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Original Article: ATTEMPT OF OBTAINING THE SORBENT SELECTIVE WITH RESPECT TO BIOLOGICALLY ACTIVE COMPONENTS OF ESSENCIAL OIL EUCALYPTUS DIVES

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Abstract
Attempt of obtaining the sorbent selective with respect to biologically active components of essential oil Eucalyptus dives. The shifting of optical activity of Eucalyptus dives liquid oil under the chiral selective SiO_2 is observed. It is concluded that chiral selective effect is growing for the systems under the magnetic influence.

Introduction. Numerous cases of epidemic, pandemic and epizootics including those caused by unknown pathogenic agents were observed at the term of XX-XXI centuries. Some investigators connect such phenomena with mutation of organisms under effect of unfavorable ecological factors. Therefore the task of effectiveness increase of medical product arises towards specialists of different fields [1-7].

The key role in this task solution belongs to interconnection of biological activeness of molecules and their stereochemical structure. It is well-known fact that certain enantiomers of amino acids, sugars, terpenes, antibiotics, alkaloid, etc have strict selectivity of effect upon living cell. In 1860 L. Paster indicated that asymmetry is typical for living matter chemistry and distinguishes it from nonliving matter. This property of living matter is realized in the fact that interacting components fit together on the principle of "lock-key" in biochemical reactions [8].

Modern preparative methods that allow distinguishing of optical isomers are based on the last achievements of nanotechnology, on the one hand, and on the well-known chromatographic methods with application of optical active phases, on the other hand. Application of hardphase chiral-selective catalyst in reaction with organic compounds is also considered to be prospective. In this respect it is necessary to use method of optically active cells (L. Poling, 1949). It lies in the chiral agent insertion in the mother solution in order to prepare sorbent with asymmetric nanopores. Up till now different polymers without high chemical inertness were used as starting materials for sorbents with optical active nanopores. This property of material can be decisive for tasks solution of pharmacology. The polysilicic acid gells meet such requirements [9, 10].

Unlike polymer sorbents silicates do not have adsorbtion ability of organic molecules and ability to from spatially oriented optical active cells. In this respect it is necessary to use method of complex substances composition: sorbents preparation by means of colloidal solutions coagulation in the nonequilibrium conditions created by external electric and magnatic field. Disorder of the solid bodies sythesized in such way is decreased due to Faraday effect [8].

The principle of molecular asymmetry was founded in our experiments of preparing immunity protraction preparations It's having ability of chiral selective extraction of components from essential hydrocarbon oils: Eucalyptus dives. This substations are used as immunity modulators in Pharmacology and traditional (Tibet) medicine. CAP is a most acceptable model object in experiments: it is optical active antibiotic, which has a long research history [4-6].

The purpose of this research is experimental check of synthesis possibility and application of chiral selective nanostructures for pharmacological products enrichment by way of essence eucalyptus.

Experimental technique and methods.

Silicate sorbents were prepared in teflon vessels by means of silica acid gels from water colloidal solutions Na_2SiO_3 and K_2SiO_3 (pH>10). Their coagulation was achieved by means of salting-out resulting from mixing of equal volume of ethanol (70% solution in water).

Optical active matrix substance, antibiotic chloramphenicol (CAP) were injected to the colloid system as 0.1-0.25% solution in C_2H_5OH at the rate of about 100 μg of chiral agent per 1 g of silicate material. Further treatment of sediment was executed by 5% solution of HCl with distilled water ablution till pH is about 8 and heating of N_2 during 3 hours at 120 ^{0}C. To our options such treatment should have lead to removal of most chiral agent from silicate sorbent. The fraction with size of 0.016 mm was sieved away after triturating in the experimental faience mortar.

The coagulation in the magnetic field was executed under influence of permanent magnet.

Essences were treated by received sorbents in the glass boxes during 1.5-2 days. The establishment of adsorption equilibrium was achieved in this way. The mass of silica gel. Taken for experiments, was 1 g. The volume of essence was 7 ml.

Polarimetric control of the optic active liquid samples was executed at temperature +19 ^{0}C at the polarimeter SU-4(USSR). The length of cuvette was 5.5 cm. Measurement inaccuracy was ± 0.02 ^{0}.

Chromatomass-spectrometer investigations of essences were executed at the device LKB-2091 (Sweden), chromatographic column DB-5, temperature program 50-250^{o}C, 3^o/mines.

