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Supplementary materials for: Evaluation of soda lignin from wheat straw/Sarkanda grass as a potential future consolidant for archaeological wood

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Further details on the reference specimens from Py-GC/MS analyses

Distributions of categorized pyrolysis products of holocellulose and lignin are shown in Figures S1a and Figure S1b respectively. Percentage distribution of holocellulose pyrolysis products obtained from untreated archaeological pine are very similar to those from fresh pine, where the most abundant are cyclopentenones, followed by anhydrosugars. Wood soaked in ethyl acetate is similar to the untreated specimen, but has slightly higher relative abundance of anhydrosugars. This may be either due to differences in initial state of preservation or due to leaching of compounds in solvent.

Regarding the lignin fraction (Figure S1b), the profile of untreated archaeological wood (untr archeo 47) is very similar to that of fresh, undegraded wood [1-3]. In fact, the monomers group (in case of softwood lignin, coniferyl alcohols) is most abundant, highlighting the very good state of preservation of lignin in this specimen. The abundances of monomers can indicate the state of the lignin polymeric structure. The decrease in the abundance of monomers and increase in short chain in archaeological wood is considered the degradation/alteration index of this polymer. The increase in the yield for secondary reactions (formation of short-chain lignin pyrolysis products) may be related to a less reticulated structure, not only of lignin polymer, quite stable in waterlogged condition, but also of lignin-hemicellulose bonds. It is known that structure with reduced cross-linking is relatively more suited to undergo further pyrolysis degradation [3]. Thermal energy in an altered/partially degraded structure causes not only breaks in the inter-monomeric bonds (formation of monomers) but also cleavage of lignin-hemicellulose linkages, and consequently increasing the pyrolysis products of the lignin with shorter side chains. The class of pyrolysis products whose abundance in archaeological woods differs from those of fresh undegraded wood comprises of carbonyl pyrolysis products. These pyrolysis products are present in sound lignin in very small relative amounts and cannot be formed during pyrolysis due to the absence of oxygen. The increase of these pyrolysis products indicates oxidation of lignin in the archaeological specimens. The fact that the group of acidic products (carboxylic functionalities) remained as low as in fresh wood indicates the oxidation process was not advanced. The lignin profiles of ethyl acetate-treated specimen nr. 37 is very similar to those for specimen nr. 47. They do, however, have lower relative abundances of monomers, indicating slightly more degradation of lignin. Otherwise, both archaeological specimens show similar lignin profiles.

