

DEJAN SKALA<sup>1</sup>  
RADMILA KUŽIĆ<sup>1</sup>  
IRENA ŽIŽOVIĆ<sup>1</sup>  
VESNA NIKOLIĆ<sup>2</sup>  
DUŠAN JOVANOVIĆ<sup>3</sup>

<sup>1</sup>Faculty of Technology and Metallurgy, Belgrade, Yugoslavia

<sup>2</sup>Faculty of Technology, Leskovac, Yugoslavia

<sup>3</sup>ChTM, Department of Catalysis and Chemical Engineering, Beograd, Yugoslavia

SCIENTIFIC PAPER

582.572.225+66.048+66.061

## ETHERIC OIL FROM GARLIC (*ALLIUM SATIVUM L.*) OBTAINED BY CO<sub>2</sub>-SFE: COMPARISON WITH STEAM DISTILLATION

*The main focus of the present work was to obtain qualitative and quantitative information on etheric oil produced by the steam distillation of garlic homogenate, by steam distillation after previously applied microwave (MW) treatment of garlic cloves, by steam distillation under reduced pressure, and by supercritical fluid extraction with carbon dioxide.*

Etheric oil from garlic (*Allium sativum L.*) contains many bioactive compounds and has been extensively used for many years as a pharmacological substance. Many other products from garlic (garlic oil, garlic powder, garlic salt, garlic paste and garlic flakes) have been used worldwide in the home or in the food industry. All garlic products can be divided into the following forms according to their preparation methods: raw garlic, dried garlic, boiled garlic, baked garlic, and fried garlic.

Etheric oil from garlic (EOG) is mainly produced by conventional methods (steam or water-steam distillation). It is not originally present in garlic; many researchers have reported that intact garlic cloves contain a flavor precursor, alliin (S-allylcysteine S-oxide), and an enzyme *alliinase*, which converts alliin into allicin, responsible for the pungent principle of garlic, when the cellular tissue of garlic is disrupted. Many S-compounds are formed from allicin and garlic oil and, of course, etheric oil from garlic gains a strong and specific flavor. Namely, after the enzyme *alliinase* was deactivated (boiling the garlic bulb or homogenizing it with alcohol containing limited quantities of water), no pungent odor was detected from the garlic samples because alliin was not converted to allicin.

Different preparations are in use today also giving different flavors of garlic products. Its qualitative and quantitative composition depends on many factors (origin, applied procedure, storage etc.). In this study the composition and yield of EOG obtained by the water-steam distillation of garlic clove homogenate (with and without MW preheating) at normal and reduced pressure (vacuum) and extraction by supercritical CO<sub>2</sub> were analyzed. Interest in the application of supercritical

fluid extraction (SFE-CO<sub>2</sub>) of garlic has increased because of its effectiveness in the extraction and analysis of many other natural products and concern related to the use and disposal of conventional organic solvents for extraction.

The volatile components of raw garlic, dried garlic, and boiled garlic have been well studied; the contributions of alk(en)yl thiosulfonates and their transformation products in the flavor sensation of garlic products have also been well researched, as well as volatile compounds from microwave-heated garlic slices (Yu et al., 1993). Also several studies were reported concerning the application of SFE technologies in the extraction of garlic (Calvey et al., 1994; 1997). Yu et al. identified 41 volatile compounds from microwave-ripened garlic samples (garlic slices mixed with soybean oil) after being isolated by a steam distillation/solvent extraction procedure applying GC and GC-MS techniques. Among these volatile components di-allyl disulfide, methyl allyl disulfide, vinyl dithiols and di-allyl trisulfide were the dominant compounds found in MW-baked garlic samples. A similar experimental procedure and preparation of volatile compounds was applied in this study: microwaved heating of garlic homogenate (only garlic slices) in the first, followed by water-steam distillation under normal and reduced pressure in the second step. The prepared samples of EOG were analysed using GC and GC-MS with a specific detector appropriate for S-compound identification.

Calvey et al. (1997) analyzed the supercritical fluid extract of homogenized garlic cloves applying liquid chromatography and the LC-MS combination. The presence of propyl compounds (in traces) and ajoene (a potent antithrombotic agent) were verified among major thiosulfonates. These compounds were not readily evident in the previous analysis of other investigations using GC-MS analysis because the complete decomposition of allicin and other thiosulfonates is very rapid (garlic juice after 3 h at room temperature followed

Author address: D. Skala, Faculty of Technology and Metallurgy, Karnegijeva 4, PO Box 494, YU-11001 Beograd;  
e-mail: skala@vesta.tmf.bg.ac.yu; dnskala@eunet.yu  
Paper received: August 17, 2000.  
Paper accepted: December 7, 2000.

by SFE, Wagner and Breu, 1989). Lawson (1993) as opposed to Wagner and Breu (1989) showed that the half-life of allicin at room temperature in water is 4 days, which was also proven by Calvey et al. (1997). Different results of extract composition prepared by SFE are the consequence of different identifications of those compounds that are primarily responsible for the characteristic flavor of freshly cut garlic. Namely, thermal decomposition or artifact formation (Block, 1992) during GC and GC-MS analysis are mainly responsible that compounds of allylcine and thiosulfinate types could not be detected.

