Electronic Supplementary Information (ESI) for

Catalytic depolymerisation of suberin rich with precious metal catalysts

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Suberin is a natural biopolymer with a structure, originally proposed by Bernards[1] (Figure S1), comprising two separate layers: poly-alphatic layers (SPAD) and poly-phenolic layer (SPPD). The SPAD layer contains long chain α,ω-dicarboxylic acids, ω-hydroxyacids and alkanoic acids with the SPPD layer containing mainly aromatic precursors such as lignin[1]

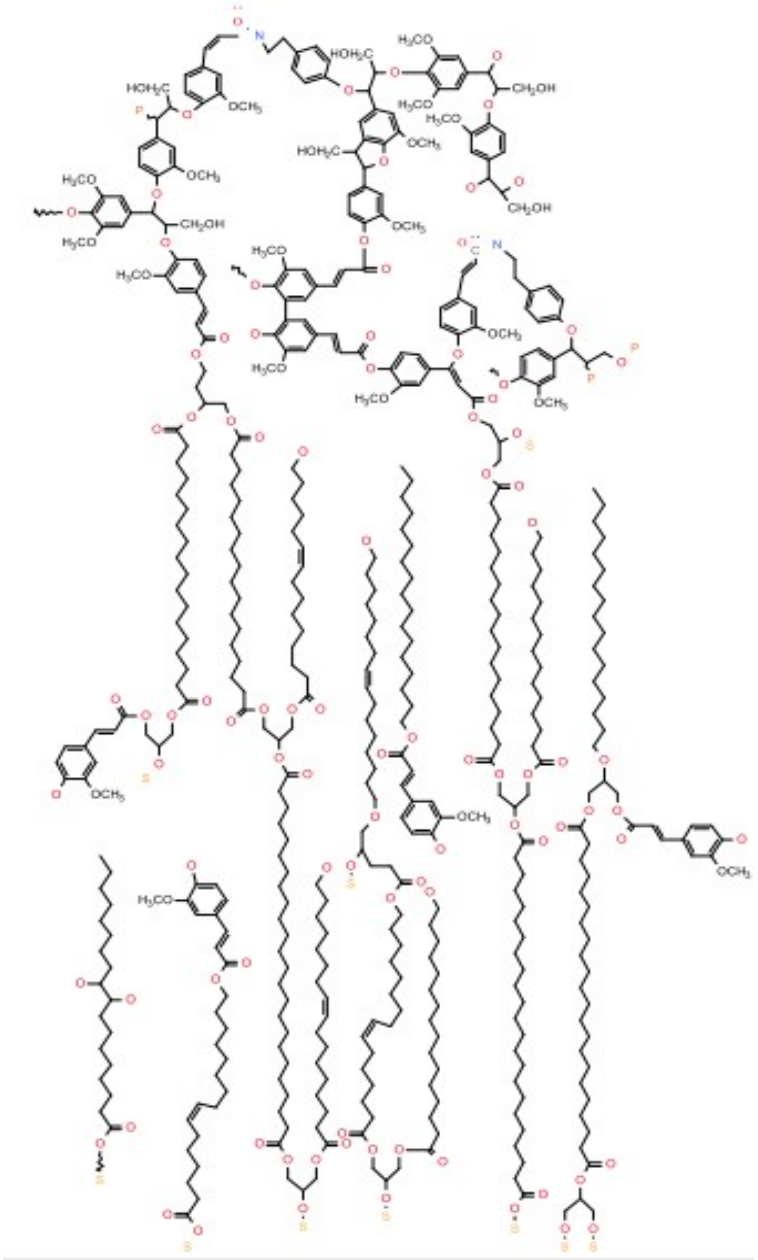


Figure S1 - Suberin Structure (drawn based on Bernards[1])

Experimental

Materials

All cork samples were obtained from commercial wine bottles and pulverised and sieved to <0.2 mm using a Kinematica Polymix PX-MFC 90D. The samples were used without any pre-extraction. 1,4 dioxane was supplied by Alfa Aesar. Double distilled water was used in all reactions. All other solvents and reagents used were obtained from Sigma Aldrich and used as received, unless otherwise stated. Commercial rhodium on carbon (5 wt.% Rh, 64 % wet) was supplied by Johnson Matthey. 5 wt.% rhodium supported on hydrotalcite was prepared by adding synthetic hydrotalcite (0.5 g) to a mortar and concentrated Rh(acac) (0.025 g, 5 wt%) in chloroform (0.25 mL) solution was pipetted evenly over the hydrotalcite. This mixture was then ground thoroughly with a pestle. This solid was left in an oven at 60 °C overnight to dry, and then calcined at 500 °C under air for 5 hours (heated at 1 °C min^{-1}, cooled at 10 °C min^{-1}).

