THE ANALYSIS OF CUMIN SEEDS ESSENTIAL OIL AND TOTAL POLYPHENOLS FROM POSTDESTILLATION WASTE MATERIAL

Milica G. Aćimović[1,2*], Vele Tešević[3], Dimitrije Mara[3], Mirjana Cvetković[4], Jovana Stanković[4], Vladimir Filipović[5]

(ORIGINAL SCIENTIFIC PAPER)
UDC 582.794.1:66.061.34:615.322

[1] Institute of Food Technology (FINS), University of Novi Sad, Serbia
[2] Institute of Field and Vegetable Crops, Novi Sad, Serbia
[3] Faculty of Chemistry, University of Belgrade, Serbia
[4] Institute of Chemistry, Technology and Metallurgy (ICTM), University of Belgrade, Serbia
[5] Institute of Medicinal Plant Research "dr Josif Pančić", Belgrade, Serbia

The essential oil content in cumin samples from Serbian market ranged between 2.0 and 4.0%, with 22 identified compounds, among which the most abundant were cumin aldehyde, *β*-pinene, *γ*-terpinene, *γ*-terpinene-7-al and *p*-cymene. Postdistillation cumin seeds waste material that remained after the essential oil extraction contains total polyphenols of between 30.1 and 47.5 mg GAE/g dry extract, as estimated by the Folin–Ciocalteu method. Hydroxybenzoic and hydroxycinnamic acids, as well as glycosides of flavonones and flavonoles, are the dominant polyphenols. However, according to DPPH method, the antioxidative potential of cumin postdistillation seeds waste was poor and it ranged between 0.02 and 0.04 mM TE/g. Further research will be focused on agro-food implementation of postdistillation waste material of cumin and other plants which are used for the essential oil production.

Keywords: *Cuminum cyminum*, essential oil, postdistillation waste material, total polyphenols, DPPH

Introduction

Cumin (*Cuminum cyminum* L.) is a herbaceous plant from Apiaceae family, originating from the Eastern Mediterranean. It is mainly grown in India, Syria, Iran and Turkey [1]. Cumin is a characteristic spice of the oriental cuisine and one of the main ingredients of curry powder. In Serbia, cumin is not very popular but recently there has been the increasing interest for healthy nutrition and functional food supplements, as well as traditional remedies approved by modern scientific methods.

The essential oil obtained from cumin seeds is light brownish yellow, with a slightly bitter, spicy and aromatic flavor and a somewhat disagreeable odor [2] originating from cumin aldehyde, the main compound in the oil [3]. Cumin essential oil has a wide range of application, such as anti-nociceptive [4], antiinflammatory [5], antimicrobial [2; 6] and antioxidative [7].

The essential oil content in cumin seeds ranged from 1.8 to 5.1% [8], and the majority of the produced plant material remained unused [9]. There is no data about postdistillation waste material of cumin seeds and its potential application. Therefore, the main aim of our investigation was to determine total polyphenoles and the antioxidative capacity of the aqueous extract that remained after hydrodistillation of four different samples of cumin seeds from the Serbian market, apart from the essential oil content and the composition of these samples.

Experimental

Plant material.

Four different commercial samples of cumin seeds (*Cumini fructus*) were bought at the local market in Novi Sad. All samples originated from India, but importers are different (cumin 1- Lay začini doo Laćarak, cumin 2 - Eko Iko doo Beograd, cumin 3 – Spices of the World doo Beograd, and cumin 4 - Jishan Agro Private Limited, Durgapur).

Chemicals.

Methanol (HPLC grade) were purchased from Merck (Darmstadt, Germany). Folin-Ciocalteu reagent was from the Institute Mol (Stara Pazova, Serbia), Na_2CO_3 was from Merck (Darmstadt, Germany), Trolox was from Fluka (Steinheim, Germany), and gallic acid and DPPH were from Sigma-Aldrich (St. Louis, the USA). These chemicals were of the analytical reagent grade. Milli Q water 18.2 MΩ cm was obtained from the purification system.

Essential oil isolation.

The dried samples of cumin were subjected to hydrodistillation using an all glass Clevenger-type apparatus to extract essential oils according to the method outlined by the European Pharmacopoeia [10].

***Author address:** Milica Aćimović, Institute of Field and Vegetable Crops, 21000 Novi Sad, Serbia
E-mail: acimovicbabicmilica@gmail.com
The manuscript received: March, 08, 2016.
Paper accepted: May, 23, 2016.

GC/MS analysis.

