

SULFATION OF BIRCH WOOD XYLAN WITH SULFAMIC ACID IN THE PRESENCE OF ACTIVATORS: EXPERIMENT AND THEORY

ALEKSANDR S. KAZACHENKO,^{*,**} FERIDE AKMAN,^{***} YAROSLAVA D. BEREZHNYAYA,^{**}
 NATALYA VASILIEVA,^{*,**} OLGA YU. FETISOVA,^{**} NOUREDDINE ISSAOUI,^{****}
 ZHOUYANG XIANG,[§] ANNA S. KAZACHENKO,^{*} TIMUR IVANENKO,^{**}
 SVETLANA NOVIKOVA,^{**} OMAR M. AL-DOSSARY[†] and LEDA G. BOUSIAKOU[#]

^{*}*Siberian Federal University, Pr. Svobodny 79, Krasnoyarsk, 660041 Russia*

^{**}*Institute of Chemistry and Chemical Technology, Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Akademgorodok 50, Blvd. 24, Krasnoyarsk, 660036 Russia*

^{***}*Vocational School of Food, Agriculture and Livestock, University of Bingöl, Bingöl 12000, Turkey*

^{****}*Laboratory of Quantum and Statistical Physics (LR18ES18), Faculty of Sciences, University of Monastir, 5079 Tunisia*

[§]*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640 China*

[†]*Department of Physics and Astronomy, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia*

[#]*IMD Laboratories Co, R&D Section, Lefkippos Technology Park, NCSR Demokritos, PO Box 60037, 15130 Athens, Greece*

✉ *Corresponding author: A. S. Kazachenko, kazachenko.as@icct.krasn.ru*

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Xylan is a polysaccharide found in plant cell walls. It is considered to be a biodegradable polymer, which does not affect negatively the environment. Sulfated xylan derivatives exhibit valuable bioactive properties, in particular, anticoagulant and hypolipidemic. We report on the development of a new method for sulfation of birch wood xylan. Activators of the sulfation reaction with sulfamic acid have been evaluated. Numerical methods have been used to establish the optimum process parameters that ensure the maximum sulfur content in the reaction product. The incorporation of a sulfate group has been confirmed by infrared and nuclear magnetic resonance spectroscopy, and elemental analysis. The initial and sulfated xylans have been comprehensively studied by theoretical methods and the most favorable conformations of the initial xylan and its sulfate have been established.

Keywords: xylan, xylan sulfate, sulfamic acid, birch, density functional theory

INTRODUCTION

Xylan, a structural polysaccharide, is a component of hemicelluloses of many plant materials. Xylan molecules are built mainly from xylose units, which are β -D-xylopyranose residues.¹ Along with cellulose, xylan is a building material of cell walls, which is used in the production of xylose, xylitol, organic acids, fodder yeast, *etc.* Xylan and its ethers and esters have found application in the food, perfume, and pharmaceutical industries as environmentally sound thickeners, emulsifiers, and stabilizers.^{2,3} In addition, xylan is a feedstock for production of bioactive sulfated derivatives.⁴ Xylan sulfate with

the brand name Elmiron is commercially produced in the US. It was approved by the US Food and Drug Administration for use as a drug in the treatment of cystitis.⁵ Xylan sulfate is also known for its antiviral, anti-inflammatory, antitumor, and anticoagulant activity.⁶⁻⁹

Xylan sulfates are obtained by several major methods, first of all, using aggressive agents: SO_3 , H_2SO_4 , ClSO_3H , and their complexes with organic solvents.^{10,11} The advantage of this method is a short process time, but the drawbacks are corrosion aggressiveness, which requires special equipment to be prevented, and partial

hydrolysis of xylan. The second method is sulfation of xylan with sulfamic acid in an organic base medium in the presence of urea.¹² This method uses non-toxic sulfamic acid, but the time of the sulfation procedure is long and it is difficult to extract urea from the reaction mass. An alternative to the above-mentioned methods is sulfation of xylan in a flow-type setup.¹³ This method makes it possible to scale the sulfation process, but toxic chlorosulfonic acid is used.

The development of alternative methods for sulfation of xylan is an urgent task. The use of sulfamic acid and solid catalysts can help eliminate the drawbacks of the other synthesis methods.

The aim of this study was to optimize the process of sulfation of xylan with sulfamic acid in pyridine and to study the obtained products by infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and density functional theory (DFT).

EXPERIMENTAL

Materials and methods

An initial raw material was birch wood (*Betula pendula* Roth.) harvested in the vicinity of the Krasnoyarsk city. The main components of birch wood were (content, wt%): cellulose (41.3), hemicelluloses and uronic acids (30.3), lignin (19.9), extractives (4.2), and ash (0.3). Birch wood was crushed and the (3–5)-mm fraction was used in the experiments.

Xylan was isolated from birch wood using the method proposed in the literature.¹² The first stage is delignification of birch wood with hydrogen peroxide in acetic acid in the presence of sulfuric acid at a temperature of 95–100 °C for 4 h. The second stage is the extraction of xylan from holocellulose with a 5% aqueous solution of sodium hydroxide.

Xylan was analyzed by a well-known method,¹⁴ consisting of xylan hydrolysis and subsequent chromatography analysis.

Xylan obtained from birch wood is a loose white powder consisting of xylose (95.13%), mannose (1.52%), glucose (1.48%), galactose (0.97%), and arabinose (0.89%).¹²

Xylan sulfation

In a 100-mL three-necked flask equipped with a stirrer, a thermometer, and a reflux condenser with a calcium chloride tube, 50 mL of pyridine was poured and 1.5 g of xylan isolated from birch wood, 2.5 g of sulfamic acid, and 1.5 g of urea were loaded. The process was carried out at 90–100 °C for 0.5–2.0 h. The reaction mass was cooled to a temperature of 20 °C, the solvent was decanted, and 50 mL of a 4% aqueous solution of sodium hydroxide was added to

pH 9–10. The resulting solution was purified by dialysis using an MF-8030-25 dialysis bag (MFPI, US) with a pore size of 6–8 kDa and a width of 25 mm. The xylan sulfate aqueous solution was dried in a Petri dish in an oven at 50 °C until water was completely removed.

The sulfur content in the obtained sodium salts of xylan sulfates was determined on a Flash EATM-112 elemental analyzer (ThermoQuest, Italy).

The Fourier-transform infrared (FTIR) spectra of the initial and sulfated xylan were recorded on a Shimadzu IRTracer-100 FTIR spectrometer (Japan) in the wavelength range from 400 to 4000 cm⁻¹. The spectral data were analyzed using the OPUS software, version 5.0. Solid specimens in the form of tablets in a KBr matrix (2-mg specimen/1000 mg of KBr) were prepared.

Proton-decoupled ¹³C NMR spectra were recorded at 25 °C on a Bruker Avance III 600 MHz spectrometer in D₂O and processed after accumulation of 4096 transients with a 10-s relaxation delay.

