Supporting information

Authors: *Danila Morais de Carvalho, Maarit H. Lahtinen, Martin Lawoko, and Kirsi S. Mikkonen*

Enrichment and identification of lignin-carbohydrate complexes in softwood extract

Number of pages: 10

Number of figures: 4

Number of tables: 6

Table S1. Mass balance and chemical characterization of galactoglucomannan (GGM) samples[a].

Samples		sdGGM	esGGM	epGGM
Mass balance based on original spruce wood (%)		21.6	4.5 ± 0.2	16.0 ± 0.4
Normalized chemical composition of sugars and lignin (%)	Man	51.1 ± 0.2	38.9 ± 0.4	55.4 ± 0.0
	Glc	14.7 ± 0.3	9.9 ± 0.4	16.3 ± 0.7
	Gal	6.4 ± 0.2	3.7 ± 0.1	7.7 ± 0.2
	Xyl	9.5 ± 0.2	7.9 ± 0.3	10.5 ± 0.5
	GlcA	1.6 ± 0.1	2.7 ± 0.2	1.9 ± 0.2
	Ara	0.6 ± 0.1	3.1 ± 0.1	0.3 ± 0.0
	Fuc	0.2 ± 0.0	0.0 ± 0.0	0.1 ± 0.1
	Rha	0.4 ± 0.1	1.0 ± 0.2	0.3 ± 0.1
	GalA	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
	Lignin	15.4 ± 2.5	32.9 ± 1.7	7.4 ± 0.6
GGM purity (%)[b]		72.2 ± 0.5	52.5 ± 0.6	79.4 ± 0.5
Acetyl groups	Content (%)[c]	3.8	4.9	3.2
	DS_{Ac}[d]	0.23	0.27	0.27
	Distribution[e]	1.0:0.8	1.0:0.8	1.0:0.8
Molar mass	Mn (kDa)	1.7 ± 0.0	0.7 ± 0.0	2.6 ± 0.0
	Mw (kDa)	7.1 ± 0.1	1.5 ± 0.0	9.3 ± 0.6
	DI	4.3 ± 0.0	2.0 ± 0.1	3.6 ± 0.3

[a]In the table: sdGGM: spray-dried galactoglucomannan; es: ethanol-soluble galactoglucomannan; epGGM: ethanol-precipitated galactoglucomannan; Man: mannose; Glc: glucose; Gal: galactose; Xyl: xylose; GlcA: glucuronic acid; Ara: arabinose; Fuc: fucose; Rha: rhamnose; GalA: galacturonic acid, DS_{Ac}: degree of acetylation of galactoglucomannan samples; Mn: number-average molar mass; Mw: weight-average molar mass; and DI: dispersity index.

[b]For the estimation of the purity of galactoglucomannan were considered the content of mannose, glucose, and galactose in samples. Similarly, arabinoglucuronoxylan content was estimated considering xylose, arabinose, and glucuronic acid moieties and pectin considered the content of fucose, rhamnose, and galacturonic acid.

[c]mol acetyl per 100 mol hexose.

[d]DS_{Ac} was calculate considering only those sugars present in the galactoglucomannan backbone, *i.e.*, mannose and glucose.

[e]Acetylation distribution in mannosyl units (C-2:C-3) obtained by semi-quantitative analysis from NMR spectra.

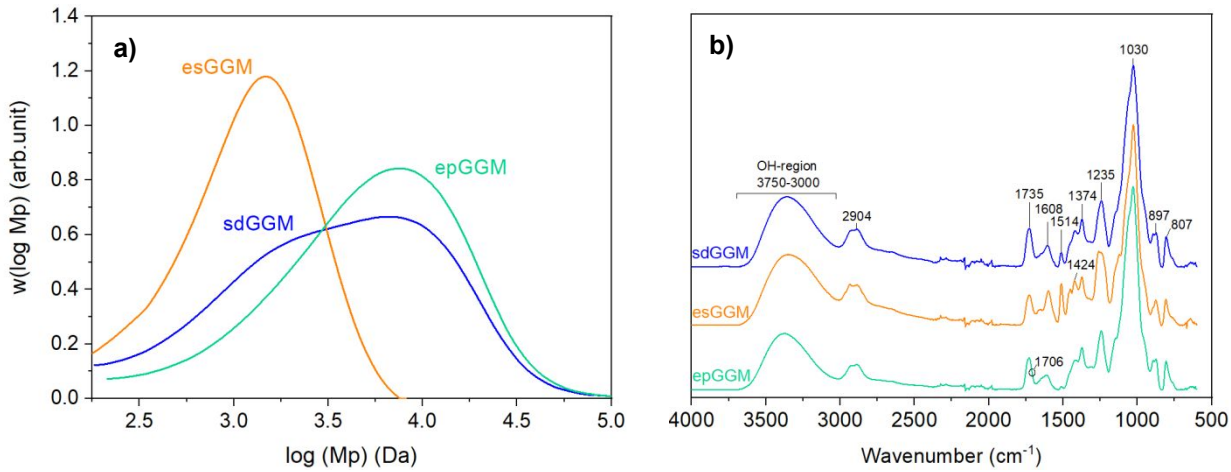

Figure S1. Molar mass distribution (**a**) and FTIR spectra (**b**) of sdGGM, esGGM, and epGGM samples.