Gas chromatographic-mass spectrometric analysis was performed using an Agilent 6890 gas chromatograph coupled with an Agilent 5973 Network mass selective detector (MSD), in a positive ion electron impact (EI) mode. The separation was effected using Agilent 19091S-433 HP-5MS fused silica capillary column with 30 m × 0.25 mm i.d., 0.25 μm film thickness. The GC oven temperature was programmed from 60 °C to 285 °C at the rate of 3°C/min. Helium was used as a carrier gas; the inlet pressure was 20.3 kPa; linear velocity was 1 ml/min at 210 °C. Injector temperature: 250 °C; injection mode: splitless. MS scan conditions: MS source temperature, 230 °C; MS Quad temperature, 150 °C; energy, 70 eV; mass scan range, 40–550 amu. The identification of the components from the essential oil was carried out on the basis of the retention index and by comparison with the reference spectra (Wiley and NIST databases).

Determination of the total polyphenolics.

The amount of total phenolics in water soluble extracts which remains after the essential oil distillation (postdistillation waste material) was determined using the Folin-Ciocalteu reagent with gallic acid as a standard. The reagent was prepared by diluting a stock solution with distilled water (1:10, v/v). The samples (1 ml, three replicates) were placed into test cuvettes, and 5 ml of Folin-Ciocalteu phenol reagent and 4 ml of Na_2CO_3 (7.5 %) were added. The absorbance of the samples was measured at 765 nm using a UV/VIS spectrophotometer Cintra 40 after incubation at 20 °C for 1 h. The results were expressed as milligrams of gallic acid equivalent per 1 g of fresh weight, (mg GAE/g).

Characterisation of phenolics compounds.

The water soluble extracts of cumin seed which remains after the essential oil distillation were dissolved in methanol to an approximate concentration of 5 mg/ml. The LC/DAD/MS analyses were carried out by an Agilent 1200 HPLC instrument (Agilent Technologies, Waldbronn, Germany) with a binary pump, an autosampler, a column compartment equipped with a Zorbax Eclipse Plus C18 column (1.8 μm, 4.6 mm × 150 mm, Agilent Technologies) and a diode-array detector coupled with a 6210 time-of-flight LC/MS system (Agilent Technologies). The mobile phase consisted of water containing 0.2% formic acid (A) and acetonitrile (B). The combination of isocratic and gradient modes of elution was used as follows: 0–1.5 min 5% B, 1.5–26 min, 5–95% B, 26–35 min, 95% B. The mobile phase flow rate was 1.4 mL/min, the column temperature was 40 °C and the injection volume was 5 μl. Spectral data from all the peaks were accumulated in the range of 190–450 nm and chromatograms were recorded at 260, 280, 290 and 320 nm. MS-data were collected by applying the following parameters: ionization negative ESI, capillary voltage 4000 V, gas temperature 350 °C, drying gas 12 L/min, nebulizer pressure 45 psi, fragmentor voltage 140 V, mass range 100–2000 m/z. A personal computer system running MassHunter Workstation software was used for data acquisition and processing. Phenolic compounds were detected as $[M-H]^-$ or $[2M-H]^-$ signals using these parameters. Compounds were characterized by their retention times (*tr*), mass spectra and UV spectra, and were tentatively identified based on the previous data published by other authors. Their complete identification was not possible since the full scan mass spectra of the chromatographically separated compounds gave only deprotonated $[M-H]^-$ ions, and MS/MS experiments were not possible with the instrumentation used.

Antioxidant activity.

The antioxidant activity of the samples was evaluated by means of the 2,2-diphenyl-1-picrylhydrazil (DPPH) radical scavenging method. This spectrophotometric assay uses stable DPPH radical as a reagent. The methanolic solution of the investigated sample (200 μl) (with starting concentrations of 200, 300, 400, 500 μl/ml of solution) was added to the 1800 μl methanolic solution of DPPH radical (concentration of 0.04 mg/ml) and after shaking, the reaction mixture was left to react in the dark for 30 min at room temperature. Then, absorbance of the remaining DPPH radical was measured at 517 nm (A_1) on Cintra 40 UV–Visible spectrophotometer. Every concentration was done in triplicate and the same experiment was done with Trolox standard, a well-known synthetic antioxidant. The results were expressed as mM of trolox equivalent per 1 g of fresh weight, (mM TE/g). Blank probes were used in the same way, with methanol instead of the investigated solution (A_0). The decrease in the absorption of DPPH solution at 517 nm is calculated by the following equation:

$$I = \frac{A_0 - A_1}{A_0} * 100\%$$

The concentrations of the extracts which reduce the absorption of DPPH solution by 50% (EC_{50}) were obtained from the curve dependence of the absorption of DPPH solution at 517 nm from the concentration for each extract and a standard antioxidant. Origin 8.0 software was used to calculate these values. Tests were carried out in triplicate.

Statistical Analysis.

Data was the subject to a statistical analysis using the program package Statistica 10 (StatSoft Inc., 2011, University of Novi Sad license) and were expressed as mean value.

Results and discussion

The essential oil content in four samples of cumin seeds from the Serbian market was between 2.0 and 4.0% (Table 1). Many studies performed in the last ten years have confirmed that the essential oil content in cumin seeds varied depending on many factors such as

a genotype, a growing region, growing technology etc. [8; 11; 12]. This indicated that cumin samples on the Serbian market are of different origin.