So, the main focus in this study was directed to the analysis of differences in the yields of EOG obtained under different working conditions knowing that some changes in EOG compositions could be varied with time and applied procedure of identification.

## MATERIALS AND METHODS

### Garlic characteristics and composition

The garlic used in this study was originally produced (Summer, 1998) in the south of Serbia (Leskovac) on a field near the high-way. Also, garlic produced in 1998 in China was used in this study.

Etheric oil from garlic has been analysed by many authors because of its complex composition and the pharmaceutical effects of some of them. Table 1 shows the most important constituents of garlic cloves and Table 2 the contents of macro- and micro-elements in garlic cloves (Vučetić et al. 1986).

Garlic is also a very important source of different vitamins: B1, which makes a complex with allicin increasing resorption in the human organism (Jung et al.

Table 1. Chemical composition of garlic clove

Component	Mass %
Water	60-70
Organic acids	0.1
Carbohydrates	0.3-3.2
Lipids	0.15
Cellulose	1.00
Nitrogen compounds	6.7-8.0
Ash	1.5

Table 2. Mineral matters present in garlic

Macro elements	mg /100g	Micro elements	µg/ 100g
Potassium	260	Iron	1500
Calcium	38	Zinc	1025
Magnesium	36	Manganese	810
Sodium	32	Copper	130
Phosphorus	234	Iodine	9
Chlorine	30	Cobalt	9

1991); B2 and B6, and C. Content of selenium which is about 9 ppm is also very important for metabolic processes in the human organism among many other mineral materials present in garlic (Table 2).

### Etheric oil from garlic

Etheric oil from garlic (EOG) was prepared 70 years ago, before any investigation and research of its composition was conducted, indicating the presence of many active components. EOG is formed after cutting garlic clove under the influence of the enzymatic activity of *alliinase*. Originally garlic clove contains **alliin**, a soluble and odorless compound which has no antimicrobial effect. The destruction of **alliin** creates **allicin** with a characteristic odor and antimicrobial (bactericidal) activity. Allicin is an unstable and volatile compound, which, in the presence of oxygen from air can further be decomposed to secondary oily products (polysulfides, sulfides) with the unpleasant and characteristic flavor of garlic (Lukić, 1985).

Etheric oil can be obtained by water-steam distillation of the garlic-homogenate, and its composition is given in Table 3 (Kim et al. 1995).

The basic physical characteristics of EOG are: clear orange-red liquid; relative density  $d_{25} = 1.040 - 1.090$ ; index of refraction  $n_D^{20} = 1.559 - 1.579$ ; the odor of di-allyl disulphide is characteristic for EOG.

Table 3. Composition of etheric oil from garlic

No	Component	Yield mg/100 g of garlic
1.	2-propen-1-thiol	0.06
2.	methyl allyl sulfide	0.37
3.	di-methyl sulfide	0.27
4.	2-vinyl acropoanal	0.51
5.	2-propen-1-ol	1.00
6.	di-allyl sulfide	1.04
7.	(Z)-1-propenyl methyl disulfide	0.25
8.	methyl allyl disulfide	8.16
9.	(E)-1-propenyl methyl disulfide	0.81
10.	dimethyl trisulfide	1.08
11.	propyl allyl disulfide	0.03
12.	3-methyl thiopropanol	tr.
13.	(Z)-1-propenyl allyl disulfide	3.07
14.	di-allyl disulfide	48.56
15.	(E)-1-propenyl allyl disulfide	7.67
16.	1,2-di-thionclop-3-ene	0.54
17.	methyl allyl trisulfide	12.82
18.	allyl thiopropanol	1.62
19.	propyl allyl trisulfide	0.53
20.	3-vinyl-4H-1,2-ditiin	0.77
21.	di-allyl trisulfide	71.67
22.	2-vinyl-4H-1,2-ditiin	0.42

## Usage of EOG

Products on the basis of EOG, because of the low content in fresh garlic bulb, are dissolved in edible oils and sold on the market in the form of gelatinized capsules or pastilles. They are used in medicine mainly as antidiabetic, antiseptic and diuretic agents, against arterioscleroses and against high blood pressure. Many of these antibiotic activities are changed and lost during the preparation of EOG capsules. Namely, according to some investigations, the influence of only one fresh clove of garlic is equivalent to the influence of 5 to 10 such prepared capsules. The yield of EOG mostly depends on the quality of fresh garlic, the procedure of its storage, as well as on the procedure used during EOG preparation.

