Supplementary Information

Variable lignin structure revealed in *Populus* leaves

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Enzymatic hydrolysis yields of select samples

| Sample	Leaf biomass pre-EH (mg)	Leaf biomass post-EH (mg)	Mass loss during EH (mg)	Mass loss during EH (%)
1121-N-1-17-9	412.4	211	201.4	49%
1121-N-2-23-77	351.1	186.1	165	47%
GW-9591-N-1-17-8	447.9	171.4	276.5	62%

FTIR absorbance values of spectra after baseline correction and normalization between [0,1].

Sample	1620-1625 cm^{-1}	1515-1520 cm^{-1}	1315-1320 cm^{-1}	1230-1235 cm^{-1}	890-895 cm^{-1}	822-827 cm^{-1}
425-S-4-26-30	0.552	0.263	0.117	0.111	0.112	0.115
1121-N-1-17-9	0.632	0.260	0.078	0.050	0.034	0.049
1121-N-2-23-77	0.544	0.196	0.062	0.043	0.045	0.037
1121-S-3-8-39	0.606	0.256	0.071	0.067	0.028	0.063
GW-9591-N-1-17-8	0.605	0.254	0.069	0.066	0.046	0.059
425-N-1-25-5	0.808	0.199	0.464	0.030	0.088	0.077
856-S-4-26-29	1	0.452	0.442	0.106	0.079	0.120
1025-N-2-7-47	1	0.559	0.387	0.084	0.047	0.114
1031-N-1-3-32	1	0.612	0.278	0.104	0.051	0.146
1121-S-4-24-25	1	0.563	0.290	0.065	0.042	0.123
1181-S-4-27-3	1	0.513	0.341	0.057	0.031	0.080
GW-9589-S-3-5-9	1	0.450	0.421	0.069	0.063	0.091
GW-9591-S-4-22-27	1	0.582	0.346	0.167	0.071	0.116
GW-9860-N-1-22-44	1	0.326	0.588	0.068	0.071	0.098
GW-9953-N	1	0.335	0.560	0.034	0.048	0.061
LILC-26-4-S-23-13	1	0.341	0.636	0.089	0.097	0.105

Ratios of FTIR peaks of interest and NMR S/G ratio for comparison

Sample	830 cm^{-1} / $1230\text{-}1235\text{cm}^{-1}$	$1620\text{-}1625\text{cm}^{-1}$ / $1515\text{-}1520\text{cm}^{-1}$	$1315\text{-}1320\text{cm}^{-1}$ / $1230\text{-}1235\text{cm}^{-1}$	830cm^{-1} / $890\text{-}895\text{cm}^{-1}$	NMR S/G ratio
425-S-4-26-30	0.50	2.10	1.05	1.02	
1121-N-1-17-9	0.23	2.43	1.55	1.44	2.9
1121-N-2-23-77	0.20	2.77	1.43	0.82	1.5
1121-S-3-8-39	0.33	2.37	1.06	2.24	
GW-9591-N-1-17-8	0.26	2.38	1.05	1.27	
425-N-1-25-5	0.30	4.07	15.59	0.88	0.6
856-S-4-26-29	0.47	2.21	4.17	1.53	0.7
1025-N-2-7-47	0.55	1.79	4.61	2.43	3.4
1031-N-1-3-32	0.55	1.63	2.68	2.88	9.8
1121-S-4-24-25	0.57	1.78	4.46	2.93	8.1
1181-S-4-27-3	0.46	1.95	6.02	2.57	2.8
GW-9589-S-3-5-9	0.42	2.22	6.07	1.46	1.2
GW-9591-S-4-22-27	0.40	1.72	2.07	1.64	0.5
GW-9860-N-1-22-44	0.38	3.06	8.70	1.39	0.7
GW-9953-N	0.38	2.99	16.59	1.26	0.6
LILC-26-4-S-23-13	0.37	2.93	7.12	1.09	0.3

FTIR absorbance ratio of the 830cm^{-1} (associated with syringyl units) and 1230cm^{-1} (associated with guaiacyl units) peaks. Statistical tests reveal these two measurements are correlated (CC=0.58, *p*-value=0.03).

FTIR vs. NMR
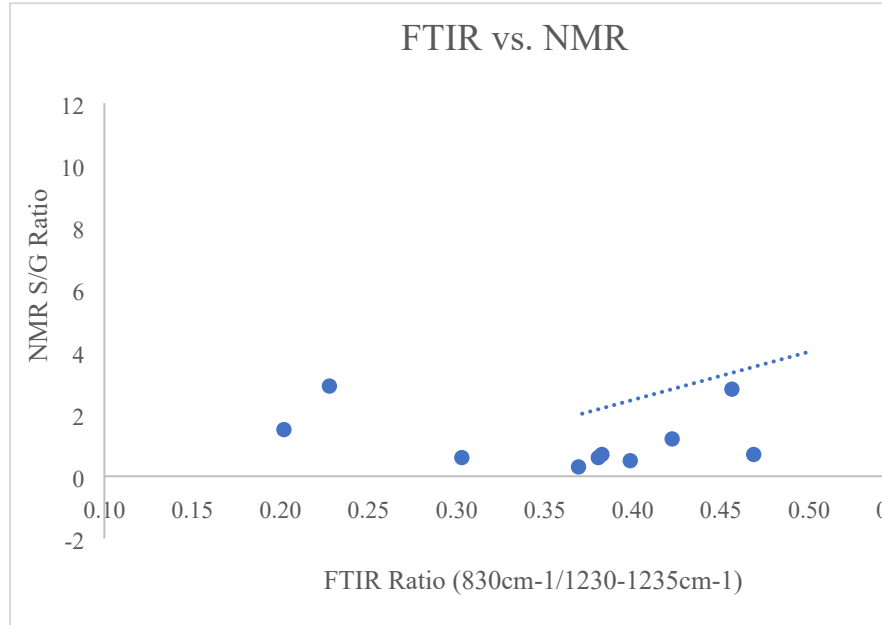
Linear Fit

Column 1 = 0.3488194 + 0.022383*Column 2

Summary of Fit

RSquare	0.345962
RSquare Adj	0.286504
Root Mean Square Error	0.097724
Mean of Response	0.40581
Observations (or Sum Wgts)	13

