by the presence of mainly sesquiterpenes and their oxygenated derivatives. The essential oil from wild chamomile contained 16 components. The most abundant compounds were the bisabolol oxides: α-bisabolol Oxide B and α-bisabolol Oxide A. The chemical composition of the commercial samples varied widely.A total of 13, 25, and 35 volatile constituents were identified in each sample respectively. All the samples contained significant amounts of (E)-β-farnesene, while the content of bisabololoids was lower.

KEYWORDS: Matricaria chamomilla L., essential oil, GC-MS

I. INTRODUCTION

Matricaria chamomilla L. (M. chamomilla) (synonymsMatricaria recutita L. and Chamomilla recutita L. Rauschert), also known as German chamomile, is an annual aromatic plant native to to Europe and Western Asia, commonly used for its medicinal properties in herbal teas, as well as a source of essential oil (EO) [1]. It is an important medicinal plant and is widely used in the traditional medicine of different countries. M. chamomilla is usually prepared as infusion or decoction and it's used for wide range of conditions including gastrointestinal and digestive disorders such as gastralgia, spasms and nausea, nervous disorders, infections of the mouth, throat, skin, and the eyes [2].

The M. chamomilla essential oil (MEO) is produced primarily from the flowers and flower heads of the plant, and it differs from other EOs by its chemical composition, consisting mainly of sesquiterpenes and their derivatives and only trace amounts of monoterpenes [3]. The principal sesquiterpenes present in the MEO are farnesene, α-bisabolol, α-bisabolol oxides A and B, as well as the sesquterpene lactone matricin and its derivative chamazulene [4]. Chamazulene is not naturally present in the plant and is formed by the decomposition of matricin during the process of obtaining the EO by hydrodystillation [5]. In addition, the MEO contains significant amounts of acetylenic compounds such as polyacetylenic spiroethers and matricaria ester [6,7].

The MEO and its components are associated with diverse biological and pharmacological properties including anti-inflammatory, anti-allergic, and anti-microbial activities [8]. MEO exhibited psychopharmacological activities in vivo, demonstrating stimulant effect similar to that of caffeine [9]. Bisabolol-Oxides-Rich MEO showed antihyperalgesic and antiedematous activities in rats [10]. In a randomized controlled clinical trial, MEO applied topically significantly reduced the analgesic demand in patients with osteoarthritis and demonstrated safety [11]. In another randomized double-blind placebo-controlled trial topical MEO showed significant improvement of severe carpal tunnel syndrome symptoms [12].

In aromatherapy, the MEO is one of the three main types of chamomile EOs used[13]. The effects of MEO in aromatherapy has been assessed by different studies. A randomized controlled clinical trial showed that the inhalational aromatherapy using combination of lavender and chamomile EOs significantly improved the symptoms associated with psychological conditions such as depression, anxiety and stress in elderly [14]. In addition, massage with the combination of lavender and chamomile aromatherapy reduced the anxiety and improved the quality of sleep in patients with burns [15]. In another clinical trial, chamomile aromatherapy alone and especially in combination with oxygen, showed a reduction of the pain in women following cesarian section with spinal anesthesia [16].

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The MEO is included in the European Pharmacopoeia (EP). According to the monograph, there are two types of MEO – one that is rich in bisabolol oxides and one that is rich in (-)-α-bisabolol. The EP monograph sets requirements for the percentage content of these compounds and chamazulene depending on the type of the oil [17].

The aim of the present study was to evaluate the chemical composition of EO obtained from the flowers of wild-grown M. chamomilla and to compare it to the composition of commercial chamomile EOfound in the Bulgarian market.

II. MATERIALS AND METHODS

Chemicals and Reagents:

For the determination of the retention indices (RI) of the volatile constituents, the following hydrocarbons were used: nonane (≥99%), decane (≥99%), undecane (≥99%), dodecane (99%), tridecane (≥99%), tetradecane (≥99%), hexadecane (≥99%), heptadecane (99%), octadecane (99%), nonadecane (99%), eicosane (99%), heneicosane (≥99.5%), docosane (99%), and tricosane purchased from Merck KGaA (Darmstadt, Germany). For the dilution of the EOs, hexane purchased from Thermo Fisher Scientific GmbH (Bremen, Germany) was used.