## Applied methods of EOG preparation

In this study different methods for EOG production were used: water–steam distillation, water–steam distillation under reduced pressure, water–steam distillation after MW heating of the garlic homogenate, supercritical extraction by CO<sub>2</sub> (with or without previous MW heating of the garlic homogenate).

a) The apparatus of *Clevenger* (IV Yugoslav Pharmacopea, 1975), and *Unger* (European Pharmacopea, 1997) was used for water–steam distillation.

b) EOG production with water–steam distillation was performed under reduced pressure enabling distillation at lower temperature which can suppress some unfavorable thermally induced decomposition processes at higher temperatures of garlic treatment. For such a procedure the same unit as those described in a) was used; the unit is connected to a water vacuum pump and with the aim of suppressing losses of volatile compounds from the EOG, the vapor from the unit prior to suction by the vacuum pump was bubbled through cooled benzene as a trap (273 K). The main advantage of such an experimental procedure is the lower temperature of the garlic–water solution boiling at reduced pressure, and its disadvantages are some loss of more volatile compounds despite all precautions and the usage of a cooled benzene trap.

c) Micro–wave heating of the garlic homogenate before water–steam distillation shortens the time for obtaining EOG. This technique of heating uses electromagnetic energy which is easily transformed into heat energy and in some cases, influences different chemical reactions. In this study MW preheating of the garlic–water homogenate was performed with the aim of seeing if such a procedure had any influence on the processes of alliin decomposition and the formation of alliin and other S–compounds.

A commercial MW heater was used which has a magnetron producing electromagnetic 12.2 cm wavelength at 2,45 GHz. The problem created during MW preheating is that applied MW oven does not allow precise control of the working parameters (temperature, applied power), so at first standard MW conditions were established enabling control of the MW field.

The power of the MW field was determined by detection of the absorbed MW energy of pure water on the basis of the simple energy balance (Kingston and Haswell, 1997):

$$P = \frac{Kc_p m \Delta T}{t}$$

where:

P – power, W

K – conversion factor (kcal / s = 4,184 J / s)

c<sub>p</sub> – specific heat capacity of water, kJ/kg.K

m – mass of water (heating medium), kg

ΔT – temperature change of water caused by radiation, K

t – time of exposure, s

The above equation could be used for determining the MW heating procedure. For example, the known absorption of MW energy by the garlic homogenate, could be used for the calculation of the temperature which can be established by MW heating

$$T_f = T_0 + \frac{P \cdot t}{K \cdot c_p \cdot m}$$

## Supercritical extraction with CO<sub>2</sub>

Supercritical fluid extraction (SFE) with CO<sub>2</sub> has been extensively used as possibly the best method for the extraction of many compounds and for obtaining different plant extracts (aroma and flavor production). It is also possible to perform selective extraction by applying the simple reduction of pressure in the separation step. Because CO<sub>2</sub> is a non–toxic, non–flammable and cheap compound, its removal from the extract (usually liquid or solid phase at ambient temperature) is almost complete. Moreover, the critical parameters for CO<sub>2</sub> are: 304 K and 7.38 MPa which enables effective extraction at very low temperatures (305 K and higher) above 7.5 MPa. This evidence is very important for the extraction of unstable compounds which can easily degrade at higher temperatures, usually applied in the processes of water steam distillation or extraction with commonly used organic solvents.

The solubility of different compounds in supercritical CO<sub>2</sub> is the basis for determining the technological route, as well as for the design of a SFE process and its application on an industrial scale. These data are often used for determining the working conditions for SFE, conditions of extract separation (fractionation) and calculation of solvent (CO<sub>2</sub>) consumption and its recirculation in the SFE process (Sokić, 1989; Žižović, 1996).

## EXPERIMENTS

### Hydrodistillation

The Unger method was used for EOG determination. In a 2 dm<sup>3</sup> vessel filled with distilled water (50 vol%) and 1 cm<sup>3</sup> of xylene and boiled for 30 min.