The optimum xylan sulfation mode was selected by the DOE (Design of Experiments) block from the Statgraphics Centurion software package.¹⁵

Quantum chemical calculation technique

The optimization and quantum chemical calculations of xylan and xylan sulfate molecules were carried out by the B3LYP/6–311G(d, p) DFT method in the Gaussian 09 program.^{16,17} The Fukui functions (*f*⁺(r), *f*[−](r), *f*⁰(r), and Δ*f*(r)) were calculated using the multifunctional wavefunction analyzer (Multiwfn).¹⁸

RESULTS AND DISCUSSION

Effect of activators on the sulfation process

It was previously thought that alcohols could be sulfated in the reaction with sulfamic acid. However, this reaction is slow: it requires two to ten hours or more to complete.¹⁹ It is known well that the organic bases, for example, pyridine, accelerate the reaction to a certain extent, and have a dissolving effect on the reaction mass.²⁰ When comparing the activating effect of pyridine, urea, thiourea, acetamide, and picoline in the process of sulfation of higher aliphatic alcohols with sulfamic acid, urea was found to be the most efficient.²¹ Sulfation of polysaccharides revealed also the activating nature of urea, in contrast to other additions. The esterification of sulfamic acid in the presence of urea is explained by the formation of a donor–acceptor complex,²² which is highly reactive to sulfation. The formation of the donor–acceptor complex is schematically illustrated in Figure 1. A schematic of sulfation of birch wood xylan with sulfamic acid in pyridine is shown in Figure 2.

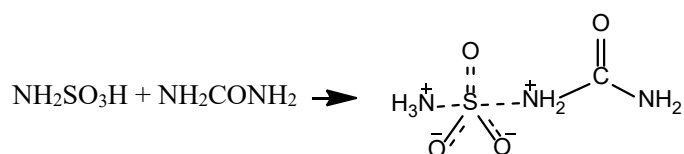


Figure 1: Schematic of formation of a donor–acceptor complex

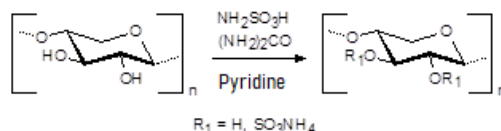


Figure 2: Schematic of the xylan sulfate synthesis using sulfamic acid

Table 1
Effect of activators of sulfation with sulfamic acid on the sulfur content in xylan sulfate
(sulfation conditions: pyridine, 100 °C, 2 h)

No.	Activator	Formula	Sulfur content, wt%
1	Urea		16.0
2	Thiourea		8.9
3	Methyl urea		9.1
4	Ethyl urea		8.0
5	Hydroxyethyl urea		7.9
6	Biuret		7.4

Previously, we studied the urea-based activators of sulfation of guar gum galactomannan with sulfamic acid,²³ xanthan,²⁴ and arabinogalactan.²⁵ Urea was shown to be the most effective activator of this process. These reactions, however, occurred in the 1,4-dioxane medium and on branched polysaccharides (galactomannan, arabinogalactan, and xanthan). Birch wood xylan is known to have a linear structure.⁷ In this work, we considered the process of sulfation with sulfamic acid in the presence of activators from a slightly different angle.

The data on the effect of the urea-based activators on the process of xylan sulfation with

sulfamic acid are given in Table 1. According to the data given in Table 1, the urea derivatives activate the process of sulfation of xylan with sulfamic acid in different degrees. Biuret was proven to be the least efficient process activator: the sulfur content in the resulting xylan sulfate was 7.4 wt%. The N-methylurea activator ensured the highest sulfur content in xylan sulfate among the urea derivatives. However, the highest sulfur content (16.0 wt%) in the xylan sulfate was obtained with urea.

Thus, it was shown that the N- and C-substituted ureas are less efficient as activators of sulfation of xylan with sulfamic acid than the

original urea. It was noticed that the activating ability of a substituent in the N-substituted ureas

Numerical optimization of sulfation of xylan with sulfamic acid

In the numerical study, two factors were included as independent variables: process temperature X_1 (90, 95, and 100 °C) and process time X_2 (0.5, 1.0, 1.5, and 2.0 h). The result of the sulfation process was characterized by the output parameter: sulfur content Y_1 in the sulfated xylan (wt%). A combined multilevel experiment plan (Users Design) was used. The confidence intervals were calculated according to the parallel

decreases with an increase in its length.

experiments on sulfation under similar conditions. Each experiment was carried out in two parallels.

The mathematical processing and optimization of the xylan sulfation process were performed using the experimental results listed in Table 2. The dependences of the output parameters on the variable process parameters were approximated by the second-order regression equations. The results of the analysis of variance are given in Table 3.

Table 2
Experimental design data of sulfation xylan process

Xylan sample no.	Reaction temperature, °C	Reaction time, h	Sulfur content, wt%
—	X_1	X_2	Y_1
1	80	0.5	6.1
2	90	0.5	9.4
3	100	0.5	10.7
4	80	1.0	8.2
5	90	1.0	14.5
6	100	1.0	17.2
7	80	1.5	9.9
8	90	1.5	15.7
9	100	1.5	16.9
10	80	2.0	10.8
11	90	2.0	16.1
12	100	2.0	16.0

Table 3
Results of the analysis of variance

Source of variance	Output parameter: sulfur content, Y_1	
	Statistical characteristics	
	Variance ratio F	Significance level P
X_1	72.34	0.0001
X_2	41.39	0.0007
X_1^2	7.47	0.0341
X_1X_2	0.1	0.7637
X_2^2	10.65	0.0172
R^2_{adj}	92.0	

The analysis of variance showed that, within the limits of the experimental conditions, the great contribution to the total variance of the output parameter is made by both the temperature and time of the sulfation process. This is indicated by the high variance ratios F for the main effects, which are also called the influence efficiencies. The P data from Table 3 are interpreted similarly. The influence of a source of variance on the

output parameter is considered to be statistically significant if the significance level is lower than a specified critical value.

The dependence of the sulfur content Y_1 in xylan sulfates on the process variables is approximated by the regression equation:

$$Y_1 = -173.175 + 3.635X_1 + 12.11X_2 - 0.0185X_1^2 + 0.022X_1X_2 - 4.1667X_2^2 \quad (1)$$

The predictive properties of Equation (1) are illustrated in Figure 2, which compares the output parameters Y_1 obtained in the experiment and calculated using Equation (1). The straight line corresponds to the calculated Y_1 values and dots are the results of the observations. The proximity of the experimental points to the straight line is indicative of the good predictive properties of Equation (1).

The approximation quality is additionally characterized by the determination coefficient

R^2_{adj} . In our case, this coefficient is $R^2_{adj} = 92.0\%$, which proves the high quality of the approximation. This evidences for the adequacy of Equation (1) to the results of the observation and makes it possible to use this equation as a mathematical model of the investigated process.

The mathematical model was used to plot the output parameter Y_1 as a function of the variable factors X_1 and X_2 in the form of a response surface (Fig. 3).

