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Essential oils analysis in dried materials and granulates obtained from *Thymus vulgaris* L., *Salvia officinalis* L., *Mentha piperita* L. and *Chamomilla recutita* L.

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ABSTRACT: The aim of the research was to evaluate the influence of herbal raw materials granulation on changes in the content and composition of essential oil. The following ground materials and granulates were subjected to analysis: *Thymi Herba* (*Thymus vulgaris* L.), *Salviae Herba* (*Salvia officinalis* L.), *Menthae Piperitae Herba* (*Mentha piperita* L.) and *Chamomillae Anthodium* (*Chamomilla recutita* L.). Studies revealed that granulation of raw materials causes an increase in the final product density. i.e. for *C. recutita* it increased about 4.0-fold, for *S. officinalis* about 3.4-fold, for *T. vulgaris* about 2.6-fold, and for *M. piperita* about 1.6-fold. Moreover, granulation negatively affected the essential oil content in the evaluated raw materials, resulting in the following losses: about 56.6% for *T. vulgaris*, about 73.6% for *S. officinalis*, about 71.3% for *M. piperita* and about 43.9% for *C. recutita*. Furthermore, significant changes in the composition of essential oils isolated from granulates were observed with reference to ground materials, e.g. the percentage of iso-menthol in oil achieved from *M. piperita* granulate increased from about 29% to about 40%, that of camphor in oil from *S. officinalis* granulate was 14% in relation to about 8%, and that of thymol in oil from *T. vulgaris* granulate increased from about 44% to about 67%, whereas the percentage of α-bisabolol oxide A in oil from *C. recutita* granulate decreased from about 34% to about 18%. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: granulation; granulates; essential oil; *Thymus vulgaris*; *Salvia officinalis*; *Mentha piperita*; *Chamomilla recutita*

Introduction

The World Health Organization (WHO) stated that in the 1990s, about 70–80% of developing countries' populations used unconventional medicine.[1] A wide spectrum of plants was described as easily available, bio-renewable sources of natural antioxidants, which are important in prophylaxis of the diseases of civilization, e.g. tumours or disturbances to the circulatory system.[2,3] Most plants used for the purpose originate from their natural habitats, and their properties depend on genetic and environmental diversity. The raw material quality is significantly determined by such post-harvest factors as processing (type of drying and storage). Plants dried at low temperatures retain their original look and texture.[4] More often, plant materials such as herbs and spices are subjected to a granulation process. Granulation consists of combining small fragments of raw material into larger particles whose final shape can be formed during grinding.[5] The main goals of granulation are: to achieve uniform mixtures of solids; to obtain products with a minimized amount of dust; to increase product quality; to improve storage, transport and dosage parameters (particularly important in the automation of production processes, elevating volume/weight:bulk density); to produce particles of a given condition to improve solubility or to avoid agglomeration, etc.; and to modify composition due to various additives.[5–7] Granulation is also applied to stabilize some groups of unstable biologically active substances. However, granulation technology is associated with the application of mechanical, thermal and pressure factors that may exert negative effects on active components contents. Easily volatile components of essential oils occurring in herbs and spices, along with compounds with multiple bonds, are particularly sensitive to high temperatures. Essential oil, whose composition and content strongly affects the medical properties of a final product, is one of a group of substances particularly sensitive to quantitative changes during technological processes. In literature references there are no data on quantitative changes of essential oils in materials subjected to the granulation process. Only studies related to comparisons of commercial tea products (tea-bags prepared from unprocessed material or tea-bags made from granulates)[8] that, despite their origin from the same producer, may be produced from different raw material lots of different physicochemical parameters, could be found.

Therefore, the aim of the research was to study the influence of the industrial granulation process on the content and composition of essential oils in popular herbal products. As compounds with various structures (both saturated and unsaturated; alcohols, aldehydes, ketones), components of essential oils are good receptors of qualitative and quantitative changes during the granulation process.