Table S2. Assignment for the relevant bands observed in FTIR spectra

Absorption band (cm^{-1})	Band assignments[a]
3360	O-H stretching vibration of hydrogen-bonded
2904	Aliphatic C-H stretching
1735	C=O stretching vibration carbonyl groups
1706	Free acetic acid (absent in the spectra)
1608	Water absorption
1514	Aromatic skeletal vibration of lignin rings
1424	Asymmetric aliphatic C–H deformation of methoxyl
1374	Symmetric aliphatic C–H bending of methoxyl in acetyl groups
1235	C-O stretching
1030	C-O and C-C stretching or C-OH bending
897	β-glycosidic linkage between sugar units
807	Aromatic out-of-plane-rings region

[a]Band assignments were assessed according to the literature.[1-8]

Table S3. Assignment for the relevant carbon-hydrogen correlation signals of lignin structures in sdGGM, esGGM, and epGGM samples and fractions.

Structural units[a]	δ_C (ppm)	δ_H (ppm)	Assignments[b]	Identified in[c]
β-*O*-4	59.5	3.70/3.44	C_γ/H_γ in β-*O*-4	1-27
β-*O*-4	71.4	4.71	C_α/H_α in γ-hydroxylated β-*O*-4	1-27
β-*O*-4 S	85.3	4.16	C_β/H_β in γ-hydroxylated β-*O*-4 in S-units	2, 5-10, 15, 16, 19, 29, 22-24
β-*O*-4 G	83.4	4.28	C_β/H_β in γ-hydroxylated β-*O*-4 in G-units	1-27
β-*O*-4 BE	84.6	4.34	C_β/H_β in β-*O*-4 in benzylether structures	2, 6-10, 16, 19, 20, 22-24
β-*O*-4 GE	81.1	4.64	C_γ/H_γ in γ-acylated β-*O*-4	1, 2, 4, 6, 7, 16, 20, 22
β-*O*-4 BE	61.5	3.80	C_γ/H_γ in β-*O*-4 in benzylether structures	1-17, 19, 20, 22-27
Phenylcoumaran	87.0	5.40	C_α/H_α in phenylcoumaran	1-27
Phenylcoumaran	54.7	3.45	C_β/H_β in phenylcoumaran	1-10, 12, 14-24
Resinol struct.	85.1	4.61	C_α/H_α in resinol structures	1, 2, 4-10, 12, 14, 16-18, 20-24
Resinol struct.	53.6	3.04	C_β/H_β in resinol structures	1-4, 6-10, 12, 16, 17, 20-24
Resinol struct.	71.2	4.14/3.85	C_γ/H_γ in resinol structures	1-20, 22
DBD	83.3	4.80	C_α/H_α in dibenzodioxin	1, 2, 6-10, 12, 16, 17, 20, 22, 23
DBD	85.5	4.01	C_β/H_β in dibenzodioxin	1, 2, 4-11, 16, 19, 20, 22, 23, 27
DBD	60.3	3.42	C_γ/H_γ in dibenzodioxin	1-14, 16-27
OSC (G_2)	111.8	7.30	C_2/H_2 in $(C=0)_\alpha$ in G-units	1-4, 6-10, 12, 16, 17, 20-23
OSC (G_6)	122.8	7.64/7.56	C_6/H_6 in $(C=0)_\alpha$ in G-units	2, 3, 6-8, 10, 16, 20, 23
OSC ($S_{2,6}$)	106.4	7.20/7.03	$C_{2,6}/H_{2,6}$ in $(C=0)_\alpha$ in S-units	7, 20
OSC_α	153.8	7.60	C_α/H_α in cinnamyl aldehyde	1-4, 6-9, 11, 12, 16-23
OSC_β	126.6	6.79	C_β/H_β in cinnamyl aldehyde	1-4, 6-12, 14, 16, 17, 20-24
Methoxyl	55.4	3.73	C/H in -OMe in G- and S-units	1-27
CA	61.7	4.05	C_γ/H_γ in cinnamyl alcohol	1, 2, 4-12, 14-24, 26, 27
$SECO_\alpha$	33.6	2.53/2.46	C_α/H_α in secoisolariciresinol	1, 2, 5-17, 20, 22, 23, 25, 26
$SECO_\beta$	42.3	1.84	C_β/H_β in secoisolariciresinol	1-10, 12, 14,16-24
DCA_α	31.4	2.52	C_α/H_α in dehydroconiferyl alcohol	1-11, 14, 16-24
DCA_β	34.4	1.65	C_β/H_β in dehydroconiferyl alcohol	1-12, 14, 16-27
$S_{2,6}$	103.9	6.68	C_2/H_2 and C_6/H_6 in S-units	2, 6, 7, 16, 20, 22
G_2	110.7	6.94	C_2/H_2 in G-units	1-27
G_5	115.0	6.82	C_5/H_5 in G-units	1-27
G_6	118.7	6.76	C_6/H_6 in G-units	1-27
$H_{2,6}$	127.8	7.19	C_2/H_2 and C_6/H_6 in H-units	1-4, 6-10, 12, 14, 16-18, 20-24

[a]β-*O*-4: β-*O*-4 linkage between lignin including syringyl (S) and guaiacyl (G) units and in lignin involved in benzylether (BE) and gamma-ester (GE) linkages; Phenylcoumaran (β5); Resinol structures (ββ); Dibenzodioxin (DBD); Oxidized side chain (OSC); Methoxyl in S and G units; Cinnavyl alcohol (CA), Secoisolariciresinol (SECO – ββ); Dehydro conyferyl alcohol (DCA); and p-hydroxyphenyl (H) unit.