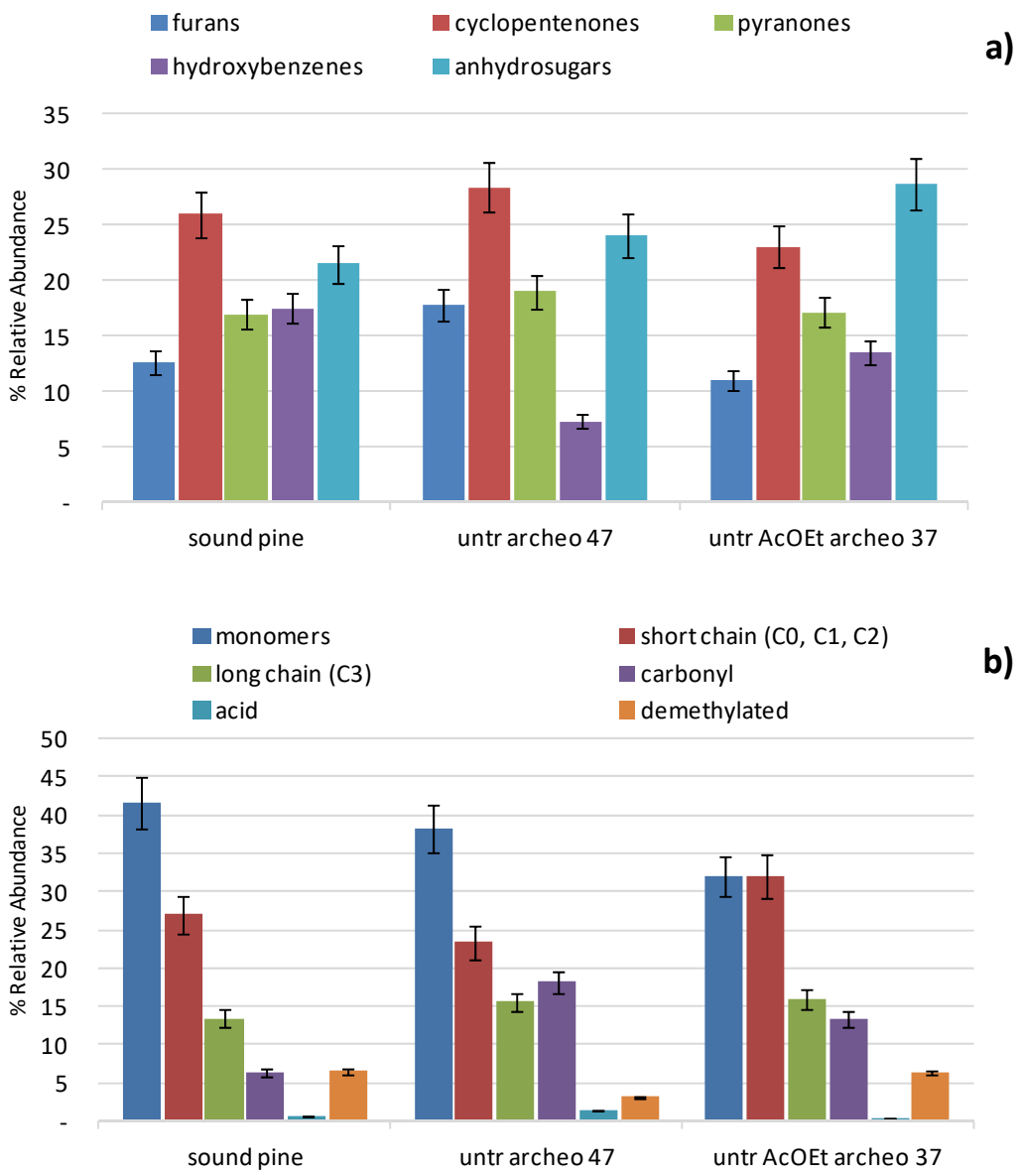

Figure S1. Distribution of categories of a) holocellulose and b) lignin pyrolysis products for sound pine wood, untreated and soaked in ethyl acetate archaeological pine wood specimens. Relative abundances are expressed as percentages relative to total holocellulose (a) and total lignin fractions (b), respectively.

Pure soda lignins

As expected, in the soda lignins most pyrolysis products originated from lignin in both P1000 (92.7%) and FB01 (94.5%) preparations, as seen in Table S1. However, a small fraction of pyrolysis products derived from holocellullose (cellulose and hemicellulose) were also identified in both P1000 (7.3%) and FB01 (5.5%) lignins. This demonstrates that a proportion of carbohydrates are firmly bound to lignin, likely covalently (as for example seen in lignin-carbohydrate complexes, LCCs), bonds which can even survive harsh lignin isolation processes [4].

Lignin pyrolysis products mainly originated from three types of lignin units in both P1000 (isolated by the Soda method) and FB01 preparations (ethyl acetate-extracted fraction from P1000): guaiacyl (G-lignin), syringyl (S-lignin) and para-hydroxyphenyl (H-lignin) (Table S1). Minor lignin components such as coumarates and ferulates, were also identified. This is expected when sourced from straws and grasses [5]. In comparison, wood mainly has G-type units (softwoods) or both S- and G-type units (hardwoods). H-type lignins also occur in some woods but in much lower amounts than S and G types [6].

Relative abundances of lignin groups for both soda lignins, P1000 and FB01, indicate differences in polymeric structures (Figure S2) compared to native lignin from sound pine (Figure S1b). The S/G ratios indicate a semi-condensed lignin structure with moderate molecular rigidity. In FB01, the relative pyrolytic G-content is lower and so this lignin is likely to have fewer condensed structures [7].

