

ESI

Strikingly High Amount of Tricin-lignin Observed from Vanilla (*Vanilla planifolia*) Aerial Roots

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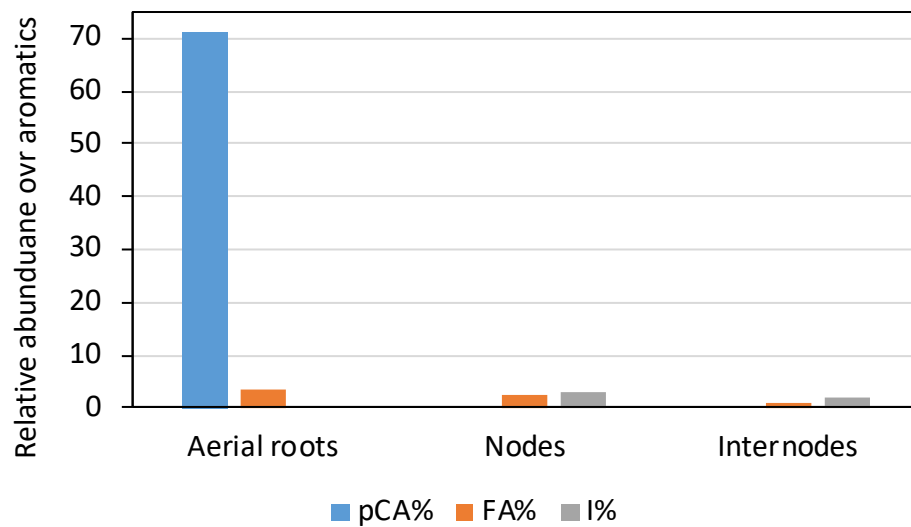


Fig. S1. ^{13}C - ^1H HSQC contour relative abundance of pCA (*p*-coumarate), FA (ferulate), and I (cinnamyl alcohol) over the total aromatics (S+G+H) of lignins isolated from aerial roots, nodes, and internodes of vanilla.

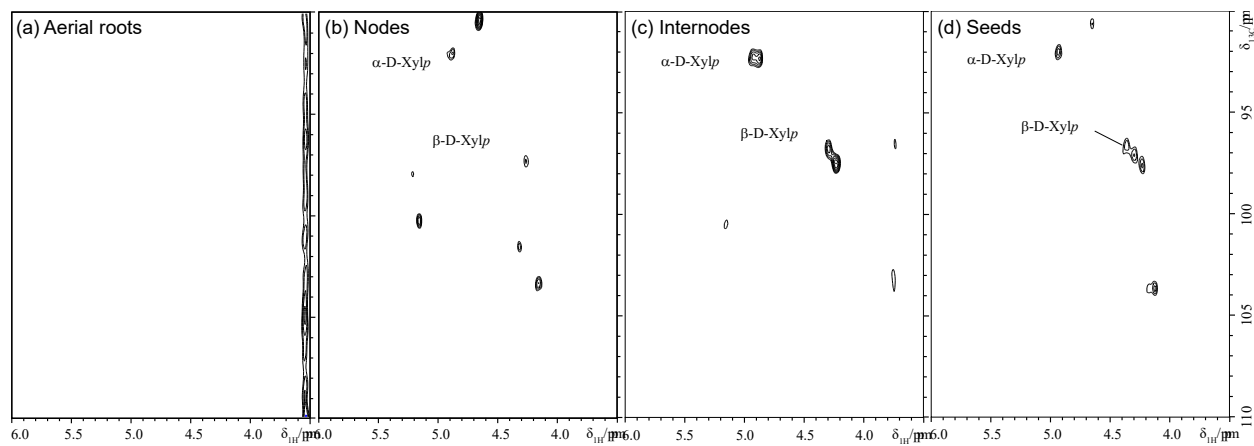


Fig. S2. ^{13}C - ^1H HSQC 2D NMR spectra revealing polysaccharide anomeries of acetylated CEL isolated from aerial roots, nodes, internodes, and seeds of vanilla. Unlabeled contours remain uncertain or unidentified.