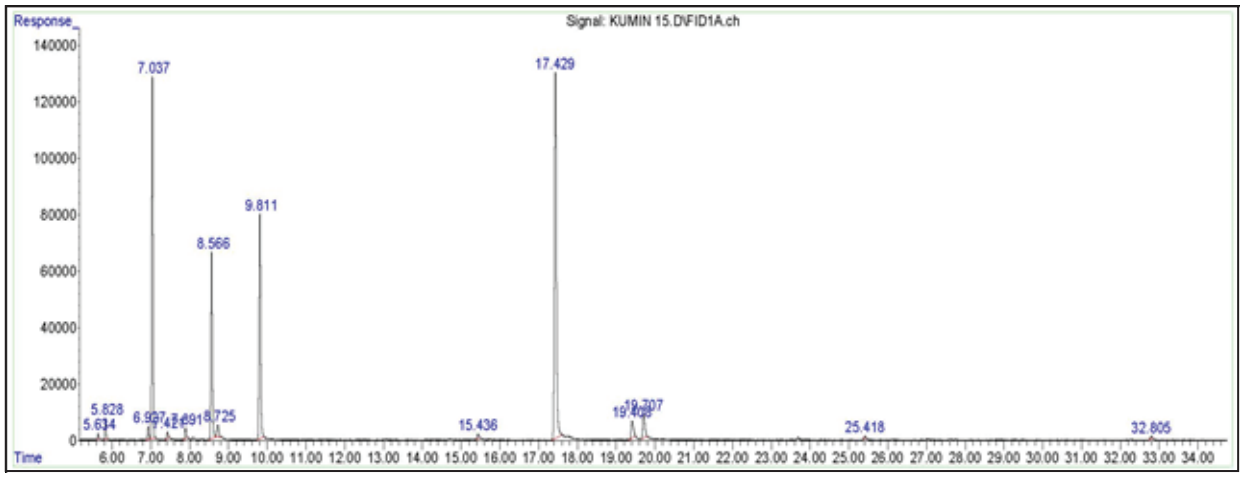
Table 1. The essential oil content in cumin seeds, total polyphenol content and antioxidative capacity of postdistillation waste material of cumin seeds.

	Essential oil content (%)	Total polyphenole content (mg GAE/g sample)	Antioxidative capacity (mM Trolox/g sample)
Cumin 1	2.0	30.1 ± 0.3	0.0217 ± 0.0034
Cumin 2	3.3	41.6 ± 1.3	0.0326 ± 0.0005
Cumin 3	4.0	40.6 ± 2.4	0.0353 ± 0.0002
Cumin 4	3.3	47.5 ± 1.5	0.0341 ± 0.0002

Table 2. Cumin seeds essential oil composition

Compound	RT	RI	Cumin 1	Cumin 2	Cumin 3	Cumin 4
α-thujene	5.606	926	0.3	0.2	0.2	0.2
α-pinene	5.794	933	1.2	0.8	0.7	0.9
sabinene	6.885	973	0.8	0.8	0.8	0.8
β-pinene	6.999	977	23.7	16.7	15.6	18.4
myrcene	7.378	991	0.3	0.6	0.7	0.8
α-phellandrene	7.848	1006	0.6	tr	0.2	0.2
δ-3-carene	8.038	1011	nd	nd	tr	tr
α-terpinene	8.267	1017	nd	nd	0.1	tr
p-cymene	8.516	1023	13.7	4.9	6.0	8.0
β-phellandrene	8.675	1027	1.0	0.3	0.5	0.4
1,8-cineole	8.763	1031	nd	0.1	0.1	tr
γ-terpinene	9.768	1059	17.6	11.8	20.2	20.1
terpinen-4-ol	14.627	1176	nd	nd	tr	0.1
1,3-ciclohexadiene-1-methanol	15.340	1194	0.2	0.4	0.7	0.9
cumin-aldehyde	17.385	1241	36.1	26.2	19.5	23.6
α-terpinene-7-al	19.320	1284	1.9	6.8	5.1	7.5
γ-terpinene-7-al	19.676	1292	2.4	30.2	29.2	17.8
p-metha-1,4-diene-7-ol	21.324	1331	nd	tr	0.1	nd
daucene	23.600	1381	nd	tr	0.1	0.1
trans-caryophyllene	25.318	1422	0.1	0.1	tr	0.1
10-epi-β-acoradiene	27.675	1478	nd	nd	0.1	0.1
carotol	32.713	1601	0.1	0.1	0.1	tr

RT – retention time, RI – retention index, tr- compound present in traces (less than 0.1%), nd – compound not detected



Picture 1. A typical GC/MS chromatogram of the cumin seed essential oil

The GC/MS analysis of the seeds essential oil of cumin from the Serbian market resulted in the identification of 22 compounds, among which the most abundant were cumin aldehyde (19.5-36.1%), *β*-pinene (15.6-23.7%), *γ*-terpinene (11.8-20.2%), *γ*-terpinene-7-al (2.4-30.2%) and *p*-cymene (4.9-13.7%) (Table 2). A typical GC/MS chromatogram of cumin seed essential oil from our research is shown in Picture 1. However, variations in the chemical composition of the essential oil are also influenced by numerous factors such as variety, weather conditions during the vegetation period, fertilization, plant density and harvest time [6; 13; 14; 15; 16].

