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Thermal and Oxidative Stability of the *Allium Sativum* L. Bioactive Compounds/ α - AND β -Cyclodextrin Nanoparticles

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This paper presents the thermal and oxidative stability of the Allium sativum L. (garlic) bioactive compounds and the corresponding α - and β -cyclodextrin nanoparticles. The complexation of the essential oil of A. sativum L. in β -cyclodextrin was achieved by alcohol-water solution method, and nanoparticles were analyzed by thermogravimetry (TG), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). In order to obtain the type and the relative concentration of compounds encapsulated in cyclodextrins, the GC-MS analysis was used. The essential oil was analyzed by GC-MS before encapsulation and after successive extraction from the complex. The higher relative concentrations in the complex were obtained for diallyl-disulfide and diallyl-trisulfide. The nanoencapsulation yields were >60%, the higher ones being obtained for the case of β -cyclodextrin. The biocompound/cyclodextrin ratio is important for the complexation yield, the best results being obtained for equimolar ratios, for all alcohols used. For the degradation of the raw samples in the presence of air and higher temperatures a decrease of the concentration of cyclic sulfide compounds was observed, compared with the case of nanoparticle degradation, where this tendency is not observed; although, the acyclic compounds were encapsulated in higher concentrations compared to the cyclic ones.

Keywords: nanoparticles, cyclodextrins, volatile oils, garlic, stability, thermogravimetry, differential scanning calorimetry, scanning electron microscopy, gas chromatography-mass spectrometry

Garlic (*Allium sativum* L.) was used by human from the ancient time in food seasoning and for some disease treatment [1,2]. The main medicinal properties are: as hypotensive, in the treatment of the cardiovascular diseases, antimicrobial in the treatment of respiratory diseases like bronchitis or influenza, antihelminthic [2,3]. Due to the decrease of the blood lipidic level in the case of consumption or administration of *Allium sativum* L. formulations, various studies were performed in order to establish the influence of these biocompounds to the ratio of total cholesterol/high density lipoproteins (TC/HDL) as well as for women and men; a significative decrease of this ratio was observed especially for women, this effect being probably determined by the reduction of the platelet aggregation [4,5]. The antimicrobial effect of the *Allium sativum* L. formulations is determined by the major sulfide compounds resulted from alliin (S-allyl-L-cystein-sulfoxid), especially allicin; the skeleton of allicin was used as model for the development of new compounds with antibacterial activity [6] and anticancerous [7-9]. Allicin is degraded in the presence of water and provide the compounds responsible for the garlic flavor [2,10-12]. When the garlic tissue is destroyed the precursors (alliin and the corresponding methyl and propyl derivatives) are transformed in allicin, diallyl-disulfide and other sulfide compounds with characteristic odor. Due to the specific sulfurous odor or the necessity of transportation to the biological targets and controlled release of these compounds, the micro/nanoencapsulation in various matrices in order to obtain pharmaceutical and/or food

products is a permanent goal. Some natural and synthetic matrices, like oligo- or polysaccharides, are used for the obtaining these supramolecular systems. Cyclodextrins (CDs) belong to the cyclic oligosaccharide class, having 6-8 glucopyranosyl units corresponding to the natural α -, β - and γ -cyclodextrin, respectively (α CD, β CD, γ CD); these compounds have a conoidal-like structure, with solubilizing hydrophilic groups at the exterior and a hydrophobic centre which allow the formation of van der Waals bonds with hydrophobic molecules or moieties (host-guest supramolecular systems); consequently, these guest molecules are protected to the degradative action of different factors (storing, transportation, alimentary, and biological factors). Due to these properties, cyclodextrins were used in various fields, especially pharmaceutical and alimentary fields [13-15] (e.g. pharmaceutical formulations containing garlic volatile oil/cyclodextrin complexes, with antiarteriosclerotic activity, were marketed in Europe and America [13], and low-sulfurous odor food formulations containing *Allium sativum* L. extracts or cyclodextrin-containing systems capable to retain the compounds with disagreeable odor were developed [16,17]).

Studies on the composition of the CDs nanoencapsulated *Allium sativum* L. volatile oil and on the degradation and stability of these compounds and nanoparticles in various conditions (storing, transportation etc.) were not realized yet. Our earlier studies [18-21] indicate important modifications on the composition of biosystems at the action of different degradative factors like air/oxygen, temperature, humidity, and the nanoencapsulation of these compounds in cyclodextrin-

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like matrices lead to biosystems with higher stability and bioavailability.

In this paper a study concerning the stability of the raw bioactive compounds from *Allium sativum* L. compared with those nanoencapsulated in α - and β -cyclodextrin at the action of degradative factors like air and temperature was done.

Materials and methods

The essential oil of garlic (*Allium sativum* L.) was purchased from SC Natex SA, Cluj Napoca-Romania; α - and β -cyclodextrin were purchased from Merck&Co. Inc., New Jersey, USA, and were reagent grade products (> 99%). The aliphatic alcohols used for the obtaining of nanoparticles (ethanol 96%, methanol and propanol, reagent grade) were obtained from Chimopar SA – Bucureşti, Romania. The hexane used for recovering of the bioactive compounds from nanoparticles has GC purity and was achieved from Merck&Co, Inc. Alkane standard solution $C_8 - C_{20}$, used for the determination of Kovats indices (KI) for flavoring compounds from GC-MS analysis, was purchased from Fluka Chemie AG, Switzerland.