The volume of distilled xylene was determined in a graduated tube after 30 min, and then 100 g of garlic (pelled and mixed in a mixer to make homogenate) were added to the vessel. Distillation was carried out for the next 2 hours. After 10 min when distillation was stopped, the level of etheric oil soluble in xylene was determined in a graduated tube and the EOG calculated from the difference of the volumes of pure xylene and xylene containing EOG.

#### MW preheating followed by hydrodistillation

The same procedure was applied as those described in the previous section, and the only difference which was made is that the garlic sample was pre-heated in the MW oven for 10 min using a MW energy equal to 170 W.

#### Distillation under reduced pressure

The same working procedure was applied as in the case of water–steam distillation using a set–up which enabled working under reduced pressure. The experimental standard set–up for water steam distillation in this case had a special connection with a water vacuum pump and U–manometer. The desired pressure inside the system was achieved by opening a needle valve mounted on the vacuum bottle. The experiments were performed under pressures of 66 and 79 kPa. Garlic homogenate was prepared using the previously described procedure.

#### Supercritical extraction

Experiments were performed using an Autoclave Engineers SCE Screening System (Figure 1).

The extractor vessel (E2 – 300 cm<sup>3</sup>) was heated to the desired temperature and the content mixed by a magnetic stirrer; CO<sub>2</sub> from a cylinder passed through

the tube immersed in a cryostat (cooled to 268 K) and pumped into the extraction vessel using a piston pump (P1; 268 K was the temperature of the pump head). The pressure inside the extraction vessel was measured and regulated by a back–pressure valve (BPR–1). By using a system of valves (V–5–9), the flow rate of CO<sub>2</sub> through the extractor was adjusted, and CO<sub>2</sub> carrying extracted materials (extract) was passed through valve V6 to the separator S. A reduction valve, used for pressure decrease, was heated thus suppressing its plugging during the expansion of compressed CO<sub>2</sub>. The separation of extract from CO<sub>2</sub> was performed at ambient temperature, while the pressure inside the separator was kept constant using a back–pressure regulator (BPR–2). The solute was taken–off from the separator opening valve at its bottom, while the CO<sub>2</sub> flow rate was measured by using a water gas–meter at the outlet from the extraction unit and then passed to the atmosphere. The used CO<sub>2</sub> (its consumption for extraction) was also measured by weighting the cylinder with CO<sub>2</sub> at the beginning and at the end of each extraction test. This value, as well as the collected amount of solute were used for determination of garlic oil solubility at different working conditions (Sokić, 1989).

#### ANALYTICAL METHODS

##### Gas chromatography and GC–MS analysis

A Shimadzu GC – 17A gas chromatogram with flame photometric detector (FPD with S–filter) was used to investigate the sulfur compounds in the EOG samples. The sulfur compounds were identified using the specially designed GC fused silica capillary column SPB–1 SULFUR, length: 30.0 m; i.d.: 0.32 mm; d.f. : 4.0 μm (SUPELCO, USA) under optimal operating condition. The GC–MS analysis was performed using the Shimadzu QP–5050 with appropriate column.

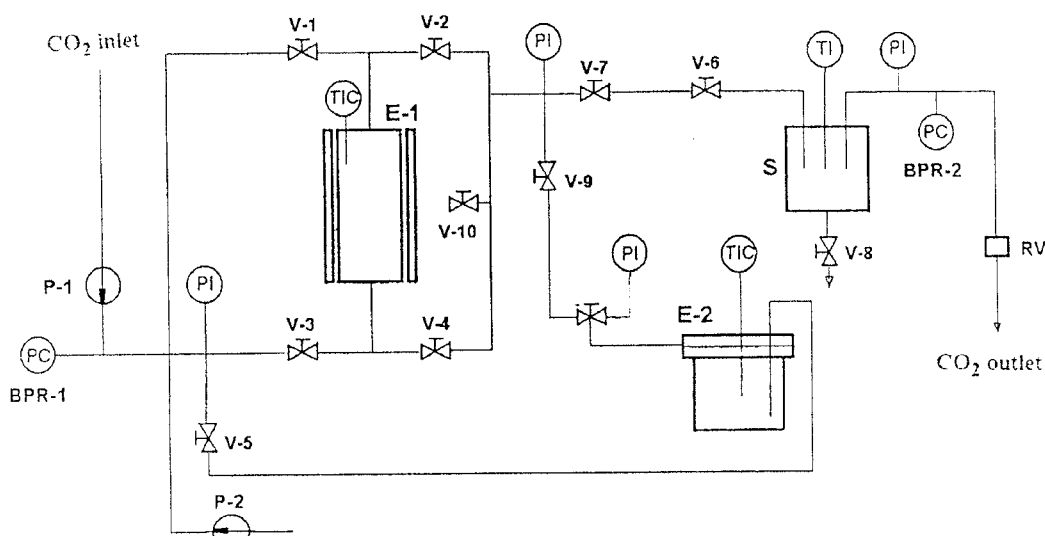


Figure 1. Experimental set-up of SFE unit

## RESULTS AND DISCUSSION

### Analysis of the quality of EOG

On the basis of the data presented in Figures 2 and 3 (a, b and c), there evidently exist large differences between the EOG composition obtained by water–steam distillation with or without MW pre–heating of the garlic homogenate and extract obtained by SFE.