[b]Contours assignments were assessed according to the literature.[9, 10]

[c]The numbers refer to the following samples: 1: sdGGM raw; 2: sdGGM SSEH pellet/large; 3: sdGGM SSEH pellet/small; 4: sdGGM SSEH supernatant/large; 5: sdGGM SSEH supernatant/small; 6: esGGM raw; 7: esGGM SSEH pellet/large; 8: esGGM SSEH pellet/small; 9: esGGM SSEH supernatant/large; 10: esGGM SSEH supernatant/small; 11: epGGM raw; 12: epGGM SSEH pellet/large; 13: epGGM SSEH pellet/small; 14: epGGM SSEH supernatant/large; 15: epGGM SSEH supernatant/small; 16: sdGGM reference pellet/large; 17: sdGGM reference pellet/small; 19: sdGGM reference supernatant/large; 19: sdGGM reference supernatant/small; 20: esGGM reference pellet/large; 21: esGGM reference pellet/small; 22: esGGM reference supernatant/large; 23: esGGM reference supernatant/small; 24: epGGM reference pellet/large; 25: epGGM reference pellet/small; 26: epGGM reference supernatant/large; and 27: epGGM reference supernatant/small.

Table S4. Assignment for the relevant lignin substructures in sdGGM, esGGM, and epGGM samples and fractions.

Structural units	δ_C (ppm)	δ_H (ppm)	Assignments[a]	Identified in[b]
β-aryl ether (β-*O*-4)	71.3	4.90	β-*O*-4 signal in α	1-10, 12-20, 22-5, 27
β-aryl ether (β-*O*-4)	83.8	4.26	β-*O*-4 signal in β of guaiacyl	1- 27
β-aryl ether (β-*O*-4)	86.0	4.08	β-*O*-4 signal in β of syringyl	2, 5, 6, 7, 10, 13, 15, 16, 20
β-aryl ether (β-*O*-4)	61.7	3.40	β-*O*-4 signal in γ	1-27
Phenyl coumaran (β-5)	87.4	5.46	β-5 signal in α	1-12, 16-24, 26
Phenyl coumaran (β-5)	52.6	3.46	β-5 signal in β	1-26
Phenyl coumaran (β-5)	62.4	3.72	β-5 signal in γ	1-27
Cinnamyl alcohol	128.5	6.42	Cinnamyl alcohol signal in α	1-3, 6-10, 16-23, 25
Cinnamyl alcohol	127.5	6.21	Cinnamyl alcohol signal in β	1, 2, 6-10, 16-23
Cinnamyl alcohol	62.8	3.90	Cinnamyl alcohol signal in γ	1-20, 22-27
Resinol (β-β)	83.4	4.86	β-β signal in α	1, 2, 5- 10, 16, 18, 20, 22
Resinol (β-β)	53.4	3.04	β-β signal in β	1-4, 6-10, 1216, 17, 20-23
Resinol (β-β)	73.1	4.09	β-β signal in γ	1, 4, 9
Dibenzodioxocin (5-5/β-*O*-4)	82.9	4.80	5-5/β-*O*-4 signal in α	1, 2, 6-8, 10, 16-18, 20, 20, 23
Dibenzodioxocin (5-5/β-*O*-4)	86.2	3.90	5-5/β-*O*-4 signal in β	2, 6, 7, 16, 20
Spirodienone (β-1)	81.2	5.00	β-1 signal in α	2, 6, 7, 16, 20, 22
Spirodienone (β-1)	59.7	2.70	β-1 signal in β	1, 7, 20
Spirodienone (β-1)	80.1	4.10	β-1 signal in β´	2, 6, 7, 11, 12

[a]Contours assignments were assessed according to the literature.[11]

[b]The numbers refer to the following samples: 1: sdGGM raw; 2: sdGGM SSEH pellet/large; 3: sdGGM SSEH pellet/small; 4: sdGGM SSEH supernatant/large; 5: sdGGM SSEH supernatant/small; 6: esGGM raw; 7: esGGM SSEH pellet/large; 8: esGGM SSEH pellet/small; 9: esGGM SSEH supernatant/large; 10: esGGM SSEH supernatant/small; 11: epGGM raw; 12: epGGM SSEH pellet/large; 13: epGGM SSEH pellet/small; 14: epGGM SSEH supernatant/large; 15: epGGM SSEH supernatant/small; 16: sdGGM reference pellet/large; 17: sdGGM reference pellet/small; 19: sdGGM reference supernatant/large; 19: sdGGM reference supernatant/small; 20: esGGM reference pellet/large; 21: esGGM reference pellet/small; 22: esGGM reference supernatant/large; 23: esGGM reference supernatant/small; 24: epGGM reference pellet/large; 25: epGGM reference pellet/small; 26: epGGM reference supernatant/large; and 27: epGGM reference supernatant/small.

Table S5. Assignment for lignin-carbohydrates bonds signals in sdGGM, esGGM, and epGGM samples and fractions.