Obtaining the *Allium sativum* L. bioactive compounds/cyclodextrin nanoparticles. α - or β CD was dissolved in 2-4 mL distilled water at 30-70°C, and then 4 mL alcoholic solution (ethanol, methanol or propanol), containing 90-270 mg volatile garlic oil (*Allium sativum* L.), was added in

0.5 h to the cyclodextrin solution, with continuous stirring; the suspension was stirred for another 15 min at the same temperature. The suspension was then cooled at the environment temperature in 0.5-4 h, in a water bath, and stored at 4°C for 1-18 h in a refrigerator, in order to complete the crystallization. The suspension was then filtered, washed with 1.5 mL alcohol and dried in an exicator (table 1).

Degradation of the raw *Allium sativum* L. bioactive compounds and cyclodextrin nanoparticles. ~100 μ L raw *Allium sativum* L. bioactive compounds or ~100 mg cyclodextrin nanoparticles were uniformly distributed on the bottom of the degradation flasks (40 x 40 mm²), which are then purged with air (oxidative atmosphere) or argon (inert atmosphere), sealed, and put in a thermostable bath or under ultraviolet light (UV), with the possibility of varying and measuring the temperature and wavelength, respectively. The samples were maintained under degradative conditions according to tables 2 and 3. After cooling, the samples of raw biocompounds were dissolved in 5 . 1 mL hexane, and the solution was analyzed by GC-MS; in the case of degraded nanoparticles, these are suspended in water and the nanoencapsulated compounds were recovered by hexane extraction.

Recovering of the bioactive compounds from nanoparticles. After cooling the degraded samples of nanoparticles these were dissolved/suspended in 4.1 mL

No	Code	m _{CD} (g)	V _{H₂O} (ml)	Temp (°C)	m _{biocomp} (g)	V _{alcohol} (ml)	cool. time (h)	perfect. time (h)	Yield (%)
1	AbCDE-r1	0.6717 β CD	2	50	0.0915	4+1.5 EtOH	4	18	91.35
2	AbCDE-r2	0.6719 β CD	2	50	0.1810	4+1.5 EtOH	4	18	84.66
3	AbCDE-r3	0.6717 β CD	2	50	0.2704	4+1.5 EtOH	4	18	79.79
4	AbCDE-v1	0.6716 β CD	4	50	0.0900	2+1.5 EtOH	4	18	85.83
5	AbCDE-v2	0.6713 β CD	2	50	0.0915	4+1.5 EtOH	4	18	90.99
6	AbCDE-t1	0.6711 β CD	2	30	0.0902	4+1.5 EtOH	4	18	88.65
7	AbCDE-t2	0.6714 β CD	2	70	0.0916	4+1.5 EtOH	4	18	93.32
8	AbCDE-c1	0.6714 β CD	2	50	0.0905	4+1.5 EtOH	0.5	18	86.24
9	AbCDE-c2	0.6718 β CD	2	50	0.0904	4+1.5 EtOH	2	18	90.44
10	AbCDE-f1	0.6713 β CD	2	50	0.0913	4+1.5 EtOH	4	1	89.63
11	AbCDM-r1	0.6713 β CD	2	50	0.0900	4+1.5 MeOH	4	18	92.30
12	AbCDM-r2	0.6713 β CD	2	50	0.1807	4+1.5 MeOH	4	18	82.11
13	AbCDM-r3	0.6714 β CD	2	50	0.2705	4+1.5 MeOH	4	18	79.05
14	AbCDP-r1	0.6713 β CD	2	50	0.0909	4+1.5 PrOH	4	18	86.96
15	AbCDP-r2	0.6715 β CD	2	50	0.1808	4+1.5 PrOH	4	18	76.67
16	AbCDP-r3	0.6715 β CD	2	50	0.2704	4+1.5 PrOH	4	18	71.44
17	AaCDE-r1	0.5408 α CD	2	50	0.0902	4+1.5 EtOH	4	18	84.64
18	AaCDE-r2	0.5404 α CD	2	50	0.1809	4+1.5 EtOH	4	18	74.39
19	AaCDE-r3	0.5409 α CD	2	50	0.2708	4+1.5 EtOH	4	18	63.09
20	AaCDM-r1	0.5403 α CD	2	50	0.0908	4+1.5 MeOH	4	18	86.02
21	AaCDP-r1	0.5402 α CD	2	50	0.0904	4+1.5 PrOH	4	18	83.43