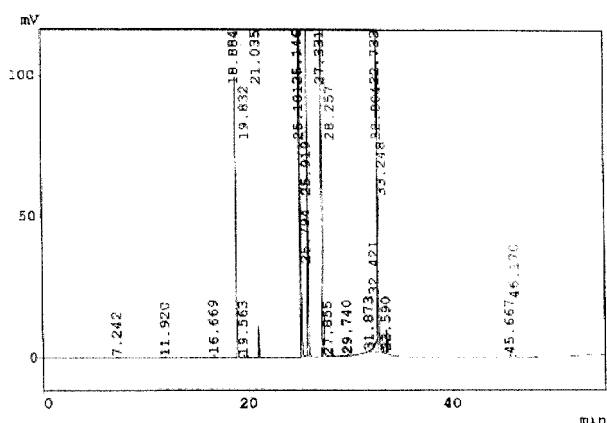


Figure 2. GC of EOG obtained by water–steam distillation

Figures 3 (a, b and c) indicates differences between different samples of EOG: (a) W–S distillation and W–S distillation with a sample pre–heated in the MW oven, (b) W–S distillation and W–S distillation with a collected sample kept in a sealed ampule at 277 K prior GC analysis, and (c) W–S distillation with a sample collected as an extract of the SFE with CO<sub>2</sub>. Obviously there are major differences between the analysed samples in the content of vinyl–di–tiene. Namely, the content of components with the retention times between 19 and 21, 25–27, 29–30 and 32–33 minutes are different which is also indicated by data on identified sulfur compounds which are presented in table 4.

By comparing GC chromatograms of EOG obtained by SFE (two layers, one of these layers was soluble in n–hexane, the other in methylene chloride) it seems that the same components according to their retention times exist in both layers of EOG extract.

The data presented in Table 4 indicates that all the samples practically have the same qualitative compositions but different relative percentages (%) according to the area of GC characteristic peaks. EOG obtained by water–steam distillation had large quantities diallyl sulfide (17.5%), methyl–allyl trisulfide (25.0%) and diallyl tetrasulfide (38.2%).

Maximal amounts of allyl tetrasulfide (59.1%), diallyl sulfide (19.0%) and large amount of methyl allyl trisulfide (18.5%) were detected in the EOG samples produced after MW pre–heating of garlic homogenate before water–steam distillation. The mechanism of polysulfide formation from allicin is promoted by the very