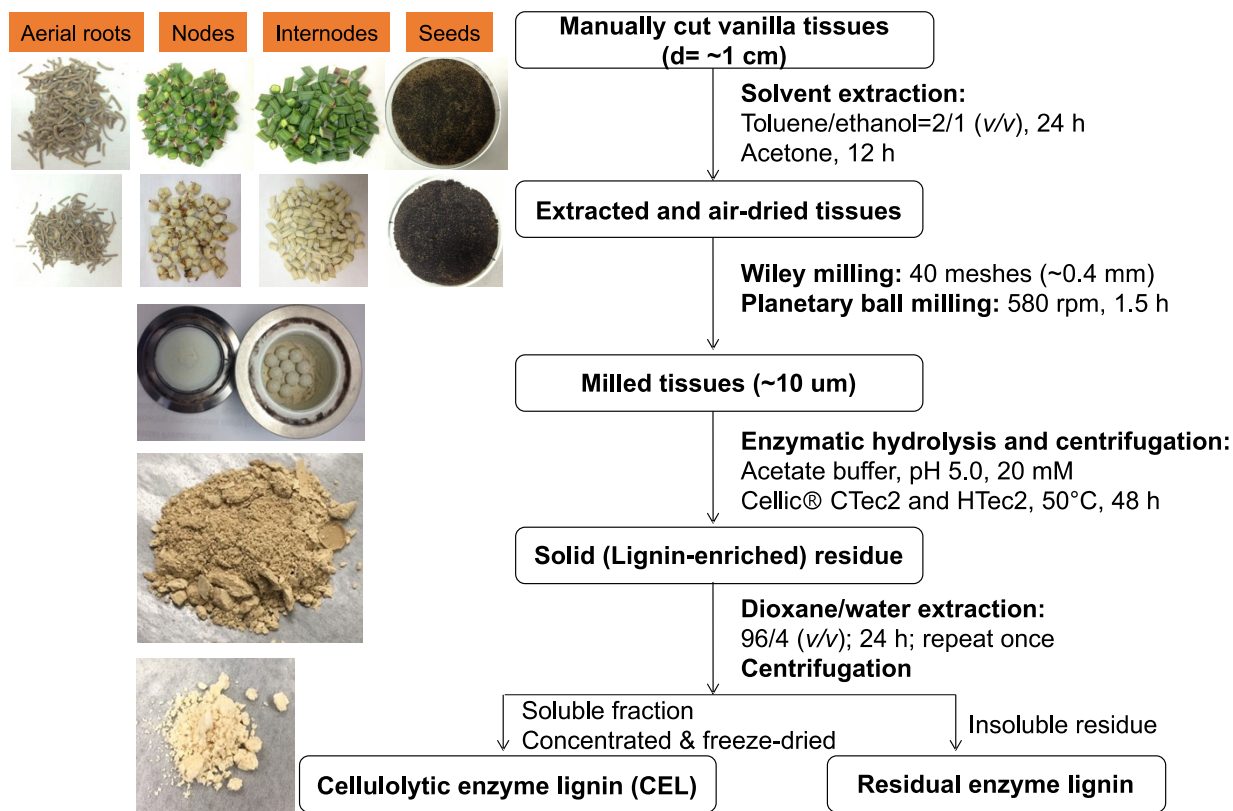


Fig. S3. Cellulolytic enzyme lignins (CEL) isolation from vanilla tissues. Inset pictures: vanilla tissues before (first row) and after (second row) solvent extraction.

Table S1 Assignments of the ^{13}C - ^1H correlation signals in the HSQC spectra of the lignins.