Table 1
CONDITIONS AND RESULTS FOR
THE OBTAINING OF THE *ALLIUM*
SATIVUM L. BIOCOMPOUNDS/
 α - AND β CD NANOPARTICLES

No	Code	m _{sample} (g)	Degradation factor	Factor value	Time (h)
1	A-O-t1	0.1102	air-temp	30°C	2
2	A-O-t2	0.0995	air-temp	60°C	2
3	A-O-t3	0.1038	air-temp	90°C	2
4	A-O-t4	0.1065	air-temp	30°C	6
5	A-O-t5	0.1009	air-temp	60°C	6
6	A-O-t6	0.1038	air-temp	90°C	6
7	A-N-t7	0.1033	argon-temp	90°C	6
8	A-O-UV1	0.1028	UV	250-350 nm	0.5
9	A-N-UV1	0.1025	UV	250-350 nm	0.5

Table 2
DEGRADATION CONDITIONS FOR
THE RAW *ALLIUM SATIVUM* L.
BIOACTIVE COMPOUNDS

No	Code	m _{sample} (g)	Degradation factor	Factor value	Time (h)
1	AbCD-Ot1	0.1113	air-temp	30°C	2
2	AbCD-Ot2	0.1009	air-temp	60°C	2
3	AbCD-Ot3	0.1016	air-temp	90°C	2
4	AbCD-Ot4	0.0974	air-temp	30°C	6
5	AbCD-Ot5	0.1033	air-temp	60°C	6
6	AbCD-Ot6	0.1025	air-temp	90°C	6
7	AbCD-Nt7	0.1026	argon-temp	90°C	6
8	AbCD-Ouv	0.1016	UV	250-300 nm	0.5
9	AbCD-Nuv	0.1010	UV	250-300 nm	0.5

Table 3
DEGRADATION CONDITIONS FOR
THE *ALLIUM SATIVUM* L. BIOACTIVE
COMPOUNDS/CYCLODEXTRIN
NANOPARTICLES

distilled water and the bioactive compounds were extracted in a liquid-liquid extractor with 2 mL hexane at 60°C for 20 min three times (the fourth extract do not contain any kind of flavor compound, revealed by GC-MS analysis). The combined extracts were dried over anhydrous CaCl_2 and analyzed by GC-MS.

GC-MS analysis. For the analysis of raw *Allium sativum* L. bioactive compounds, those degraded in various conditions and those recovered from non-degraded or degraded nanoparticles a Hewlett Packard HP 6890 Series gas chromatograph coupled with a Hewlett Packard 5973 mass selective detector (GC-MS) system was used (calibration factor 1.0). A HP-5 MS capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) was used for the GC system. The temperature program was set up from 50°C to 250°C with 6°C/min, both the injector and detector temperatures were 280°C and He was used as carrier gas. 1 μL sample was injected in all cases. Ionization energy EI of 70eV was used for mass detector, with a source temperature of 150°C, scan range 30-600 amu, scan rate 1s⁻¹. The compounds were identified by comparing the mass spectra with those from the NIST/EPA/NIH Mass Spectral Library 2.0 or by using the Kovats indices computed from the GC-MS analysis of the C₈-C₂₀ alkane standard mixture.

TG analysis. A TG 209 NETZSCH thermogravimetric apparatus was used for the thermal analysis of the *Allium sativum* L. bioactive compounds/cyclodextrin nanoparticles. The temperature program was 20 to 550°C with 10°C/min. All determinations were conducted under nitrogen atmosphere. Data acquisition was performed with the TG Netzsch 209-Acquisition Soft/2000 and the data analysis was realized with the Netzsch Proteus-Thermal Analysis ver. 4.0/2000 soft.

DSC analysis. Differential scanning calorimetry of the nanoparticles was carried out on a DSC 204 Netzsch apparatus, with a temperature program of -50 ÷ 400°C, the heating rate being 10°C/min. The acquisition and the processing of the data were performed with the DSC 204 Netzsch-Acquisition Soft/2000 and Netzsch Proteus-Thermal Analysis, ver. 4.0/2000, respectively.

SEM analysis. For morphological and dimensional evaluation of the *Allium sativum* L. bioactive compounds/cyclodextrin nanoparticles scanning electron microscopy (SEM) technique was used. A JEOL JSM 5510-LV SEM apparatus was used, at different magnitude levels.

Results and discussion

High yields were obtained in the case of nanoencapsulation of *Allium sativum* L. bioactive compounds in cyclodextrins, which vary with the *Allium* biocompounds/ α - and β CD molar ratio, alcohol and water volume ratio (the solvent system used for nanoencapsulation), temperature nanoencapsulation, cooling time of the suspension, time of crystallization, and the hydrophobicity of the alcohol used in the process.