Structural units[a]	δ_C (ppm)	δ_H (ppm)	Assignments[b]	Identified in[c]
PG	101.1-99.8	5.18-5.00	Phenylglycoside	1, 2, 6-12, 17, 20, 22-24
PG	101.8	4.98-4.90	Phenylglycoside	1, 4, 6-10, 17, 19-23
PG	100.8	4.89-4.84	Phenylglycoside	3, 6, 8-11, 14, 21-23
BE (BE_1)	80.2	4.50	Benzylether	2, 6, 7, 16, 20, 22
GE	62.0-65.0	4.50/4.00	γ-ester	1-27

[a]PG: phenylglycoside; BE: benzylether; and GE: γ-ester.

[b]Contours assignments were assessed according to the literature.[10, 12, 13]

[c]The numbers refer to the following samples: 1: sdGGM raw; 2: sdGGM SSEH pellet/large; 3: sdGGM SSEH pellet/small; 4: sdGGM SSEH supernatant/large; 5: sdGGM SSEH supernatant/small; 6: esGGM raw; 7: esGGM SSEH pellet/large; 8: esGGM SSEH pellet/small; 9: esGGM SSEH supernatant/large; 10: esGGM SSEH supernatant/small; 11: epGGM raw; 12: epGGM SSEH pellet/large; 13: epGGM SSEH pellet/small; 14: epGGM SSEH supernatant/large; 15: epGGM SSEH supernatant/small; 16: sdGGM reference pellet/large; 17: sdGGM reference pellet/small; 19: sdGGM reference supernatant/large; 19: sdGGM reference supernatant/small; 20: esGGM reference pellet/large; 21: esGGM reference pellet/small; 22: esGGM reference supernatant/large; 23: esGGM reference supernatant/small; 24: epGGM reference pellet/large; 25: epGGM reference pellet/small; 26: epGGM reference supernatant/large; and 27: epGGM reference supernatant/small.

Table S6. Assignment for the relevant carbon-hydrogen correlation signals of polysaccharides linkages in sdGGM, esGGM, and epGGM samples and fractions.

Structural units	δ_C (ppm)	δ_H (ppm)	Assignments[a]	Identified in[b]
Acetyl	20.9	2.01	-CH_3 in acetyl	1-27
Ara_1	107.8	4.76	C_1/H_1 in β-L-arabinopyranoside	1-27
Ara_2	83.2	3.76	C_2/H_2 in β-L-arabinopyranoside	1-23, 25, 27
Ara_4	84.8	4.00	C_4/H_4 in β-L-arabinopyranoside	2, 6, 7, 9, 10, 11, 16, 20, 22
Ara_5	62.3	3.42/3.36	C_5/H_5 in β-L-arabinopyranoside	1-25, 27
Glc_1	102.0	4.32	C_1/H_1 in β-D-glucopyranoside	1-27
Glc_2	74.8	2.90	C_2/H_2 in β-D-glucopyranoside	1-19, 21-27
Glc_3	76.7	3.05	C_3/H_3 in β-D-glucopyranoside	1- 27
Glc_4	79.9	3.38	C_4/H_4 in β-D-glucopyranoside	1-27
Glc_5	70.2	3.18	C_5/H_5 in β-D-glucopyranoside	1, 3-15, 17-27
Glc_6/Man_6	60.0	3.59	C_6/H_6 in β-D-gluco-/mannopyranoside	1-27
Xyl_1	101.5	4.38	C_1/H_1 in β-D-xylopyranoside	1-27
Xyl_2	72.7	3.03	C_2/H_2 in β-D-xylopyranoside	1-27
$Xyl_2(r_\alpha)$	69.7	3.27	C_2/H_2 in β-D-xylopyranoside of xylans reduction end	1-19, 21-27
Xyl_2-Ac	73.0	4.40	C_2/H_2 in 2-*O*-acetyl-β-D-xylopyranoside	2, 6-11, 14-17, 20, 22, 23, 25
$Xyl_1(_2Ac)$	100.8	4.49	C_1/H_1 in 2-*O*-acetyl-β-D-xylopyranoside	1-27
Xyl_3	74.5	3.28	C_3/H_3 in β-D-xylopyranoside	1-23, 25-27
Xyl_3-Ac	74.5	4.81	C_3/H_3 in 3-*O*-acetyl-β-D-xylopyranoside	1-20, 22-27
$Xyl_{2,3}$-Ac	71.6	4.54	C_2/H_2 in 2,3-*O*-acetyl-β-D-xylopyranoside	1, 2, 4-11, 12, 15-20, 22-27
$Xyl_{2,3}$-Ac	72.9	4.90	C_3/H_3 in 2,3-*O*-acetyl-β-D-xylopyranoside	1-20, 22-27
$Xyl_1(_{2,3}Ac)$	99.3	4.68	C_1/H_1 in 2,3-*O*-acetyl-β-D-xylopyranoside	1-27
Xyl_4	75.7	3.51	C_4/H_4 in β-D-xylopyranoside	1-27
Xyl_5	62.8	3.78/3.17	C_5/H_5 in β-D-xylopyranoside	1-27
Xyl_4(nr)	66.0	3.31	C_4/H_4 in β-D-xylopyranoside of xylans non-reducing end	1-15, 17-19, 22-27
Xyl_5(nr)	65.3	3.62/2.98	C_5/H_5 in β-D-xylopyranoside of xylans non-reducing end	1-27
Xyl_t(nr)	103.4	4.15	C_1/H_1 in β-D-xylopyranoside of xylans non-reducing end	1-6, 8-19, 22-27
$Xyl_t(r_\alpha)$	92.3	4.85	C_1/H_1 in α-D-xylopyranoside of xylans reduction end	1-20, 22-27
$Xyl_t(r_\beta)$	97.3	4.21	C_1/H_1 in β-D-xylopyranoside of xylans reduction end	1-20, 22-27
Man_1	100.3	4.51	C_1/H_1 in β-D-mannopyranoside	1-27
Man_2	74.5	2.90	C_2/H_2 in β-D- mannopyranoside	1-19, 21-27
Man_2-Ac	70.9	5.24	C_2/H_2 in 2-*O*-acetyl-β-D- mannopyranoside	1-27
Man_3	76.6	3.08	C_3/H_3 in β-D- mannopyranoside	1-20, 22-27
Man_3-Ac	73.0	4.82	C_3/H_3 in 3-*O*-acetyl-β-D- mannopyranoside	1-27
Man_4	79.3	3.38	C_4/H_4 in β-D- mannopyranoside	1-19, 21-25, 27
Man_5	76.9	3.63	C_5/H_5 in β-D- mannopyranoside	1-27
Man_6-Ac	63.5	4.29/4.03	C_6/H_6 in 6-*O*-acetyl-β-D- mannopyranoside	1-15, 17-19, 22-27
$Man_t(r_\alpha)$	93.5	4.86	C_1/H_1 in α-D-mannopyranoside of mannan reduction end	1-19, 21-27
$Man_t(r_\beta)$	93.6	4.59	C_1/H_1 in β-D-mannopyranoside of mannan reduction end	1-15, 17-20, 22-77
Gal_1	105.0	4.28	C_1/H_1 in β-D-galactopyranoside	1-27
U_1	97.6	5.10	C_1/H_1 in 4-O-methyl-α-D-glucuronic acid	2, 4, 7, 12, 14, 16, 18, 22, 23, 24, 26
U_4	81.6	3.09	C_1/H_1 in 4-O-methyl-β-D-glucuronic acid	1-19, 22-27
U*	91.6/94.4	5.19/4.89	C_1/H_1 in galacturonic acid	1-19, 22-27