The electron-microscopic researches were executed on "Teiss Merlin". Specific surface size of silica samples (S) was measured by Gurvich's adsorption method [10]. S = 20-50 m/g. The specific surfaces of samples were are measured with an error no more than 10 %. X-ray analysis were executed on the device DRON 3.0 (Russia), radiation Fe Kα. The magnetic density (H) measurements in experiments with permanent magnet were executed at the device IMP-05 (Russia) . H was about 50 A/m.

The electron-microscopic researches were executed on "Zeiss Merlin" devise.

Results and discussions.

In the executed experiments left isomer, antibiotic D-(-)-threo-1-(p-introphenyl)-2-dichloracetyl-aminopropanediol-1,3, chloramphenicol ($[\alpha]_D^{25}$= -25.5 ^{0}(EtOAc)) [8] was injected to the mother solution at the obtaining of silica acid gels. Sorbents on their basis were used for essence Eucalyptus dives treatment. All silica samples were non-crystalline.

As result, modification of optic activity of this essence was observed. This effect was much more significant in the experiments with silica gel received in the magnetization conditions (see table). The phenomena observed may be explained on the basis of well-known Cotton effect that consist in additivity of rotation power of optic active substances mixture [8]. It is possible to suggest that the angles of rotation essence after treatment will increase due to extraction of left isomer components from it.

On the ground of Chromatomass-spectrometric investigations results and chromatographic indexes (times) comparison of terpene hydrocarbon the attempt to determine components adsorbed by silica gels in the indicated investigations was made. In spite of some difficulties connected with compounds identification according to their mass-spectrum it can be determined that the main components of essence received from Eucalyptus dives are terpene hydrocarbons: α-phellandrene, $C_{10}H_{16}$, wich according to chromatographic data was adsorbed by the chiral-prepared silica gels the most effectively, and α-terpinene, $C_{10}H_{16}$, γ-terpinene, $C_{10}H_{16}$, α-thujene, $C_{10}H_{16}$ and terpenoigs 1,8-cineol $C_{10}H_{18}O$, menthol, $C_{10}H_{20}O$, citronellal, $C_9H_{15}O$, and aromatic hydrocarbon cimole, $C_{10}H_{14}$ [12].

Among the main active extracted hydrocarbon component of studied oil is

Trans-(-)-5-methyl-3-(1-methylethenyl)-cyclohexen [3-isopropenyl-5-methyl-cyclohexen] (CAS#56816-08-1 172-175 ^{0}C b.p.). Mass-spectra is in Fig. 1.

However, the structure of this hydrocarbon is not typical for biology objects. Indeed, in special literature [12] there are some differences of mass-spectra of this compound. Most likely the hydrocarbon, which is observed in our experiments has structure agrees: trans-(-)-6-methyl-3-(1-methylethenyl)-cyclohexen [3-isopropenyl-6-methil-cyclohexen]. This minor agent can take part in pharmacology effects with 1,8-cineol because this structure has a type of optical active antibiotic CAP.

The investigations of hydrocarbons emissions of affected plants where executed by author that allow to make conclusions concerning protective functions of terpenes and terpenoids. Their properties as antioxidant determine immunomodulatory action as far as it is connected with formation of free radicals that destroy organism's cells [6]. Possibility of molecules penetration through biological membrane is determined, on the one hand, by their space structure and, on the other hand, by their lipophilic properties. It is likely to be the reason why terpenes are able to prevent biological cells affection by free-radical particles and similar to antibiotic by their structure.

Coagulation of colloid silicate solution at alcohol draining and lack of magnetic field was carried out for 0.5-1 min. The sediment in the solution precipitated instantly under influence of permanent magnet. Obviously such difference in colloid systems behavior is caused by bigger non-equilibrium of deposition modes during magnetization. This phenomenon can be explained by destruction of double electric layer of ions that surrounds colloid particles due to ions orientations on the magnetic field. Faraday effect consists in the following: due to induced moment the substances show additional optic activity that may contributed to the decrease of system disarray [8].

The method we applied can be used for catalysts synthesis that model ferments according to the method of matrix indentation. It can improved in order to use molecular layering with the chemical assembly application for regulation of nanonporous size. The magnetization penetration for optic active chromatographic phases and optical pure drugs obtaining requires further development [10].

Conclusion. It is clear, that we observed chiral selective adsorption, because, the non-magnetic-carried (Fig. 2) and magnetic-carried (Fig. 3 and 4) solid samples have electron microscopic difference only and identical other characteristics.