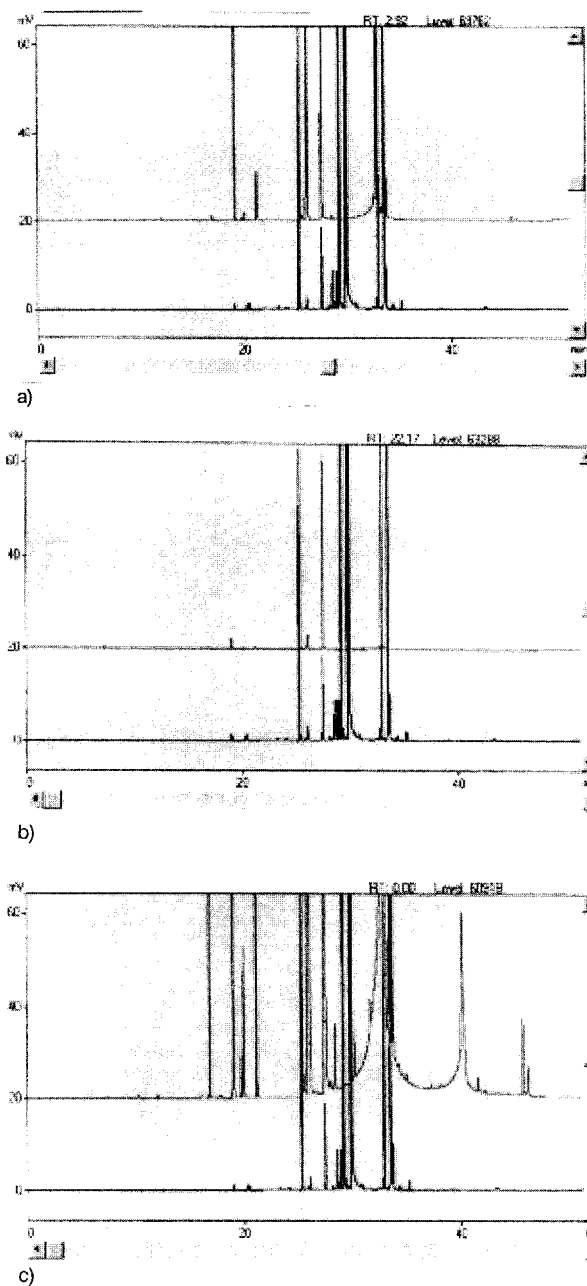


Figure 3. Comparative results of GC's of EOG obtained by different methods: a) water–steam distillation; b) W–S distillation and sample pre–heating in the MW oven; c) W–S distillation under reduced pressure.

rapid degradation of allicin in the garlic cells under the influence of a polar medium (water) when MW is applied prior to the water–steam distillation. Water–steam distillation is usually followed by the formation of a large amount of foam. However, foam formation was suppressed in the case of MW pretreatment of garlic homogenate.

Also, in the case of water–steam distillation depending on applied storage procedure of EOG samples (samples A and C, Table 4) difference in their composition was detected. Namely, the sample stored

Table 4. Qualitative identification of EOG obtained under different conditions

No	RT, min	A	B	C	D	Identification
1	7.24	0.01	/	/	/	*
2	11.92	0.01	0.01	/	/	Allyl monosulfide
3	16.67	0.03	0.04	0.72	/	*
4	18.88	2.08	1.07	5.31	0.13	2-propen-1-thiol
5	19.56	0.02	0.01	0.08	/	methyl 2-propenyl sulfide
6	19.83	0.05	0.03	0.27	/	methyl 1-propenyl sulfide
7	20.11	/	/	/	0.10	*
8	20.28	/	/	/	0.12	*
9	21.04	0.25	0.21	1.21	/	di-methyl sulfide
10	23.12	/	/	/	0.05	*
11	25.15	11.91	/	9.53	4.61	2-propen-1-ol
12	25.18	17.50	19.02	10.34	/	di-allyl sulfide
13	25.92	4.20	1.89	19.46	0.36	di-allyl disulfide
14	27.33	25.00	18.48	21.05	1.65	methyl allyl trisulfide
15	27.86	0.01	/	/	0.09	*
16	28.26	0.02	/	0.18	0.05	*
17	28.41	/	/	/	0.83	*
18	28.78	/	/	/	0.80	*
19	29.08	/	/	/	10.13	3-vinyl-4H-1,3-dithiin
20	29.30	/	/	/	0.13	*
21	29.48	/	/	/	0.08	*
22	29.74	0.01	0.01	/	63.79	3-vinyl-4H-1,2-dithiin
23	30.05	/	/	0.10	0.08	
24	31.87	0.01	/	0.07	/	
25	32.42	0.32	0.03	14.04	0.02	
26	32.73	38.23	59.06	28.72	5.32	diallyl tetra sulfide
27	33.25	0.06	0.02	0.22	0.06	*
28	33.39	/	/	/	9.98	*
29	33.59	0.24	0.11	0.75	1.06	*
30	34.02	/	/	/	0.02	*
31	34.249	/	/	/	0.17	*
32	34.61	/	/	/	0.03	*
33	35.089	/	/	/	0.19	*
34	38.88	/	/	/	0.23	*
35	39.07	/	/	/	0.04	*
36	40.031	/	/	/	1.76	*
37	43.19	/	/	/	0.06	*
38	43.33	/	/	/	0.04	*
39	45.67	0.03	/	0.17	/	*
40	46.17	0.01	/	0.08	/	*
41	48.071	/	tr.	/	/	*
42	49.83	/	tr.	/	/	*
43	50.91	/	tr.	/	/	*
44	51.02	/	tr.	/	/	*
45	51.50	/	tr.	/	/	*
Σ		100.00	100.00	100.00	100.00	

A–water–steam distillation; B–as A and MW pre-heating of garlic homogenate; C–water–steam distillation – samples stored in a refrigerator (277 K) in a sealed ampoule; D – SFE with CO<sub>2</sub>; \* – nonidentified S–compounds

at ambient temperature in an ordinary closed vial (A) did not have volatile compounds compared to samples stored in a refrigerator (277 K) in a sealed ampoule (C).