Batch reaction conditions for cork hydrogenolysis

Under identical conditions to those reported in the previous study[1] the catalyst (Rh/C; 0.5 g or Rh/Htc; 0.5 g), cork powder (0.2 mm, 2.0 g) and the appropriate solvent system were added together in a mini-reactor (Hastelloy® 100 mL volume, Autoclave Engineers). Air was expelled from the reactor by exchange of the headspace with hydrogen, and the pressure was set to 40 bar H_2 with the stirring set to 1000 rpm. Thereafter, the temperature was increased to 200 °C (at a rate of 10 °C min^{-1}) and, thereafter, this temperature was maintained for 4 h.

Using the previously reported conditions[1] of a 1:1 dioxane: water (44 mL) solvent system, the effect on the hydrogenolysis by the addition of base (0.25-0.5 g of hydrotalcite or dolomite) was investigated.

Additionally, five different solvent systems have been investigated for the hydrogenolysis of cork; 1,4-dioxane, 2-methyl-tetrahydrofuran (MeTHF), ethylene glycol, methanol and ethanol. For the comparison of solvent systems a solvent to water ratio of 6:4 was used unless otherwise stated.

Product Extraction Methods

After cooling, the reaction mixture was filtered and the filter cake washed. For the dioxane, ethylene glycol, ethanol and methanol solvent systems, the filter cake was washed with 1 : 1 dioxane : water (3 × 20 mL). The combined filtrates were extracted with chloroform (3 × 200 mL), dried over anhydrous magnesium sulphate and concentrated under vacuum resulting in the isolation of the bio-oil. This bio-oil was dissolved in 1 : 1 dioxane: water (30 mL) to which sodium hydroxide (0.5 g) was added to neutralise free acids. After refluxing for 4 hours the mixture was extracted with chloroform (3 × 100 mL). For the MeTHF solvent system, the resulting biphasic mixture was separated and the aqueous layer was extracted with 2-MeTHF (2 x 100 mL).

In all cases, the organic phase was then dried with anhydrous magnesium sulphate and filtered. The solvent was then removed under reduced pressure and remaining traces of solvent removed under high vacuum. This extraction process resulted in the production of a brown bio-oil (the crude product) for each of the solvent systems.

Analysis and Characterisation

Analysis of the crude yield for all reactions investigated has identified two main product streams, namely lipids and aromatics.

Quantitative GC-MS analysis of the lipids in the bio-oil was performed using a Perkin-Elmer autosystem XL GC with a Perkin-Elmer Turbomass detector and BP5 column. The bio-oil (20 mL) was dissolved in a solution of 1.25 M hydrochloric acid (HCl) in anhydrous methanol (2 mL). This mixture was heated under reflux for 4 h under nitrogen after which the methanol was removed by evaporation using a nitrogen stream. The residue was suspended in water (5 mL) and extracted with chloroform (3 × 5 mL). The organic layer was dried and concentrated using a nitrogen stream to an oily residue which was further dried under vacuum for 2 h. After this time the bio-oil was dissolved in anhydrous pyridine (0.3 mL), *N,O*-bis(trimethylsilyl)-trifluoroacetamide (0.5 mL containing 10% chlorotrimethylsilane) was then added. This mixture was heated at 70 °C with agitation for 1 h under nitrogen. After cooling, 0.2 mL of a standard of 1 mg mL^{-1} (trimethylsilyl)cholesterol was added. This mixture was injected directly into the GC-MS for characterisation.