Plant Material and Oil Extraction:

The flowers of wild-grown M. chamomilla were collected in The Tundja Hilly Plane floristic region, South Bulgaria (42°01'42.9"N 26°28'06.9"E). The air-dried flowers were subjected to hydrodistillation using Clevenger-type apparatus for 4 h to obtain the EO. The collected EO was dried over anhydrous sodium sulfate and stored at 4°C in dark glass vials until future GC-MS analysis. The commercial EOs were purchased from local pharmacies.

Chromatographic conditions:

For the analysis of the EOs gas chromatography with mass spectrometry (GC-MS) was used. The analyses were performed using Bruker Scion 436-GC SQ MS (Bremen, Germany) equipped with a Bruker BR-5ms fused silica capillary column (0.25 µm film thickness and 15 m × 0.25 mm i.d.). The carrier gas was helium at a constant flow rate of 1mL/min. The volume of the injection was 1µL with split ratio of the injector 1:60 and temperature of the injector set to 250 °C. The temperature of the oven was initially set at 50 °C for 1 min, then it was increased to 130 °C at a rate of 10 °C/min, and increased to 160 °C at a rate of 2 °C/min, and after that it was increased to 270 °C at a rate of 15 °C/min and held for 1 min. The temperature of the detector was set to 300 °C. The mass spectra were obtained in full scan mode with a mass range of 50–350 m/z. The identification of the constituents was performed by comparing their MS spectra with spectral data within the Wiley NIST11 Mass Spectral Library (NIST11/2011/EPA/NIH) and the literature data. The RIs were calculated using the retention times of the n-alkane series (C8–C30) injected under the same conditions described above.

III. RESULTS AND DISCUSSION

The extracted MEO was dark blue in colour with characteristic smell. The samples from the distilled EO and the commercial EOs were diluted with hexane and analyzed with GC-MS. In the EO from wild M. chamomilla (WEO) a total of sixteen constituents were identified, representing 85.67% of the total EO. The results from the analysis are present in table 1 and the chromatograms are present in figure 1.

All the analyzed EOs were characterized by the presence of mainly sesquiterpenes and their oxygenated derivatives. In the EO from wild M. chamomilla (WEO) small amounts of oxygenated monoterpenes (MO) were found representing 2.26 % of the total EO. Among the MO artemisa ketone (1.54%) and yomogi alcohol (0.72%) were identified. Compared to the commercial EO, in the extracted EO only limited amounts of sesquiterpene hydrocarbons (SH) were present (1.64%), represented by (E)-β-farnesene. The most abundant compounds were the oxygenated sesquiterpenes (SO), representing 71.75% of the total EO. The prevailing components from the SO were the two bisabolol oxides - α-bisabolol oxide B (27.26%) and α-bisabolol oxide A (21.37%), as well as α-bisabolone oxide A (11.41%). The higher amounts of bisabolol oxides (48.63%) compared to the limited amounts of bisabolol (0.68%) determine the type of the EO as bisabolol oxides-rich type of Matricaria EO. In addition, the EO from wild M. chamomilla meets the requirements of the EP monograph of Matricaria oil for content of bisabolol oxides (29-81%). The chamazulene content was 3.64% of the total EO, which also meets the requirements of the EP (≥1%). The WEO also contained significant amounts of spiroethers (13.66%).

The samples from the commercial EOs (CP1, CP2, CP3) contained 13, 25, and 35 volatile constituents, representing 90.02%, 84.98%, and 85.49% of the total EO respectively. The chemical constituents of the commercial EO samples differ from that of the wild EO. The main class of volatile compounds present in two of the samples (CP1 and

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CP3) are the sesquiterpene hydrocarbons (SH), representing 59.22% and 58.88% of the total EOs respectively, whereas CP2 contained predominantly

Table 1. Volatile chemical compound, identified in the EO from wild-grown M. chamomilla (WEO) and commercial products containing MEO (CP1, CP2, CP3), where tr-traces (less than 0.05%).