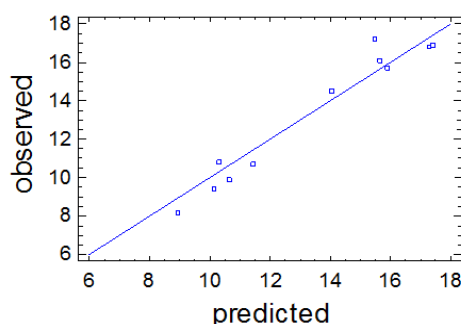


Figure 2: Observation (dots) versus prediction by mathematical model (1) for output parameter Y_1

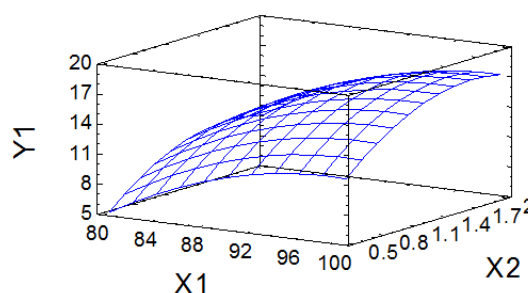


Figure 3: Response surface of sulfur content (wt%) in sulfated xylan as a function of sulfation time and temperature

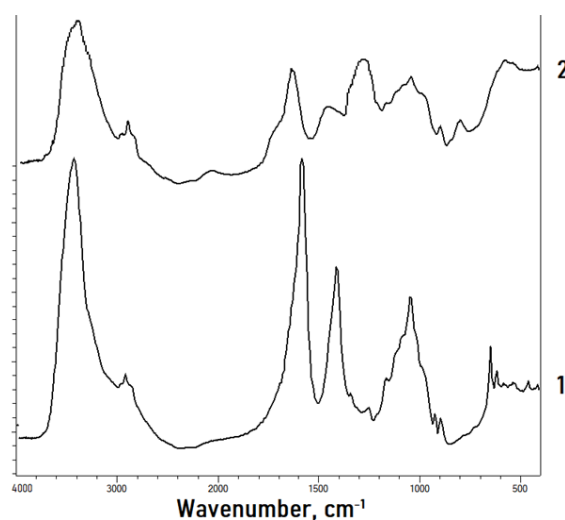


Figure 4: FTIR spectra of (1) xylan and (2) xylan sulfate

According to the calculation using mathematical model (1), the maximum predicted sulfur content (17.6 wt%) in the investigated factor space range is obtained at the point corresponding to a process temperature of 99 °C and a process time of 1.72 h.

The incorporation of a sulfate group into the xylan macromolecule was proven by the IR and NMR spectroscopy data. The presence of a sulfate group in the sulfated xylan molecule was proven

by IR spectroscopy (Fig. 4). The high-intensity absorption band at 1257 cm^{-1} corresponds to the asymmetric stretching vibrations of the sulfate group and the band at 1020 cm^{-1} is related to the symmetric stretching vibrations of the SO_2 group. The band with a maximum at 802 cm^{-1} belongs to the stretching vibrations of the C–O–S group. The low-frequency absorption band at 578 cm^{-1} refers to the bending vibrations of the SO_2 group. These

data are consistent with the results reported in the literature.¹²

Figures 5 and 6 present the NMR spectra of xylan sulfate. They contain the absorption bands of all five carbon atoms of β -D-xylose. The additional signals observed point out the modification of the xylan macromolecule. In particular, the high-intensity signal at 97.6 ppm belongs to the C3 atom of the β -D-xylopyranose units linked to the sulfate group. The presence of

sulfate groups at the C2 and C3 atoms in a quite a few β -D-xylopyranose units of xylan sulfate is revealed by the appearance of additional strong signals from the neighboring C1 carbon atoms at 100.2 ppm and C4 atoms at 72.8 ppm. The chemical shifts of the C1 and C4 atoms of the β -D-xylopyranose units of xylan sulfate, which contain no sulfate groups, are 101.7 and 73.8 ppm, respectively.¹²

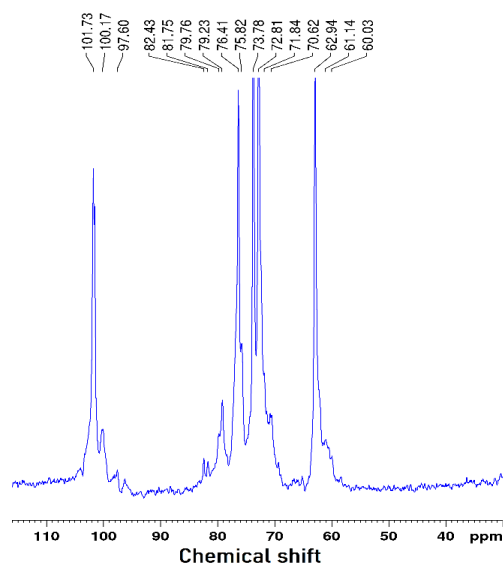


Figure 5: ^{13}C NMR spectrum of xylan sulfate

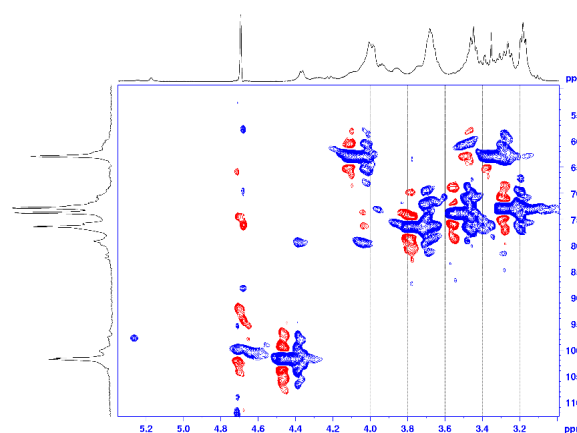


Figure 6: HSQC NMR spectrum of xylan sulfate

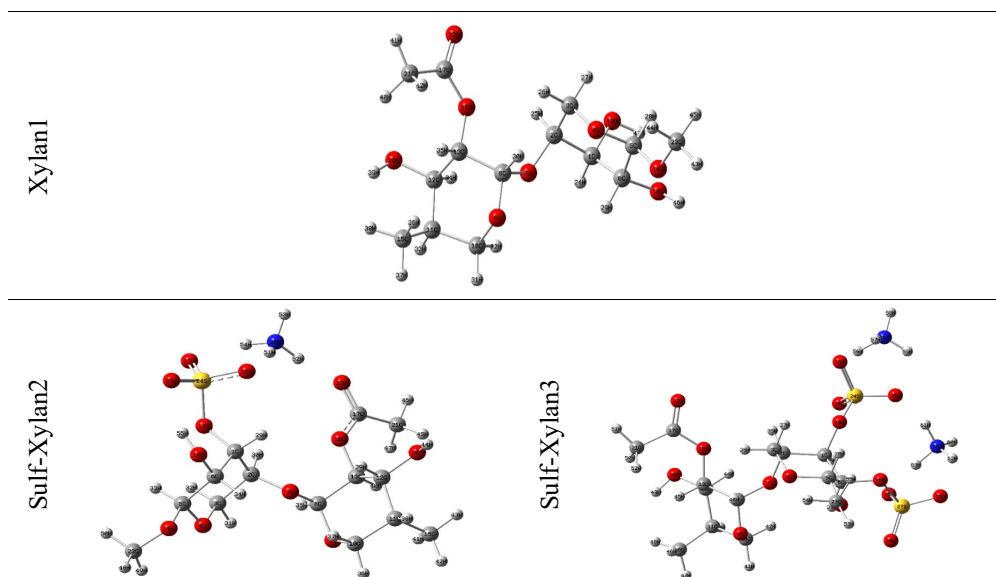


Figure 7: Molecular geometry of xylan and xylan sulfates

Optimizing the structures of xylan and sulfated xylan

The DFT is widely used in the theoretical studies of the structures of polysaccharides and their derivatives.²⁶⁻²⁹ In this case, the

MP2(fc)/aug-cc-pVDZ,²⁸ B3LYP/6-311+G(2d,p)//B3LYP/6-311G(d,p),³⁰ B3LYP/6-31 G + (d),³¹ M05-2X/6-31 + G*,³² and other levels of theory are used. Previously, theoretical calculations for xylan were made for the

processes of dissolution in an ionic liquid³³ and destruction during pyrolysis.³⁴

The first step to understanding the structural and functional properties of polysaccharides should be to optimize and elucidate the conformations of their monomer units.³⁵ At the first stage of our theoretical study, we optimized the dimer structure for xylan and its sulfated derivatives using the B3LYP/6–311G(d, p) DFT calculation. The optimized structures are shown in Figure 7 and described in Table 4.