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Materials and Methods

Plant Materials/Granulation Process

The following ground materials and granulates were subjected to study: *Thymi Herba* (*Thymus vulgaris* L.), *Salviae Herba* (*Salvia officinalis* L.), *Menthae Piperitae Herba* (*Mentha piperita* L.) and *Chamomillae Anthodium* (*Chamomilla recutita* L.). These were purchased from the herbal production plant, Trans-Herbost Kębłów, near Lublin. Samples were collected from uniform raw materials before granulation and directly after the process performed in a production plant according to given technological parameters. Material was conditioned with steam before granulation by adjusting its temperatures to 60 °C (the required temperature was achieved due to steam at 250 kPa pressure). Granulates were produced in a granulator (own design and construction; nominal efficiency, 100 kg/h; rotational velocity, 150 r.p.m.) equipped with a sieve of 5 mm diameter perforation. Pellets of 5 mm length and 5 mm diameter were cooled in an air stream and ground in a cylindrical mill. The granulate produced was fractionated through a sieve and the 0.8–2.0 mm fraction was collected. Granulates obtained in the above manner are part of the production plant range of semi-products for further processing, which can be used to produce different types of pharmaceutical extracts or for composing bag teas. Before study and measurements, raw material and granulates were preliminarily dried in a drier (25 °C) until the moisture content was rediced to 10%. Studies involved the mean sample prepared from 10 randomly collected initial samples of raw material and granulates. Analytical determinations were performed in three replications.

Material Density

The density of the raw materials and granulates was determined by means of the gravimetric method, in accordance with standard PN-92/C-04504.[9]

Light Microscopy (LM)

Observations and photographs were taken by means of a stereoscopic light microscope, Olympus SZX12, equipped with an Olympus C-7070 digital camera.

Essential Oils

The essential oil content in the studied raw materials was determined in accordance with the *Polish Pharmacopoeia VI*.[10] The oil obtained was collected in dark glass vessels, dried using dehydrated sodium sulphate and stored at below −10 °C until chromatographic determination.

Qualitative and Quantitative Analysis

GC–MS

The GC–MS instrument ITMS Varian 4000 GC–MS/MS (Varian, USA) was used, equipped with a CP-8410 auto-injector and a 30 m × 0.25 mm i.d. VF-5ms column (Varian, USA), film thickness 0.25 μm; carrier gas, helium at a rate of 0.5 ml/min; injector and detector temperature, 220 °C and 200 °C, respectively; split ratio, 1:20; injection volume, 1 μl. A temperature gradient was applied (60 °C for 0.5 min, then incremented by 3 °C/min to 246 °C and held at this temperature for 10 min); ionization energy, 70 eV; mass range, 40–1000 Da; scan time, 0.80 s.

GC–FID

A Varian 3800 Series (Varian, USA) instrument with a DB-5 column (J&W, USA) was used, operated under the same conditions as GC–MS; FID, 256 °C; split ratio, 1:50.

Qualitative Analysis

The qualitative analysis was carried out on the basis of MS spectra, which were compared with the spectra of the NIST library[11] and with data available in the literature.[12,13] The identity of the compounds was confirmed by their retention indices, taken from the literature[12,13] and our own data.

Quantitative Analysis

Quantitative analysis was performed by means of the internal standard addition method (alkanes C_{12} and C_{19}), according to previously described procedures.[14] Essential oil was diluted 1000 times using *n*-hexane to achieve a 1 $cm^{[3]}$ volume, then 1 mg C_{12} and 1 mg C_{19} were added to the diluted oil. Such prepared samples were subjected to GC–MS and GC–FID determinations. The quantitative analysis was performed on the basis of calibration curves for α-pinene, camphene, sabinene, β-pinene, limonene, 1,8-cineole, linalool, menthol, *iso*-menthol, carvone, thymol, carvacrol, (*E*)-caryophyllene, α-humulene, germacrene D, spathulenol, caryophyllene oxide, α-bisabolol oxide B, chamazulene, α-bisabolol oxide A and alkanes C_{10}–C_{25}) within the concentration range 0.05–70%.

Because of the lack of proper standards, we made the assumption that a component's physical and chemical properties were similar to those for the closest standard in our possession: α-pinene for myrcene, α-terpinene and γ-terpinene; limonene for *p*-cymene; linalool for borneol, terpinen-4-ol, isobornyl acetate and menthyl acetate; iso-menthol for *neoiso*-menthol, thymol methyl ether and carvacrol methyl ether; carvone for *cis*-thujone, *trans*-thujone, camphor, menthone, menthofuran, *iso*-menthone, pulegone and piperitone; germacrene D for β-bourbonene, β-elemene and (*Z*)-β-farnesene; spathulenol for viridiflorol and manool; caryophyllene oxide for humulene epoxide II and epoxy-*allo*-alloaromadendrene.