№	Compound	RI	Formula	Class of compound	% WEO	% CP1	% CP2	% CP3
1	Yomogi alcohol	1001	C10H18O	MO	0.72	–	–	–
2	o-Cymen	1032	C10H14	MH	tr	–	–	tr
3	Limonene	1040	C10H16	MH	–	–	–	0.06
4	Eucalyptol	1044	C10H18O	MO	tr	–	–	–
5	cis-β-Ocimen	1057	C10H16	MH	–	1.15	0.05	0.37
6	Artemisia ketone	1068	C10H16O	MO	1.54	–	–	0.19
7	Artemisia alcohol	1087	C10H18O	MO	tr	–	–	–
8	Limona ketone	1131	C9H14O	MO	–	–	–	0.39
9	Melilotal	1179	C9H10O	MO	–	–	–	0.08
10	Anethole	1267	C10H12O	PP	–	–	0.07	–
11	δ-Elemene	1314	C15H24	SH	–	–	0.11	–
12	α-Copaene	1374	C15H24	SH	–	–	–	0.11
13	Berkheyaradulene	1379	C15H24	SH	tr	0.59	0.47	0.23
14	Longifolene	1388	C15H24	SH	–	–	–	0.27
15	β-Caryophyllene	1397	C15H24	SH	–	0.48	0.28	0.5
16	α-cis-Bergamotene	1402	C15H24	SH	–	–	–	0.08
17	α-Himachalene	1416	C15H24	SH	–	–	–	7.56
18	(E)-β-Farnesene	1428	C15H24	SH	1.64	34.13	23.33	15.39
19	Alloaromadendrene	1449	C15H24	SH	–	–	–	5.4
20	Germacrene D	1454	C15H24	SH	–	7.02	2.02	2.46
21	β-Selinene	1460	C15H24	SH	–	–	0.23	0.3
22	Viridiflorene	1465	C15H24	SH	–	–	0.7	–
23	Bicyclogermacrene	1469	C15H24	SH	–	–	1.68	1.02
24	α-Muurolene	1472	C15H24	SH	–	–	tr	–
25	Elixene	1475	C15H24	SH	–	4.33	–	–
26	α-Cuprenene	1480	C15H24	SH	–	–	–	21.34
27	(E,E)-α-Farnesene	1486	C15H24	SH	–	12.67	2.92	3.41
28	cis-α-Bisabolene	1509	C15H24	SH	–	–	–	0.81
29	γ-Cadinene	1515	C15H24	SH	–	–	0.06	–
30	δ-Cadinene	1526	C15H24	SH	–	–	0.28	–
31	Nerolidol	1563	C15H26O	SO	0.1	–	0.24	–
32	Dendrolasin	1572	C15H22O	SO	–	–	0.12	–
33	(-)-Spathulenol	1583	C15H24O	SO	7.29	–	0.7	0.36
34	Globulol	1590	C15H26O	SO	–	–	0.17	–
35	Viridiflorol	1601	C15H26O	SO	–	–	0.08	–
36	β-Himachalen oxide	1620	C15H24O	SO	–	–	–	0.34
37	1-epi-Cubenol	1630	C15H26O	SO	–	–		0.55
38	α-Acorenol	1635	C15H26O	SO	–	–	–	0.75
39	α-Bisabolol Oxide B	1648	C15H26O	SO	27.26	9.85	6.57	1.5
40	Allohimachalol	1664	C15H26O	SO	–	–	–	0.51
41	E-Bisabol-11-ol	1667	C15H26O	SO	–	–	0.25	–
42	E-10,11-Dihydroatlantone	1671	C15H24O	SO	–	–	–	0.82
43	α-Bisabolol	1685	C15H26O	SO	0.68	1.4	36.33	–

44	α-Bisabolone Oxide A	1687	C15H26O2	SO	11.41	–	–	6.62
45	(Z)-γ-Atlantone	1691	C15H22O	SO	–	–	–	2.73
46	(E)-γ-Atlantone	1702	C15H22O	SO	–	–	–	2.59
47	(Z)-α-Atlantone	1714	C15H22O	SO	–	–	–	1.25
48	Chamazulene	1725	C14H16	SO	3.64	5.27	2.41	0.71
49	α-Bisabolol Oxide A	1740	C15H26O2	SO	21.37	7.99	4.74	3.95
50	(E)-α-Atlantone	1779	C15H22O	SO	–	–	–	1.42
51	Z-spiroether	1882	C13H12O2	O	10.83	5.14	–	–
52	E-spiroether	1895	C13H12O2	O	2.83	–	1.17	1.42
	Terpene classes							
	Monoterpene hydrocarbons (MH)				–	1.15	0.05	0.43
	Oxygenated monoterpenes (OM)				2.26	–	–	0.66
	Sesquiterpene hydrocarbons (SH)				1.64	59.22	32.08	58.88
	Oxygenated sesquiterpenes (SO)				71.75	24.51	51.61	24.10
	Phenylpropanoids (PP)				–	–	0.07	–
	Others (O)				13.66	5.14	1.17	1.42
	Total identified				89.31	90.02	84.98	85.49