It can be seen from Figure 7 and Table 4 that the incorporation of sulfate groups into the xylan dimer structure affects almost all bond lengths and bond angles. In particular, in the initial xylan, the C1–C2 bond length is 1.5383 Å; when one sulfate group is introduced into the xylan structure, this length decreases to 1.5367 Å and, after adding the second sulfate group, it increases to 1.5379 Å. A different picture is observed for the C1–C6 bond: its lengths in the initial xylan, xylan monosulfate, and xylan disulfate are

1.5349, 1.5406, and 1.5370 Å, respectively. The C1–O19 bond length increases from 1.4239 to 1.4725 Å with the growing content of sulfate groups in the xylan molecule. The C2–O7 bond lengths in the initial xylan and its mono- and disulfates are 1.4410, 1.4379, and 1.4337 Å, respectively. A similar dynamics is observed for the C3–O4 bond lengths: in the initial xylan and its mono- and disulfate, the values are 1.4306, 1.4175, 1.4231 Å, respectively. The C8–O9 bond lengths decrease almost uniformly from 1.4059 to 1.4012 Å with an increase in the content of sulfate groups in the xylan structure. The shortest length in the initial xylan corresponds to the C17–O22 bond: 1.2094 Å, which is consistent with the data on different carbonyl compounds.^{36,37} The longest bond (1.5491 Å) is C8–C13. In the ammonium salts of sulfated xylyns, the minimum length corresponds to the N–H bond in the ammonium cation, which is consistent with the data reported previously.^{38–40}

Table 4
Selected bond parameters of xylan and xylan sulfates

Bond length (Å)					
Xylan1		Sulf-Xylan2		Sulf-Xylan3	
Bond	Length	Bond	Length	Bond	Length
C1-C2	1.5383	C1-C2	1.5367	C1-C2	1.5379
C1-C6	1.5349	C1-C6	1.5406	C1-C6	1.5370
C1-O19	1.4239	C1-O19	1.4472	C1-O19	1.4725
C2-C3	1.5276	C2-C3	1.5311	C2-C3	1.5278
C2-O7	1.4410	C2-O7	1.4379	C2-O7	1.4337
C3-O4	1.4306	C3-O4	1.4175	C3-O4	1.4231
O4-C5	1.4248	O4-C5	1.4398	O4-C5	1.4361
C5-C6	1.5307	C5-C6	1.5371	C5-C6	1.5357
C5-O14	1.3941	C5-O14	1.3834	C5-O14	1.3794
C6-O18	1.4277	C6-O18	1.4087	C6-O18	1.4286
O7-C8	1.4125	O7-C8	1.407	O7-C8	1.4170
C8-O9	1.4059	C8-O9	1.4035	C8-O9	1.4012
C8-C13	1.5491	C8-C13	1.5471	C8-C13	1.5476
O9-C10	1.4373	O9-C10	1.4409	O9-C10	1.4392
C10-C11	1.5361	C10-C11	1.5385	C10-C11	1.5365
C11-C12	1.5475	C11-C12	1.5506	C11-C12	1.5484
C12-C13	1.5368	C12-C13	1.5275	C12-C13	1.5369
C12-O20	1.4281	C12-O20	1.4321	C12-O20	1.4289
C13-O16	1.4374	C13-O16	1.4497	C13-O16	1.4391
O16-C17	1.3649	O16-C17	1.3432	O16-C17	1.3638
C17-O22	1.2094	C17-O22	1.2253	C17-O22	1.2102
		O19-S24	1.6769	O19-S24	1.6199
		S24-O25	1.4678	S24-O25	1.4529
		S24-O26	1.5112	S24-O26	1.5627
		S24-O27	1.4808	S24-O30	1.4812
		N28-H51	1.0753	S27-O28	1.4596
		N28-H52	1.0396	S27-O29	1.5166

		N28-H53	1.0181	S27-O32	1.4847
		N28-H54	1.029	N31-H56	1.4999
				N31-H57	1.0177
				N31-H58	1.0176
				N31-H59	1.0191
				N33-H60	1.0168
				N33-H61	1.0345
				N33-H62	1.0345
				N33-H63	1.0750
Bond angle (°)					
C1-O19-H47	106.9277	C1-O19-S24	120.184	C1-O19-S24	120.5146
C2-O7-C8	122.6848	C2-O7-C8	116.9027	C2-O7-C8	122.8252
C3-O4-C5	111.4253	C3-O4-C5	113.4742	C3-O4-C5	113.7071
C5-O14-C23	114.6583	C5-O14-C23	114.5876	C5-O14-C23	114.8169
C6-O18-H46	107.7052	C6-O18-H55	111.2588	C6-O18-S27	116.8849
C8-O9-C10	113.7291	C8-O9-C10	113.117	C8-O9-C10	113.632
C12-O20-H39	109.1055	C12-O20-H44	109.2325	C12-O20-H49	113.632
C13-O16-C17	125.1565	C13-O16-C17	123.7566	C13-O16-C17	125.2985
O16-C17-C21	119.1653	O16-C17-C21	120.4062	O16-C17-C21	119.1515
O16-C17-O22	117.6002	O16-C17-O22	117.7102	O16-C17-O22	117.5824
		O19-S24-O25	105.2898	O19-S24-O25	110.1848
		O19-S24-O26	104.7124	O19-S24-O26	100.1665
		O19-S24-O27	101.9714	O19-S24-O30	107.5167
		O25-S24-O26	114.0589	O25-S24-O26	111.0513
		O25-S24-O27	117.3254	O25-S24-O30	118.3508
		O26-S24-O27	111.6246	O26-S24-O30	107.9765
		H51-N28-H53	111.4693	H56-N31-H57	113.5836
		H52-N28-H54	112.4913	H56-N31-H59	105.3502
		H53-N28-H54	110.0046	H57-N31-H58	108.106
				O18-S27-O28	107.7957
				O18-S27-O29	103.3261
				O28-S27-O29	113.8032
				O28-S27-O32	118.1546
				H60-N33-H61	112.2696
				H60-N33-H62	112.6111
				H60-N33-H63	113.6528

According to the data listed in Table 4, the largest bond angle in the initial xylan is observed for the C13–O16–C17 bond: 125.1565°. The smallest bond angle corresponds to the C1–O19–H47 bond: 106.9277°. The C8–O9–C10 angle for the initial xylan and its sulfated derivatives ranges within 113.1–113.8°. The incorporation of one and two sulfate groups into the xylan molecule leads to a change in the C13–O16–C17 bond angle to 123.7566 and 125.2985°, respectively. The angles of the H–N–H bonds lie in the range of 108.1–113.7°.