[a]Contours assignments were assessed according to the literature.[9]

[b]The numbers refer to the following samples: 1: sdGGM raw; 2: sdGGM SSEH pellet/large; 3: sdGGM SSEH pellet/small; 4: sdGGM SSEH supernatant/large; 5: sdGGM SSEH supernatant/small; 6: esGGM raw; 7: esGGM SSEH pellet/large; 8: esGGM SSEH pellet/small; 9: esGGM SSEH supernatant/large; 10: esGGM SSEH supernatant/small; 11: epGGM raw; 12: epGGM SSEH pellet/large; 13: epGGM SSEH pellet/small; 14: epGGM SSEH supernatant/large; 15: epGGM SSEH supernatant/small; 16: sdGGM reference pellet/large; 17: sdGGM reference pellet/small; 19: sdGGM reference supernatant/large; 19: sdGGM reference supernatant/small; 20: esGGM reference pellet/large; 21: esGGM reference pellet/small; 22: esGGM reference

supernatant/large; 23: esGGM reference supernatant/small; 24: epGGM reference pellet/large; 25: epGGM reference pellet/small; 26: epGGM reference supernatant/large; and 27: epGGM reference supernatant/small.

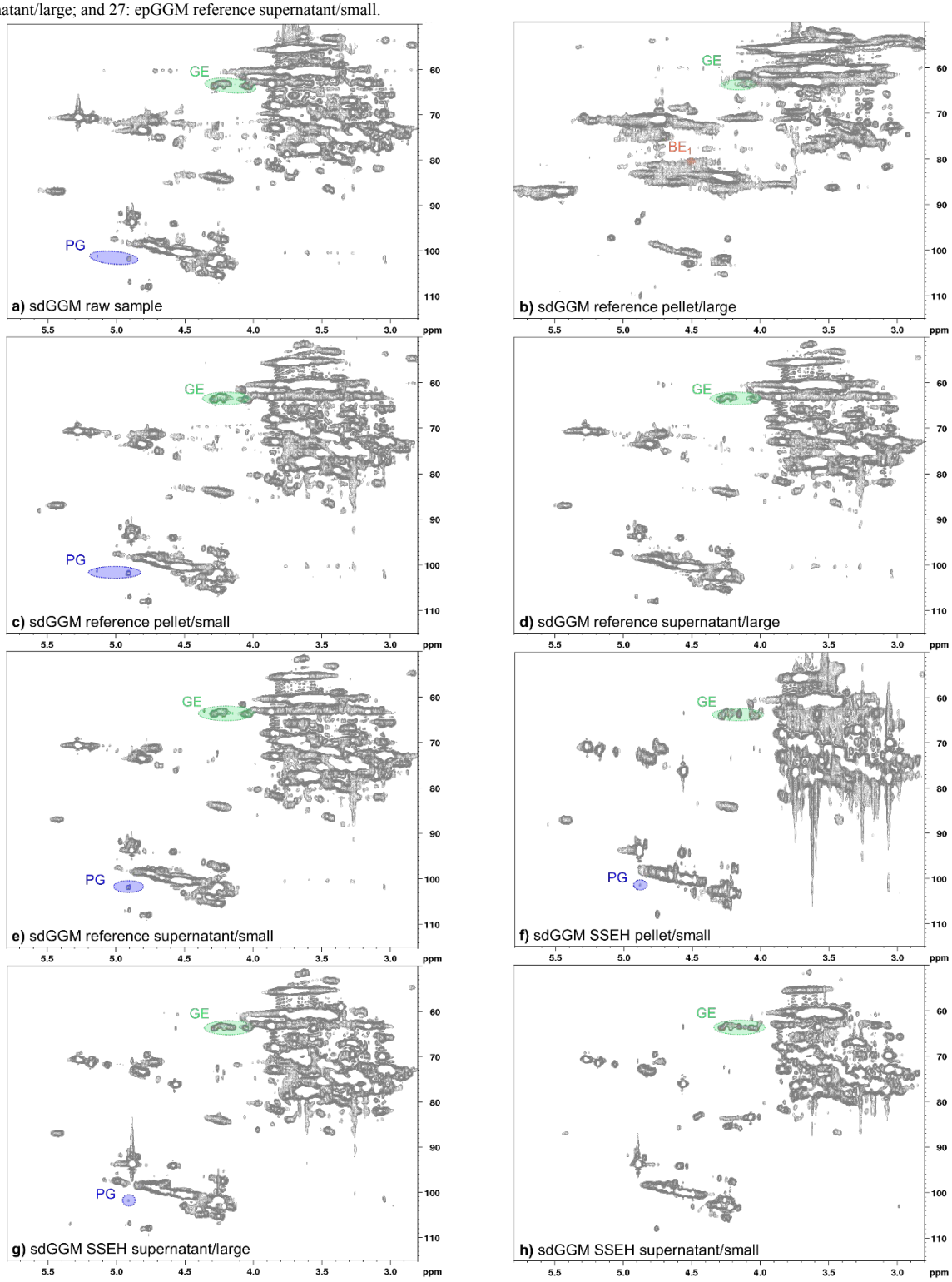

Figure S2. HSQC spectra of sdGGM raw sample (**a**), sdGGM reference pellet/large (**b**), sdGGM reference pellet/small (**c**), sdGGM reference supernatant/large (**d**), sdGGM reference supernatant/small (**e**), sdGGM SSEH pellet/small (**f**), sdGGM SSEH supernatant/large (**g**), and

sdGGM SSEH supernatant/small (**h**) fractions. Cross-signal for the various LCC bonds identified are highlighted in spectra.

