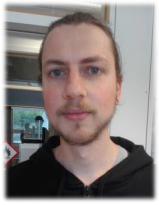
Pressurized liquid extraction and liquid chromatography-mass spectrometry analysis of phenolic oligomers from Lignin samples



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Introduction

Lignin is the second most abundant biopolymer on earth and has a high potential to become a biorenewable raw material for high value aromatic chemicals.

The biopolymer consists of three main aromatic subunits. The aromatic subunits are connected via different linkages. Three main linkages are shown in Figure 1.

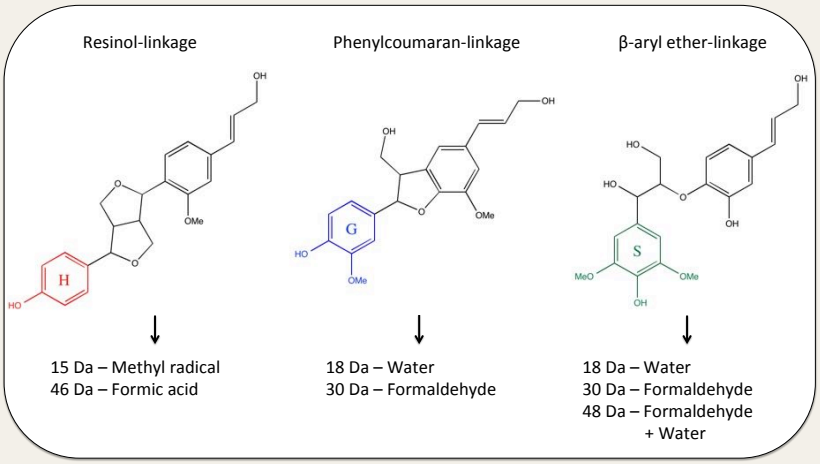

Figure 1: Lignin-related dimeric phenolic compounds with different aromatic subunits, different linkages and dominant mass loses of MS/MS fragments.

Results

- Dimers and trimers are identified in ethyl acetate, ethyl acetate/methanol and acetone/ethanol solvent fractions (Table 2)
- Possible phenolic oligomers could be identified by using dominant MS/MS fragments of oligomer linkages
- Unknown compounds with reasonable MS/MS fragments could be detected in ethyl acetate, ethyl acetate/methanol and acetone/ethanol solvent fractions (Table 2)

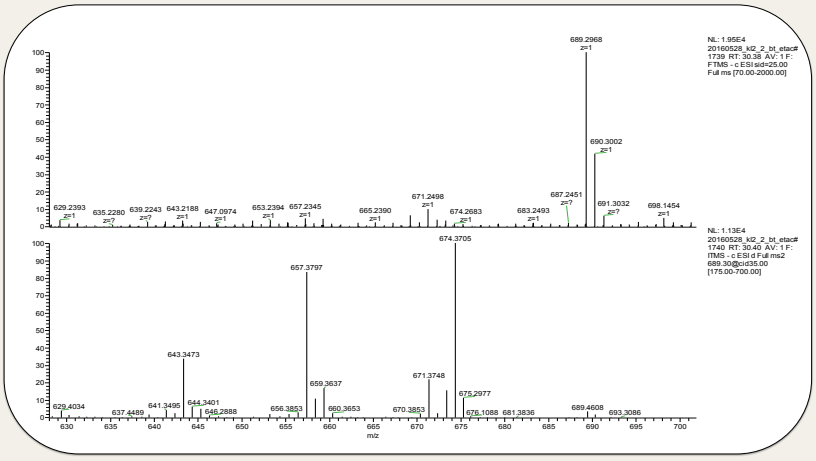

Figure 2: Molecular ion peak (top) and MS/MS spectrum (bottom) with major fragment ions of a unknown compound with m/z 689.2968. (m/z 674: - •CH_3; m/z 671: -H_2O; m/z 659: -H_2CO; m/z 657: -$HOCH_3$; m/z 643: -HCOOH)

Conclusions

- Dimers, trimers and suspected lignin-related phenolic oligomers could be identified
- Most compounds are detected in the ethyl acetate and ethyl acetate/ methanol solvent fractions
- First identifications of phenolic oligomers are possible by using a suspect list and dominant MS/MS fragments of oligomer linkages

Challenges

- How to fractionate industrial produced lignin (LignoBoost lignin) into fractions with a distribution of phenolic oligomers depending on their molecular size?
- How to search for lignin-related phenolic oligomers using liquid chromatography-high resolution tandem mass spectrometry (LC-HRMS^n) without availabe reference standards?

Methods

- Pressurized liquid extraction is a extraction method for solid samples using solvents at high pressures and temperatures
- Extraction were done at 100 bar, a extraction time of 30 minutes (2 x 15 minutes) and temperatures depending on the solvent (Table 1)
- Extraction solvents were selected by increasing polarity and hydrogen bonding hansen solubility parameters (Table 1)
- Analysis of solvent fractions using reversed phase LC coupled to a linear ion trap-Orbitrap hybrid mass spectrometer
- Identification using suspect list based on literature [1,2,3] and dominant MS/MS fragments of oligomer linkages [4] (Figure 1)

Table 1: Pressurized liquid extraction fractionation sequence, solvent mixtures in (v/v), Temperature and calculated Hansen solubility parameters of the used solvents.

Order	Solvent	T / °C	Hansen solubility parameters		
			δ_D	δ_P	δ_H
1	Ethyl acetate	80	14.4	4.8	6.4
2	Ethyl acetate/Methanol (80/20)	40	15.3	6.5	10.0
3	Acetone/Ethanol (40/60)	50	15.0	9.0	13.8
4	Acetone/Water (70/30)	50	14.9	11.7	17.1

δ_D: dispersion parameter; δ_P: polarity parameter; δ_H: hydrogen bonding parameter

Table 2: Number of detected possible lignin-related compounds in the pressurized liquid extraction fractions of the lignin sample.

Compound class	Pressurized liquid extraction solvent fractions			
	Ethyl acetate	Ethyl acetate/ Methanol	Acetone/Ethanol	Acetone/Water
Monomers	3	3	0	0
Dimers	4	2	1	0
Trimers	2	3	1	0
Unknowns	24	20	1	0
Sum	33	28	3	0

Acknowledgements

The project is part of the lignin project at Lund University (www.lignin.lu.se). We acknowledge funding by the Swedish Foundation for Strategic Research (SSF, RBP 14-0052).

References

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