The total polyphenole content in the cumin postdistillation seeds waste material, as estimated by the Folin–Ciocalteu method, was between 30.1 and 47.5 mg GAE/g dry extract (Table 1). However, other research was focused on the phenol content in the cumin seeds dry weight (DW). The amount of total phenolic compounds in cumin seeds samples from the Italian market ranged from 2.9 to 11.6 mg GAE/ g DW depending on the extraction technique. In particular, the results showed four times higher recoveries with the application of the microwave assisted extraction in comparison to the ultrasound assisted extraction [17]. Similarly, Soxhlet extraction of cumin fruit showed a significantly higher content of polyphenoles (from 12.2 to 25.2 mg GAE/g DW) than maceration (from 6.9 to 17.7 mg GAE/g DW) [18].

The phenol content is significantly different when the sample origin is in question. Tunisian cumin contained more phenolic acids (9.5 mg GAE/g DW) than Indian (6.4 mg GAE/g DW) [19]. Apart from this, the ripe stage also significantly influenced the phenol content, i.e. the polyphenol content was lower at unripe seeds when compared to fully ripe ones [18]. Water deficit during growth periods of cumin significantly influenced the total phenolic content. Drought caused a significant increase of the total phenolic content, which was more pronounced in moderate water deficit than that observed under severe water deficit [19].

According to the above mentioned, the differences in the total polyphenole content in the cumin postdistillation waste material can be a consequence of the plant origin, the weather conditions during the growing season, as well as the ripening stage during the harvest time.

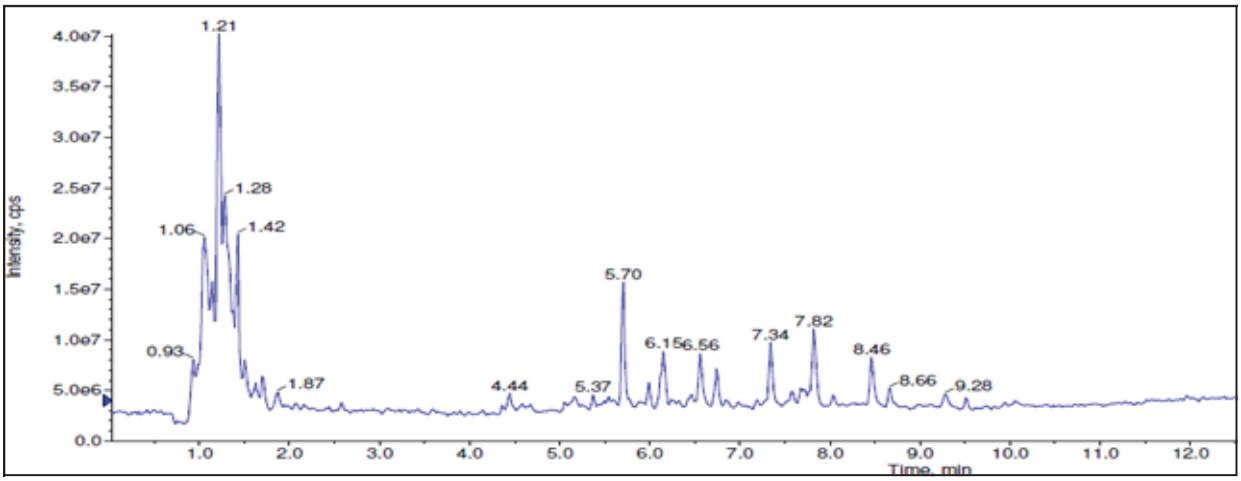
By applying the LC/DAD/MS analysis, 41 phenolic compounds were detected in the postdistillation waste material of cumin seeds (Table 3, Pictures 2 and 3). Hydroxybenzoic and hydroxycinnamic acids were most abundant, as well as glycosides of flavonones and flavonoles. In another study, conducted on Tunisian and Indian cumin, 19 phenolic compounds were identified, among which the *p*-coumaric acid was the major phenolic acid (with 4.8 mg/g DW in Tunisian, and 2.3 mg/g DW in Indian cumin) [19]. Other phenolic compounds were luteolin, syringic, cinnamic and *trans*-2-dihydrocinnamic acid, as well as flavones [19]. The comparison of extraction methods showed that Soxhlet extracts contained the greatest amount of polyphenols and flavonoids, in comparison to maceration samples [18]. As in case of the total polyphenole content, their composition can be different depending on many factors.

