

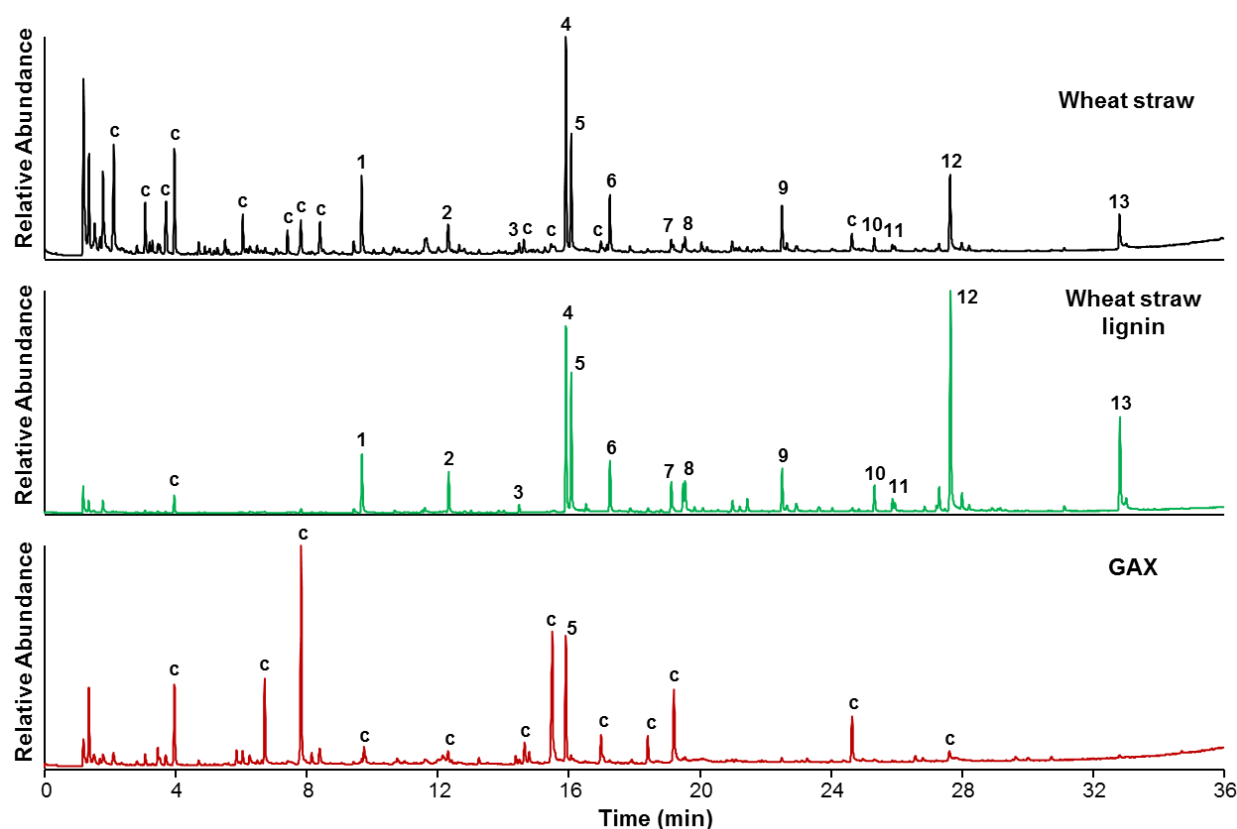


Figure S1. Py-GC-HR-MS pyrograms (TIC) of wheat straw, wheat straw lignin and glucuronoarabinoxylan (GAX). Numbers refer to major lignin-derived compounds: 1 guaiacol; 2 4-methylguaiacol; 3 4-ethylguaiacol; 4 4-vinylphenol; 5 4-vinylguaiacol; 6 syringol; 7 *trans*-isoeugenol; 8 vanillin; 9 4-vinylsyringol; 10 *trans*-propenylsyringol; 11 syringaldehyde; 12 *trans*-coniferyl alcohol; 13 *trans*-sinapyl alcohol. Carbohydrate-derived products (c) are not further specified.

Table S1. Py-GC-HR-MS relative abundance of lignin compounds in wheat straw lignin isolate used for fermentations with *P. anserina*. Corrected for relative response factors and relative abundance of ^{13}C internal standard analogues. Sum on the bases of structural classification according to van Erven et al. (1, 2). Average and standard deviation of analytical duplicates.

wheat straw lignin	
Lignin subunits (%)	
H	8.6 ± 0.3
G	58.9 ± 0.2
S	32.4 ± 0.2
S/G	0.55 ± 0.0
Structural moieties (%)	
Unsubstituted	5.6 ± 0.2
Methyl	3.4 ± 0.1
Vinyl	27.0 ± 0.5
4-VP ^a	7.1 ± 0.3
4-VG ^b	16.4 ± 0.1
C _α -ox	4.8 ± 0.0
C _β -ox ^c	1.1 ± 0.0
C _γ -ox	55.7 ± 0.8
Miscellaneous	3.5 ± 0.1
PhC _γ ^d	60.1 ± 0.7

^a 4-vinylphenol. ^b 4-vinylguaiacol. ^c excluding diketones. ^d phenols with intact α,β,γ carbon side chain.

Table S2. Semiquantitative ^1H - ^{13}C HSQC NMR structural characterization of wheat straw lignin isolate used for fermentations with *P. anserina*.

wheat straw lignin	
Lignin subunits (%)^a	
H	3
G	63
G _{ox}	0
S	34
S _{ox}	0
S/G	0.5
Hydroxycinnamates (%)^b	
<i>p</i> -coumarate	8
ferulate	6
Flavonolignin (%)^b	
tricin	15
Lignin interunit linkages (%)^{b,c}	
β -O-4' aryl ethers	56 (91)
β -5' phenylcoumarans	4 (7)
β - β' resinols	1 (2)
total	62 (100)

^a relative distribution of lignin subunits (H+G+G_{ox}+S+S_{ox}=100)

^b relative volume integral of substructure versus volume integral of total lignin subunits

^c relative distribution of total interunit linkages in parentheses

References

1. Van Erven G, Nayan N, Sonnenberg AS, Hendriks WH, Cone JW, Kabel MA. Mechanistic insight in the selective delignification of wheat straw by three white-rot fungal species through quantitative ^{13}C -IS py-GC-MS and whole cell wall HSQC NMR. *Biotechnol Biofuels*. 2018;11:262.
2. Van Erven G, Hilgers R, de Waard P, Gladbeek E-J, van Berkel WJH, Kabel MA. Elucidation of in situ ligninolysis mechanisms of the selective white-rot fungus *Ceriporiopsis subvermispota*. *ACS Sustainable Chem Eng*. 2019;7:16757-64.