HOMO–LUMO analysis

Molecular orbitals and their properties, including energy, are necessary for understanding the fundamental characteristics and predicting properties of substances, for example, the most reactive sites in π -electron systems.^{41,42} The highest occupied molecular orbital–the lowest

unoccupied molecular orbital (HOMO–LUMO) analysis is an effective tool widely used to interpret the optical and electronic properties of organic compounds.⁴³ The knowledge of the HOMO–LUMO and their properties, specifically, the energies, provides valuable assistance in measuring the chemical reactivity of molecules. During molecular interactions, the LUMO accepts electrons and its energy corresponds to electron affinity (EA), while the HOMO serves as an electron donor and its energy is related to the ionization potential (IP).^{41,42}

The HOMO–LUMO energy gap explains the intramolecular charge-transfer interactions and is used to determine the properties of electron transport in molecules.⁴¹ A molecule with a wide boundary orbital gap (the HOMO–LUMO energy gap) is characterized by the low chemical activity and high kinetic stability.⁴⁴ Substances with a wide HOMO–LUMO energy gap are stable.⁴⁵

Figure 8 shows the molecular orbital energy diagram of xylan and xylan sulfates. The HOMO–LUMO energy gap in the initial xylan is wider than in its sulfated derivatives, which explains its higher stability as compared with xylan sulfates or other derivatives.⁴⁶ A decrease in

the HOMO-LUMO energy gap after the incorporation of sulfate groups into the molecule of a natural substance was also observed in lignin,⁴⁷ monolignols,⁴⁸ DEAE cellulose,⁴⁹ chitosan,⁵⁰ galactomannan,⁵¹ starch,⁵² betulin,⁵³ etc.

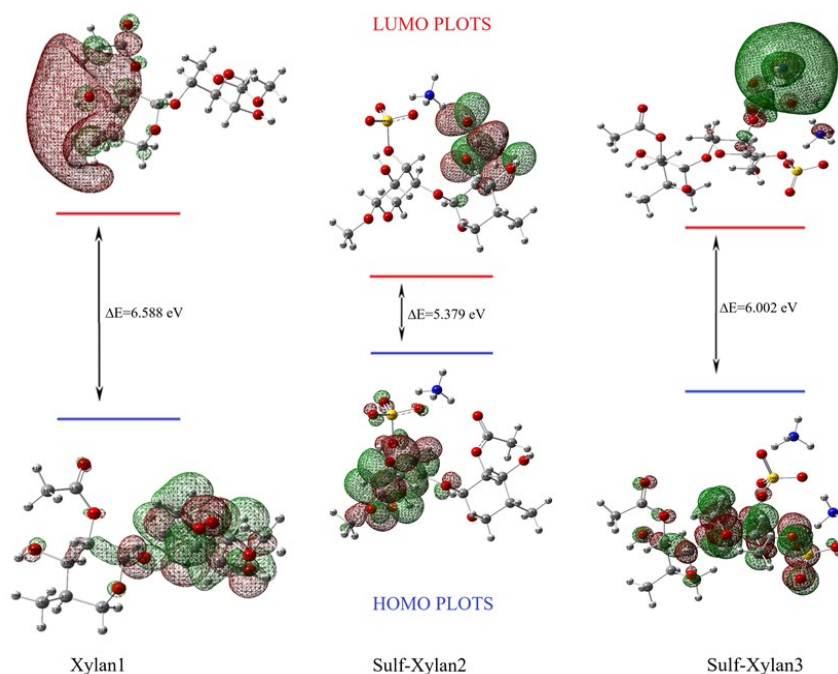


Figure 8: Molecular orbital energy diagrams for xylan and xylan sulfates

Table 5
Some reactivity descriptors calculated for xylan and xylan sulfates

Parameter	Value (eV)		
	Xylan1	Sulf-Xylan2	Sulf-Xylan3
E_{LUMO}	-0.4944	-1.2093	-0.9581
E_{HOMO}	-7.0829	-6.5887	-6.9609
ΔE	6.5884	5.3794	6.0028
μ	-3.7886	-3.8990	-3.9595
EA	0.4944	1.2093	0.9581
IP	7.0829	6.5887	6.9609
σ_o	0.1518	0.1859	0.1666
ζ	0.3036	0.3718	0.3332
η	3.2942	2.6897	3.0014
χ	3.7886	3.8990	3.9595
N	0.4590	0.3539	0.3829
ω	2.1786	2.8260	2.6117
ΔN_{max}	1.1501	1.4496	1.3192

E_{LUMO} – LUMO energy, E_{HOMO} – HOMO energy, ΔE – energy gap, μ – chemical potential, EA – electron affinity, IP – ionization potential, σ_o – optical softness, ζ – chemical softness, η – chemical hardness, χ – electronegativity, N – nucleophilicity index, ω – electrophilicity index, and ΔN_{max} – maximum charge transfer index

The energies of the frontier orbitals are important parameters of the electronic structure of a molecule. The HOMO and LUMO energies,

along with the other general descriptors of the reactivity,^{54,55} including ionization potential I, electron affinity A, electronegativity χ , chemical

hardness η , chemical softness s , chemical potential μ , electrophilicity ω , and nucleophilicity N , calculated from the HOMO and LUMO energies are given in Table 5.

According to the data given in Table 5, with an increase in the number of sulfate groups in the xylan molecule, the chemical potential changes from -3.7886 to -3.9595 and the electronegativity changes from 3.7886 to 3.9595 . The electron affinity of the initial xylan is 0.4944 , while for the xylan mono- and disulphate, its values are 1.2093 and 0.9581 , respectively. The chemical softness

values for the initial xylan and its mono- and disulfate are 0.3036 , 0.3718 , and 0.3332 , respectively. The maximum charge transfer indices for the initial xylan and its mono- and disulfate are 1.1501 , 1.4496 , and 1.3192 , respectively. It can be seen that most parameters (ΔE , EA , IP , σ_o , ζ , η , N , ω , and $\Delta N_{\max}$) change nonlinearly with a uniform increase in the number of sulfate groups in the xylan molecule.