According to the obtained results, the antioxidative potential of cumin postdistillation seeds waste is poor and it ranged between 0.02 and 0.04 TE/g (Table 1). The comparison of two extraction methods showed that Soxhlet extracts contained the greatest amount of polyphenols and flavonoids, while maceration samples exhibited higher antiradical and bleaching power assay. Total phenolic contents and EC_{50} (the concentration required to cause a 50% DPPH inhibition) values in cumin seeds during their ripening led to the conclusion that the antioxidant activity does not depend only on the high content of total phenolics but also on the phenolic composition. A total of 19 phenolic compounds were successfully identified by HPLC analysis during the ripening of cumin seeds. Fully ripe seeds were dominated by *p*-coumaric acid [18].

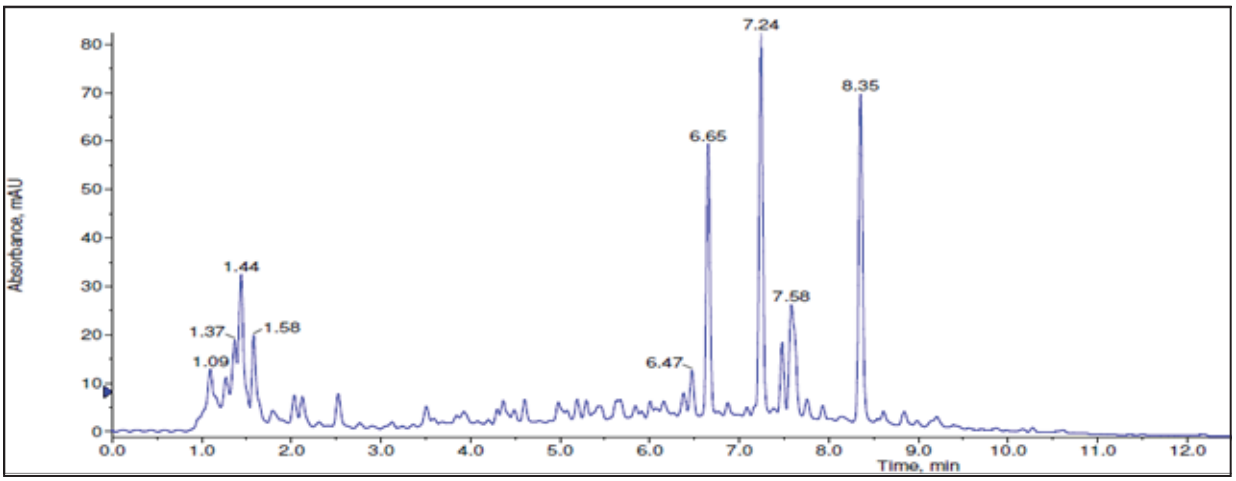
Table 3. The phenolics compounds of cumin seeds postdistillation waste identified by LC/DAD/MS

