BOOK OF PROCEEDINGS

AgroSym

VII International Scientific Agriculture Symposium
Jahorina, October 06-09, 2016

agro 2016 sym

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VII International Scientific Agriculture Symposium
“Agrosym 2016”

AGROSYM 2016

Jahorina, October 06 - 09, 2016

Impressum

VII International Scientific Agriculture Symposium „Agrosym 2016“

Book of Proceedings

Published by

University of East Sarajevo, Faculty of Agriculture, Republic of Srpska, Bosnia
University of Belgrade, Faculty of Agriculture, Serbia
Mediterranean Agronomic Institute of Bari (CIHEAM - IAMB) Italy
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CIP - Каталогизација у публикацији
Народна и универзитетска библиотека
Републике Српске, Бања Лука

631(082)(0.034.2)

INTERNATIONAL Scientific Agricultural Symposium "Agrosym 2016" (7 ; Jahorina)
Book of Proceedings [Elektronski izvor] / VII International Scientific Agriculture Symposium "Agrosym 2016", Jahorina, October 06 - 09, 2016 ; [editor in chief Dušan Kovačević]. - East Sarajevo =Istočno Sarajevo : Faculty of Agriculture =Poljoprivredni fakultet, 2016. - 1 elektronski optički disk (CD-ROM) : tekst, slika ; 12 cm

CD ROM čitač. - Nasl. sa nasl. ekrana. - Registar.

ISBN 978-99976-632-7-6

COBISS.RS-ID 6216984

10.7251/AGRENG1607115

ANALYSIS OFTOTAL POLYPHENOLS FROM POSTDESTILLATION WASTE MATERIAL OF DIFFERENT CORIANDER ACCESSIONS GROWN IN SERBIA

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Abstract

Coriander (*Coriandrum sativum* L.) is an aromatic plant grown for seed (*Coriandri fructus*) which contains essential oil (*Coriandri aetheroleum*) with a specific fragrance originating from the main component, limonene. Essential oil is obtained by steam distillation from the dried ripe seed. However, the content of essential oil in seed is low, between 0.1 and 1.8%, depending on variety, geographical origin, agroecological conditions, growing technology, etc. Still, the majority of the produced plant material remained unused. The aim of our investigation was to determine the total polyphenols content in postdistillation waste material which remains after coriander essential oil distillation. Evaluation of its antioxidative capacity was the other purpose of this study. Six coriander accessions of different origins were grown on an experimental field in Mošorin, Serbia, during 2014. According to the obtained results, postdistillation coriander seed waste material, as estimated by the Folin–Ciocalteu method, contained between 40.9 and 57.2 mg GAE/g dry extract of total polyphenols. However, according to DPPH method the antioxidative potential of coriander postdistillation seed waste was poor and it is ranged between 0.03 and 0.04 TE. Further research will be focused on agro-food implementation of postdistillation waste material of coriander and other plants which are used for essential oil production.

Keywords: *Coriandrum sativum*, postdistillation waste material, total polyphenols, DPPH, antioxidative capacity

Introduction

Coriander (*Coriandrum sativum* L.) is annual aromatic plant from the Apiaceae family. It is grown for seed (*Coriandri fructus*) which can be used as spice or for essential oil distillation (*Coriandri aetheroleum*). The dry, ripe fruit and oil have a specific fragrance, sweet, hot and pungent. The scent originates from the main components in the essential oil: limonene, α-pinene and geranyl-acetate. However, the content of essential oil in seed is low, between 0.1 and 1.8% (Diederichsen 1996). The amount of the essential oil and its quality can vary depending on: varieties and cultivars, the geographical position of the region of production, the climate and weather conditions, soil type, agro technology, the stage in which the harvest is performed, drying, storage and applied extraction techniques (Aćimović 2014).

Material efficiency is nowadays an essential topic to promote the sustainable use of natural resources, waste materials and industrial by-products, in agreement with the principle of sustainable development and life cycle assessment (Prokkola et al., 2012). Because of this, the biological potential of various plant waste materials is in focus of numerous studies. These studies are important, both in terms of economy and ecology, in order to elucidate the way to exploit post-distillation waste material of aromatic plants and other plant waste materials more efficiently (Gavarić et al., 2015).

The aim of our investigation was to determine the total polyphenols content in postdistillation waste material which remains after coriander essential oil distillation. Thestudy of antioxidant activity of postdistillation waste material was the other purpose of this paper.