EOG obtained by SFE with CO<sub>2</sub> had a larger quantity of vinyl–ditiine. According to the literature data such compounds is usually used for the explanation of the allicin degradation mechanism. Analysis of EOG obtained by SFE after MW pretreatment of garlic homogenate did not indicate the presence of cyclic–vinyl–ditiines, and this results leads to the conclusion that allicin was completely degraded before SFE.

#### Yield analysis

As presented in Tables 5 and 6, the yield of EOG differs and depends on the applied procedure of its preparation. The usage of MW pretreatment of garlic homogenate gave a smaller yield compared to the yield of EOG obtained by simple water–steam distillation. Furthermore a stable emulsion of EOG and water was obtained when water–steam distillation was used after MW pretreatment. This effect could be caused by the dehydration of garlic homogenate and the loss of some specific volatile compounds during MW pretreatment. The formation of emulsion causes additional difficulties in separating the EOG samples from water.

Table 5. Yields of EOG obtained by water–steam distillation

Sample	Procedure	Yields, %
A	Water–steam distillation	0.237 – 0.312
B	As A with MW pretreatment of garlic homogenate	0.053 – 0.187
C (66 kPa) (79 kPa)	Water steam distillation under reduced pressure	0.30 0.28

Note: Water–steam distillation under reduced pressure was performed using garlic originating from China.

Table 6. Yields of EOG obtained by SFE

Sample	Working conditions	Yields (%)
SFE 1	20 MPa, 323 K	0.071
2	25 MPa, 323 K	0.051
3	30 MPa, 323 K	0.071
SFE 1 + MW	MW pretreatment	0.172
SFE 2 + MW	MW pretreatment	0.091
SFE 3 + MW	MW pretreatment	0.117

Yields of EOG obtained by SFE are higher in the cases of MW pretreatment of garlic homogenate. That means that the degradation of components caused by MW preheating creates such components which are more soluble in the supercritical carbon dioxide. The yield of SFE is generally smaller than those obtained by conventional methods (water–steam distillation) and depends on the working conditions of SFE. It was found that a larger yield could be obtained under smaller pressure of supercritical extraction with CO<sub>2</sub>. This study showed that some minimal yield of EOG exists if SFE is

performed under a pressure of app. 25 MPa whether or not MW preheating of garlic homogenate was applied before extraction.

## CONCLUSION

MW preheating of garlic homogenate before water–steam distillation or SFE caused changes of EOG quality and its composition. Such an applied procedure also resulted in EOG yield changes. MW preheating in the case of water–steam distillation decreases the EOG yield, contrary to the observed effect in the case of applied SFE where preheating increases the extract yield. It is not possible to define the effect of MW preheating in the garlic cells according to the results of this study. However, this study indicates that there was no presence of allicin in MW preheated homogenate.

Water–steam distillation under reduced pressure gave only smaller amounts of more volatile compounds in EOG. The process is much faster compared to the common mode of water–steam distillation which is an advantage of such an operation.

Allicin was detected in the sample obtained by SFE with CO<sub>2</sub> (without MW preheating). That means that the lower temperature of extraction favors extraction of allicin, i.e. it does not cause its degradation.

## REFERENCES

[1] Block E., The Organosulfur Chemistry of the Genus *Allium*: Implications for the Organic Chemistry of Sulfur, *Angew. Chem., Int. Ed. Engl.* **31** (1992) 1135–1178.