▷ **Lack Of Fit**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	0.05556687	0.055567	5.8186
Error	11	0.10504875	0.009550	Prob > F
C. Total	12	0.16061562		0.0345*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.3488194	0.035956	9.70	<.0001*
Column 2	0.022383	0.009279	2.41	0.0345*

▼ Multivariate

Correlations

	Column 1	Column 2
Column 1	1.0000	0.5824
Column 2	0.5824	1.0000

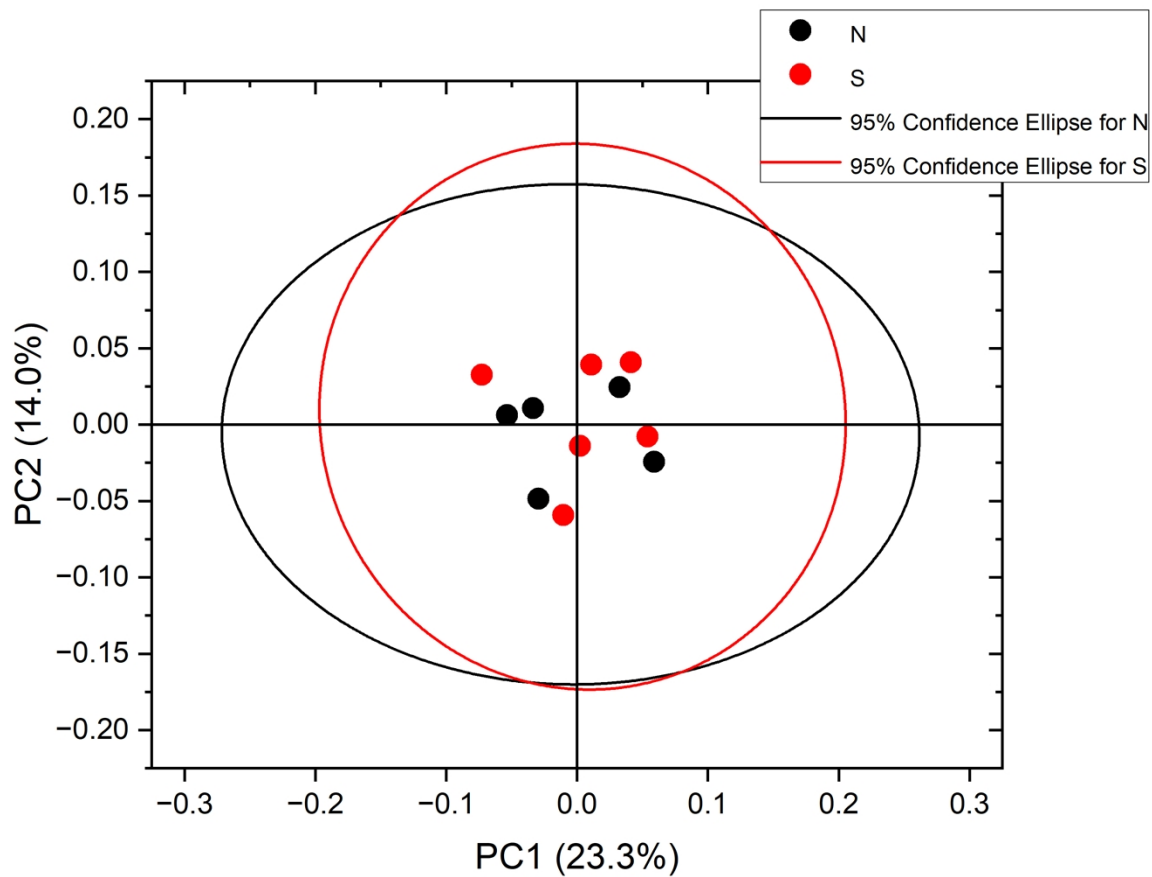Correlations between S/G ratio and β-O-4 linkage abundance
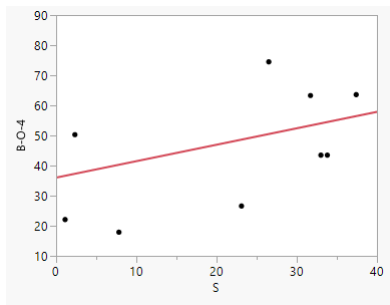
S units (uncondensed) vs. β-O-4 content for all data points. p-value=0.28. CC=0.36.
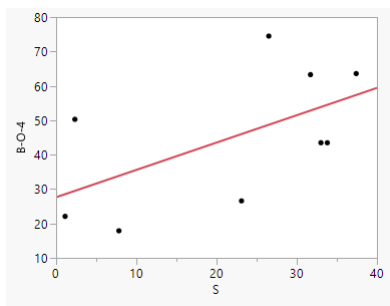
S units (uncondensed) vs. β-O-4 content, two S/G outlier samples removed. p-value=0.11. CC=0.57.

Principal component analysis of FTIR specta from Figure 4 in the main text, re-scaled to illustrate 95% confidence intervals.

Principal component analysis of metabolite abundance from Figure 6 in the main text, re-scaled to illustrate 95% confidence intervals.