The nanoencapsulation yields increase with the molar ratio between the *Allium* bioactive compounds and β CD (from 91.4% for a ratio of 1:1 to 79.8% for a ratio of 3:1). This fact is probable due to an additional solubilization of the complex in the biocompounds excess and clears out at alcohol washing step. Not important variation of the yield were observed in the case of nanoencapsulation of the biocompounds in β CD at different ratios of alcohol/water volumes, but the nanoencapsulation temperature play an important role for the yield. Thus, the yield increases with the nanoencapsulation temperature, the dependence being close to the ideality (88.7% at 30°C, 91% at 50°C, and

93.3% at 70°C). The cooling time has influence on the nanoencapsulation yield, a lower time being detrimental to the performance of the process (86.2% for a cooling time of 0.5 h), compared with 2-4 h cooling time, which lead to higher yields (~91%). The time necessary for the complete crystallization has no influence (~90% for one hour of perfection compared with ~91% for 6-18 h). The yield of nanoencapsulation in the case of modifying the hydrophobicity of the alcohol decrease with the increase of the hydrophobicity of the alcohol (expressed as logarithm of the octanol/water partition coefficient, logP; for methanol, logP = -0.5 and the yield was 92.3%; for ethanol logP = -0.31, with the yield of 91.4%, and for propanol logP = 0.25 and the yield of nanoencapsulation was 87%).

In the case of nanoencapsulation of *Allium sativum* L. bioactive compounds in α CD the yields were generally lower, probably due to a higher solubility of the complex in the alcohol-water system. Thus, the nanoencapsulation yield in ethanol-water system was in the range of 63-85% at biocompounds/ α CD molar ratios between 1:1 – 3:1, with statistically significative dependence. In this case the yield of nanoencapsulation decreases with the increasing of the alcohol hydrophobicity (from 86% for methanol, to 84.6% for ethanol and 83.4% for propanol).

The thermogravimetric data for *Allium sativum* L. bioactive compounds/cyclodextrin nanoparticles indicate a mass loss of ~13% up to 110°C and 14% at 150°C for the pure β CD, while for the nanoparticles obtained with a molar ratio of 1:1 this mass loss was only 9.8% up to 150°C (fig.1); for samples corresponding to a molar ratios of 2:1 and 3:1 the mass changes were 11.5% and 13.5%, respectively. In the case of use of methanol in the process, the TG analysis indicates a mass loss of 11.5%, and for propanol 11.8%. The mass loss – molar ratio dependence in the case of methanol is similar to that of ethanol, but for propanol, this dependence is reversed, probably due to the competitiveness of this more hydrophobic alcohol to nanoencapsulation.

From the DSC data obtained for the *Allium sativum* L. biocompounds/ β CD nanoparticles endothermic peaks are observed (probable due to the decomplexation processes) at ~178°C (decomplexation of alkyl/allyl-sulfides), at ~80°C (water molecules elimination), and ~260°C (β CD decomposition) (fig. 2).

From the SEM analysis, *Allium sativum* L. biocompounds/ β CD nanoparticles seem to have a rhombohedral-parallelepipedic crystallization form, with dimensions between hundred of nanometers and 1-2 micrometers for the particle sides (figs. 3 and 4).

For the *Allium sativum* L. biocompounds/ α CD the dimensions of the particles were slightly higher. From the TG analysis of these α CD nanoparticles the mass loss was 12% for a molar ratio of 1:1, with a decrease to 11% for 3:1 molar ratio; the pure α CD has a lower mass change of 9.4% (fig. 5).

The GC-MS analysis of the raw *Allium sativum* L. bioactive compounds indicates the presence of the sulfide compounds from the gradually transformation of alliin and its derivatives. Thus, the GC-MS analysis of the non-degraded samples and for those degraded at 30°C (A-O-t1; fig. 6), indicates the presence of the same sulfide compounds: dialkyl- and diallyl-sulfides, alkyl-allyl-sulfides, cycloalkyl-sulfides (figs. 7-9). The main compounds identified by MS and KI for the *Allium sativum* L. volatile oil are presented in table 4. Relative concentrations of almost 20% for diallyl-disulfide, 16% for diallyl-trisulfide, and 4.6% for 1,3-dithiane are observed.

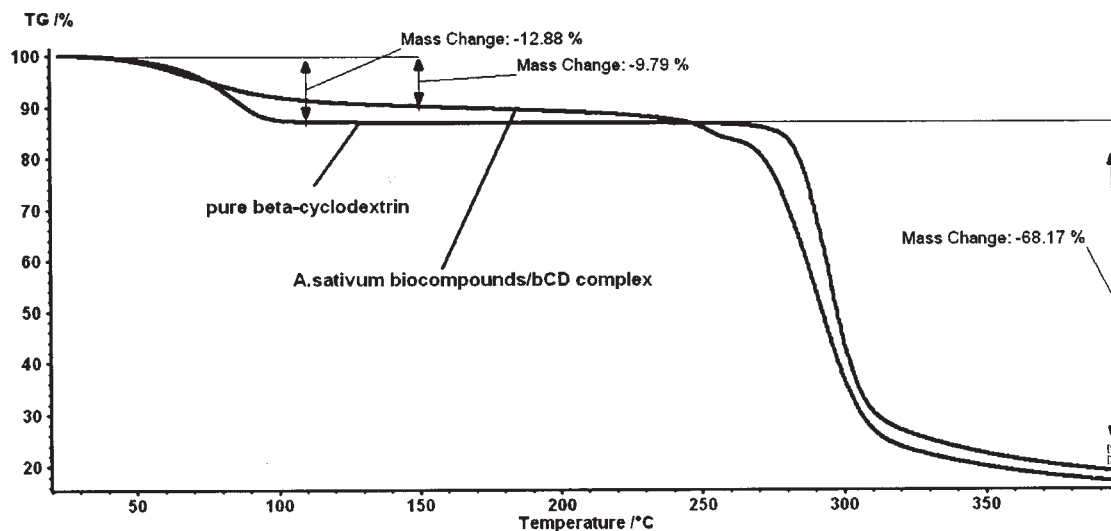


Fig. 1. Thermograms superposition for pure β CD and *Allium sativum* L. biocompounds/ β CD nanoparticles

