Synthesis of the sulfated arabinogalactan
tetramethylammonium complex

A S Kazachenko¹,², N Yu Vasilyeva¹,², Yu N Malyar¹,² and A V Miroshnikova¹

¹Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center
“Krasnoyarsk Science Center SB RAS”, 50/24, Akademgorodok, Krasnoyarsk, 660036, Russia
²Siberian Federal University, 79, Svobodny av., Krasnoyarsk, 660041, Russia

E-mail: leo_lion_leo@mail.ru

Abstract. Sulfated polysaccharides, due to the presence of anionic groups, are able to form complexes with positively charged molecules. This work presents the results of obtaining complexes of the sulfated polysaccharide arabinogalactan with tetramethylammonium bromide. The resulting complex was shown to be soluble in water and methylene chloride. The introduction of tetramethylammonium bromide into the molecule of sulfated arabinogalactan has been proven by elemental analysis and FTIR spectroscopy.

1. Introduction
Polysaccharides are important plant polymers that play important roles in plants [1]. Polysaccharides are long-chain polymers of mono-, di- and oligosaccharides [2,3]. Modification of polysaccharides with different functional groups can give them different properties for use in pharmaceuticals, medicine, building materials, etc. [4-6].

One of the important derivatives of polysaccharides is sulfated derivatives. They have anticoagulant, lipid-lowering activity [6].

Larch wood arabinogalactan is a water-soluble polysaccharide that has anticoagulant, hypolipidemic and antimicrobial activity [1]. Sulfated arabinogalactan containing acidic sulfo groups, like heparin, can interact with nitrogen-containing compounds to form complex compounds. We have previously obtained derivatives of sulfated arabinogalactan with glycine, ornithine [7], arginine, histidine [8], and copper [9]. In addition, the possibility of obtaining an intermolecular complex of sulfated starch with casein was investigated [10].

Amino acid derivatives with polysaccharides are of great interest for medicine, since the introduction of an amino acid into the structure of a polysaccharide opens up new possibilities for varying their lipophilic-hydrophilic properties, selectivity, and duration of action [11–13].

There is information in the literature that molecular complexes of heparin with amino acids, formed with the participation of acidic groups of heparin and amino groups of amino acids, have a powerful anticoagulant effect, and are also antiplatelet agents and fibrinolytics [14-16].

Tetramethylammonium has the ability to protonate, which opens up the possibility of its use in the preparation of complexes with anionic polysaccharides.
In this work, a method was proposed for the synthesis of a complex of sulfated arabinogalactan with tetramethylammonium bromide, as well as its characterization by IR spectroscopy and elemental analysis.

2. Experimental part

The raw material used was arabinogalactan (AG) of Siberian larch wood (Larix sibirica Ledeb.), produced by OOO «Chemistry of Wood» (Irkutsk, Russia) under the name of the drug «FibrolarS».

Sulfation of arabinogalactan was carried out with sulfamic acid in dioxane in the presence of urea according to the method described in [17]. For the synthesis of the complex, a sulfated arabinogalactan with a sulfur content of 9.8 wt. %.

Method of obtaining a complex of sulfated arabinogalactan with tetramethylammonium bromide. A weighed portion of sulfated arabinogalactan 0.40 – 0.45 g (sulfur content 9.5%) was dissolved in 10 ml of water, and a 6% aqueous solution of tetramethylammonium bromide was added with stirring. The solution was kept for 3 hours. Then the resulting solution was evaporated by ½, extracted with methylene chloride, the residue was filtered off. The structure and composition of the solid product remaining after removal of the solvent was determined from the data of elemental analysis and IR spectroscopy.

FTIR - spectra were recorded on an IR Fourier spectrometer (Vector 22) in the wavelength range of 400–4000 cm$^{-1}$. Spectral information processing was carried out using the OPUS / YR software (version 2.2). Solid samples (3 mg) for analysis were prepared in the form of tablets in a KBr matrix.

FlashEA-1112 elemental analyzer (ThermoQuest, Italia) was used for elemental analysis.

3. Results and discussion

Obtained complexes of sulfated arabinogalactan with tetramethylammonium bromide (TMAB) dissolve in water and, unlike the initial sulfated arabinogalactan (SAG), dissolve in methylene chloride. The results of elemental analysis showed that the content of sulfur and nitrogen in the products is much lower than in the initial reagents. Table 1 shows the results of the experiment.

| № | Molar ratio SAG : TMAB | Product yield, wt. % | Nitrogen content, wt. % | Sulfur content, wt. % |
|---|------------------------|----------------------|------------------------|----------------------|
| 1 | 1:1                    | 62.34                | 1.39                   | 3.50                 |
| 2 | 1:2                    | 56.90                | 1.25                   | 3.44                 |
|   | SAG                    | -                    | -                      | 9.80                 |
|   | TMAB                   | -                    | 9.10                   | -                    |

The resulting complexes were investigated by FTIR spectroscopy, the spectra of the samples are identical; Figures 2, 3 show the FTIR spectra of the starting tetramethylammonium bromide and the SAG complex with TMAB.

Compared with the FTIR spectrum of the initial reagents - SAG Na-salt (Figure 1) and TMAB (Figure 2), the spectrum of the obtained polymer complexes (Figure 3) increases the intensity of the absorption band in the region of 3430-3440 cm$^{-1}$ as a result of close values of the absorption regions bonds NH and O-H. Changes in the nature of absorption corresponding to CH vibrations in the range of 2960-2730 cm$^{-1}$ in the complex, compared with stretching vibrations of the initial TMAB. The absorption band belonging to the S = O stretching vibrations, contained in the FTIR spectrum of the SAG Na-salt, broadens in the range of 1240-1257 cm$^{-1}$. 
Figure 1. FTIR spectrum of sulfated arabinogalactan.

Figure 2. FTIR spectrum of tetraammonium bromide.

Figure 3. FTIR spectrum of the polymer complex.
4. Conclusions
For the first time, a complex of sulfated arabinogalactan with tetramethylammonium bromide was obtained. The obtained SAG: TMAB complex was shown to dissolve in water and methylene chloride. When using a molar ratio of SAG: TMAB 1:1, a product yield of up to 63 wt.% is achieved.

The composition of the resulting complex was determined by FTIR spectroscopy and elemental analysis. In the FTIR spectrum of the obtained complex of sulfated arabinogalactan with tetramethylammonium bromide, absorption bands appear corresponding to the vibrations of the N-H and C-H groups.

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