	t_r (min)	MW	MF	λ (nm)	ID compound (based on literature data)	Literature source
1	1.05	196,0595	$C_6H_{12}O_7$		UNC	
2	1.05	602,1426	$C_{32}H_{26}O_{12}$		UNC	
3	1.05	504,1715	$C_{24}H_{24}O_{12}$		Luteolin-3'-(3''-O-acetyl)-O-glucuronide; or Luteolin-3'-(4''-O-acetyl)-O-glucuronide	20
4	1.14	210,074	$C_{12}H_{18}O_3$	212;274sh	Jasmonic acid	21
5	1.15	182,0798	$C_9H_{10}O_4$		Homovanillic acid	22
6	1.21	192,0281	$C_6H_8O_7$		UNC	
7	1.22	134,0222	$C_4H_6O_5$		UNC	
8	1.28	104,0124	$C_3H_4O_4$		UNC	
9	1.35	174,0174	$C_6H_6O_6$		UNC	
10	1.43	192,0284	$C_6H_8O_7$	200;208sh;212sh;242;288	UNC	
11	1.70	118,0278	$C_4H_6O_4$		UNC	
12	1.84	174,0174	$C_6H_6O_6$		UNC	
13	1.86	162,0538	$C_6H_{10}O_5$		UNC	
14	4.43	354,0971	$C_{16}H_{18}O_9$	244;296sh;326	Chlorogenic acid	22
15	5.05	356,1122	$C_{16}H_{20}O_9$	236;292sh;316sh	Ferulic acid-O-hexoside	22
16	5.17	446,1445	$C_{21}H_{18}O_{11}$		Apigenin-7-O-glukuronid	23
17	5.37	354,0958	$C_{16}H_{18}O_9$	240;222sh;300sh;326	Chlorogenic acid	22
18	5.70	504,1853	$C_{24}H_{24}O_{12}$	220	Luteolin-3'-(3''-O-acetyl)-O-glucuronide; or Luteolin-3'-(4''-O-acetyl)-O-glucuronide	20
19	5.99	484,2108	$C_{20}H_{36}O_{13}$		Di-O-galloyl-hexoside	24
20	6.12	506,2009	$C_{23}H_{22}O_{13}$		Quercetin-3-acetylhexoside	25
21	6.16	364,1307	$C_{22}H_{20}O_5$	218;272;334	UNC	
22	6.16	374,1596	$C_{19}H_{18}O_8$	218;272;334	5,6-dihydroxi-7,8,3',4'-tetramethoxyflavone	26
23	6.33	342,1332	$C_{15}H_{18}O_9$		Caffeic acid-O-hexoside 1	22
24	6.56	342,1335	$C_{15}H_{18}O_9$	238	Caffeic acid-O-hexoside 2	22
25	6.74	624,1333	$C_{28}H_{32}O_{16}$	254;266sh;348	Isorhametin-3-O-rutinoside	27
26	6.84	372,1083	$C_{16}H_{20}O_{10}$	224;322	UNC	
27	7.19	368,1621	$C_{17}H_{20}O_9$		Feruloylquinic acid	28
28	7.19	576,2432	$C_{26}H_{40}O_{14}$ $C_{44}H_{32}O$		UNC	
29	7.34	608,1382	$C_{28}H_{32}O_{15}$	222sh;266;336	Diosmin	23
30	7.58	638,1496	$C_{46}H_{22}O_4$ $C_{21}H_{34}O_{22}$	220;250sh;266sh;348	UNC	
31	7.68	448,1022	$C_{21}H_{20}O_{11}$	254;266sh;348	Kaempferol-3-O-glucoside	27
32	7.72	444,1435	$C_{23}H_{24}O_9$ $C_{16}H_{28}O_{14}$	234;276;294sh;390	UNC	
33	7.72	548,2477	$C_{25}H_{40}O_{13}$	234;276;294sh;390	UNC	
34	7.82	346,1110	$C_{20}H_{26}O_5$		Rosmanol; epirosmanol; isorosmanol	21
35	8.03	444,1433	$C_{23}H_{24}O_9$	232;340	UNC	
36	8.46	432,1078	$C_{21}H_{20}O_{10}$	266; 336	Apigenin-7-O-glucoside	22
37	8.67	442,1858	$C_{21}H_{30}O_{10}$ $C_{22}H_{18}O_{10}$		UNC	
38	9.28	138,0315	$C_7H_6O_3$	236;302	p-hydroxybenzoic acid	22
39	9.51	456,212	$C_{22}H_{32}O_{10}$		UNC	
40	9.51	446,1725	$C_{21}H_{18}O_{11}$		Apigenin-7-O-glucuronide	26
41	9.72	468,2229	$C_{20}H_{36}O_{12}$		UNC	

tr – Retention time, MW – Molecular Weight, MF – molecular formula, λ – Absorbance maxima, UNC – Unknown compound



Picture 2. A typical HPLC-ESI-ToF-MS(-) chromatographic profile of the cumin extract



Picture 3. A typical HPLC-UC (260 nm) chromatographic profile of the cumin extract

Conclusion

The essential oil content in cumin seeds usually constitutes up to 5%, with cumin aldehyde, *β*-pinene, *γ*-terpinene, *γ*-terpinene-7-al and *p*-cymene as main compounds. However, a large amount of postdistillation waste material which remains unused contains between 30.1 and 47.5 mg GAE/g of total polyphenolics, and possesses a poor antioxidative capacity (0.02-0.04 TE/g). Further research will be focused on agro-food implementation of the postdistillation waste material of cumin seeds and other plants which are used for the essential oil production.

References

[1] P.R. Moghaddam, R. Moradi, H. Mansoori, Influence of planting date, intercropping and plant growth promoting rhizobacteria on cumin (*Cuminum cyminum* L.) with particular respect to disease infestation in Iran. Journal of Applied Research on Medicinal and Aromatic Plants, 1 (2014) 134-143.

[2] A.H. Chaudhry, A. Tanveer, A. Shar, M.S. Akhtar, M.K. Shahid, K.M. Ashfaq, T.A. Malik, R.H. Siddiqui, Physico-chemical investigation and antimicrobial activity of essential oil of *Cuminum cyminum* L. World Applied Sciences Journal, 19 (2012) 330-333.

[3] Q. Chen, X. Hu, J. Li, P. Liu, Y. Yang, Y. Ni, Preparative isolation and purification of cuminaldehyde and p-menta-1,4-dien-7-al from the essential oil of *Cuminum cyminum* L. by high-speed counter-current chromatography. Analytica Chimica Acta, 689 (2011) 149-154.