Quantitative ^{1}H NMR spectroscopy was performed on a Bruker Avance spectrometer at 300 MHz with tetramethylsilane (TMS) as internal standard (unless indicated otherwise). The extracted bio- oil (50 mg) and vanillin (10 mg), as an internal standard, was measured into a sample vial, and dissolved in deuteriated chloroform (1 mL).

Errors were calculated via the following equation:

$$Reported\ error = \Delta x_{avg} \pm \frac{Range}{2\sqrt{Number of\ samples}}$$

Quantification of yields from NMR

MestReNova (v.5.2.3.) NMR analysis software was used and the aldehyde hydrogen on vanillin was used to calibrate the spectra (set at 9.73ppm) and was integrated as 1.

Determination of fatty acid yields

In the region between 2.0 ppm and 3.0 ppm there are resonances resulting from the CH_2 groups alpha and beta to the benzene ring of the aromatic products, as well as alpha to the carboxylic acid of the lipid products. Previously, triplets have been assigned in this region[2]. The CH_2 group adjacent to the carboxylic acid group of lipids is found at 2.24 (2H, t, J = x Hz); propyl-guaiacol CH_2 alpha to the ring is found at 2.42 (2H, t, J = x Hz); dihydroconiferyl alcohol CH_2 alpha to the ring is found at 2.55 (2H, t, J = x Hz). Previously not observed in the spectra is dihydroferulic acid {DFA/ 3-(4-Hydroxy-3-methoxyphenyl)propanoic acid}. The CH_2 beta to the ring of DFA is found at 2.78 (2H, t, J = x Hz); further, the CH_2 group alpha to the ring is observed at 2.50 (2H, t, J = x Hz). Each triplet can be integrated to calculate the mass of each individual product of the hydrogenolysis, this calculation is found in Equation S1:

$$weight\% = \frac{\left(\frac{\frac{int.}{2} \times n_V \times M_M}{M_S}\right) \times M_O}{M_C} \times 100$$

Equation S1: where: int. = integration of CH_2 triplet; n_V = moles of vanillin in sample; M_M = molecular mass of species; M_S = mass of sample submitted; M_O = mass of oil (as crude yield); M_C = mass of cork used.

Molecular weights of the products can be found in Table S1. The wt% values calculated here are shown as weight percentages of the starting material (cork), allowing comparisons to be drawn across all of the results. To calculate the yield of the lipids an arbitrary weight of 170 g mol^{-1} was used, based on in depth analysis of fatty acid chain length from previous work.[2]

Determination of aromatic yields

In the region between 6.4 ppm and 7.4 ppm the aromatic hydrogens on the guaiacyl substituent are evident. The area of 6.5 – 6.8 was integrated and taken to represent 3 CH groups on the guaiacyl substituent of the aromatic products, this integration is used to calculate an arbitrary value representing the weight percentage of the aromatic products. To do this, an arbitrary molecular weight was taken to be 180 (the average M_M of compounds 1-3) using Equation S2.

$$weight\% = \frac{\left(\frac{\frac{int.}{3} \times n_V \times 180}{M_S}\right) \times M_O}{M_C} \times 100$$

Equation S2. where: int. = integration 3x aromatic hydrogens; n_V = moles of vanillin in sample; 180 = molecular mass average; M_S = mass of sample submitted; M_O = mass of oil (as crude yield); M_C = mass of cork used.

GC-MS

Crude product

Table S1: The identified products from GC-MS data of non-derivative oil

Time	*m/z*	Compound
11.7	124	guaiacol
13.46	138	methyl guaiacol
14.76	152	ethyl guaiacol
16.02	166	propyl guaiacol
17.88	220	C16 alcohol
19.51	182	DCA
20.11	240	C15 acid
20.84	240	C16 alkene acid
21.19	254	C16 acid
22.22	268	C17 acid

Time	*m/z*	Compound
22.8	256	C18 alkene acid
23.22	282	C18 acid
24.15	296	C19 acid
24.7	284	C20 alkene acid
25.06	310	C20 acid
25.93	324	C21 acid
26.79	338	C22 alkene acid
27.65	429	C22 epoxide acid
27.93	341	C20 diacid

GC-MS was performed crude yield. The gas chromatograph and mass spectra for 2 compounds are shown in the supporting information. Most of the identified products are listed in Table S1. Aromatic products, lipids and alcohols are observed.

