Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supporting Information

Accessing suberin from cork via ultrafast supercritical hydrolysis

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Fig. SF1 Photos of the original cork biomass (A) in comparison with the UFC-2 (B) and UFC-3 (C) solid hydrolysis products and the carbohydrate-lignin complex after suberin extraction (D)

SF2 GC MS data for suberin acid monomer samples

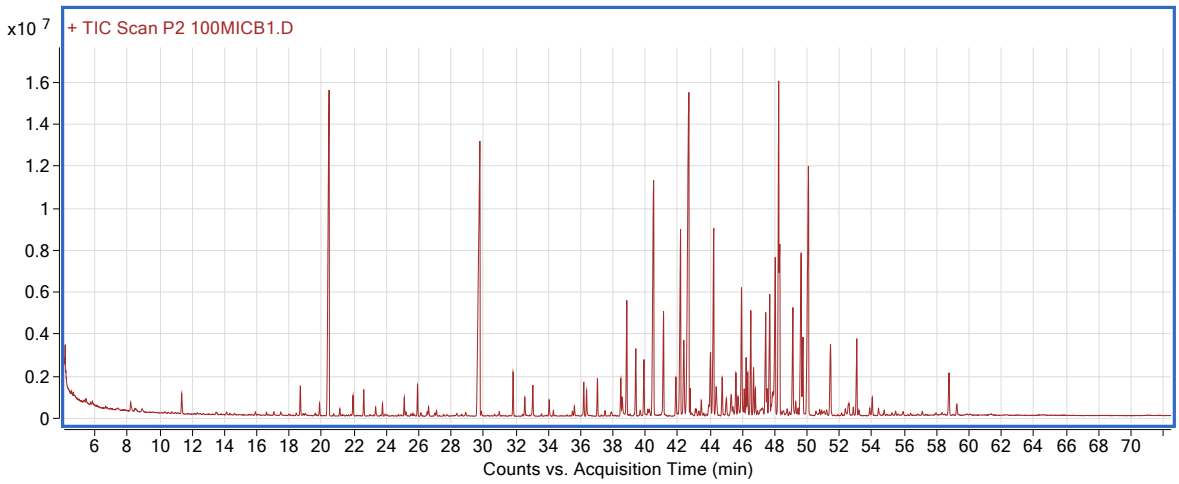

Figure SF2. Representative GC-MS chromatogram for suberin obtained via alkaline methanolysis (sample based from chemical summative analysis)

SF3. Formation of repolymerization products

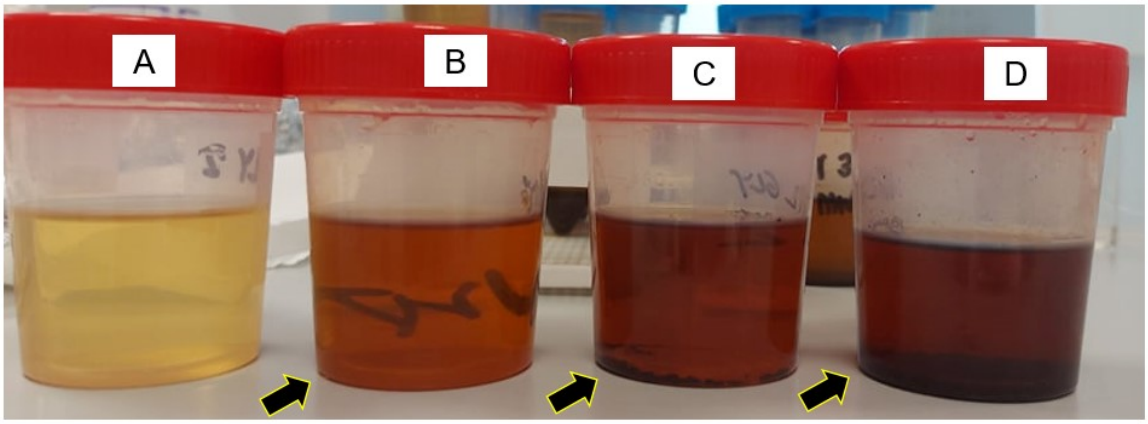

Figure SF3. Observed formation of repolymerization products at the bottom of the solution denoted “char”. Aqueous fraction after acidification post-methanolysis (suberin hydrophilics parts) [A] original cork biomass; [B] UFC-3 (395^{O}C, 265 bar, 250 ms); [C] UFC-1 (389^{O}C, 272 bar, 430 ms); [D] UFC-2 (386^{O}C, 265 bar, 1270 ms)

Table ST1 Chemical summative data

Table ST1: Chemical summative analysis data for as-received cork from Ainia Technologies, in comparison with data reported in literatures. Data in the current study is reported as g compound per 100 g of oven dry weight (o.d.w.) cork. Suberin determination for all entries was carried out via alkaline methanolysis.

