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Micellar extractions with anionic surfactant SDS and the mixture of SDS/OSAS for determination lovastatin in river samples

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ABSTRACT

The potential of the micellar extractions techniques for the preconcentration of lovastatin (LOV) was studied. The analyte has created micelle with anionic surfactant sodium dodecyl sulfate (SDS). Moreover, we have noticed that it is possible to isolate LOV using a binary mixture of SDS and 1-octanesulfonic acid sodium salt (OSAS). Therefore, two independent procedures were described in this study. Here we demonstrate the optimum analytical conditions for LOV assay such as pH of solution, concentration of surfactants, centrifugation time and electrolyte type. The linear calibration curves were obtained. The method range for LOV-SDS was of 10^{-6} mol L^{-1} to 5×10^{-5} mol L^{-1} with detection and quantification limits of 0.69×10^{-6} mol L^{-1} and 1.11×10^{-6} mol L^{-1}, respectively, and the range for LOV-SDS/OSAS was of 10^{-6} mol L^{-1} to 6×10^{-5} mol L^{-1}, with detection and quantification limits of 1.38×10^{-6} and 2.10×10^{-6} mol L^{-1}. The recoveries of the method using SDS surfactant were 93.5–101% and for the mixture of SDS/OSAS were 85–107.5%. The proposed preconcentration methods after validation were successfully applied to spectrophotometric and chromatographic determination of LOV in water samples from the local river.

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1. Introduction

Among the classical pollutants in the environment, the new contaminants have been recently extended. Pharmaceuticals, estrogens, algal, cyanobacterial toxins, metalloids, pesticides are considered to be new emerging pollutants [19]. Pharmaceuticals are in particular interest because of the fact that the large quantities of drugs are used in human and veterinary medicine. After their medicinal application and excretion via urine and feces, residual drugs and their metabolites are mainly entered to municipal sewage treatment plants. Most of the pharmaceutical preparations are not completely removed, and they reach the aquatic environment almost in 90% of unchanged form. Depending on the mobility, they can be transported to surface waters, sediments, groundwaters or soil. Concentration of pharmaceuticals in the water samples is at the level of ng L^{-1} or μg L^{-1}.

Lovastatin $C_{24}H_{36}O_5$ (LOV) [8-[2-(4-hydroxy-6-oxooxan-2-yl) ethyl]-3,7-dimethyl-1,2,3,7,8,8a-hexahydronaphthalen-1-yl]-2-methylbutanoate (Fig. 1) is one of the available statins, which are used for the treatment of the patients suffering from hypercholesterolemia. LOV as a potent inhibitor of 3-hydroxy-3-methylglutaryl coenzyme A reductase (HMG-CoA) possesses high effectiveness in reducing total cholesterol and the low density lipoprotein cholesterol levels in the body [2]. It is first generation drug derived from the fungus *Aspergillus terreus* [3]; other compounds which belong to this therapeutic group are produced by semi-synthetic (simvastatin, pravastatin) or totally synthetic (fluvastatin, atorvastatin) processes. LOV exists in two forms—lactone and hydroxy acid [5]. The hydroxy acid forms are the active drugs, but the lactone is known as inactive prodrugs [9]. This lactone form is absorbed from the gastrointestinal tract and hydrolysed to the hydroxyl acid in the liver [17].

The common use of lovastatin resulting from increasingly frequent cardiovascular diseases poses a risk of escaping of this drug residue to the environment. Therefore, it is essential to monitor the concentration levels of statins in the environment. A review of the literature suggests that the most frequently used methods for determining lovastatin, and its derivatives are the chromatographic and electrochemical methods.

Several methods have been already reported for the determination of LOV, including techniques such as HPLC-UV [3,8,13], UPLC-MS/MS [18], polarographic [16] and spectrophotometric methods [7]. In these articles, the solid phase extraction SPE and liquid–liquid extraction LLE are the most popular methods for isolation LOV from different samples. Alternative approach to the conventional and widely used sample preparation process is micellar extraction.

On the ground of the review of literature, it can be stated that micellar extraction is described especially for metal analysis [10,14] and organic compounds such as polycyclic aromatic hydrocarbons, polychlorinated compounds, pesticides, vitamins, aromatic amines, fulvic and humic acids and others [1]. Up to our knowledge, an isolation method is known for some drugs for example flurbiprofen from rat plasma [4], terazosin from pharmaceutical formulations and biological fluid samples [15], carbamazepine and phenobarbital from blood plasma and saliva [12] and arbidol from rat plasma [6]. Nevertheless, the number of

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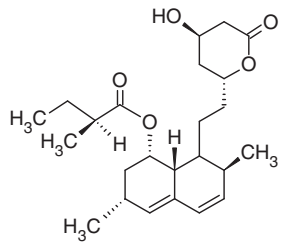

Fig. 1. Molecule structure of lovastatin (MW = 404.55 g · mol^{-1}).

micellar extraction methods dedicated to applications of drugs is very limited.

The aim of the presented study is to use micellar extraction for isolation LOV from samples of aqueous solutions. This extraction procedure is based on forming micelles by introducing surface active substances to the aqueous solution. Surfactants are able to dissolve organic nonpolar compounds such as pharmaceuticals in their own hydrophobic core. The surfactant-rich phase, containing the analyte which is viscous, must be usually diluted in small volume of organic solvent before being injected into the apparatus.

This article focuses on the optimization of extraction parameters such as surfactant selection, electrolyte type and its concentration, adding acid, influence of shaking and centrifugation time. The content of isolated analyte was directly determined by the spectrophotometric and chromatographic methods by comparison to the previous one. The water sample was taken from the local river Horodnianka that flows in the northeastern Poland.