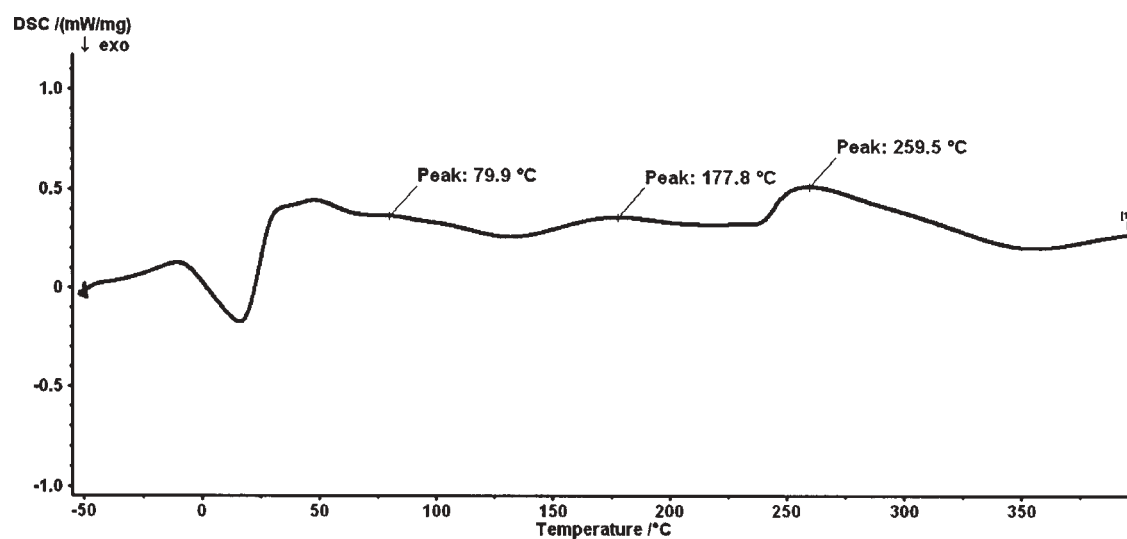


Fig. 2. DSC analysis for the *Allium sativum* L. biocompounds/ β CD nanoparticles

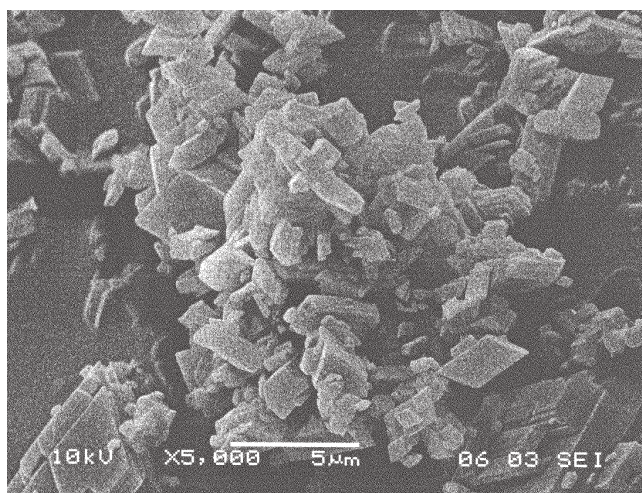


Fig. 3. SEM micrograph for the *Allium sativum* L. biocompounds/ β CD nanoparticles (x 5 000 magnification)

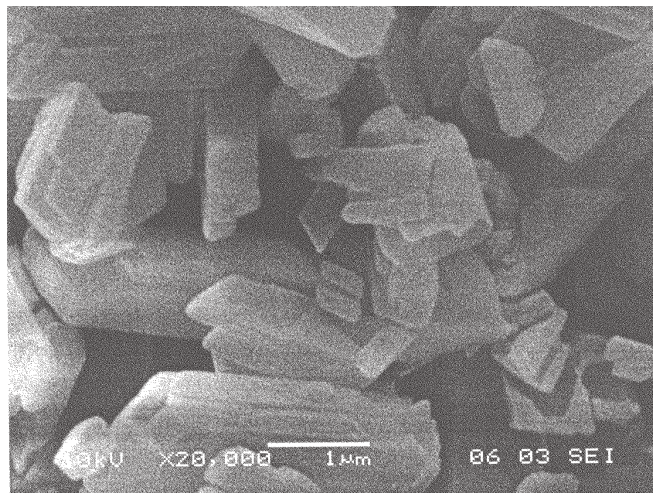


Fig. 4. SEM micrograph for the *Allium sativum* L. biocompounds/ β CD nanoparticles (x 20 000 magnification)