Statistical Analysis

Data were analysed by analysis of variance (Duncan's test) at the 5% significance level, using the SAS statistical system (SAS Version 9.1, SAS Institute, Cary, NC, USA).

Results and Discussion

Due to the high temperature used during the granulation process, the structure of plant material is damaged and smaller fragments agglomerate to form larger particles (Figure 1). The density of the material increases notably, as follows: for *T. vulgaris* about 2.6-fold; for *S. officinalis* about 3.4-fold; for *M. piperita* about 1.6-fold; and for *C. recutita* about 4.0-fold (Table 1).

The contents of the essential oils in the materials studied were as follows: *T. vulgaris*, 2.19 ± 0.09% (dried), 0.95 ± 0.08% (granulate); *S. officinalis*, 0.91 ± 0.02% (dried), 0.24 ± 0.02% (granulate);

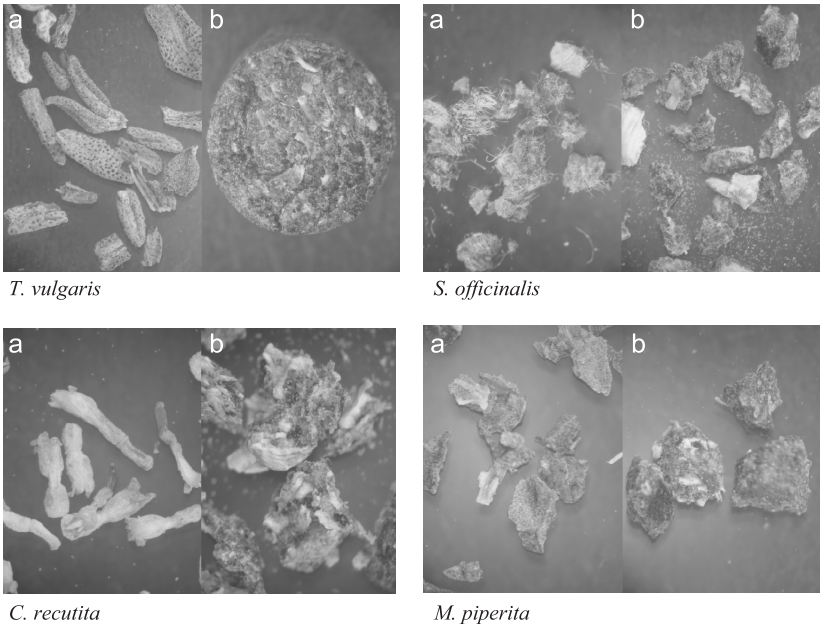

Figure 1. Microscope image of unprocessed plant-origin materials, (a) dried and (b) granulated (magnification, × 40)

Table 1. Density of unprocessed plant-origin materials and granulates: *Thymus vulgaris* L., *Salvia officinalis* L., *Mentha piperita* L. and *Chamomilla recutita* L.

Plant	Density (g/ml)	
	Dried materials	Granulates
T. vulgaris	0.219 ± 0.054b	0.576 ± 0.094a
S. officinalis	0.171 ± 0.043b	0.580 ± 0.096a
M. piperita	0.349 ± 0.084b	0.572 ± 0.086a
C. recutita	0.143 ± 0.032b	0.572 ± 0.086a

Values designated with the same letters (a, b) within line do not significantly differ at 5% error (Duncan's test).

M. piperita, 1.08 ± 0.02% (dried), 0.31 ± 0.04% (granulate), *C. recutita*: 0.66 ± 0.05% (dried) and 0.37 ± 0.04% (granulate) (Figure 2). The study revealed that granulation negatively affected the essential oil content in the raw materials evaluated, causing the following losses: ca. 57% for *T. vulgaris*, ca. 73% for *S. officinalis*, ca. 71% for *M. piperita* and ca. 43% for *C. recutita*.

The content of essential oil in dried *Salvia* before granulation was similar to that found in the literature—about 1%.[16] That oil contains the following main components (Table 2): manool (17.15%), viridiflorol (14.39%), borneol (7.75%), camphor (13.60%), *cis*-thujone (6.66%), and *trans*-thujone (3.26%). During the granulation process, the content of the main component, viridiflorol, increased by almost one-third (from 14.39% to 20.92%), the content of manool remained at a constant level (17.10–17.15%) and the amount of camphor decreased (from 13.60% to 7.53%).

