SUPPORTING INFORMATION

Characterization of Organosolv Switchgrass Lignin by Using High Performance Liquid Chromatography / High Resolution Tandem Mass Spectrometry Using Hydroxide-Doped Negative-Ion Mode Electrospray Ionization

Tiffany M. Jarrell, Christopher L. Marcum, Huaming Sheng, Benjamin C. Owen, C. J. O'Lenick, Hagen Maraun, Joseph J. Bozell, and Hilkka I. Kenttämaa*

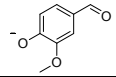
**E-mail: hilkka@purdue.edu*

Table of Contents

Table S1. Elemental compositions obtained from exact mass measurements for the deprotonated carbohydrates and fatty acids in the organosolv switchgrass sample.

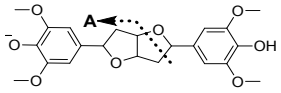
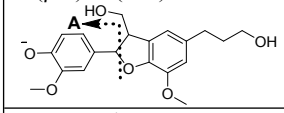
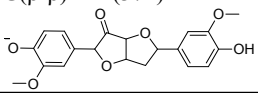
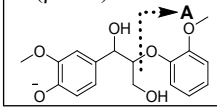
Elemental Composition	Retention Time	Exact Mass	Error (± mmu from expected mass)	DBE	Analyte Type
$C_{12}H_{23}O_2$	26.74	199.1706	1.4	1	Fatty Acid
$C_{14}H_{27}O_2$	29.01	227.2019	1.3	1	Fatty Acid
$C_{15}H_{29}O_2$	29.62	241.2176	1.4	1	Fatty Acid
$C_6H_9O_5$	3.56	161.0459	1.4	2	Saccharide
$C_{10}H_{15}O_7$	3.60	247.0825	1.3	3	Saccharide

Table S2. Deprotonated molecules formed upon negative-ion mode ESI from monomeric lignin model compounds, and the fragment ions of the deprotonated molecules with their relative abundances, and the fragment ions' fragment ions with their relative abundances, formed in consecutive ion isolation/CAD experiments.[a]

Model Compounds (m/z of [M-H]$^-$)	**MS^2/CAD Product Ions (m/z) and Their Relative Abundances**		**MS^3/CAD Product Ions[a] (m/z) and Their Relative Abundances**	
Vanillin (151) 	151-CH_3 (136)	100%	136-CO (108) 136-CO_2 (92)	100% 15%

[a] MS^3 was performed only for the most abundant product ion in the MS^2 spectra to avoid sacrificing the duty cycle of the instrument.

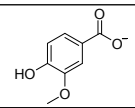
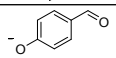
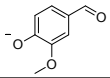
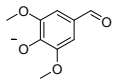
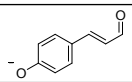
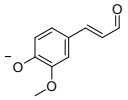
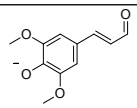
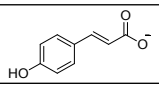
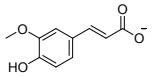
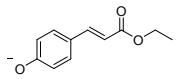
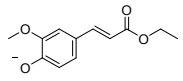
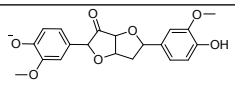
Table S3. Deprotonated molecules formed upon negative-ion mode ESI from dimeric lignin model compounds, the fragment ions of the deprotonated molecules with their relative abundances, and the fragment ions' fragment ions with their relative abundances, formed in consecutive ion isolation/CAD experiments.[a] Data for G(8-8)G, G(8-5)G, and G(8-8)FA were obtained from literature.[b]

Model Compounds (m/z of [M-H]$^-$)	**MS^2/CAD Product Ions (m/z) and Their Relative Abundances**		**MS^3/CAD Product Ions[a] (m/z) and Their Relative Abundances**	
G(β-β)G[b] (357) 	357-A (151) 357-CH_2O (327) 357-A-CH_3 (136) 357-HCOOH (311) 357-CH_3 (342)	100% 34% 23% 15% 14%	Not reported[b]	
G(β-5)G[b] (359) 	359-A (223)	100%	Not reported[b]	
G(β-β)FA[b] (371) 	371-CO_2 (327)	100%	Not reported[b]	
G(β-O-4)G: 319 	319-H_2O-CH_2O(271) 319-A (195)	100% 8%	271-CH_3 (256) 271-A (164)	100% 18%

[a] MS^3 was performed only for the most abundant product ion in the MS^2 spectra to avoid sacrificing the duty cycle of the instrument.

[b] Reference 40.