For the evaluation of the stability of the bioactive compounds from *Allium sativum* L. volatile oil, only the bolded structures from the table 4 were evaluated from the modification of the relative concentration under action of different degradative factors (air-oxygen, temperature, UV light) point of view. The codes used for these compounds were: diallyl-monosulfide (DAMS, retention time 4.63 min), 1,3-dithiane (DT, retention time 5.75 min), diallyl-disulfide (DADS, retention time 9.58 min), allyl-

methyl-trisulfide (AM3S, retention time 11.00 min), 1,3,5-trithiane (TT, retention time 11.51 min), diallyl-trisulfide (DA3S, retention time 14.85 min), and diallyl-tetrasulfide (DA4S, retention time 16.67 min). For the degradation of raw *Allium sativum* L. biocompounds at temperatures between 30-90°C, in the presence of air-oxygen, for 2 h, the relative concentration of the compounds DAMS, DADS, and AM3S (determined from the chromatograms obtained by GC-MS analysis) remains approximately the same, but

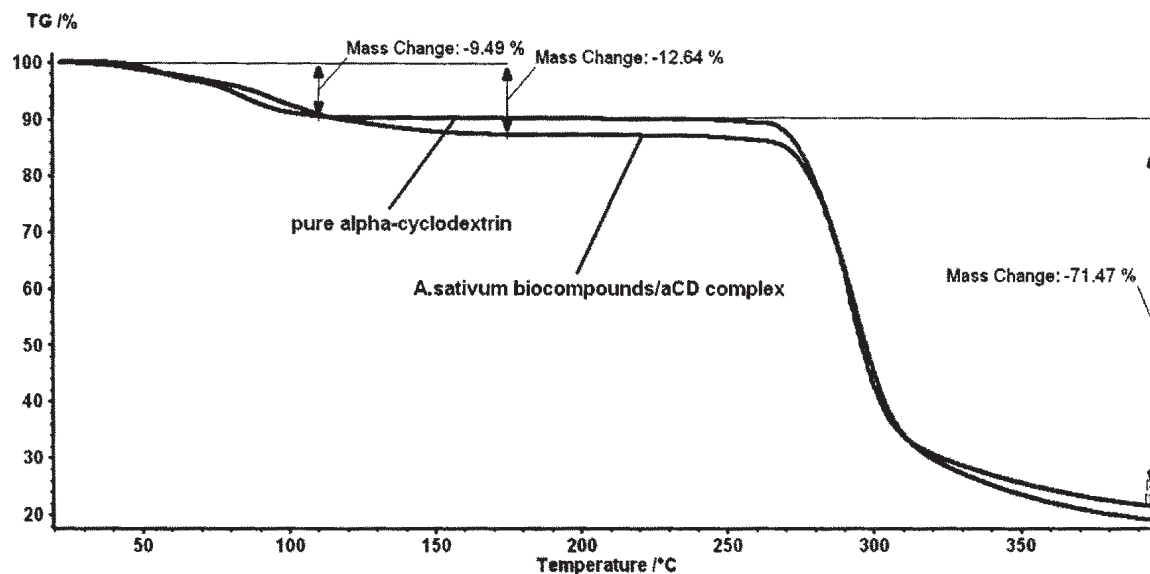


Fig. 5. Thermograms superposition for pure α CD and *Allium sativum* L. biocompounds/ α CD nanoparticles

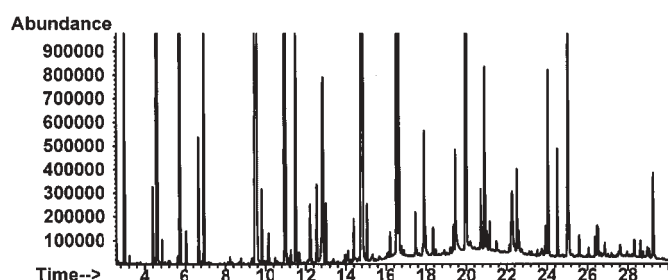


Fig. 6. The GC chromatogram from the GC-MS analysis of the essential oil of *Allium sativum* L.