Material and methods

Plant material. Six different ecotypes of coriander plants were grown for the trial purposes. The local ecotype of coriander seed, widely grown in province of Vojvodina was obtained from medicinal plants grower from Kulpin (plants used for extraction of the oil marked as Coriander 1), while other five types of seed were bought at the local market. The seed producers were: Institute for Medicinal Plant Research “drJosifPančić” Serbia, “Semenarnacoop” Serbia, “Master seeds” Serbia, “Sgaravatti” Italy and “Blumen” Italy (plants used for extraction of the oils marked as Coriander 2, 3, 4, 5 and 6, respectively). Coriander was sown in the first decade of April, by hand at row spacing 35 cm, and around 70 seeds per meter in a row (density of 200 plants per m^2). The size of the experimental plots was5m^2. Weeds were controlled by hoeing and weeding when needed. Disease and insect control measures were not applied. Harvest was carried out by hand in the phase of full maturity, at the end of July. After harvest, the seed waskept in paper bags at room temperature until required for further analysis.

Experiment location and growing conditions. The experimental field was set in a village called Mošorin (45°18' N, 20°09' E) in 2014. Mošorin is located in the north part of the Republic of Serbia. This area has moderate continental climate with some tendencies towards continental. The whole region is located in a semi-arid area where variations in the amount of precipitation, air temperature and other important climatic elements are substantial over the years. The soil at experimental field had a neutral reaction to soil solution (pH 7.3 in KCl) and was moderately supplied with humus (2.7%). The soil is classified as highly calcareous loamy chernozem (with 8.4% $CaCO_3$). The content of readily available phosphorus and potassium was high (81.6 and 75.1 mg/100gof soil, respectively).

Essential oil isolation. The dried samples of coriander were subjected to hydro-distillation using an all glass Clevenger–type apparatus to extract essential oils according to the method outlined by the European Pharmacopoeia.

Determination of the total polyphenolics.The amount of total phenolics in water soluble extracts which remains after essential oil distillation (postdistillation waste material) wasdetermined using the Folin-Ciocalteu reagent with gallic acid as astandard. The reagent was prepared by diluting a stock solutionwith distilled water (1:10, v/v). Samples (1 ml, three replicates)were placed into test cuvettes, and 5 ml of Folin-Ciocalteuphenol reagent and 4 ml of Na_2CO_3 (7.5 %) were added. Theabsorbance of the samples was measured at 765 nm using aUV/VIS spectrophotometer Cintra 40 after incubation at 20 °C for 1 h. The resultswere 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 coriander seed which remains after 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). A 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 ($\mathbf{t}_r$), mass spectra and UV spectra, and were tentatively identified based on 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 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 a 1800 μlmethanolic 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 resultswere 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:

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

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

Statistical Analysis. Data was subject to 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 average content of essential oil in different accessions of coriander seed grown in Serbiawas 0.57%, and varied between 0.42 and 0.95%(Table 1). The highest content of essential oil wasdetermined in local ecotype (Coriander 1). It is well known that essential oil content depends on many factors, among whichthe genotype is a major determinant for the synthesis of secondary metabolites(Gil et al., 2002).

Still, the majority of the produced plant material remained unused (more than 99%). However, the total polyphenole content in coriander postdistillation seeds waste material as estimated by

the Folin–Ciocalteu method in average was 53.78 mg GAE/g dry extract (Table 1). The lowest amount of total phenolic compounds was determined in Coriander 3 (40.9 mg GAE/g dry extract), and highest in Coriander 4 (57.2 mg GAE/g dry extract). However, data about total polyphenole content in methanolic coriander seed extract is very different, and ranged between 18.70 GAE/g dry weight (Dua et al., 2014), up to 65.58 mg GAE/g dry weight (Sriti et al., 2012).
According to DPPH method, the antioxidative potential of coriander postdistillation seed waste was poor and it is ranged between 0.03 and 0.04 mMTrolox Equivalents/g sample(Table 1). However, in the study with fruit methanolic extract of three coriander varieties (Tunisian, Syrian and Egyptian) EC_{50}values of reducing power activity varied significantly from 54.20 to 122.01 μg/mL (Msaada et al., 2014).

Table 1. Essential oil content (%) in coriander seed, total polyphenole content (mg Gallic Acid Equivalent/g sample) and antioxidative capacity (mMTrolox Equivalent/g sample) of methanolic extract of coriander postdistillation waste material.

	Essential oil content (%)	**Total polyphenole content (mg GAE/g sample)**	**Antioxidative capacity (mM TE/g sample)**
Coriander 1	0.95	55.7	0.04
Coriander 2	0.56	55.9	0.03
Coriander 3	0.45	40.9	0.03
Coriander 4	0.42	57.2	0.04
Coriander 5	0.49	56.2	0.04
Coriander 6	0.56	56.8	0.04
Average	**0.57**	**53.78**	**0.037**

by applying the lc/dad/ms analysis,43 phenolic compounds were detected in the postdistillation waste material of coriander seed. there are a couple of groups: hydroxybenzoic and hydroxycinnamc acids, as well as glycosides flavanones and flavanols. the most abundant are different hydroxycinnamic acids and their derivates, and glycosides flavanols. esculin, glycosides coumarines,is found in methanolic extract of coriander seed.

