Non-targeted analysis of lignin-related oligomers

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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.

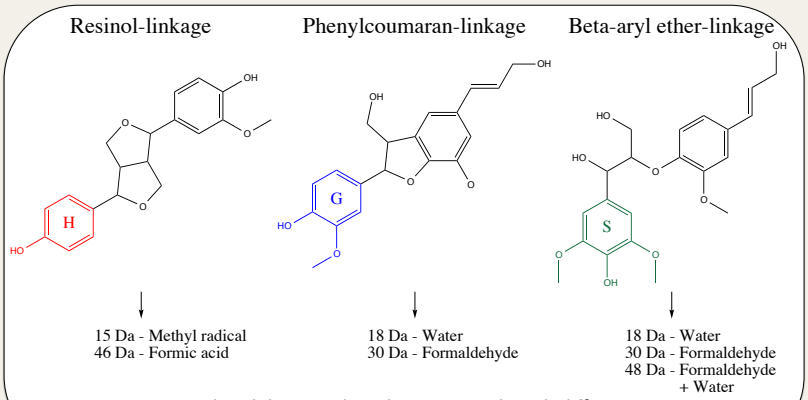

Figure 1. Lignin-related dimeric phenolic compounds with different aromatic subunits, different linkages and dominant mass losses of MS/MS fragments.

Challenges

- How to search for lignin-related oligomers using liquid chromatography-high resolution tandem mass spectrometry (LC-HRMS^n) without availabe reference standards?

Results

- Several possible lignin-related oligomers could be identified by neutral loss scans showing characteristic neutral losses.
- A detected compound at m/z 467.1696 ([M-H]$^-$, figure 2) hes been not detected yet in literature.
- For the compound at m/z 467.1696 ([M-H]$^-$) a chemical structure could be supposed based on lost neutral fragments, determined elemental composition and ring double bond equivalents (figure 3).
- A possible tandem MS fragmentation pathway for m/z 467.1696 ([M-H]$^-$) has been proposed (figure 3).
- Using the suspect list, two trimers could be identified.

Methods

- Lignin-related oligomers were extracted from LignoBoost lignin using pressurized liquid extraction (PLE).
- Extraction were done using Acetone/Water (70/30) at 100 bar, 80 °C and an extraction time of 30 min (2 x 15 min).
- The obtained extract was diluted and analyzed by reversed phase LC coupled to a linear ion trap-Orbitrap hybrid mass spectrometer.
- A non-targeted analysis strategy using HRMS in neutral loss scan mode, determination of possible elemental compositions by heuristic filtering of molecular formulas, ring double bound (RDB) equivalents and fragmentation pathways in tandem MS.
- A MS^3-ion tree experiment with screening for dominant neutral losses in MS^2 experiments [3] (figure 1) for lignin-related oligomers has been created using a MS resolution of 30000.
- A suspect list of lignin-related oligomers has been created based on detected compounds in the literature [1,2,3,4].

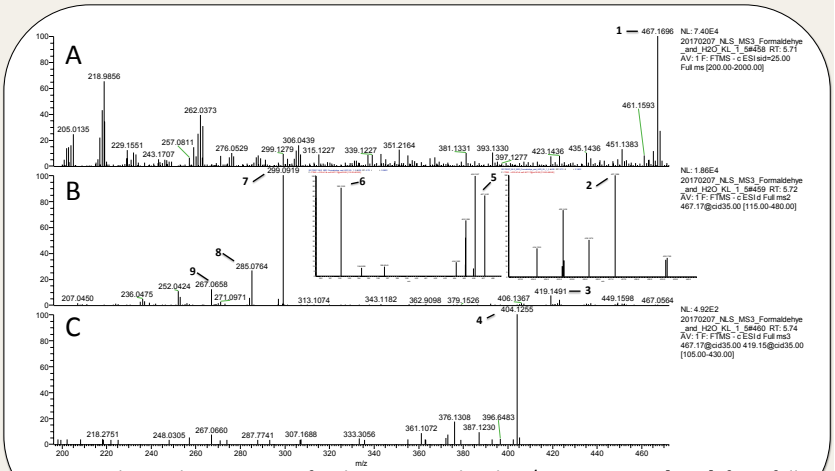

Figure 2. Obtained mass spectra for the compound with m/z 467.1696. A: [M-H]$^-$ from full scan, B: MS^2 from m/z 467.1696, C: MS^3 from 419.1491.

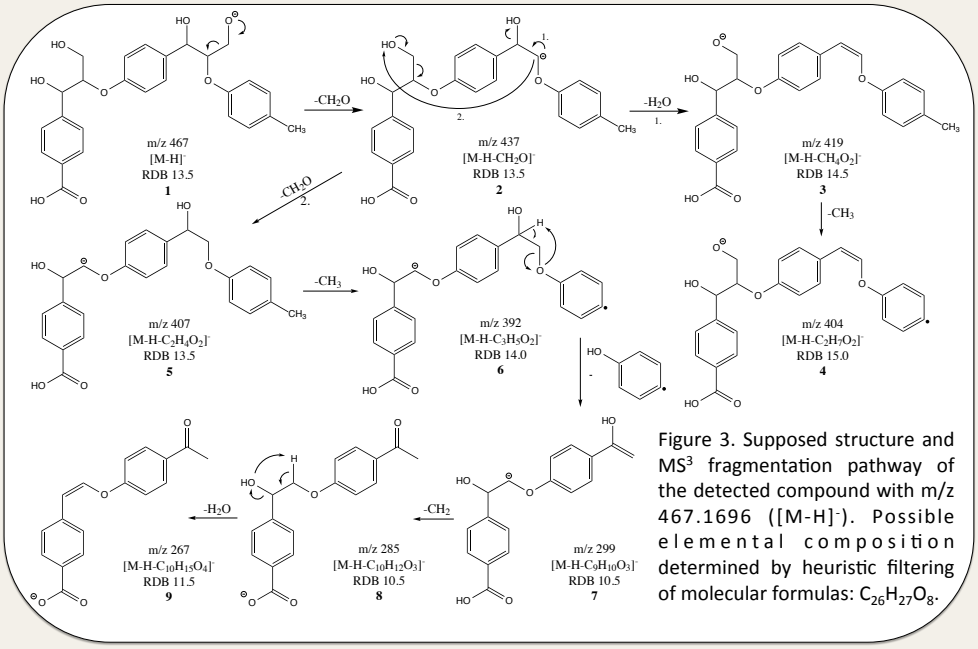

Figure 3. Supposed structure and MS^3 fragmentation pathway of the detected compound with m/z 467.1696 ([M-H]$^-$). Possible elemental composition determined by heuristic filtering of molecular formulas: $C_{26}H_{27}O_8$.

Conclusions and outlook

- With the developed non-targeted strategy possible lignin-related oligomers can be identified without using reference standards.
- The data evaluation will be continued and possible lignin-related oligomers will be identified by tandem MS fragmentation pathways.

Acknowledgements

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References

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