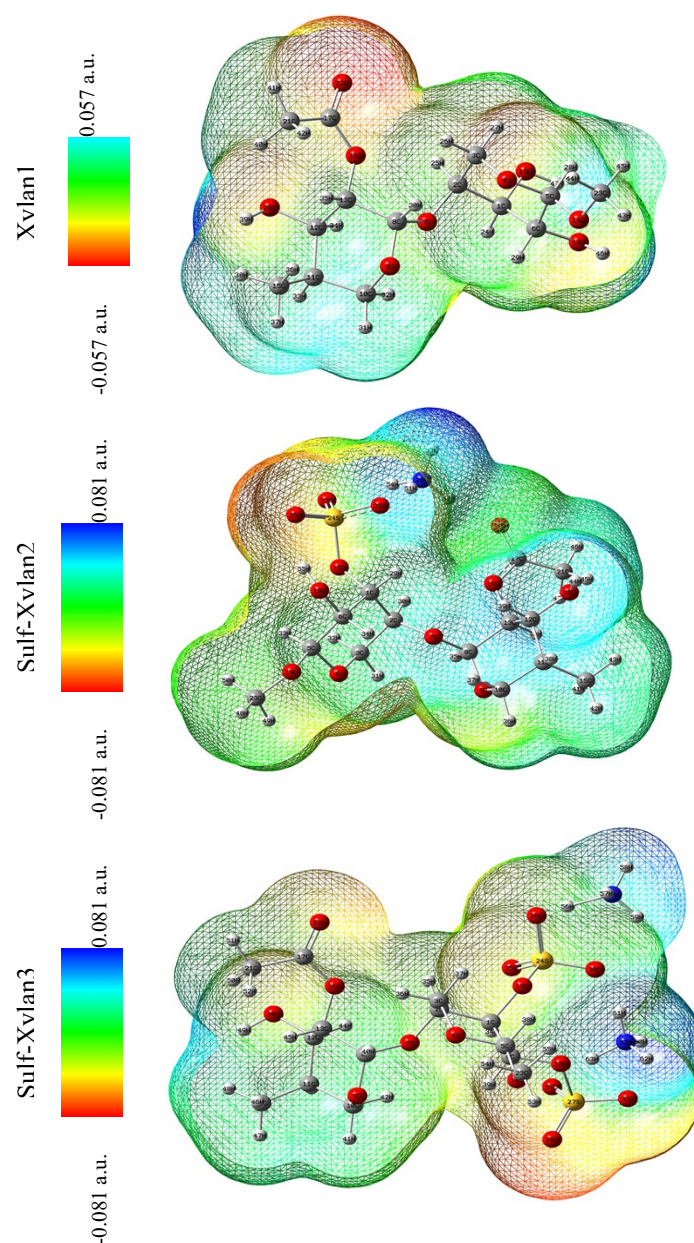


Figure 9: Molecular electrostatic potential maps of xylan and xylan sulfates

Molecular electrostatic potential

The common electrostatic effect induced by the distribution of the total charge of a molecule at a point in its vicinity is known as the molecular electrostatic potential (MEP). MEP relates the total charge distribution to dipole moments, partial charges, electronegativity, and a reactive site of a molecule.⁵⁶ It provides a tool to visualize the understanding of the relative polarity of a molecule and serves as a quantity useful for explaining the hydrogen bonding, reactivity, and structure–activity interplay in molecules, including biomolecules and drug molecules.⁵⁷ Different MEP values on the surface are reflected by different colors; the red color marks areas with the most negative electrostatic potential; the blue color, areas with the most positive electrostatic potential; and the green color, zero-potential areas. The negative electrostatic potential corresponds to the attraction of a proton by the total electron density in a molecule (shades of red) and the positive electrostatic potential corresponds to the repulsion of a proton by atomic nuclei (shades of blue).⁵⁸ It can be seen in Figure 9 that the red color in the MEP maps is localized mainly over oxygen atoms, while the blue color, over nitrogen atoms in the ammonium cation. The areas above carbon are mainly colored in shades of green.

Fukui functions

The use of the Fukui functions, along with other theoretical methods, finds wide application in predicting the reactivity of chemicals.^{59,60} The Fukui functions are measures of the sensitivity of a particular area in an N -electron system to an external chemical potential.^{61,62} The Fukui functions are used to determine atomic centers with the high regional electrophilic reactivity, local nucleophilic reactivity, and local radical reactivity in a molecule. According to the definition given by Kollandaivel *et al.*,⁶³ the Fukui functions $f^+(r)$, $f^-(r)$, and $f^0(r)$ are calculated as:

$$f^+(r) = q_{(N+1)}(r) - q_{(N)}(r) \text{ for the nucleophilic attack} \quad (2)$$

$$f^-(r) = q_{(N)}(r) - q_{(N-1)}(r) \text{ for the electrophilic attack} \quad (3)$$

$$f^0(r) = 1/2 [q_{(N+1)}(r) - q_{(N-1)}(r)] \text{ for the radical attack} \quad (4)$$

In the above equations, $q(r)$ is the atomic charge obtained from the electrostatically derived charge and the Mulliken population analysis for neutral (N), anionic ($N-1$), and cationic ($N+1$)

chemical structures at the n^{th} atomic site and the plus, minus, and zero superscripts correspond to the nucleophilic, electrophilic, and radical attack, respectively. The data on the Fukui functions are listed in Table 6. The high Fukui function value for an atom indicates that the molecular reactivity is high as well.⁶⁴ As compared to these three attacks, the molecule is more nucleophilic. The dual identifier $\Delta f(r)$ in the last row of Table 6 is the difference between the signs and nucleophilic and electrophilic attacks in a particular region, which is calculated using the equation:

$$\Delta f(r) = f^+(r) - f^-(r) \quad (5)$$

In the case of $\Delta f(r) > 0$, the site can be considered as a nucleophilic attack and, at $\Delta f(r) < 0$, the site can be considered as an electrophilic attack.⁶⁵

It can be seen from Table 6 that, in the initial xylan, the nucleophilic effect weakens in the series 17(C) > 22(O) > 16(O) > 21(C) > 42(H) > 40(H) > 41(H) > 39(H) > 37(H) > 38(H). The electrophilic effect weakens in the series 4(O) > 7(O) > 2(C) > 5(C) > 3(C) > 6(C) > 18(O) > 8(C) > 28(H) > 20(O) > 13(C) > 25(H) > 19(O) > 14(O) > 27(H) > 30(H) > 1(C) > 9(O) > 24(H) > 29(H) > 12(C) > 23(C) > 10(C) > 46(H) > 26(H) > 33(H) > 45(H) > 11(C) > 47(H) > 44(H) > 34(H) > 32(H) > 15(C) > 31(H) > 43(H) > 35(H) > 36(H).

In xylan monosulfate, a decrease in the nucleophilic effect is observed in the series 17(C) > 22(O) > 16(O) > 47(H) > 45(H) > 21(C) > 53(H) > 46(H) > 54(H) > 28(N) > 39(H) > 37(H) > 52(H) > 38(H) > 42(H) > 44(H) > 51(H) > 36(H) > 13(C) > 10(C) > 12(C) > 11(C) > 9(O). The electrophilicity of xylan monosulfate decreases in the series 18(O) > 4(O) > 27(O) > 30(H) > 6(C) > 33(H) > 5(C) > 29(H) > 55(H) > 34(H) > 32(H) > 26(O) > 31(H) > 3(C) > 14(O) > 2(C) > 25(O) > 20(O) > 48(H) > 1(C) > 19(O) > 7(O) > 23(C) > 50(H) > 49(H) > 24(S) > 43(H) > 35(H) > 41(H) > 40(H) > 15(C) > 8(C).

In xylan disulfate, a decrease in the nucleophilic effect is observed in the series 57(H) > 58(H) > 17(C) > 59(H) > 31(N) > 60(H) > 24(S) > 25(O) > 22(O) > 50(H) > 52(H) > 19(O) > 26(O) > 33(N) > 56(H) > 30(O) > 21(C) > 61(H) > 62(H) > 16(O) > 63(H) > 1(C) > 51(H) > 39(H). The electrophilicity of xylan monosulfate decreases in the series 29(O) > 18(O) > 28(O) > 4(O) > 7(O) > 32(O) > 20(O) > 35(H) > 38(H) > 37(H) > 27(S) > 9(O) > 2(C) > 3(C) > 40(H) > 13(C) > 8(C) > 36(H) > 5(C) > 55(H) > 6(C) >

14(O) > 45(H) > 43(H) > 53(H) > 23(C) > 12(C) > 41(H) > 54(H) > 44(H) > 10(C) > 48(H) > 11(C) > 34(H) > 49(H) > 46(H) > 42(H) > 47(H) > 15(C).

Thus, when a sulfate group is incorporated into a xylan molecule, the number of atoms naturally increases, both with the nucleophilic and electrophilic effects.