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Table

Changes of the angle of rotation of essence Eucalyptus dives during treatment by chiral-prepeared sorbents with matrix nanostructure of chloramphenicol

Silica gel taken for experiment (receiving conditions)		Angle of rotation of polarized light in the essence Eucalyptus dives		Image of silica surface
chloramphenicol.	Magnatic field	S^o	degrees	
-	-	+7,55	+2,61	Fig. 2.
+	-	+7,65	+2,65	Fig. 3.
+	+	+8,50	+2,94	Fig. 4.
Virgin sample of essence Eucalyptus dives		+7,55	+2,61	

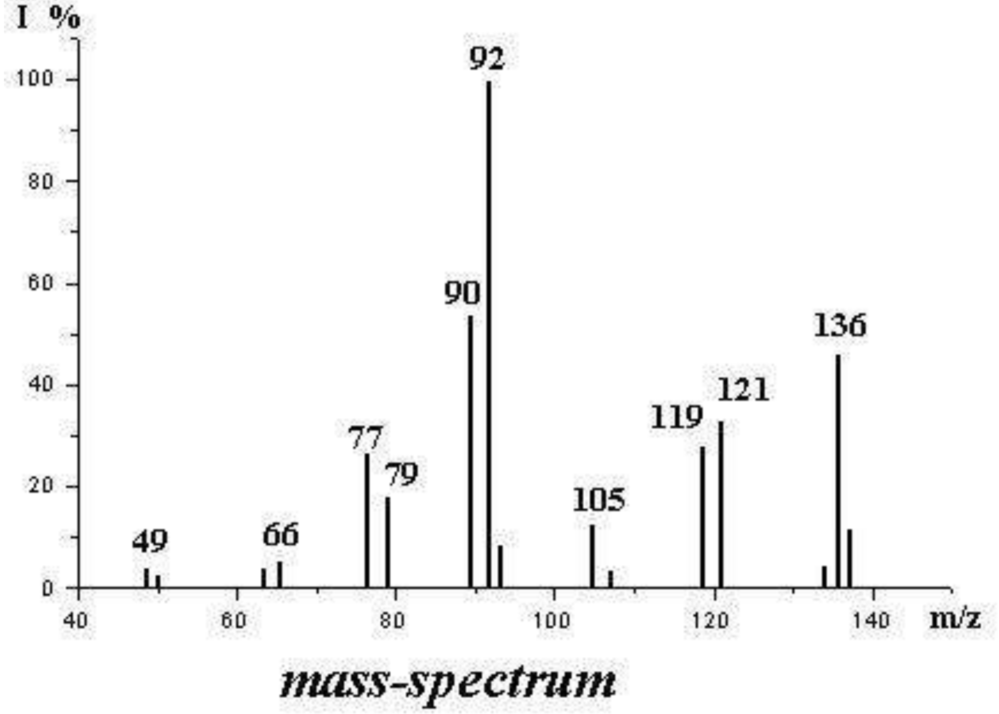
I %
100
80
60
40
20
0
40
60
80
100
120
140
m/z
49
66
77
79
90
92
105
119
121
136
mass-spectrum

Fig. 1.