Unprocessed dried *Mentha* contains: iso-menthol (28.66%), menthone (21.25%), iso-menthone (6.68%), 1,8-cineole (3.65%), and menthol (3.45%). After granulation, iso-menthol increased by about 11% (from 28.66% to 39.85%) and menthone, *iso*-menthone and 1,8-cineole decreased by about 4%, 1% and 3%. Zitterl-Eglseer *et al.*[8] found that the percentage of menthone decreased from 12.7% and 21.8% in leaves (tea-bags) to 2.5% and 6.6% in pellets (tea-bags), respectively. Moreover, in an earlier study, the authors recorded 3.4% and 4.8% of 1,8-cineole in peppermint leaves (tea-bags), while finding no presence of that component in pellets (tea-bags).[8]

Thymol is the main component of dried thyme (about 44.32% of the total oil from the herb), and its content increased by about 23% due to granulation. The level of carvacrol also increases (from 3.58% to 8.01%), whereas the content of *p*-cymene decreases (by about 22%). The similarity of thymol, carvacrol and *p*-cymene structures indicates that *p*-cymene can isomerize to the other two. Moreover, the content of γ-terpinene in the sum of the essential oil components decreases as compared to the oil before granulation (from 3.59% to 0.14%). In the present experiment, quantitative changes observed in the contents of γ-terpinene, *p*-cymene, carvacrol and thymol can be attributed to their localization in the biosynthetic pathway.[17,18]

The increase of γ-terpinene concentration may result from the granulation influences on the shift of chemical balance through the conversion of thymol, carvacrol, and *p*-cymene in the biosynthetic pathway in the γ-terpinene synthesis direction. No doubt the main factors determining the quantitative changes are temperature (60 °C) and mechanical processing during granulation. In an earlier study,[19] the authors did not record changes of quantitative composition in thyme oil heated to 80–180 °C (3 h), which could be affected by closing the raw oil in vials within the thermostat and lack of mechanical factors in the experiments due to different methodology.

Oil made of chamomile flowers as the main constituents contains a mixture of α-bisabolol oxide B (30.64%) with α-bisabolol

Table 2. Concentrations of primary components in essential oil from *Mentha piperita*, *Thymus vulgaris*, *Salvia officinalis* and *Chamomilla recutita* and their granulates