oxygenated sesquiterpenes (53.61%). The most abundant compound in CP1 and CP2 was (E)-β-farnesene, representing 34,13% of the total EO. (E,E)-α-farnesene was also identified in CP1 in significant amount, representing 12.67% of the total EO, while its amount in CP2 was only 2.92% and in CP3 – 3.41%. Other SH identified in CP1 were germacrene D (7.02%) and elixene (4.33%). The content of bisabolol oxides compared to that of bisabolol in CP1 was higher, however, the total content of bisabolol oxides (17.84%) did not meet the requirements of the Ph.Eur. The content of chamazulene (5.27%) was in the described limits given by EP monograph. CP2 was the only sample in which the content of α-bisabolol (38.33%) was higher than that of bisabolol oxides. CP3 differs from the other samples by the limited amounts of bisabolol oxides present in the EO. The most prominent compound in that sample was the sesquiterpene α-cuprenene, representing 21.34% of the total EO. All samples contained more than 1% chamazulene except CP3, which contained only 0.71% of this compound.

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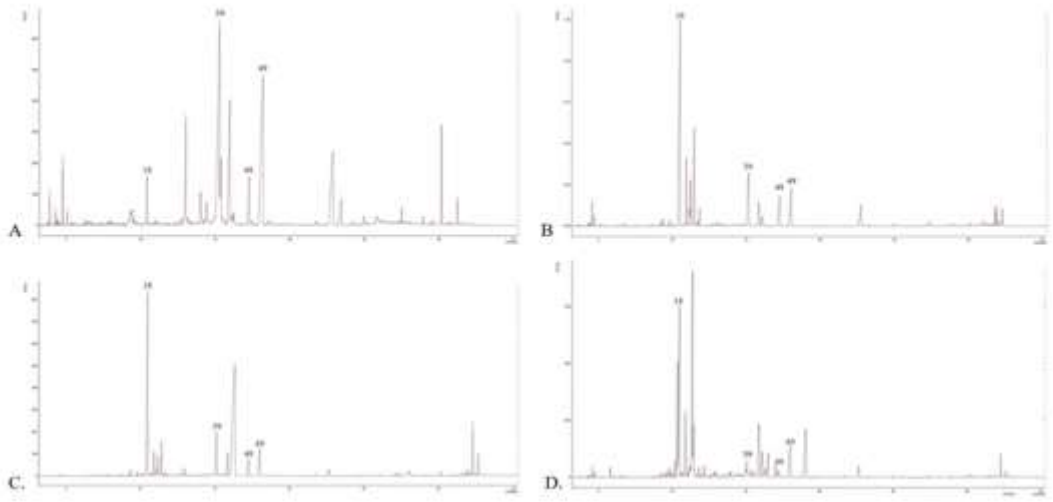

Figure 1. Chromatograms of the EO samples from wild grown M. chamomilla (A) and commercial products containing MEO (B, C, and D), where the numbers refer to the following compounds: 18-(E)-β-Farnesene, 39-α-Bisabolol Oxide B, 48-Chamazulene, 49-α-Bisabolol Oxide A

The MEO quality depends on genetic and environmental factors. The content of chamazulene is determined by the genetics of the plant, while the growing conditions are more important for the content of bisabolol and its derivatives [18]. The commercial samples are characterized by the significant content of (E)-β-farnesene. The higher amounts of (E)-β-farnesene can be attributed to premature harvesting of the flowers or the use of green plant parts like stems and leaves [19]. In addition, commercial MEOs may be adulterated with different synthetic compounds or other cheaper EOs, which can impact their overall chemical composition [20,21].

IV. CONCLUSION

In the present study the chemical composition of the EO of wild-grown Bulgarian M. chamomillawas evaluated. The oil was rich in sesquiterpenes, most abundant of which were the bisaboloids α-bisabolol oxide B and α-bisabolol oxide A, as well as spiroethers. Moreover, the chemical composition of 3 commercial products containing M. chamomillaEO found in the Bulgarian market were also evaluated. The chemical constituents of the commercial samples varied widely, but all contained significant amounts of (E)-β-farnesene compared to the content of bisabolol oxides, which most likely can be attributed to premature harvesting or the use of vegetative plant parts. The complexity of the composition of the available MEOs could reflect negatively on the biological activities of these EOs. For this reason, it is important to assure the quality of the commercial EOs on the market.

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