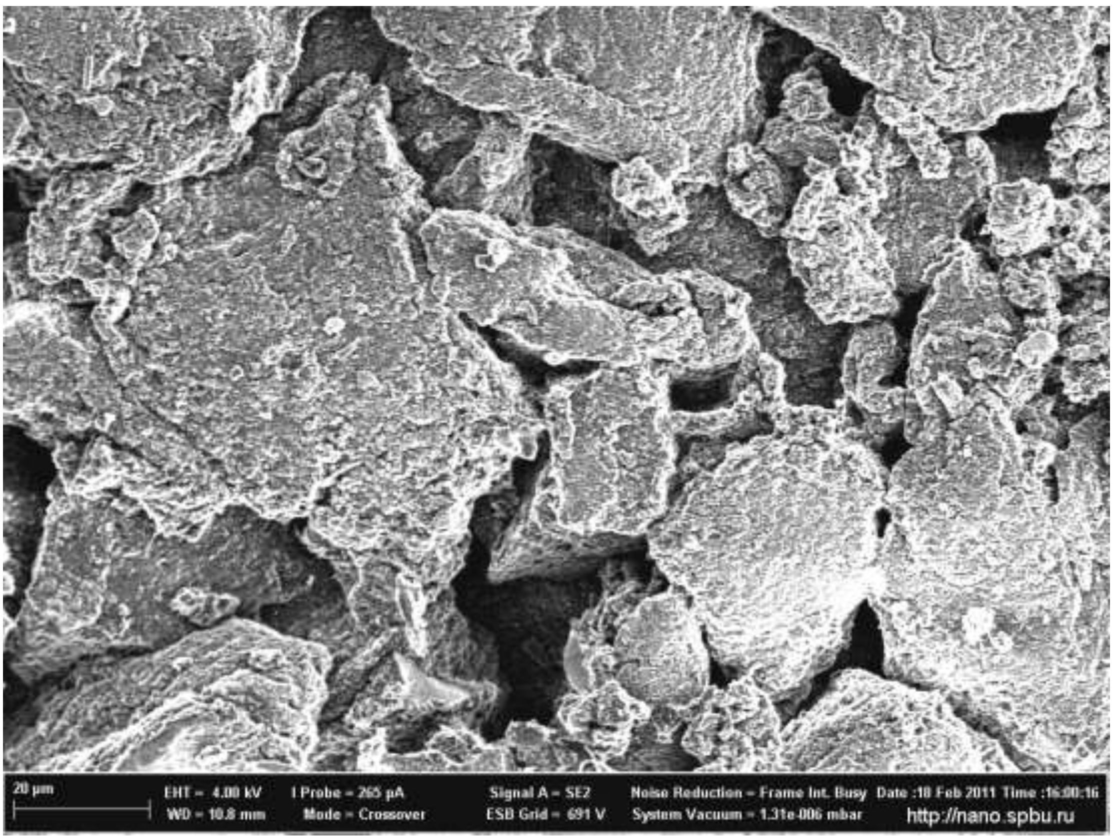
20 µm
EHT = 4.00 kV
WD = 10.8 mm
I Probe = 265 pA
Mode = Crossover
Signal A = SE2
ESB Grid = 691 V
Noise Reduction = Frame Int. Busy
System Vacuum = 1.31e-006 mbar
Date :10 Feb 2011 Time :16:00:16
http://nano.spbu.ru

Fig. 2.

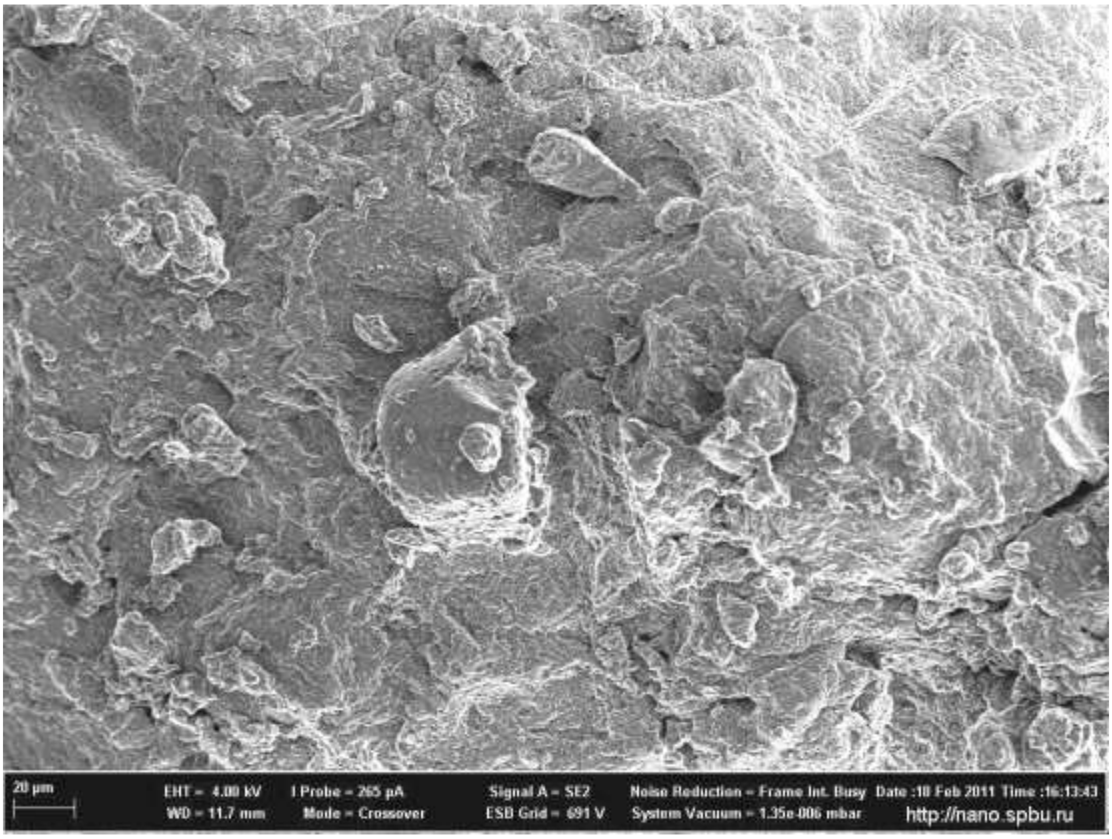
20 µm
EHT = 4.00 kV
WD = 11.7 mm
I Probe = 265 pA
Mode = Crossover
Signal A = SE2
ESB Grid = 691 V
Noise Reduction = Frame Int. Busy
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Fig. 3.