- [2] Calvey E.M., J.E. Matusik, K.D. White, J.M. Betz, E. Block, M.H. Littlejohn, S. Naganathan and D. Putman, Off-Line Supercritical Fluid Extraction of Thiosulfates from Garlic and Onion, *J.Agric.Food. Chem.*, **42** (1994) 1335 – 41
- [3] Calvey E. M., J.E. Matusik, K.D. White, R. DeOrazio, D. Sha, E. Block, Allium Chemistry: Supercritical Fluid Extraction and LC–APCI–MS of Thiosulfates and Related Compounds from Homogenates of Garlic, Onion and Ramp. Identification in Garlic and Ramp and Synthesis of 1–Propanesulfinothioic Acid S–Allyl Ester, *J. Agric. Food Chem.* **45** (1997) 4406–4413.
- [4] European Pharmacopeia, Europa, 1997.
- [5] Jung E.M., F. Jung, C. Mrowietz, H. Kiesewetter, G. Pinolur, E. Wenzel, *Drug Res.*, **41** (1991) 626.
- [6] Kim S.M., C.M. Wu, K. Kubota, A. Kobayashi, *J. Agric.Food. Chem.*, **43** (1995) 449–52
- [7] Kingston H.M.S., S.J. Haswell, *Microwave–Enhanced Chemistry*, American Chemical Society, Washington, DC, 1997.
- [8] Lawson L. D., Bioactive organosulfur Compounds of Garlic and Garlic Products, and Their Role in Reducing Blood Lipids, In *Human Medicinal Agents from Plants*, Kinghorn A. D., Balandrin M.F., Eds., ACS Symposium Series 534, ACS, Washington, 1993, p. 306–330.
- [9] Lukić D., *Farmakognozija, Farmaceutski fakultet, Beograd*, 1995.
- [10] *Pharmacopea Jugoslavica, Editio quarta, Zagreb*, 1975.
- [11] Sokić M., Determination of solubility in supercritical fluids, *Hem.ind.* **43** (1989) 437–44.
- [12] Vučetić J., M. Jaredić i M. Ćirović, *Hemijski pregled*, **3** (1986) 45.
- [13] Wagner H., Breu W., Antinflammatory Investigation of Garlic Extract, *Deutsch. Apoth. Ztg.* **129** (Suppl. **15**) (1989) 21–23.
- [14] Yu T.H., C.M Wu and C.T. Ho, Volatile Compounds of Deep–Oil Fried, Microwave–Heated, and Oven–Baked Garlic Slices, *J.Agric.Food. Chem.*, **41** (1993) 800 – 5.
- [15] Žižović I., Solubility of the polyunsaturated fatty acids in supercritical CO<sub>2</sub>, MS Thesis, University of Belgrade, 1996.

## IZVOD

ETARSKO ULJE BELOG LUKA (*ALLIUM SATIVUM* L.) DOBIJENO EKSTRAKCIJOM NATKRITIČNIM CO<sub>2</sub>–SFE: POREDZENJE SA DESTILACIJOM VODENOM PAROM

(Naučni rad)

Dejan Skala<sup>1</sup>, Radmila Kužić<sup>1</sup>, Irena Žižović<sup>1</sup>, Vesna Nikolić<sup>2</sup>, Dušan Jovanović<sup>3</sup>

<sup>1</sup>Tehnološko–metalurški fakultet, Beograd, Jugoslavija

<sup>2</sup>Tehnološki fakultet, Leskovac, Jugoslavija

<sup>3</sup>HTM, Centar za katalizu i hemijsko inženjerstvo, Beograd, Jugoslavija

Cilj rada je bio usmeren ka dobijanju kvalitativne i kvantitativne informacije o prinosu i sastavu etarskog ulja dobijenog iz isitnjenih i homogenizovanih češnjeva belog luka primenom različitih tehnika. Pri tome su primenjene sledeće tehnike dobijanja etarskog ulja: destilacija vodenom parom homogenizata pod normalnim i sniženim pritiskom, destilacija vodenom parom homogenizata koji je prethodno tretiran u standardnoj mikrotalnoj peći, kao i ekstrakcija etarskog ulja primenom natkritičnog ugljen dioksida.

U etarskom ulju koje je proizvedeno destilacijom pomoću vodene pare, uz prethodno tretiranje homogenizata u mikrotalnoj peći utvrđeno je kvalitativno drukčiji sastav od uzorka koji je pripremljen klasičnim putem (metode Clevenger ili Unger). Naime, prisustvo odgovarajućih jedinjenja (alicina), koja su karakteristična za ovo etarsko ulje, nije utvrđeno jer tokom tretiranja u mikrotalnoj peći dolazi do indukovanja odgovarajućih termijskih procesa njihovog razlaganja unutar ćelija belog luka. Utvrđeno je da se brzina izdvajanja etarskog ulja uvećava ako se destilacija sa vodenom parom izvodi pod sniženim pritiskom. Osnovni zaključak ovog rada je da se jedinjenja tipa alicina mogu dobiti u većim koncentracijama u etarskom ulju jedino ukoliko se za njegovo izdvajanje primeni natkritična ekstrakcija sa ugušćenim ugljen dioksidom. Objašnjenje je verovatno u tome što se u procesu ekstrakcije sa ugušćenim ugljen dioksidom, koja se izvodi na nižim temperaturama u odnosu na destilaciju vodenom parom, sprečavaju reakcije razlaganja alicina koje se lako pospešuju termijskim putem.

Ključne reči: Beli luk • Etarsko ulje • Dobijanje • Destilacija vodenom parom • Ekstrakcija ugušćenim ugljendioksidom •

Key words: Garlic • Etheric oil • Preparation • Water–steam distillation • Supercritical fluid extraction •