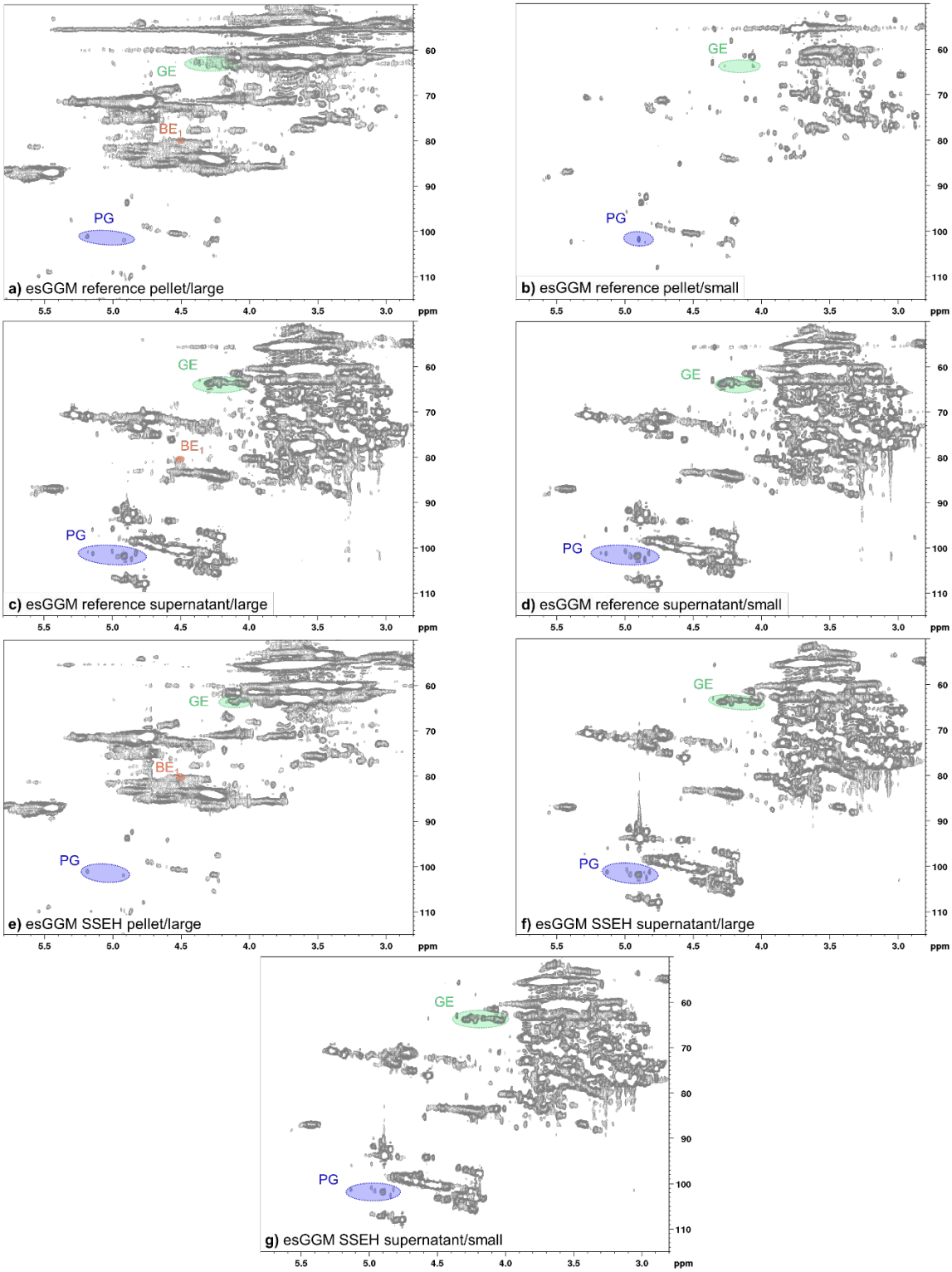

Figure S3. HSQC spectra of esGGM reference pellet/large (**a**), esGGM reference pellet/small (**b**), esGGM reference supernatant/large (**c**), esGGM reference supernatant/small (**d**), esGGM SSEH

pellet/large (**e**), esGGM SSEH supernatant/large (**f**), and esGGM SSEH supernatant/small (**g**) fractions. Cross-signal for the various LCC bonds identified are highlighted in spectra.

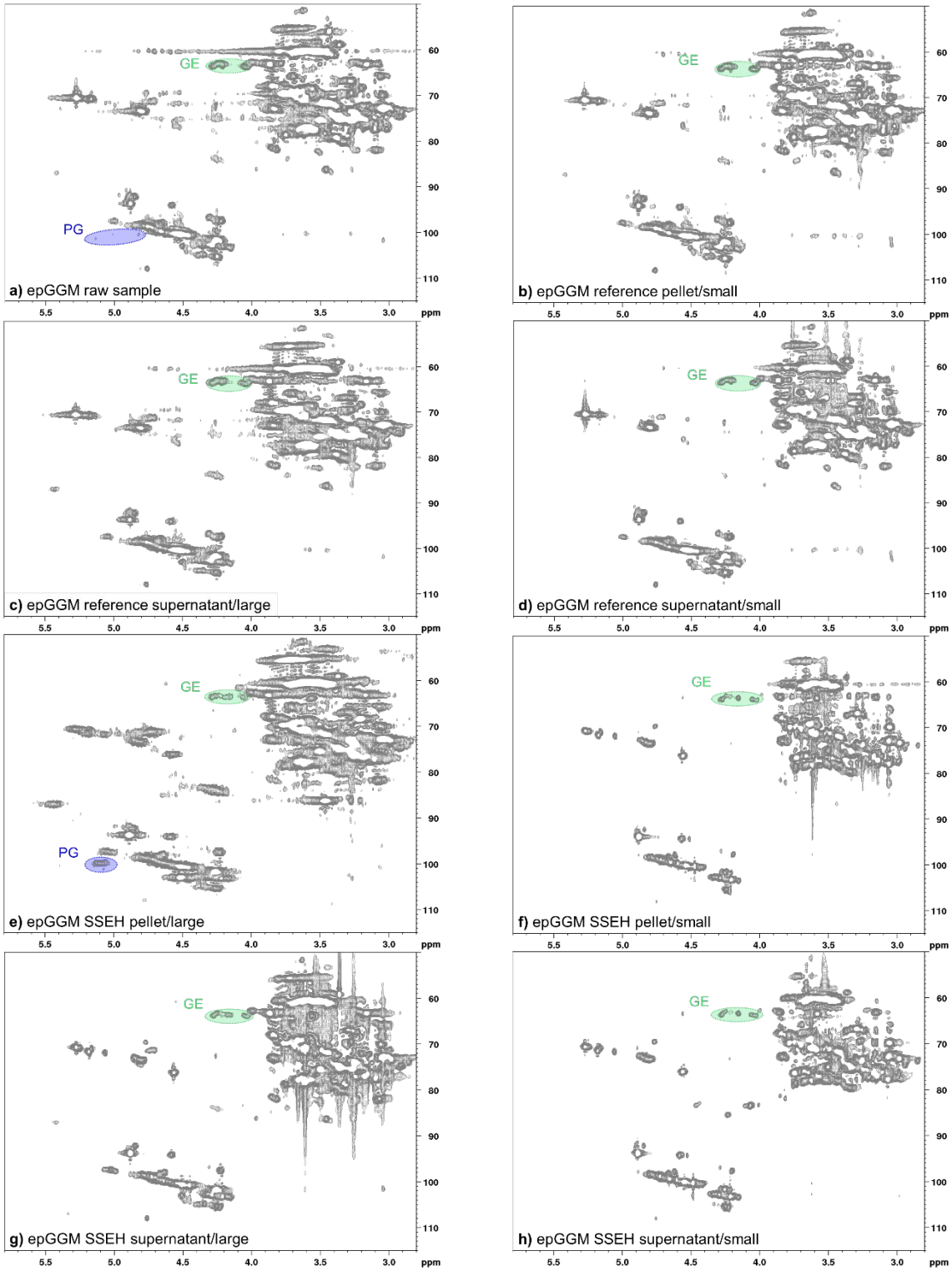

Figure S4. HSQC spectra of epGGM raw sample (**a**), epGGM reference pellet/small (**b**), epGGM reference supernatant/large (**c**), epGGM reference supernatant/small (**d**), epGGM SSEH