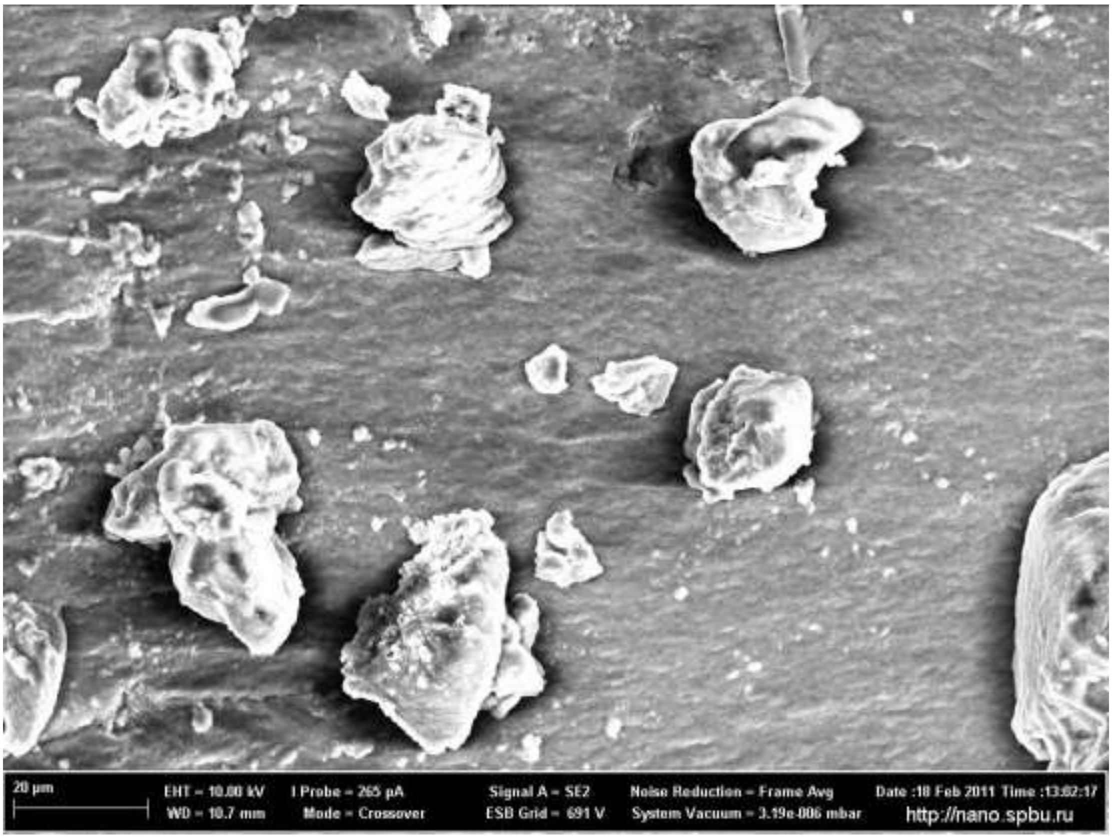
20 µm
EHT = 10.00 kV
WD = 10.7 mm
I Probe = 265 pA
Mode = Crossover
Signal A = SE2
ESB Grid = 691 V
Noise Reduction = Frame Avg
System Vacuum = 3.19e-006 mbar
Date :18 Feb 2011 Time :13:02:17
http://nano.spbu.ru

Fig. 4.