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Transformations of Bjorkman lignin from European spruce (*Picea abies*) in superacidic media

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The Bjorkman lignin and products of its destruction under the action of Brønsted and Lewis superacids (CF_3SO_3H, $AlBr_3$ and zeolite CBV-720) were analyzed by MALDI mass spectrometry and their stabilities under superacidic conditions were compared.

Renewable lignocellulose materials are an alternative to coal, natural gas and oil.[1–3] A serious effort has been made to obtain fine chemicals[4–7] and fuels[8–12] based on the chemical transformations of lignin and lignocellulose. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) has been used for estimating the molecular weights of lignin oligomers.[13–17]

Based on our preliminary data,[18] we studied the transformation of lignin in Brønsted and Lewis superacids, which promote selective chemical reactions, such as bond cleavage, electrophilic addition, substitution and coupling.[19] The conversion of Bjorkman lignin from European spruce (*Picea abies*) was performed under the action of CF_3SO_3H (Brønsted superacid), $AlBr_3$ (Lewis superacid) and zeolite CBV-720 (solid Brønsted–Lewis superacid). Ion cyclotron resonance MALDI-MS was used for the analysis of lignin conversion products (Figures S13–S16, see Online Supplementary Materials).

First, we characterized the initial Bjorkman lignin by ^{13}C NMR spectroscopy (see Online Supplementary Materials), elemental analysis and MALDI-MS (Figure S13). The molecular weight of oligomeric lignin varies from 600 to 4500 Da. The main groups of oligomers are located at 1000–2000 and 2500–3500 Da. The spectrum contains clusters of peaks with mass differences Δm of 180–196 Da, which correspond to the so-called aryl propane lignin structural unit of guaicil type. This cluster structure is very clear for light part of the spectrum in the mass range 900–2400 Da. For masses of 2500–4500 Da, the separation into definite clusters of oligomers is not so strict due to the irregular lignin structure. The highest masses of ~4500 Da correspond to lignin oligomers consisting of about 25 aryl propane units.

After treatment in CF_3SO_3H, the molecular mass distribution occupied a range of 1500–3000 Da with a broad maximum at 2000–2500 Da (Figure S14). These data show that lignin underwent intra- and intermolecular condensation to form crosslinked oligomeric structures in addition to destruction.

According to MALDI-MS data, the treatment of lignin in the $AlBr_3$–benzene system gives oligomers with masses of 700–2000 Da (Figure S15). The MALDI-MS spectrum shows sharp clusters of peaks with the difference Δm ~ 180 Da in guaicil aryl propane unit. Thus, the destruction of lignin with $AlBr_3$ is more selective compared to that with CF_3SO_3H (Figure S14).

The conversion of lignin with zeolite CBV-720 containing Brønsted and Lewis acid sites at 130 °C for 24 h resulted in deep depolymerization and condensation of lignin oligomers with masses smaller than 1800 Da (Figure S16). The MALDI-MS spectrum contains several series of peaks with the mass differences Δm 178 Da: 843, 1021, 1199, 1377, 1555, 1733; and in the heavy part of the spectrum Δm 198 Da: 823, 1021, 1219; 1043, 1241; and Δm 196: 1223, 1419; 1401, 1597; 1419, 1615; 1555, 1751.

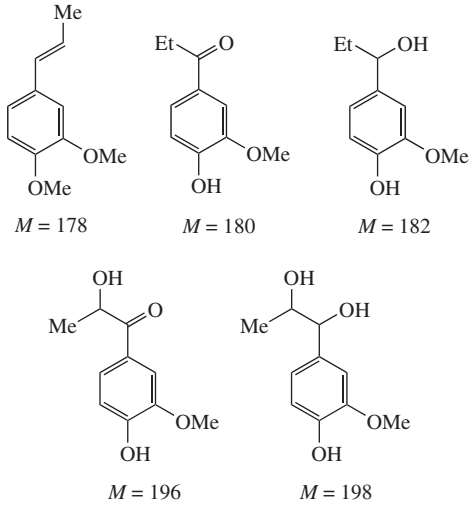


Figure 1 Aryl propane lignin units of guaicil type with masses of 178, 180, 182, 196 and 198 Da.

The possible structures of aryl propane lignin units of guaicil type with masses of 178, 180, 182, 196 and 198 Da are presented in Figure 1. The lignin oligomers detected by MALDI-MS (see Figures S13–S16) differ in these structural fragments.

The following lignin destruction products soluble in $CHCl_3$ (see Online Supplementary Materials) were detected by the gas chromatography–mass spectrometry (GC-MS) analysis of low-molecular-weight compounds formed after treatment with CF_3SO_3H, $AlBr_3$ and zeolite CBV-720 in yields of 6–10%: 4-hydroxy-3-methoxybenzaldehyde (vanillin), 4-hydroxy-3-methoxyacetophenone (acetovanillon), 4-hydroxy-3-methoxybenzoic acid (vanillic acid), 3-(4-hydroxy-3-metoxyphenyl)propenal (coniferaldehyde), 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethanone and 3-hydroxy-1-(4-hydroxy-3-metoxyphenyl)propan-1-one. These compounds were formed because of the destructive protosolvolysis of lignin macromolecules.