Labels	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm)	Assignment
B$_{\beta}$	53.2/3.47	C $_{\beta}$ /H $_{\beta}$ in β -5' phenylcoumaran substructures (B)
C$_{\beta}$	53.6/3.06	C $_{\beta}$ /H $_{\beta}$ in β - β' resinol substructures (C)
OMe	55.5/3.71	C/H in methoxyls
A$_{\gamma}$	59.8/3.36 & 3.58	C $_{\gamma}$ /H $_{\gamma}$ in normal (γ -hydroxylated) β -O-4' substructures (A)
F$_{\beta}$	59.5/2.78	C $_{\beta}$ /H $_{\beta}$ in spirodienone substructures (F)
I$_{\gamma}$	61.5/4.10	C $_{\gamma}$ /H $_{\gamma}$ in cinnamyl alcohol end-groups (I)
B$_{\gamma}$	62.5/3.75	C $_{\gamma}$ /H $_{\gamma}$ in β -5' phenylcoumaran substructures (B)
A'$_{\gamma}$	62.8/3.70	C $_{\gamma}$ /H $_{\gamma}$ in γ -acylated β -O-4' substructures (A')
C$_{\gamma}$	71.0/3.80 & 4.17	C $_{\gamma}$ /H $_{\gamma}$ in β - β' resinol substructures (C)
A$_{\alpha}$/A'$_{\alpha}$	71.5/4.75 & 71.9/4.89	C $_{\alpha}$ /H $_{\alpha}$ in β -O-4' substructures (A, A') -G&-S, respectively
K$_{\alpha}$	75.1/5.22	C $_{\alpha}$ /H $_{\alpha}$ in benzodioxane (K)
K$_{\beta}$	75.3/4.93	C $_{\beta}$ /H $_{\beta}$ in benzodioxane (K)
F'$_{\beta}$	77.0/4.39	C $_{\beta}$ /H $_{\beta}$ in spirodienone substructures (F)
E$_{\alpha}$	78.1/4.12	C $_{\alpha}$ /H $_{\alpha}$ in α,β -diaryl ether substructures (E)
F$_{\alpha}$	81.3/5.07	C $_{\alpha}$ /H $_{\alpha}$ in spirodienone substructures (F)
A'$_{\beta(S)}$	83.6/4.33	C $_{\beta}$ /H $_{\beta}$ in γ -acylated β -O-4' substructures linked to an S unit (A')
D$_{\alpha}$	83.1/4.79	C $_{\alpha}$ /H $_{\alpha}$ in 5-5' dibenzodioxocin substructures (D)
A$_{\beta(G)}$	83.6/4.31	C $_{\beta}$ /H $_{\beta}$ in β -O-4' substructures linked to a G unit (A)
C$_{\alpha}$	84.9/4.66	C $_{\alpha}$ /H $_{\alpha}$ in β - β' resinol substructures (C)
A$_{\beta(S)}$	86.1/4.13	C $_{\beta}$ /H $_{\beta}$ in β -O-4' substructures linked to an S unit (A)
B$_{\alpha}$	86.9/5.46	C $_{\alpha}$ /H $_{\alpha}$ in β -5' phenylcoumaran substructures (B)
T$_{8}$	94.1/6.54	C $_{8}$ /H $_{8}$ in triclin units (T)
T$_{6}$	98.8/6.21	C $_{6}$ /H $_{6}$ in triclin units (T)
S$_{2/6}$	103.9/6.72	C $_{2}$ /H $_{2}$ and C $_{6}$ /H $_{6}$ in etherified syringyl units (S)
T$_{2'}/6'$	104.1/7.30	C $_{2'}$ /H $_{2'}$ and C $_{6'}$ /H $_{6'}$ in triclin units (T)
T$_{3}$	104.8/7.04	C $_{3}$ /H $_{3}$ in triclin units (T)
J$_{2/6(S)}$	106.5/7.05	C $_{2}$ /H $_{2}$ and C $_{6}$ /H $_{6}$ in cinnamaldehyde end-groups in S units (J)
G$_{2}$	110.9/6.99	C $_{2}$ /H $_{2}$ in guaiacyl units (G)
FA$_{2}$	111.2/7.31	C $_{2}$ /H $_{2}$ in ferulic acid units (FA)
pCA$_{\beta}$+FA$_{\beta}$	113.5/6.27	C $_{\beta}$ /H $_{\beta}$ in p-coumarate (pCA) and ferulate (FA)
G$_{5}$	115.1/6.71 & 6.97	C $_{5}$ /H $_{5}$ in guaiacyl units (G)
G$_{6}$	118.9/6.78	C $_{6}$ /H $_{6}$ in guaiacyl units (G)
FA$_{6}$	122.5/7.09	C $_{6}$ /H $_{6}$ in ferulic acid units (FA)
J$_{\beta}$	126.2/6.77	C $_{\beta}$ /H $_{\beta}$ in cinnamaldehyde end-groups (J)
I$_{\beta}$	128.2/6.24	C $_{\beta}$ /H $_{\beta}$ in cinnamyl alcohol end-groups (I)
I$_{\alpha}$	128.4/6.44	C $_{\beta}$ /H $_{\beta}$ in cinnamyl alcohol end-groups (I)
J$_{\alpha}$	153.1/7.59	C $_{\alpha}$ /H $_{\alpha}$ in cinnamaldehyde end-groups (J)