2. Experimental

2.1. Instrumentals

A Hitachi U-1900 spectophotometer (Tokyo, Japan) equipped with the deuterium discharge lamp and quartz glass was used for the measurements. The phase-separation process was accelerated by the centrifuge MPW-251 (MPW-Med. Instuments, Warsaw, Poland). A thermo-separation chromatographic system with a 2D Spectra System UV3000, a low-gradient pump P2000 and a vacuum membrane degasser SCM Thermo Separation was used (San Hose, California, USA).

2.2. Chemicals

Lovastatin from Mevinolin from *Aspergillus* sp., anionic sodium dodecyl sulfate (SDS) and 1-octanesulfonic acid sodium salt (OSAS), cationic tetrabutyloammonium bromide (TBAB) and cetyltrimethylammonium bromide (CTAB), non-ionic Triton X-114 (TX-114) and Triton X-100 (TX-100) were bought from Sigma-Aldrich (Steinheim, Germany). A standard stock solution containing 10^{-3} mol L^{-1} LOV ($\log K_{o/w} = 3.90$) was prepared in methanol. Standard working solution was freshly prepared every day before an analysis by diluting the standard solution with Milli-Q water, and then it was stored in a dark bottle at room temperature. Each ionic micellar solution 10^{-1} mol L^{-1} was prepared by appropriate weight and dilution with Milli-Q water. TX-114 and TX-100 were used as a 5% water solution. Other chemicals used in experiments, like NaCl, $CaCl_2$, KBr and Na_2SO_4 (POCh, Gliwice, Poland), were prepared by dissolving an appropriate amount of salt in Milli-Q water. Working solution of HCl was prepared by successive dilutions of appropriate volumes of concentrated acid in Milli-Q water.

2.3. General analytical procedures

2.3.1. Extraction procedure with using anionic surfactant SDS

The 2.25 mL extracting solution of SDS (10^{-1} mol L^{-1}) was mixed with 4 mL sodium chloride (4 mol L^{-1}), 0.3 mL hydrochloric acid (10^{-1} mol L^{-1}) and 0.5 mL aliquots of standard solution of LOV (10^{-3} mol L^{-1}) in the calibrated test tubes. The content of the tubes was diluted with Milli-Q water (total volume 10 mL), and then the sample was kept in a room temperature for 10 min. The solutions were being shaken for 20 min with the speed of 250 circulations per minute. After that, the mixtures were being centrifuged at 1431 ×*g* for 15 min. The surfactant-rich phase felt down as a compact layer at the bottom of the tube, and the aqueous phase could be separated by the Pasteur pipette. Diluted 10 mL of methanol surfactant-rich phases was collected into the calibrated test tubes. The absorption spectrum of LOV after this procedure of extraction was showed in Fig. 2.

2.3.2. Extraction procedure with using the binary mixture of SDS and OSAS

The 1.0 mL extracting solution of SDS (10^{-1} mol L^{-1}) and 0.75 mL second extracting solution of OSAS (10^{-1} mol L^{-1}) were mixed with 3.5 mL calcium chloride (4 mol L^{-1}), 80 μL hydrochloric acid (10^{-1} mol L^{-1}), and 0.5 mL aliquots of standard solution of LOV (10^{-3} mol L^{-1}) in the calibrated test tubes. The content of the tubes was diluted with Milli-Q water (total volume 10 mL), and the sample was being kept in a room temperature for 10 min. The solutions were shaken for 5 min with the speed of 250 circulations per minute. After that, the mixtures were centrifuged at 1431 ×*g* for 15 min. The aqueous phase was separated by the Pasteur pipette from the surfactant-rich phase, which created a slight mass at the side of the tube. The surfactant-rich phases were diluted in 10 mL of methanol.

2.3.3. Water samples

Water samples were taken from the local river Horodnianka which passes through Choroszcz (northeast Poland). The place is about 75 cm from the river bank and about 1/3 of the river depth. The samples were collected into polyethylene flasks; they were protected from the light and stored in the refrigerator. Each sample was first filtered with 0.45 μm membrane filter and then extracted by micellar extraction methods.

3. Results and discussion

3.1. Optimization of extraction parameters

3.1.1. Surfactant selection and its concentration

First of all, 5% aqueous solution of non-ionic surfactants TX-100 and TX-114 has been checked. The extraction of LOV in different pH values was carried out. Moreover, a lot of electrolytes such as NaCl, $CaCl_2$, KBr and Na_2SO_4 were looked up. The results did not allow them to use LOV from aqueous samples for isolation. The efficiency was very low in the range of 15–20%.

It was also checked if cationic surfactants like TBAB and CTAB are suitable for creating micelle with LOV. It was observed that using them for isolation of LOV from samples of aqueous solutions is possible

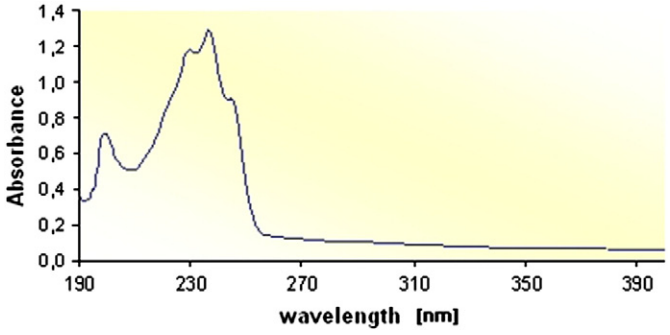

Fig. 2. Absorption spectrum of the micellar solution phase after extraction with a solution of SDS (SDS-LOV).

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