[4] M. Sayyah, A. Peirovi, M. Kamalinejad, Anti-nociceptive effect of the fruit essential oil of *Cuminum cyminum* L. in rat. Iranian Biomedical Journal, 6 (2002)141-145.

[5] S.I. Shivakumar, A.A. Shahapurkar, K.V. Kalmath, B. Shivakumar, Antiinflammatory activity of fruits of *Cuminum cyminum* Linn. Der Pharmacia Lettre, 2 (2010) 22-24.

[6] H. Hajlaoui, H. Mighri, E. Noumi, M. Snoussi, N. Trabelsi, R. Ksouri, A. Bakhrouf, Chemical composition and biological activities of Tunisian *Cuminum cyminum* L. essential oil: A high effectiveness against Vibrio spp. strains. Food and Chemical Toxicology, 48 (2010) 2186-2192.

[7] M. Moghaddam, S.N.K. Miran, A.G. Pirbalouti, L. Mehdizadeh, Y. Ghaderi, Variation in essential oil

composition and antioxidant activity of cumin (*Cuminum cyminum* L.) fruits during stages of maturity. Industrial Crops and Products, 70 (2015) 163-169.
[8] F. Moraghebi, Introduction of mirtenal as an indicator component in essential oil of *Cuminum cyminum* Isfahan variety. Journal of Biodiversity and Environmental Sciences, 3 (2013) 112-117.
[9] N. Gavaric, N. Kladar, A. Misan, A. Nikolic, I. Samojlik, N. Mimica-Dukic, B. Bozin, Postdistillation waste material of thyme (*Thymus vulgaris* L., *Lamiaceae*) as a potential source of biologically active compounds. Industrial Crops and Products, 74 (2015) 457-464.
[10] European Pharmacopoeia, 5th Ed. Cedex, Council of Europe, 2004, pp. 217–218.
[11] R. Li, Z.T. Jiang, Chemical composition of the essential oil of *Cuminum cyminum* L. from China. Flavour and Fragrance Journal, 19 (2004) 311-313.
[12] N. Chaudhary, S.S. Husain, M. Ali, Chemical composition and antimicrobial activity of volatile oil of the seeds of *Cuminum cyminum* L. World Journal of Pharmacy and Pharmaceutical Science, 3 (2014) 1428-1441.
[13] Y. Kan, M. Kartal, T. Ozek, S. Aslan, K.H.C. Baser, Composition of essential oil of *Cuminum cyminum* L. according to harvesting times. Turkish Journal of Pharmaceutical Sciences, 4 (2007) 25-29.
[14] P. Hashemi, A. Yarahmadi, K. Azizi, B. Sabouri, Study of the effects of N fertilization and plant density on the essential oil composition and yield of *Cuminum cyminum* L. seeds by HS-SME. Chromatographia, 67 (2008) 253-257.
[15] I. Bettaieb, S. Bourgou, J. Sriti, K. Msaada, F. Limam, B. Marzouk, Essential oil and fatty acids composition of Tunisian and Indian cumin (*Cuminum cyminum* L.) seeds: a comparative study. Journal of the Science of Food and Agriculture, 91 (2010) 2100-2107.
[16] I. Bettaieb-Rebey, I. Jabri-Karoui, I. Hamrouni-Sellami, S. Bourgou, F. Limam, B. Marzouk, Effect of drought on the biochemical composition and antioxidant activities of cumin (*Cuminum cyminum* L.) seeds. Industrial Crops and Products, 36 (2012) 238-245.
[17] M. Gallo, R. Ferracane, G. Graziani, A. Ritieni, V. Fogliano, Microwave assisted extraction of phenolic compounds from four different spices. Molecules, 15 (2010) 6365-6374.
[18] I. Bettaieb-Rebey, S. Kefi, S. Bourgou, I. Ouerghemmi, R. Ksouri, M.S. Tounsi, B. Marzouk, Ripening stage and extraction method effects on physical properties, polyphenol composition and antioxidant activities of cumin (*Cuminum cyminum* L.) seeds. Plant Foods for Human Nutrition, 69 (2014) 358-364.
[19] I. Bettaieb-Rebey, N. Zakhama, I. Jabri-Karoui, B. Marzouk, Polyphenol composition and antioxidant activity of cumin (*Cuminum cyminum* L.) seeds extract under drought. Journal of Food Science, 77 (2012) 634-739.
[20] L. Perez-Fons, M.T. Garzon, V. Micol, Relationship between the antioxidant capacity and effect of rosemary (*Rosmarinus officinalis* L.) polyphenols on membrane phospholipid order. Journal of Agricultural and Food Chemistry, 58 (2010) 161-171.
[21] N. Babovic, S. Djilas, M. Jadranin, V. Vlasj, J. Ivanovic, S. Petrovic, I. Zizovic, Supercritical carbon dioxide extraction of antioxidant fraction from selected Lamiaceae herbs and their antioxidant capacity. Innovative Food Science and Emerging Technologies, 11 (2010) 98-107.
[22] A. Vallverdu-Quetalz, J. Reguerio, M. Martinez-Huelamo, J.F.R. Alvarenga, L. Neto Leal, R.M. Lamuela-Raventos, A comprehensive study on phenolic profile of widely used culinary herbs and spices: rosemary, thyme, oregano, cinnamon, cumin and bay. Food Chemistry, 154 (2014) 299-307.
[23] U. Justensen, Negative atmospheric pressure chemical ionization low-energy collision activation mass spectrometry for the characterization of flavonoids in extracts of fresh herbs. Journal of Chromatography A, 902 (2000) 369-379.
[24] N. Kumar, P. Bhandari, B. Singh, S.S. Bari, Antioxidant activity and ultra-performance LC-electrospray ionization-quadrupole time-of-flight mass spectrometry for phenolics-based fingerprinting of Rose spices: *Rosa damascene, Rosa bourboniana* and *Rosa brunonii*. Food and Chemical Toxicology, 47 (2009) 361-367.
[25] A. P. Singh, T. Wilson, D. Luthria, M. R. Freeman, R. M. Scott, D. Bilenker, S. Shah, S. Somasundaram, N. Vorsa, LC-MS-MS characterization of curry leaf flavonols and antioxidant activity. Food Chemistry, 127 (2001) 80-85.
[26] J.R. Vergara-Salinas, J. Perez-Jimenez, J. L. Torres, E. Agosin, J.R. Perez-Correa, Effect of Temperature and time on polyphenolic content and atioxidant activity in the pressurize hot water extraction of deodorized thyme (*Thymus vulgaris*). Journal of Agricultural and Food Chemistry, 60 (2012) 10920-10929.
[27] I. Parejo, F. Vildomat, J. Bastida, G. Schemeda-Hirschmann, J. Burillo, C. Codina, Bioguided isolation and Identification of the nonvolatile antioxidant compounds from fennel (*Foeniculum vulgare* Mill.) waste. Journal of Agricultural and Food Chemistry, 52 (2004) 1890-1897.
[28] A. Kaiser, D. R. Kammerer, R. Carlem, Impact of blaching on polyphnol stability and antioxidant capacity of innovative coriander (*Coriandrum sativum* L.) pastes. Food Chemistry, 140 (2013) 332-339.