Chemical compound	RI	Percentage (%, g/100 g)								Identification method
		Mentha piperita		*Thymus vulgaris*		*Salvia officinalis*		*Chamomilla recutita*		
		Dried material	Granulate	Dried material	Granulate	Dried material	Granulate	Dried material	Granulate	
α-Pinene	934	0.50 ± 0.01	tr.	0.75 ± 0.05	tr.	0.18 ± 0.04	0.07 ± 0.01	—	—	IR, MS, S
Camphene	952	tr.	—	0.57 ± 0.03	tr.	0.31 ± 0.05	0.09 ± 0.01	—	—	IR, MS, S
Sabinene	974	0.30 ± 0.01	tr.	tr.	0.06 ± 0.01	—	—	0.28 ± 0.02	tr.	IR, MS, S
β-Pinene	981	0.78 ± 0.02	tr.	—	—	0.10 ± 0.03	0.08 ± 0.01	—	—	IR, MS, S
Myrcene	990	0.28 ± 0.05	tr.	0.67 ± 0.03	tr.	0.06 ± 0.01	tr.	—	—	IR, MS
α-Terpinene	1017	—	—	0.79 ± 0.05	0.12 ± 0.01	—	—	—	—	IR, MS
p-Cymene	1027	tr.	—	22.27 ± 1.13a	0.28 ± 0.03b	0.15 ± 0.03	0.20 ± 0.01	0.18 ± 0.03	0.19 ± 0.03	IR, MS
1,8-Cineole (= Eucalyptol)	1033	3.65 ± 0.27a	0.57 ± 0.03b	0.71 ± 0.04	0.07 ± 0.01	2.21 ± 0.42	1.34 ± 0.04	0.17 ± 0.02	0.22 ± 0.04	IR, MS, S
γ-Terpinene	1058	tr.	0.09 ± 0.01	3.59 ± 0.21a	0.14 ± 0.03b	tr.	0.20 ± 0.02	tr.	0.25 ± 0.02	IR, MS
Linalool	1101	0.33 ± 0.01	0.25 ± 0.05	2.45 ± 0.17	1.23 ± 0.05	—	0.50 ± 0.01	0.34 ± 0.01	1.60 ± 0.34	IR, MS, S
cis-Thujone	1112	tr.	—	—	tr.	6.66 ± 0.58a	7.27 ± 0.18a	tr.	0.17 ± 0.02	IR, MS
trans-Thujone	1110	0.06 ± 0.01	tr.	—	tr.	3.26 ± 0.16b	5.33 ± 0.15a	tr.	0.12 ± 0.02	IR, MS
Camphor	1153	—	—	0.45 ± 0.05	0.24 ± 0.04	13.60 ± 1.81a	7.53 ± 0.16b	0.14 ± 0.02	0.56 ± 0.06	IR, MS
Menthone	1159	21.25 ± 0.10a	17.69 ± 0.23b	—	—	—	—	—	—	IR, MS
Menthofuran	1165	0.23 ± 0.01	0.13 ± 0.01	—	—	—	—	—	—	IR, MS
iso-Menthone	1168	6.68 ± 0.02a	5.71 ± 0.06b	—	—	—	—	—	—	IR, MS
Menthol	1172	3.45 ± 0.01a	3.29 ± 0.09a	—	—	—	—	—	—	IR, MS, S
Borneol	1177	—	—	1.45 ± 0.09	1.30 ± 0.15	7.75 ± 0.30a	2.79 ± 0.11b	0.25 ± 0.03	0.56 ± 0.05	IR, MS
iso-Menthol	1181	28.66 ± 0.13b	39.85 ± 0.44a	—	—	—	—	—	—	IR, MS, S
Terpinen-4-ol	1183	0.71 ± 0.19	0.14 ± 0.01	0.68 ± 0.04	1.02 ± 0.12	—	—	—	—	IR, MS
neoiso-Menthol	1191	0.22 ± 0.04	0.57 ± 0.06	—	—	—	—	—	—	IR, MS
Thymol, methyl ether	1231	—	—	1.24 ± 0.02	0.22 ± 0.02	tr.	0.06 ± 0.01	—	—	IR, MS
Carvacrol, methyl ether	1242	—	—	0.81 ± 0.04	0.16 ± 0.02	—	—	—	—	IR, MS
Pulgeone	1241	0.53 ± 0.01	0.97 ± 0.08	—	—	—	—	—	—	IR, MS
Piperitone	1257	1.72 ± 0.02	2.06 ± 0.02	0.07 ± 0.01	0.18 ± 0.02	0.30 ± 0.03	0.25 ± 0.02	—	—	IR, MS
Isobornyl acetate	1286	—	—	—	—	1.16 ± 0.03	0.38 ± 0.01	—	—	IR, MS
Menthyl acetate	1291	10.26 ± 0.18a	8.24 ± 0.17b	—	—	0.46 ± 0.05	1.13 ± 0.05	—	—	IR, MS
Thymol	1293	—	—	44.32 ± 1.39b	67.32 ± 3.36a	—	—	—	—	IR, MS, S
Carvacrol	1301	—	—	3.58 ± 0.18b	8.01 ± 0.98a	—	—	—	—	IR, MS, S
β-Bourbonene	1382	0.52 ± 0.01	0.28 ± 0.02	0.06 ± 0.01	tr.	0.06 ± 0.01	0.09 ± 0.01	tr.	1.02 ± 0.23	IR, MS
β-Elemene	1388	0.61 ± 0.01	0.37 ± 0.03	—	—	0.06 ± 0.01	tr.	tr.	1.24 ± 0.19	IR, MS
E-Caryophyllene	1418	2.84 ± 0.01	2.01 ± 0.12	2.16 ± 0.16	0.59 ± 0.06	3.15 ± 0.04	1.74 ± 0.05	0.49 ± 0.08	2.13 ± 0.25	IR, MS, S
Z-β-Farnesene	1452	0.35 ± 0.01	0.28 ± 0.02	tr.	0.06 ± 0.01	—	—	1.49 ± 0.42	1.26 ± 0.48	IR, MS
α-Humulene	1455	0.17 ± 0.01	0.16 ± 0.01	0.11 ± 0.01	0.06 ± 0.02	2.95 ± 0.25	2.17 ± 0.11	0.13 ± 0.02	0.48 ± 0.05	IR, MS, S
Germacrene D	1480	2.73 ± 0.02	1.30 ± 0.11	—	—	0.13 ± 0.01	0.11 ± 0.01	0.40 ± 0.04	0.54 ± 0.05	IR, MS, S
Spathulenol	1577	0.18 ± 0.01	0.26 ± 0.05	0.10 ± 0.01	0.18 ± 0.02	0.23 ± 0.09	0.15 ± 0.01	4.00 ± 0.47b	8.15 ± 0.56a	IR, MS, S
Caryophyllene oxide	1582	0.27 ± 0.04	0.39 ± 0.09	0.85 ± 0.10	2.67 ± 0.29	1.18 ± 0.06	1.52 ± 0.11	0.85 ± 0.10	0.30 ± 0.03	IR, MS, S
Viridiflorol	1595	0.64 ± 0.01	1.16 ± 0.19	0.26 ± 0.04	0.30 ± 0.03	14.39 ± 0.19b	20.92 ± 0.80a	—	—	IR, MS
Humulene epoxide II	1610	tr.	tr.	0.10 ± 0.01	0.18 ± 0.02	1.31 ± 0.15	2.51 ± 0.16	0.59 ± 0.09	1.30 ± 0.12	IR, MS
Epoxy *allo*-aromadendrene	1648	tr.	tr.	—	—	2.19 ± 0.19	1.13 ± 0.04	—	—	IR, MS
α-Bisabolol oxide B	1655	0.21 ± 0.01	0.24 ± 0.01	0.18 ± 0.02	0.37 ± 0.04	0.99 ± 0.11	0.34 ± 0.03	30.64 ± 1.80b	42.64 ± 1.96a	IR, MS, S
Chamazulene	1740	—	—	—	—	—	—	11.74 ± 0.76a	7.18 ± 0.65b	IR, MS, S
α-Bisabolol oxide A	1750	tr.	—	0.06 ± 0.01	0.08 ± 0.02	0.51 ± 0.01	0.05 ± 0.02	33.87 ± 0.93a	18.28 ± 0.71b	IR, MS, S
Manool	2062	—	—	—	—	17.15 ± 1.29a	17.10 ± 1.98a	—	—	IR, MS
Total		88.13	86.01	88.28	84.84	80.5	75.05	85.56	88.19	