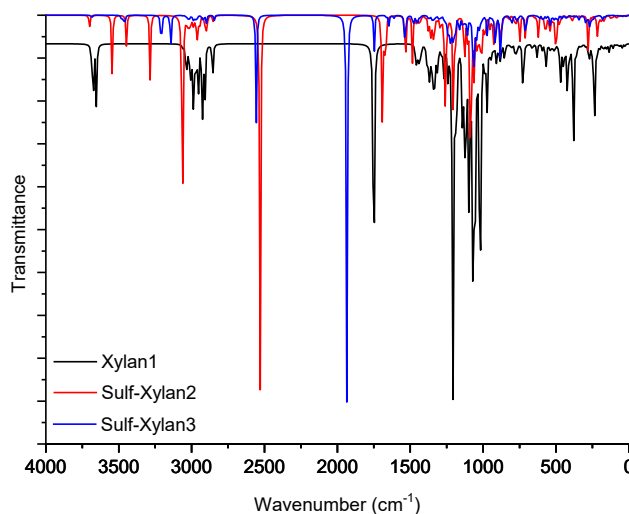


Figure 10: FTIR spectra of xylan and xylan sulfates

Theoretical FTIR spectroscopy

The spectroscopy techniques are wide-spread in the analysis of various polysaccharides.^{66,67} They help to accurately identify the structure and, consequently, to make an assumption about properties of polysaccharides.⁶⁸ Along with the experimental spectroscopy methods, the theoretical modeling of spectroscopic properties is being intensively developed.^{26,28}

The theoretical vibration characteristics of the initial and sulfated xylan are shown in Figure 10 and given in Table 7.

OH-group vibrations

According to the data from Table 7, in the theoretical spectra of the initial xylan, the absorption bands of the hydroxyl group are observed at 3684, 3673, and 3652 cm^{-1} (νOH). The incorporation of a sulfate group weakly affects the spectroscopic characteristics of the hydroxyl group vibrations.

CH-group vibrations

In the theoretical FTIR spectrum, the absorption bands corresponding to the CH group vibrations are observed in the region of 3062–2854 cm^{-1} (νCH). The incorporation of a sulfate group into the xylan molecule does not affect significantly the CH group vibration either.

CO-group vibrations

The C–O group vibrations in the initial xylan are observed in the FTIR spectra at 1208, 1057, 1128, and 1099 cm^{-1} and the vibrations of C=O groups, at 1750 cm^{-1} . The sulfate group incorporated into the xylan molecule has a minor effect on the C–O and C=O groups vibrations.

SO-group vibrations

The vibrations of the sulfate group are observed at 1243, 1227, 1071, 1063, 915, and 881 cm^{-1} . The results obtained are consistent with the data reported previously.⁶⁹

Table 6
Condensed Fukui functions for xylan and xylan sulfates

Xylan1					Sulf-Xylan2					Sulf-Xylan3				
Atoms	f_r^-	f_r^+	f_r^0	$\Delta f(r)$	Atoms	f_r^-	f_r^+	f_r^0	$\Delta f(r)$	Atoms	f_r^-	f_r^+	f_r^0	$\Delta f(r)$
1(C)	0.0157	0.0001	0.0079	-0.0155	1(C)	0.0146	-0.0007	0.0070	-0.0153	1(C)	0.0061	0.0112	0.0086	0.0051
2(C)	0.0496	0.0004	0.0250	-0.0492	2(C)	0.0174	-0.0015	0.0079	-0.0188	2(C)	0.0150	0.0005	0.0078	-0.0145
3(C)	0.0466	0.0003	0.0235	-0.0463	3(C)	0.0250	0.0024	0.0137	-0.0225	3(C)	0.0152	0.0011	0.0081	-0.0141
4(O)	0.2882	0.0000	0.1441	-0.2881	4(O)	0.1140	0.0061	0.0600	-0.1078	4(O)	0.0581	0.0069	0.0325	-0.0512
5(C)	0.0489	0.0000	0.0244	-0.0489	5(C)	0.0317	0.0018	0.0167	-0.0299	5(C)	0.0120	0.0013	0.0067	-0.0106
6(C)	0.0441	0.0000	0.0220	-0.0440	6(C)	0.0356	0.0018	0.0187	-0.0338	6(C)	0.0116	0.0032	0.0074	-0.0084
7(O)	0.1398	0.0004	0.0701	-0.1394	7(O)	0.0167	0.0042	0.0105	-0.0125	7(O)	0.0396	0.0035	0.0215	-0.0361
8(C)	0.0338	0.0036	0.0187	-0.0301	8(C)	0.0047	0.0045	0.0046	-0.0001	8(C)	0.0143	0.0029	0.0086	-0.0114
9(O)	0.0152	0.0018	0.0085	-0.0134	9(O)	0.0145	0.0150	0.0147	0.0006	9(O)	0.0268	0.0084	0.0176	-0.0184
10(C)	0.0032	0.0004	0.0018	-0.0028	10(C)	0.0033	0.0071	0.0052	0.0039	10(C)	0.0062	0.0031	0.0046	-0.0031
11(C)	0.0029	0.0017	0.0023	-0.0013	11(C)	0.0028	0.0060	0.0044	0.0033	11(C)	0.0051	0.0027	0.0039	-0.0023
12(C)	0.0122	0.0069	0.0095	-0.0053	12(C)	0.0005	0.0042	0.0023	0.0037	12(C)	0.0070	0.0018	0.0044	-0.0052
13(C)	0.0338	0.0091	0.0214	-0.0247	13(C)	0.0049	0.0094	0.0071	0.0045	13(C)	0.0174	0.0038	0.0106	-0.0136
14(O)	0.0174	0.0000	0.0087	-0.0174	14(O)	0.0235	0.0036	0.0136	-0.0199	14(O)	0.0126	0.0043	0.0084	-0.0083
15(C)	0.0007	0.0003	0.0005	-0.0004	15(C)	0.0046	0.0039	0.0042	-0.0007	15(C)	0.0051	0.0043	0.0047	-0.0008
16(O)	0.0237	0.1153	0.0695	0.0917	16(O)	-0.0089	0.0651	0.0281	0.0740	16(O)	0.0113	0.0196	0.0154	0.0082
17(C)	0.0033	0.4585	0.2309	0.4552	17(C)	0.0032	0.2075	0.1054	0.2044	17(C)	0.0136	0.0803	0.0469	0.0666
18(O)	0.0353	0.0000	0.0177	-0.0353	18(O)	0.1398	0.0102	0.0750	-0.1296	18(O)	0.0580	-0.0008	0.0286	-0.0588
19(O)	0.0190	0.0000	0.0095	-0.0189	19(O)	0.0172	0.0042	0.0107	-0.0130	19(O)	-0.0003	0.0172	0.0084	0.0175
20(O)	0.0278	0.0026	0.0152	-0.0253	20(O)	0.0096	-0.0064	0.0016	-0.0161	20(O)	0.0350	0.0050	0.0200	-0.0300
21(C)	0.0008	0.0654	0.0331	0.0646	21(C)	0.0052	0.0521	0.0286	0.0469	21(C)	0.0108	0.0234	0.0171	0.0127
22(O)	0.0091	0.2467	0.1279	0.2375	22(O)	0.0096	0.1652	0.0874	0.1556	22(O)	0.0522	0.0755	0.0639	0.0233
23(C)	0.0047	0.0000	0.0024	-0.0047	23(C)	0.0158	0.0039	0.0099	-0.0119	23(C)	0.0096	0.0041	0.0068	-0.0055
24(H)	0.0129	0.0000	0.0065	-0.0129	24(S)	0.0186	0.0100	0.0143	-0.0086	24(S)	0.0028	0.0340	0.0184	0.0312
25(H)	0.0233	0.0002	0.0117	-0.0231	25(O)	0.0419	0.0248	0.0333	-0.0170	25(O)	0.0087	0.0338	0.0212	0.0251
26(H)	0.0035	0.0012	0.0023	-0.0023	26(O)	0.0234	-0.0008	0.0113	-0.0242	26(O)	0.0113	0.0270	0.0191	0.0157
27(H)	0.0172	0.0000	0.0086	-0.0172	27(O)	0.0581	0.0088	0.0335	-0.0493	27(S)	0.0284	0.0078	0.0181	-0.0205
28(H)	0.0289	0.0000	0.0145	-0.0289	28(N)	0.0058	0.0228	0.0143	0.0170	28(O)	0.0725	0.0192	0.0458	-0.0533
29(H)	0.0064	0.0000	0.0032	-0.0064	29(H)	0.0246	-0.0043	0.0101	-0.0288	29(O)	0.0639	0.0027	0.0333	-0.0613
30(H)	0.0174	0.0005	0.0090	-0.0169	30(H)	0.0292	-0.0103	0.0095	-0.0396	30(O)	0.0118	0.0254	0.0186	0.0135
31(H)	0.0003	0.0001	0.0002	-0.0003	31(H)	0.0269	0.0031	0.0150	-0.0238	31(N)	0.0016	0.0518	0.0267	0.0502
32(H)	0.0007	0.0001	0.0004	-0.0006	32(H)	0.0309	0.0060	0.0185	-0.0249	32(O)	0.0423	0.0105	0.0264	-0.0318
33(H)	0.0019	0.0005	0.0012	-0.0014	33(H)	0.0367	0.0035	0.0201	-0.0332	33(N)	0.0095	0.0244	0.0170	0.0149