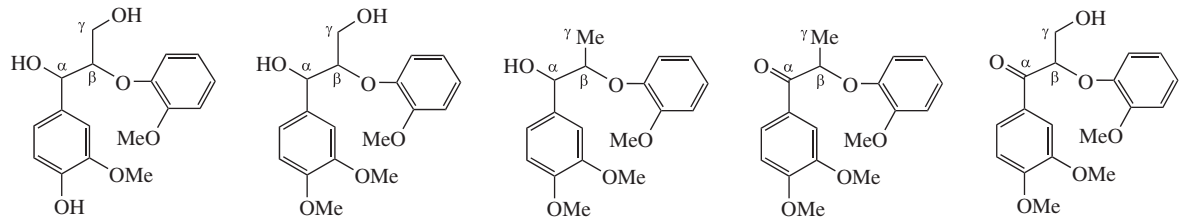


Figure 2 Lignin model compounds **1**–**5** containing β-O-4 linkage.

The initial Bjorkman lignin and products of its destruction in TfOH and $AlBr_3$ were characterized by elemental analysis. The starting lignin contained 60.16% C and 5.77% H. Lignin after treatment with TfOH or $AlBr_3$ contained 36.47% C and 2.67% H or 39.06% C and 2.20% H, respectively, due to the functionalization and condensation of lignin and the subsequent reactions of intermediate cation particles with water.

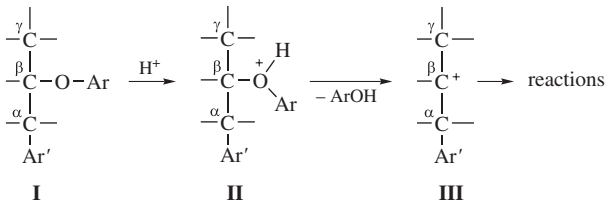
We studied the transformation of model lignin compounds **1**–**5** of guaicil type containing β-O-4 linkages[20] to elucidate the stability of this linkage under protosolvolysis in CF_3SO_3H (Figure 2). The β-O-4 bond is the most representative type of linkages between lignin structural subunits.[1] Compounds **1**–**5** have an *ortho*-methoxyphenyl group in the β-site of the propane chain and differ in substituents in the α- and γ-positions.

After the conversion of compounds **1**–**5** in CF_3SO_3H at 20 °C for 2 h, the reaction mixtures were analyzed by ^{1}H NMR spectroscopy and GC-MS. Compounds **4** and **5** bearing a carbonyl group in the α-position remained unreacted.

On the other hand, compounds **1**–**3** with α-OH group underwent complete conversion into complicated mixtures according to ^{1}H NMR data. The GC-MS analysis of these reaction residues showed the presence of no more than 20% *ortho*-methoxyphenol (guaiacol). In these cases, guaiacol was formed due to β-O-4 bond cleavage under the action of superacids. However, it is difficult to estimate quantitatively the degree of β-O-4 bond destruction for compounds **1**–**3** since guaiacol molecules as strong π-nucleophiles can participate in secondary reactions with cationic intermediate species under the reaction conditions.

We propose the following mechanism of the protosolvolytic cleavage of lignin β-O-4 bonds in superacids: the protonation of the $C^β$–O–Ar bond at the oxygen atom in lignin fragment **I** leads to oxonium cation **II** which eliminates the phenol molecule ArOH with $C^β$–O bond cleavage to give cation **III** (Scheme 1). This cation is hardly generated in the case when the α-position is occupied with the carbonyl group (like in compounds **4**, **5**) due to its electron-withdrawing character, which destabilizes the cationic center on the carbon $C^β$. α,γ-Hydroxy substituted lignin structures (like **1**–**3**) can also lose OH group from these positions under protonation in superacids, affording various reactive cationic species.

Cations **III** can undergo further inter- and intramolecular transformations, such as rearrangements, fragmentation and deprotonation. The released compound ArOH as a π-nucleophile can also participate in secondary processes, for instance, in electrophilic aromatic substitution. All these cationic reactions result in the destruction and condensation of lignin oligomers under the action of various superacids.



Scheme 1

Thus, the Bjorkman lignin from European spruce (*Picea abies*) undergoes destruction and condensation under the action of Brønsted and Lewis superacids, such as CF_3SO_3H, $AlBr_3$, and zeolite CBV-720. The superacidic destruction of lignin can be used for obtaining valuable organic compounds.

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Online Supplementary Materials

Supplementary data associated with this article (experimental procedures, ^{1}H, ^{13}C NMR and mass spectral data) can be found in the online version at doi:10.1016/j.mencom.2014.11.014.

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