RI, non-isothermal Kováts retention indices (from temperature-programming, using definition of Van den Dool and Kratz[15]) for series of *n*-alkanes C_6–C_{31}; tr., trace (<0.05%); MS, compared to mass spectrum; S, compounds identified on the basis of comparison with MS database spectra, retention indices and pure reference chemicals.
Values designated with the same letters (a, b) within line do not significantly differ at 5% error (Duncan's test).

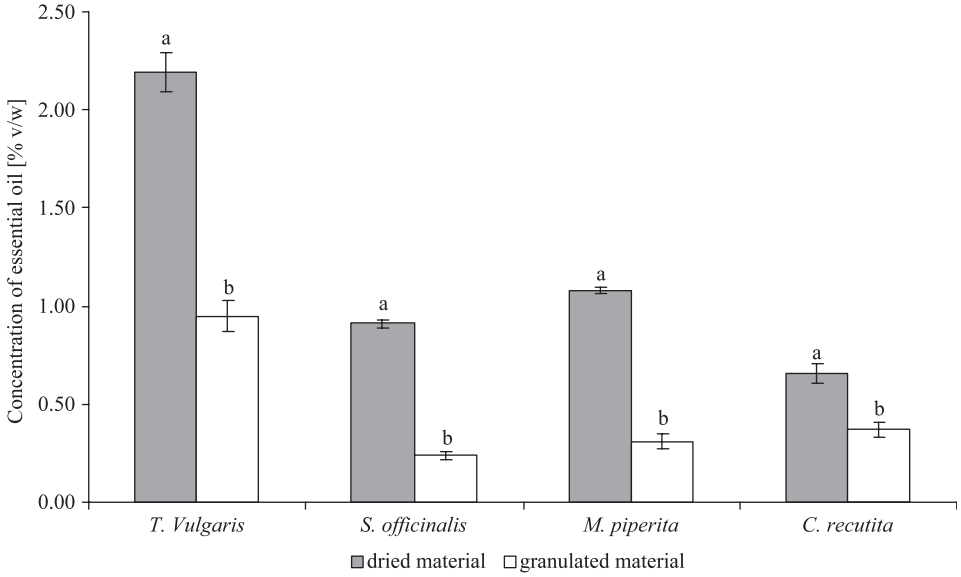

Figure 2. Contents of essential oils in unprocessed plant-origin materials and granulates: *T. vulgaris*, *S. officinalis*, *M. piperita* and *C. recutita* L. Values designated with the same letters (a, b) do not significantly differ at 5% error (Duncan's test)