Izvod

ANALIZA ETARSKOG ULJA PLODOVA KUMINA I UKUPNIH POLIFENOLA U OSTACIMA NAKON DESTILACIJE

Milica G. Aćimović[1,2], Vele Tešević[3], Dimitrije Mara[3], Mirjana Cvetković[4], Jovana Stanković[4], Vladimir Filipović[5]

[1]Institut za prehrambene tehnologije (FINS), Univerzitet u Novom Sadu, Novi Sad, Srbija
[2]Institut za ratarstvo i povrtarstvo, Novi Sad, Srbija
[3] Hemijski fakultet,Univerzitet u Beogradu, Beograd, Srbija
[4] Institut za hemiju, tehnologiju i metalurgiju (IHTM), Univerzitet u Beogradu, Beograd, Srbija
[5] Institut za proučavanje lekovitog bilja "dr Josif Pančić", Beograd, Srbija

(ORIGINALNI NAUČNI RAD)
UDK 582.794.1:66.061.34:615.322

Sadržaj etarskog ulja u plodovima kumina prisutnog na Srpskom tržištu kreće se između 2.0 i 4.0%. Primenom GC/MS identifikovane je ukupno 22 komponente u etarskim uljima kumina, među kojima su najzastupljenije: kumin aldehid, *β*-pinen, *γ*-terpinen, *γ*-terpinen-7-al i *p*-cimen. Međutim, kako je sadržaj etarskog ulja u plodovima kumina mali (ispod 5%), veliki deo biljnog materijala ostaje neiskorišćen. Primenom tzv. Folin–Ciocalteu metoda, ustanovljeno je da ostaci nakon destilacije etarskog ulja iz plodova kumina sadrže između 30.1 i 47.5 mg GAE/g suvog ekstrakta ukupnih polifenola. Hidroksibenzoeva i hidroksicimetna kiselina, kao i glikozidi flavonona i flavonola, su najzastupljeniji polifenoli. Na osnovu DPPH-metoda antioksidativni potencijal ostataka nakon destilacije plodova kumina je slab i kreće se između 0.02 i 0.04 mM TE/g. Dalja istraživanja bi trebalo usmeriti ka primeni ostataka nakon destilacije plodova kumina i drugih biljaka koje se koriste za destilaciju etarskih ulja u prehrambenoj industriji i poljoprivredi.

Ključne reči: *Cuminum cyminum*, etarsko ulje, ostaci nakon destilacije etarskog ulja, ukupni polifenoli, DPPH