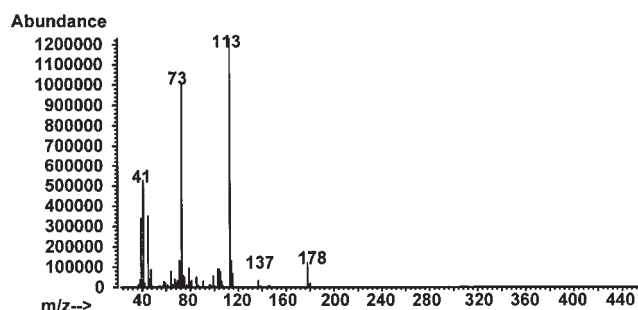


Fig. 8. Experimental and MS spectral database from NIST for diallyl-disulphide

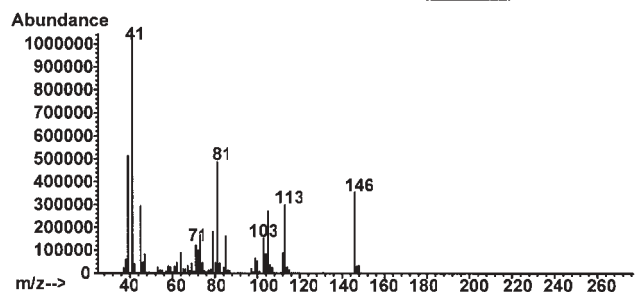


Fig. 7. Experimental and MS spectral database from NIST for diallyl-disulphide

the concentration of the cyclic compounds decreases (especially for DT, which probably is oxidized to a sulfoxidic or carbonilic compound) with the increase of the degradation temperature; the concentration of oligo-sulfides DA3S and DA4S increase slightly (table 5). For the non-encapsulated biocompounds, degraded in the same way, but for 6 h, similar behavior can be observed.

For the *Allium sativum* L. biocompounds/CDs nanoparticles, degraded in the same way, some differences can be observed compared with the results from the non-encapsulated compounds; the concentrations of the main

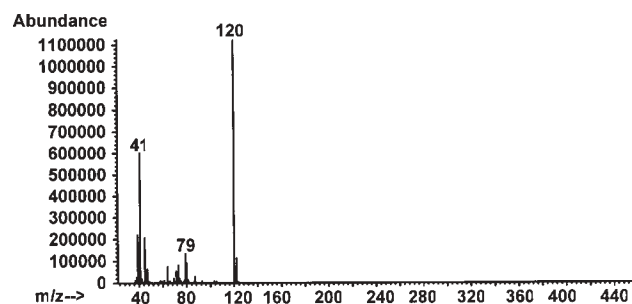


Fig. 9. Experimental and MS spectral database from NIST for 1,3-dithiane

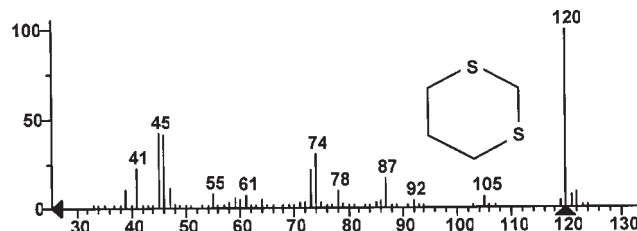


Table 4GC-MS RESULTS FOR THE MAIN BIOACTIVE COMPOUNDS FROM THE *ALLIUM SATIVUM* L. VOLATILE OIL

No	Time (min)	Area	Area %	KI	MS Identification
1	3.001	3863000	2.3	755	Disulfide, dimethyl-
2	4.399	728215	0.4	852	1,2-Dithiolane
3	4.629	20372946	12.4	865	Diallyl-monosulfide
4	5.745	7594134	4.6	923	1,3-Dithiane
5	6.045	279243	0.2	937	Disulfide, methyl propyl-
6	6.938	2708490	1.6	978	Dimethyl trisulfide
7	9.576	32701543	19.8	1090	Diallyl-disulfide
8	9.811	634518	0.4	1100	1,3-Dithiane, 2,2-dimethyl-
9	10.146	304716	0.2	1114	Disulfide, dipropyl-
10	11.003	14561387	8.8	1149	Allyl-methyl-trisulfide
11	11.509	2919961	1.8	1170	1,3,5-Trithiane
12	14.852	26758793	16.2	1314	Diallyl-trisulfide
13	16.662	7895754	4.8	1397	Diallyl-tetrasulfide
14	16.779	83106	0.1	1402	1,3-Dithian-2-one
15	17.907	1357404	0.8	1455	Propane, 2,2-bis(methylthio)-
16	18.348	285053	0.2	1477	Pentasulfide, dimethyl-
17	29.264	984723	0.6	2089	Cyclic octaatomic sulfur
18			24.8		Other minor compounds

Table 5RELATIVE CONCENTRATION (%) VARIATION FOR THE NON-ENCAPSULATED *ALLIUM SATIVUM* L. BIOCOMPOUNDS WITH THE VARIATION OF THE DEGRADATION TEMPERATURE (FOR 2 h OF ACTION)

Compound name	Code	Degradation temperature (°C)		
		30	60	90
		A-O-t1	A-O-t2	A-O-t3
Diallyl-monosulfide	DAMS	12.3	11.6	12.3
1,3-Dithiane	DT	4.6	4.2	4.2
Diallyl-disulphide	DADS	19.8	18.8	19.3
Allyl-methyl-trisulfide	AM3S	8.3	8.6	8.4
1,3,5-Trithiane	TT	1.7	1.8	2
Diallyl-trisulfide	DA3T	16.2	17.5	17.8
Diallyl-tetrasulfide	DA4S	4.9	5	4.3

Table 6RELATIVE CONCENTRATION (%) VARIATION FOR THE RECOVERED *ALLIUM SATIVUM* L. BIOCOMPOUNDS FROM THE COMPLEXES WITH THE VARIATION OF THE DEGRADATION TEMPERATURE (FOR 2 h OF ACTION)