pellet/large (**e**), epGGM SSEH pellet/small (**f**), epGGM SSEH supernatant/large (**g**), and epGGM SSEH supernatant/small (**h**) fractions. Cross-signal for the various LCC bonds identified are highlighted in spectra.

References

1. Gupta, S.; AU - Madan, R. N.; AU - Bansal, M. C., Chemical composition of Pinus caribaea hemicellulose. *Tappi journal (USA)* **1987,** *70* (8), 113-116.
2. Kačuráková, M.; Belton, P. S.; Wilson, R. H.; Hirsch, J.; Ebringerová, A., Hydration properties of xylan-type structures: an FTIR study of xylooligosaccharides. *Journal of the Science of Food and Agriculture* **1998,** *77* (1), 38-44. https://doi.org/10.1002/(SICI)1097-0010(199805)77:1<38:AID-JSFA999>3.0.CO;2-5.
3. Chaikumpollert, O.; Methacanon, P.; Suchiva, K., Structural elucidation of hemicelluloses from Vetiver grass. *Carbohydrate Polymers* **2004,** *57* (2), 191-196. https://doi.org/10.1016/j.carbpol.2004.04.011.
4. Sun, J. X.; Sun, X. F.; Sun, R. C.; Su, Y. Q., Fractional extraction and structural characterization of sugarcane bagasse hemicelluloses. *Carbohydrate Polymers* **2004,** *56* (2), 195-204. https://doi.org/10.1016/j.carbpol.2004.02.002.
5. Drobniak, A.; Mastalerz, M., Chemical evolution of Miocene wood: Example from the Belchatow brown coal deposit, central Poland. *International Journal of Coal Geology* **2006,** *66* (3), 157-178. https://doi.org/10.1016/j.coal.2005.06.004.
6. Bian, J.; Peng, F.; Xu, F.; Sun, R.-C.; Kennedy, J. F., Fractional isolation and structural characterization of hemicelluloses from Caragana korshinskii. *Carbohydrate Polymers* **2010,** *80* (3), 753-760. https://doi.org/10.1016/j.carbpol.2009.12.023.
7. Belmokaddem, F.-Z.; Pinel, C.; Huber, P.; Petit-Conil, M.; Perez, D. D. S., Green synthesis of xylan hemicellulose esters. *Carbohydrate research* **2011,** *346* (18), 2896-2904. https://doi.org/10.1016/j.carres.2011.10.012.
8. Shamekhi, M. A.; Rabiee, A.; Mirzadeh, H.; Mahdavi, H.; Mohebbi-Kalhori, D.; Eslaminejad, M. B., Fabrication and characterization of hydrothermal cross-linked chitosan porous scaffolds for cartilage tissue engineering applications. *Materials Science and Engineering: C* **2017,** *80*, 532-542. https://doi.org/10.1016/j.msec.2017.03.194.
9. Giummarella, N.; Lawoko, M., Structural Insights on Recalcitrance during Hydrothermal Hemicellulose Extraction from Wood. *ACS Sustainable Chemistry & Engineering* **2017,** *5* (6), 5156-5165. https://doi.org/10.1021/acssuschemeng.7b00511.
10. Nishimura, H.; Kamiya, A.; Nagata, T.; Katahira, M.; Watanabe, T., Direct evidence for α ether linkage between lignin and carbohydrates in wood cell walls. *Scientific reports* **2018,** *8* (1), 1-11. https://doi.org/10.1038/s41598-018-24328-9.
11. Kim, H.; Ralph, J.; Akiyama, T., Solution-state 2D NMR of ball-milled plant cell wall gels in DMSO-d_6. *BioEnergy Research* **2008,** *1* (1), 56-66. https://doi.org/10.1007/s12155-008-9004-z.
12. Balakshin, M.; Capanema, E.; Gracz, H.; Chang, H.-m.; Jameel, H., Quantification of lignin–carbohydrate linkages with high-resolution NMR spectroscopy. *Planta* **2011,** *233* (6), 1097-1110. https://doi.org/10.1007/s00425-011-1359-2.
13. Du, X.; Pérez-Boada, M.; Fernández, C.; Rencoret, J.; del Río, J. C.; Jiménez-Barbero, J.; Li, J.; Gutiérrez, A.; Martínez, A. T., Analysis of lignin–carbohydrate and lignin–lignin linkages after hydrolase treatment of xylan–lignin, glucomannan–lignin and glucan–lignin

complexes from spruce wood. *Planta* **2014,** *239* (5), 1079-1090. https://doi.org/10.1007/s00425-014-2037-y.