Both soda lignins had very low relative abundances of monomers. For P1000, short chain lignin pyrolysis products are the most abundant group, while in FB01 both short chain and carbonyl groups are most abundant. In FB01, there are lower relative abundances of long chain groups, greater abundances of demethylated groups and slightly greater abundances of acid groups than in P1000. These differences show that FB01 may have slightly different chemical properties than P1000. The greater amounts of compounds with polar carbonyl and carboxyl functionalities may increase the polarity of this preparation.

Table S1. Holocellulose(H) and Lignin (L) relative abundances from soda lignins used in the experiments expressed as percentages of all holocellulose and lignin pyrolysis products. Straw lignin units: guaiacyl (G-lignin), syringyl (S-lignin) and p-hydroxyphenyl units (H-lignin), with minor amounts of p-coumarates (C) and ferulates (F).

	P1000	**FB01 (EtOAc fraction of P1000)**
Holocellulose	7.3	5.5
Lignin	92.7	94.5
H/L	0.08	0.06
Lignin units present		
S type	46.4	46.2
G type	30.7	25.6
H type	15.6	22.7
S/G	1.51	1.80
p-coumarates (C)	3.17	1.81
Ferulates (F)	0.90	1.63

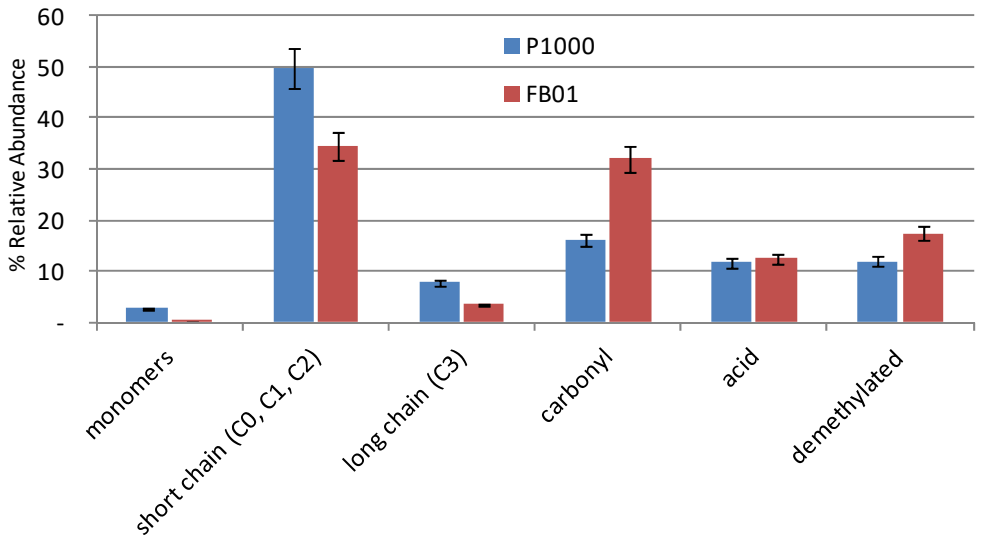

Figure S2. Distribution of lignin pyrolysis products from soda lignin P1000 and FB01, shown as % relative abundances of the total lignin pyrolysis products obtained by Py-GC/MS.

Table S2. Band heights averaged from each depth analyzed by FTIR.

	Average band height at 1328 cm^{-1}	Standard dev.	Corrected band heights for P1000	Corrected standard dev. for P1000
P1000 lignin	0.100	--	0.124	--
FB01 lignin	0.124	--	--	--
30% P1000 outer surface average	0.046	0.008	0.057	0.010
30% P1000 inner surface average	0.027	0.005	0.033	0.006
30% P1000 core edge average	0.015	0.001	0.019	0.001
30% P1000 core centre average	0.020	0.001	0.025	0.002
30% FB01 outer surface average	0.067	0.004	--	--
30% FB01 inner average	0.048	0.009	--	--
30% FB01 core edge average	0.026	0.005	--	--
30% FB01 core centre average	0.030	0.004	--	--
Ethyl acetate average	0.012	0.000	--	--

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