Compound name	Code	Degradation temperature (°C)		
		30	60	90
		AbCD-Ot1	AbCD-Ot2	AbCD-Ot3
Diallyl-monosulfide	DAMS	7	9.60	7.4
1,3-Dithiane	DT	2.2	3.1	2.6
Diallyl-disulphide	DADS	29.3	32.2	25.6
Allyl-methyl-trisulfide	AM3S	8	8.5	7
1,3,5-Trithiane	TT	1.7	1.8	1.3
Diallyl-trisulfide	DA3T	18.4	19.9	15.7
Diallyl-tetrasulfide	DA4S	3.9	4	3.1

Table 7RELATIVE CONCENTRATION (%) VARIATION FOR THE NON-ENCAPSULATED *ALLIUM SATIVUM* L. BIOCOMPOUNDS IN THE PRESENCE OF AIR (OXYGEN) AND ARGON AT HIGHER DEGRADATION TEMPERATURES (90°C)

Compound name	Code	Degradation factor	
		air	argon
		A-O-t6	A-N-t7
Diallyl-monosulfide	DAMS	12.3	10.8
1,3-Dithiane	DT	4.3	4.1
Diallyl-disulphide	DADS	18.6	20.8
Allyl-methyl-trisulfide	AM3S	8.4	9.5
1,3,5-Trithiane	TT	1.8	2.3
Diallyl-trisulfide	DA3T	17.1	17.8
Diallyl-tetrasulfide	DA4S	4.8	3.8

compounds (DADS, DATS) are increased, in detriment of the relative minor compounds like DAMS and DT. The tendency is also to decrease the relative concentrations of these minor compounds with the increase of the degradation temperature (table 6).

Similar studies were done among the behaviour of the biocompounds under the action of temperature in the presence of air-oxygen, compared with the case of the absence of this oxidant (under argon), and small differences were observed. Thus, an increase of the concentration of acyclic di- and trisulfides can be observed

(DADS from 18.6% in the presence of air to 20.8% in argon, AM3S from 8.4% to 9.5%, and DA3S from 17.1% to 17.8%). Therefore, the oxygen has an influence on the degradation of these compounds (table 7).

For the degradation of the nanoparticles in the presence of air or argon at higher temperatures (90°C), a small decrease of the relative concentration for all sulfide compounds in non-oxidative conditions was observed (it is possible due to the oxidation-polymerization effects in the presence of oxygen).

In the case of degradation of non-encapsulated and nanoencapsulated *Allium sativum* L. bioactive compounds under UV light for 30 min, a relatively small decrease of the DAMS and DA3S concentrations for the non-encapsulated samples degraded in the presence and absence of oxygen, and for TT in the case of nano-encapsulated samples can be observed.

Conclusion

The complexation of the essential oil of garlic (*Allium sativum* L.) in α - and β -cyclodextrin provides a product with no "garlic" odor, characteristic for the sulfur compounds from the raw volatile oil.

The relative concentration of the unsaturated acyclic compounds is higher than for the saturated acyclic and cyclic sulfide compounds, relative to the raw essential oils. This can be explained by the hydrophobic properties of these compounds, indicated by the logarithm of the partition coefficient between octanol and water (logP) [22]. For compounds with the ratio between the relative concentration in raw and reextracted essential oil < 1 (more competitive than others for the cyclodextrin cavity), the calculated logP were: 2.55 for diallyl-disulfide and 3.17 for diallyl-trisulfide, while for the compounds with the ratios > 1 (lower competition to the hydrophobic cavity of the cyclodextrin) the logP values were 1.68 for dimethyl trisulfide, 1.74 for dimethyl tetrasulfide, 0.98 for 1,3-dithiane, and 1.94 for 1,3,5-trithiane. The differences between the hydrophobicity of the compounds are very clear: all the compounds encapsulated in higher concentration have logP values above 2.5.

Generally, the yields of nanoencapsulation of *Allium sativum* L. bioactive compounds in cyclodextrins are higher than 60%, but they decrease with the molar ratio between biocompounds and α - or β CD; the yields also increase with the complexation temperature or with the cooling time, probably due to the possibility to adjust the association-dissociation equilibrium and to the formation of more nuclei centers in the incipient phase of crystallization; the decrease of the yields with the increase of the biocompounds/CDs molar ratio also remain in the case of other alcohol used for nanoencapsulation.

Non-significative variation can be observed in the case of degradation of *Allium sativum* L. biocompounds with the variation of the degradation temperature in the presence of oxygen, excepting 1,3-dithiane, which probable is transformed in sulfoxide or carbonyl compound (a slightly increase of the concentration of these compounds at higher temperatures and in the presence of oxygen can be observed); the degradation of the corresponding α - and β CD nanoparticles leads to an increase of the relative concentration of the diallyl-di- and

diallyl-trisulfide, compared with those for the non-encapsulated ones. Small differences exist between the composition of the degraded biosystems in the presence or absence of oxygen, and in the presence of the UV light.

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