Electronic Supplementary Information (ESI) for

Structural Characterization of Lignins from Willow Bark and Wood

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Table S1. Assignments of the Lignin $^{1}H–^{13}C$ Correlation Peaks in the 2D-HSQC Spectra of Willow Bark and Isolated EL.[a]

Label	δC/δ H (ppm)	Assignment
B_β	53.2/3.57	$C_\beta–H_\beta$ in phenylcoumaran substructures (**B**)
C_β	53.4/3.03	$C_\beta–H_\beta$ in β–β′ resinol substructures **(C)**
$–OCH_3$	55.3/3.67	C–H in methoxyls
A_γ	60.0/3.69 and 60.8/3.59	$C_\gamma–H_\gamma$ in γ-hydroxylated β-O-4′ substructures **(A)**
SD_β	60.0/2.82	$C_\beta–H_\beta$ in spirodienone substructures **(SD)**
$X1_\gamma$	61.5/4.17	$C_\gamma–H_\gamma$ in cinnamyl alcohol end-groups **(X1)**
B_γ	62.8/3.74	$C_\gamma–H_\gamma$ in phenylcoumaran substructures **(B)**
C_γ	70.9/4.15	$C_\gamma–H_\gamma$ in β–β′ resinol substructures **(C)**
$A_{\alpha(S)}$	71.9/4.97	$C_\alpha–H_\alpha$ in β-O-4′ substructures **(A)** linked to a S-unit
SD_α	81.1/5.14	$C_\alpha–H_\alpha$ in spirodienone substructures **(SD)**
$A_{\beta(H/G)}$	83.6/4.38	$C_\beta–H_\beta$ in β-O-4′ substructures **(A)** linked to a H-unit and G- unit
C_α	84.9/4.66	$C_\alpha–H_\alpha$ in β–β′ resinol substructures **(C)**
$A_{\beta(S)}$	86.1/4.15 and 87.3/4.02	$C_\beta–H_\beta$ in β-O-4′ substructures linked **(A)** to a S unit
B_α	86.9/5.55	$C_\alpha–H_\alpha$ in phenylcoumaran substructures **(B)**
$S_{2,6}$	103.9/6.76 and 106.3/7.10	$C_2–H_2$ and $C_6–H_6$ in etherified syringyl units **(S)**
G_2	110.8/7.02 and 111.0/7.29	$C_2–H_2$ in guaiacyl units **(G)**
G_5/G_6	114.7/6.71; 114.9/6.95 and 6.84/119.1	$C_5–H_5$ and $C_6–H_6$ in guaiacyl units **(G)**
$X1_\beta$	128.4/6.29	$C_\beta–H_\beta$ in cinnamyl alcohol end-groups **(X1)**
$X1_\alpha$	128.4/6.49	$C_\alpha–H_\alpha$ in cinnamyl alcohol end-groups **(X1)**

[a] Signals were assigned in comparison with the literature.

Table S2. NMR Data for Polysaccharide Components in the Willow Bark WCW in DMSO-d_6/pyridine-d_5 (4:1).[a]

Saccharide	Unit	δC/δ H (ppm)	Full name
Cellulose (blue)	β-D-Glc*p*	102.8-103.6/ 4.23-4.41	β-D-glucopyranoside
Xylan (green)	α-D-Xyl*p* (R)	92.2/5.04	α-D-xylopyranoside
	β-D-Xyl*p* (R)	96.7/4.47	β-D-xylopyranoside
	2-*O*-Ac-β-D-Xyl*p*	99.5/4.58	acetylated β-D-Xyl*p*
	2,3-di-*O*-Ac-β-D-Xylp	99.1/4.78	acetylated β-D-Xyl*p*
	4-*O*-MeGlcA	97.4/5.27	4-*O*-methyl-α-D-glucuronic acid
Pectin (red)	α-L-Rha*p*	100.3/5.20	α-L-rhamnopyranose
	β-D-Gal*p* (R)	93.0-105.5/4.38-5.05	β-D-galactopyranoside
	α-D-Gal*p*A	100.3/5.10	α-D-galactopyranuronic acid
	α-L-Ara*f*	107.0-107.8/ 4.88-4.99	α-L-arabinofuranoside
	β-L-Ara*f*	101.9-102.7/ 5.11-5.26	β-L-arabinofuranoside

[a] Signals were assigned by comparison with the literature

Figure S1. Aromatic (δ_C/δ_H 96-150/6.0-8.2 ppm) (top) and side-chain (δ_C/δ_H 48-92/2.0-6.0 ppm) (bottom) regions of 2D HSQC NMR spectra of WCW preparations from bark (left), inner bark (middle), and wood (right).