34(H)	0.0015	0.0007	0.0011	-0.0008	34(H)	0.0281	0.0022	0.0151	-0.0258	34(H)	0.0087	0.0068	0.0077	-0.0019
35(H)	0.0019	0.0018	0.0019	-0.0001	35(H)	0.0076	0.0054	0.0065	-0.0022	35(H)	0.0273	-0.0015	0.0129	-0.0287
36(H)	0.0002	0.0001	0.0001	-0.0001	36(H)	0.0104	0.0152	0.0128	0.0047	36(H)	0.0132	0.0024	0.0078	-0.0108
37(H)	0.0001	0.0001	0.0001	0.0001	37(H)	-0.0040	0.0081	0.0021	0.0121	37(H)	0.0213	0.0001	0.0107	-0.0212
38(H)	0.0001	0.0001	0.0001	0.0001	38(H)	0.0081	0.0157	0.0119	0.0075	38(H)	0.0215	-0.0006	0.0105	-0.0221
39(H)	0.0013	0.0019	0.0016	0.0005	39(H)	-0.0048	0.0090	0.0021	0.0138	39(H)	0.0070	0.0083	0.0077	0.0012
40(H)	0.0002	0.0367	0.0184	0.0365	40(H)	0.0093	0.0083	0.0088	-0.0010	40(H)	0.0174	0.0037	0.0105	-0.0137
41(H)	0.0001	0.0044	0.0022	0.0043	41(H)	0.0024	0.0002	0.0013	-0.0022	41(H)	0.0134	0.0087	0.0111	-0.0047
42(H)	0.0002	0.0380	0.0191	0.0378	42(H)	0.0085	0.0158	0.0122	0.0074	42(H)	0.0020	0.0006	0.0013	-0.0014
43(H)	0.0002	0.0000	0.0001	-0.0002	43(H)	0.0078	0.0031	0.0054	-0.0047	43(H)	0.0144	0.0078	0.0111	-0.0066
44(H)	0.0009	0.0000	0.0004	-0.0009	44(H)	0.0075	0.0148	0.0111	0.0073	44(H)	0.0052	0.0016	0.0034	-0.0036
45(H)	0.0014	0.0000	0.0007	-0.0014	45(H)	0.0045	0.0556	0.0301	0.0511	45(H)	0.0132	0.0063	0.0098	-0.0069
46(H)	0.0028	0.0000	0.0014	-0.0028	46(H)	0.0093	0.0351	0.0222	0.0258	46(H)	0.0031	0.0016	0.0023	-0.0015
47(H)	0.0010	0.0000	0.0005	-0.0010	47(H)	0.0044	0.0679	0.0362	0.0634	47(H)	0.0113	0.0101	0.0107	-0.0011
					48(H)	0.0224	0.0070	0.0147	-0.0154	48(H)	0.0094	0.0067	0.0080	-0.0027
					49(H)	0.0130	0.0024	0.0077	-0.0106	49(H)	0.0138	0.0120	0.0129	-0.0018
					50(H)	0.0151	0.0041	0.0096	-0.0110	50(H)	0.0080	0.0273	0.0176	0.0193
					51(H)	0.0013	0.0082	0.0048	0.0069	51(H)	0.0145	0.0174	0.0159	0.0029
					52(H)	0.0024	0.0120	0.0072	0.0096	52(H)	0.0086	0.0273	0.0179	0.0187
					53(H)	0.0115	0.0494	0.0305	0.0378	53(H)	0.0140	0.0080	0.0110	-0.0060
					54(H)	0.0032	0.0236	0.0134	0.0205	54(H)	0.0082	0.0036	0.0059	-0.0046
					55(H)	0.0309	0.0035	0.0172	-0.0274	55(H)	0.0115	0.0020	0.0067	-0.0095
										56(H)	0.0020	0.0156	0.0088	0.0136
										57(H)	0.0022	0.0722	0.0372	0.0700
										58(H)	0.0076	0.0769	0.0423	0.0693
										59(H)	0.0005	0.0588	0.0296	0.0582
										60(H)	0.0134	0.0565	0.0350	0.0430
										61(H)	0.0037	0.0152	0.0094	0.0115
										62(H)	0.0057	0.0166	0.0111	0.0109
										63(H)	0.0033	0.0085	0.0059	0.0052

Table 7
Some important wavenumbers (cm⁻¹) determined experimentally and theoretically (scaled by a factor of 0.9642) for xylan and xylan sulfates

Xylan1		Sulf-Xylan2		Sulf-Xylan3	
Assignment	Theor.	Assignment	Theor.	Assignment	Theor.
νO-H	3684, 3673, 3652	νO-H	3700, 3544	νO-H	3684
νC-H (aliphatic)	3062-2854	νN-H	3446, 3284, 3062, 2529	νN-H	3480, 3431, 3430, 3349, 3207, 3143, 2556, 1934
νC=O	1750	νC-H (aliphatic)	3067-2849	νC-H (aliphatic)	3062-2844
νO-C (adjacent to the carbonyl group)	1208, 1057	νC=O	1693	νC=O	1746
νO-C (connecting the rings)	1128, 1099	δN-H	1693, 1676, 1665, 1533, 1483	δN-H	1662, 1642, 1614, 1610, 1535, 1479, 1452
		νO-C (adjacent to the carbonyl group)	1255, 1040	νO-C (adjacent to the carbonyl group)	1209, 974
		νO-C (connecting the rings)	1124, 1105	νO-C (connecting the rings)	1113, 1104
		νS-O	1203, 1087, 922	νS-O	1243, 1227, 1071, 1063, 915, 881

CONCLUSION

Sulfation of birch xylan with sulfamic acid in pyridine was carried out. The incorporation of the sulfate group was confirmed by the elemental analysis and the IR and NMR spectroscopy investigations. It was found, in particular, that the characteristic absorption bands corresponding to the sulfate group vibrations appear in the IR spectra. In the NMR spectra, in addition to the peaks corresponding to the initial xylan, the carbon peaks typical of xylan sulfate were identified. The numerical optimization of the sulfation process was carried out to establish the process conditions that ensure the maximum sulfur content in xylan sulfate. The xylan and xylan sulfate molecular structure, electron localization, and other important parameters were established using the theoretical methods. The proposed method is promising for a wide range of applications, since sulfamic acid is much less corrosive and aggressive than the available sulfating agents.

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