Derivative lipids

A derivatives sample was prepared and GC-MS was performed. The identified products are listed in Table S2. The derivation converted many of the acids into methyl esters, the alcohols were converted into trimethyl-silyl groups.

Table S2: The identified products from GC-MS data of derivative oil

Time	*m/z*	Compound
15.8	236	isoeugenol
16.71	238	propyl guaiacol
19.34	292	C16 alcohol - sime3
20.23	282	DFA - ester
20.62	326	DCA - ester
20.81	340	DFA - acid sime3

Time	*m/z*	Compound
21.74	270	C16 acid - ester
23.72	298	C18 acid - ester
24.89	341	C18 diacid - ester
26.8	384	C20 diacid
27.55	415	C22 acid

Solvent Effect

Table S3: Kamlet Taft Parameters of Solvents

	Alpha	Beta	Mu	Bio-oil	Lipids	Aromatic
1,4-Dioxane[4]	0	0.37	0.35	27	17.1	6.1
MeOH[4]	0.93	0.66	0.58	17	11.1	8.7
EtOH[4]	0.52	0.16	-0.03	30.5	14.4	5.6
EtGly[5]	0.92	0.52	0.9	29.5	9.8	2.4
MeTHf[4]	0	0.58	0.53	40	19.4	4.7

Figure S2: α (H bonding ability) of Solvent vs Weight Percentage of product

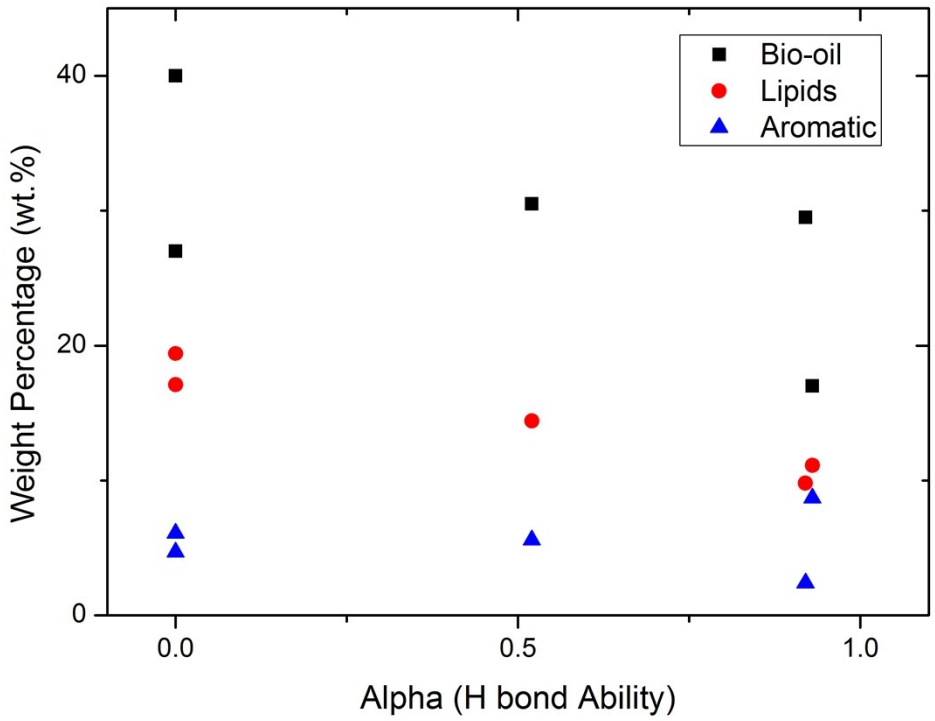


Figure S3: β (Basicity) of Solvent vs Weight Percentage of product

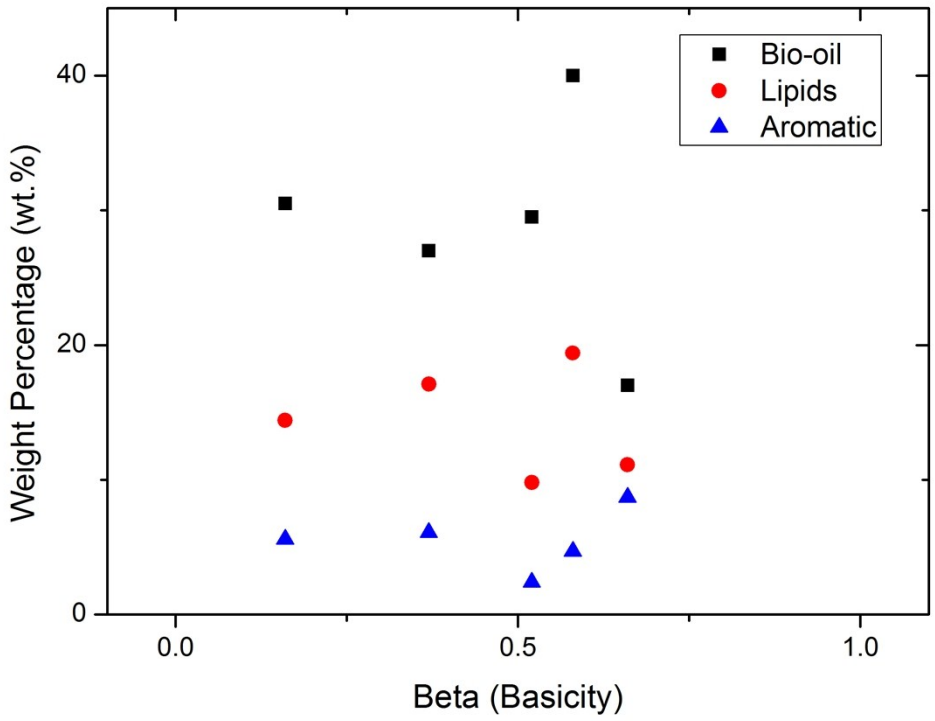
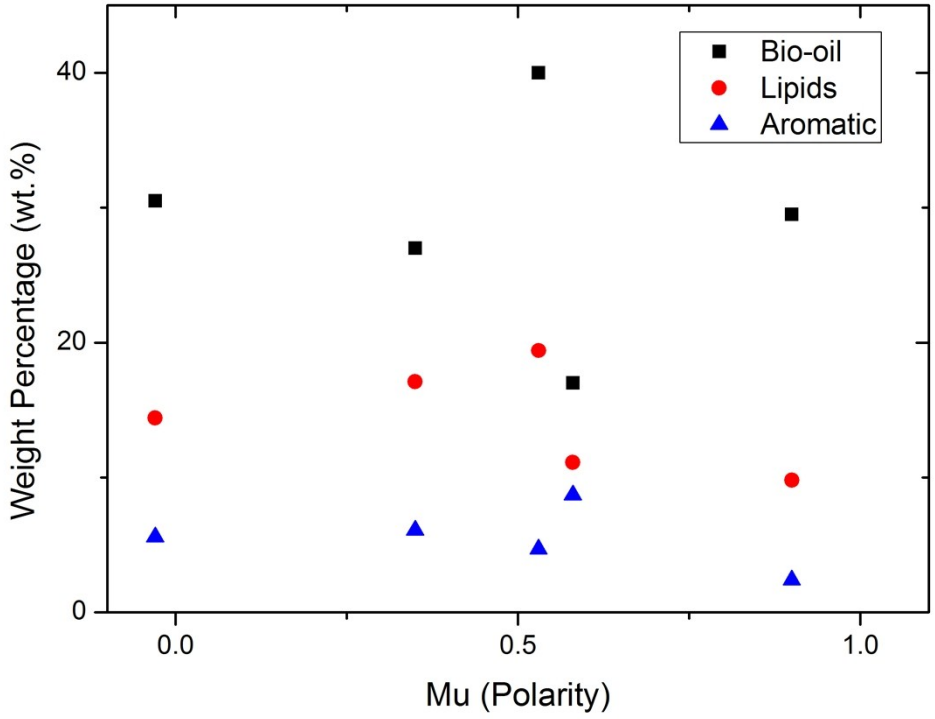


Figure S4: μ (Polarity) of Solvent vs Weight Percentage of product



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