oxide A (33.87%). It was observed that the percentage of the main components changed as a result of granulation, while their sum was at similar levels (64.51% before vs. 60.92% after the process). Zitterl-Eglseer *et al*.[8] found that the percentage of sum of A and B bisabolol oxide isomers for chamomile flowers (tea-bags) and pellets (tea-bags) increased from 51.1% to 55.8% (sample 1), while it decreased from 44.8% to 36.2% for sample 2. The lack of an unequivocal tendency in the experiments of the cited authors may be attributed to the fact that compared commercial products (flowers and pellets in sample 1 and sample 2) probably did not came from the same lot of raw material (granulate was not achieved from the material that was used in production of simple product). The presented experiment revealed an increase of spathulenol concentration from 4.0% to 8.15%. However, a decrease of the percentage of chamazulene by about 5% was observed in essential oil isolated from the granulate. Zitterl-Eglseer *et al*.[8] recorded the increase of spathulenol percentage from 0.9% and 0.0% in flowers (tea-bags) to 1.2% and 1.1% in pellets (tea-bags), respectively, while these authors did not find any chamazulene presence.

Conclusions

It can be stated that the granulation process of plant materials studied in this research has a negative effect on the essential oils content.

Differences in the essential oils composition compared to the unprocessed material were found for granulates; an apparent decrease of the volatile components was observed. The results of the analysis of the essential oils composition indicated that the granulation process affects the isomerization of some chemical compounds. Granulation results in a uniform product with higher density that is also more useful for transport and storage.

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References

[1] Akerele O. *World Health Forum* **1993**, *14*, 390–395.
[2] Castenmiller JJM, Linssen JPH, Heinonen IM *et al. Nahrung/Food* **2002**, *46*, 290–293.
[3] Javanmardi J, Stushnoff C, Locke E *et al. Food Chem*. **2003**, *83*, 547–550.
[4] Kosuke N, Ying L, Zhehong J *et al. J. Food Eng*. **2006**, *75*, 71–77.
[5] Schuchmann H. *Food Control* **1996**, *6*, 95–100.
[6] Kulig R. Conditioning of plant-origin raw materials subjected to granulating. PhD Thesis, University of Agriculture, Lublin, Poland, **2003**.
[7] Kopral W. Granulating of agricultural and food materials by means of vacuum method. Wydawnictwo Akademii Rolniczej w Lublinie, Lublin, Poland, **2005**.
[8] Zitterl-Eglseer K, Chizzola R, Franz CH. *Dtsch. Lebensmitt.-Rdsch*. **2003**, *99*, 91–96.
[9] PN-92/C-04504. *Chemical Analysis, Determination of Density of Liquid Chemical Products and Solids in Powder*. Polski Komitet Normalizacji, Miar i Jakości: Warsaw, **2002**.
[10] *Polish Pharmacopoeia VI*. Polskie Towarzystwo Farmaceutyczne: Warsaw, **2002**.
[11] *Mass Spectral Library*. NIST/EPA/NIH: USA, **2002**.
[12] Adams RP. *Identification of Essential Oil Compounds by Gas Chromatography/Quadrupole Mass Spectroscopy*. Allured: Carol Stream, IL, **2001**.
[13] Joulain D, König WA. *The Atlas of Spectral Data of Sesquiterpene Hydrocarbons*. E.B. Verlag: Hamburg, **1998**.
[14] Kowalski R. *Flavour Fragr. J*. **2008**, *23*, 164–171.
[15] Van Den Dool H, Kratz, DJ. *J. Chromatogr*. **1963**, *11*, 463–467.
[16] Sagareishvili TG, Grigolava BL, Gelashvili NE *et al. Chem. Nat. Comp*. **2000**, *36*, 360–361.
[17] Thompson JD, Chalchat J-C, Michet A *et al. J. Chem. Ecol*. **2003**, *29*, 859–880.
[18] Hudaib M, Speroni E, Di Pietra AM *et al. J. Pharm. Biomed. Anal*. **2002**, *29*, 691–700.
[19] Tomaino A, Cimino F, Zimbalatii V *et al. Food Chem*. **2005**, *89*, 549–554.