Table S4. Ions formed upon negative-ion mode ESI for organosolv switchgrass mixture that show fragmentation that matches that of a deprotonated model compound studied as well as their fragment ions, with their relative abundances, formed in consecutive ion isolation/CAD experiments.[a]

Identified Analytes: m/z of $[M-H]^-$	**MS^2/CAD Product Ions (m/z) and Their Relative Abundances**	**MS^3/CAD Product Ions[a] (m/z) and Their Relative Abundances**
A_1: 167 	167-CH_3 (152) 100% 167-CO_2 (123) 45%	152-CO_2 (108) 100%
A_2: 121 	121-CO (93) 100% 121-COH (92) 21%	93: No further fragmentation
A_3: 151 	151-CH_3 (136) 100%	136-CO (108) 100% 136-CO_2 (92) 14%
A_4: 181 	181-CH_3 (166) 100%	166-CH_3 (151) 100%
A_5: 147 	147-CO (119) 100% 147- C_3H_4O (103) 10%	119: No further fragmentation
A_6: 177 	177-CH_3 (162) 100%	162-CO (134) 100% 162-COH (133) 36% 162-C_3H_4O (106) 13%
A_7: 207 	207-CH_3 (192) 100%	192-CH_3 (162) 100%
A_8: 163 	163-CO_2 (119) 100%	119:No further fragmentation
A_9: 193 	193- CO_2-CH_3 (134) 100% 193-CO_2 (149) 45% 193-CH_3 (178) 8%	134: No further fragmentation
A_{11}: 191 	191-C_2H_4 (163) 100% 191-C_2H_6O (145) 22% 191-C_2H_4 -CO_2 (119) 14% 191- C_2H_5 (162) 7%	163-CO_2 (119) 100%
A_{12}: 221 	221-CH_3 (206) 100%	206-C_2H_5 (177) 100% 206-C_2H_5 - CO_2 (133) 33% 206-C_2H_4 (178) 25% 206-C_2H_4 - CO_2 (134) 8%
B_6: 371 	371-CO_2 (327) 100%	327-CH_2O (297) 100% 327-Y (175) 20% 327-CH_3 (312) 19%

[a] MS^3 was performed only for the most abundant product ion in the MS^2 spectra to avoid sacrificing the duty cycle of the instrument.

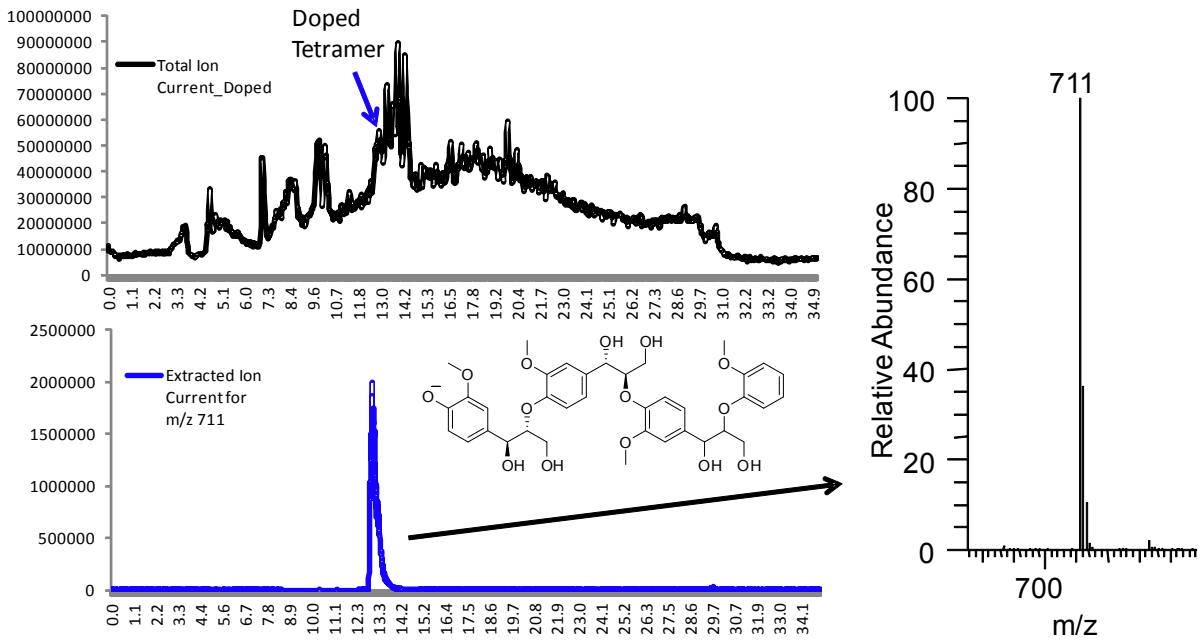


Figure S1. An HPLC chromatogram measured for the organosolv switchgrass sample after spiking it with a tetrameric model compound (0.1 mM) and the negative-ion mode ESI mass spectrum measured for the dopant.