Table 2.The phenolics compounds of methanolic extract of coriander seeds postdistillation waste material identified by LC/DAD/MS

No	RT (min)	Molecular weight	Molecular formula	Absorbance maxima (nm)	Identification	Reference
1	1,04	602,1454	$C_{32}H_{26}O_{12}$ $C_{25}H_{30}O_7$		NI	
2	1,04	210,0389	$C_{12}H_{18}O_3$		Jasmonic acid	Babovic et al., 2010
3	1,05	166,0484	$C_5H_{10}O_6$		NI	
4	1,07	440,0936	$C_{19}H_{20}O_{12}$ $C_{26}H_{16}O_7$		NI	
5	1,07	224,0545	$C_7H_{12}O_8$		NI	
6	1,14	208,2021		204;216;310	NI	
7	1,21	190,0131	$C_6H_6O_7$		NI	
8	1,21	134,0255			NI	
9	1,28	104,0119	$C_3H_4O_4$		NI	
10	1,37	192,0290	$C_6H_8O_7$		NI	
11	1,44	192,0284	$C_6H_8O_7$	216;252sh	NI	
12	1,51	129,0433		276sh;260	NI	
13	1,64	222,0395	$C_7H_{10}O_8$	248;280sh	NI	
14	1,67	116,0123	$C_4H_4O_4$		NI	
15	1,72	118,0278	$C_4H_6O_4$	218;300sh	NI	
16	1,72	148,0392	$C_5H_8O_5$		NI	
17	1,91	162,0530	$C_6H_{10}O_5$		NI	
18	2,04	531,1606	$C_{23}H_{25}N_5O_{10}$ $C_{22}H_{29}NO_{14}$ $C_{26}H_{25}N_3O_8$	208;254;292sh	NI	
19	2,20	369,1082		200;214;256;296sh	NI	
20	3,54	214,0853	$C_{10}H_{14}O_5$		NI	
21	3,54	340,1205	$C_{15}H_{16}O_9$		Esculin	Parejo et al., 2004
22	3,61	316,0890	$C_{16}H_{12}O_7$	214;236;314	Izorhameti	Hossain et al., 2010
23	4,68	204,0912		220;276	NI	
24	5,17	370,0558	$C_{16}H_{18}O_{10}$	244;304sh;328	Hydroxyl-cafeoilhinonicacid	Kaiser et al. 2013
25	5,37	176,0692	$C_7H_{12}O_5$	242;294sh;330	NI	
26	5,63	430,1529	$C_{30}H_{22}O_3$		NI	
27	5,70	254,1173	$C_{13}H_{18}O_5$		NI	
28	5,93	180,0429	$C_9H_8O_4$	218sh;233;294sh;326	Caffeicacid	Vallverdu-Quetalz et al., 2014
29	6,04	402,1543	$C_{18}H_{26}O_{10}$		NI	
30	6,20	350,0686	$C_9H_{18}O_{14}$		NI	
31	6,35	432,2016	$C_{21}H_{20}O_{10}$		Apigenin-7-O-glukozid	Vallverdu-Quetalz et al., 2014
32	6,35	384,0710	$C_{16}H_{16}O_{11}$ $C_9H_{20}O_{16}$		NI	

33	7,18	378,1905	$C_{17}H_{30}O_9$	230;296sh;312	NI	
34	7,18	368,1620	$C_{17}H_{20}O_9$	230;296sh;312	Ferouilhinonicacid	Kaiser et al., 2013
35	7,41	412,1426	$C_{30}H_{20}O_2$		NI	
36	7,53	426,1219	$C_{12}H_{26}O_{16}$ $C_{30}H_{18}O_3$	230;278	NI	
37	7,72	410,1270	$C_{12}H_{26}O_{15}$ $C_{30}H_{18}O_2$	222sh;238;296sh;322	NI	
38	7,76	194,0590	$C_{10}H_{10}O_4$	222sh;238;296sh;322	Ferulicacid	Vallverdu-Quetalz et al., 2014
39	7,76	370,1781	$C_{16}H_{18}O_{10}$	222sh;238;296sh;322	Hydroxyl-cafeoilhinonic acid	Kaiser et al., 2013
40	7,90	414,1547	$C_{19}H_{26}O_{10}$		NI	
41	8,14	410,1273	$C_{12}H_{26}O_{15}$ $C_{30}H_{18}O_2$	238;264sh;308	NI	
42	8,34	476,2269	$C_{21}H_{16}O_{13}$		NI	
43	12,64	330,2421	$C_{20}H_{26}O_4$		Carnosol	Babovic et al., 2010

Conclusion

Our findings suggest that coriander postdistillation waste material represents a source of polyphenoles, but has low antioxidative capacity according to DPPH method. However, further research needs to be focused on its implementation in agro-food industry, in order to provide high exploitation of plant material.

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