	This study	**Cunha et al. 2020** [28]	**Pereira 2013** [12]	**Pinto et al. 2009** [16]
Components	g/ 100 g o.d.w. cork			
TOTAL EXTRACTIVES	10.5 ± 1.6	11.4 ± 2.2	16.2 ± 3.9	9
Hexane	3.6 ± 0.3	-	-	-
Ethanol	4.0 ± 0.9	-	-	-
Water	3.8 ± 1.1	-	-	-
TOTAL SUBERIN	47.7 ± 3.9	-	-	-
Suberin monomers	44.1 ± 3.7	41.0 ± 3.4	42.8 ± 6.2	33
Glycerol[a]	3.7 ± 0.2	-	3.8 ± 0.6	-
POLYSACCHARIDES	14.6 ± 1.8	18.4 ± 5.2	18.2	23
Cellulose[b]	7.6 ± 0.7	-	-	-
Hemicellulose[c]	7.0 ± 1.1	-	-	-
TOTAL LIGNIN	21.1 ± 1.2	24.9 ± 3.4	22 ± 3.3	-
Klason lignin	20.6 ± 1.1	-	-	33
Acid soluble lignin	0.5 ± 0.1	-	-	-
ASH	1.7 ±	0.89 ± 0.02	1.2	4

[a]determined by HPLC [b]as glucose; [c]xylose + arabinose

Table ST2. Identification and quantification of major suberin monomers obtained via alkaline methanolysis (Chem. Summa. – conventional treatment; UFC-1 (389^{O}C, 272 bar, 430 ms); UFC-2 (386^{O}C, 265 bar, 1270 ms); UFC-3 (395^{O}C, 265 bar, 250 ms)

Compounds	Chem. summative		UFC-1		UFC--2		UFC-3	
	µg/mg	s.d.	µg/mg	s.d.	µg/mg	s.d.	µg/mg	s.d.
Glycerol	0.639	0.008	0.395	0.007	0.436	0.008	0.651	0.002
Fatty alcohols	1.149	0.094	1.588	0.105	1.704	0.105	1.624	0.072
Eicosan-1-ol	0.29	0.005	0.429	0.022	0.468	0.019	0.458	0.02
Docosan-1-ol	0.859	0.089	1.159	0.083	1.237	0.086	1.166	0.052
Fatty acids	1.182	0.107	0.898	0.051	0.913	0.069	1.398	0.051
Octadecanoic acid	0.307	0.017	0.313	0.003	0.266	0.003	0.392	0.008
Eicosanoic acid	0.076	0	0.079	0.004	0.073	0.006	0.064	0
Docosanoic acid	0.799	0.09	0.507	0.044	0.574	0.06	0.942	0.043
ω-Hydroxy-acids	11.301	0.936	5.042	0.487	6.809	0.5	8.403	0.38
16-hydroxyhexadecanoic acid	0.29	0.016	0.183	0.006	0.242	0.008	0.372	0.005
18-hydroxyoctadec-9-enoic acid	3.347	0.291	2.044	0.128	2.709	0.177	3.937	0.147
22-hydroxydocosanoic acid	3.872	0.232	0.487	0.091	0.602	0.104	0.744	0.045
24-hydroxytetracosanoic acid	1.476	0.166	0.092	0.053	0.127	0.003	0.078	0.015
9,10,18-trihydroxyoctadecanoic acid	2	0.209	1.44	0.114	1.894	0.122	2.171	0.105
9,10-epoxy-18-hydroxyoctadecanoic acid	0.317	0.022	0.795	0.095	1.236	0.086	1.1	0.063
α,ω-dicarboxylic acids	5.177	0.515	11.039	1.269	14.013	1.162	11.994	0.699
Hexadecanedioic acid	2.496	0.226	2.794	0.211	2.886	0.202	1.845	0.084
Octan-1,8-dioic acid	0.177	0.007	0.163	0.004	0.157	0.005	nd.	Nd
Nonan-1,9-dioic acid	n.d.	n.d.	0.335	0.005	0.267	0.004	0.257	0.014
9,10-dihydroxyoctadecanedioic acid	1.212	0.157	2.137	0.183	3.446	0.179	3.851	0.18
Docosanedioic acid	0.17	0.007	1.895	0.272	3.016	0.318	2.391	0.188
Decan-1,10-dioic acid	0.927	0.102	1.379	0.161	2.039	0.171	1.892	0.136
Undecanedioic acid	0.194	0.016	2.336	0.433	2.203	0.283	1.757	0.097
Phenolics	5.91	0.059	6.835	0.08	7.063	0.046	7.146	0.021
cis Ferulic	5.125	0.034	6.127	0.061	6.384	0.026	6.603	0.01
Transferulic	0.441	0.005	0.424	0.015	0.374	0.004	0.238	0.004
Vanillin	0.344	0.02	0.284	0.004	0.304	0.016	0.304	0.007
Extractives	0.939	0.074	2.383	0.507	2.66	0.391	1.781	0.056
Lupenone	0.727	0.063	1.54	0.326	1.889	0.284	0.895	0.026
Betulinic acid	0.211	0.011	0.843	0.181	0.77	0.107	0.887	0.03

SL List of Chemicals

The chemicals used in the experiments were procured from their respective suppliers and were used as-received. Methanol (99.8%), n-hexane (95%), anhydrous sodium sulphate (99%), sulfuric acid (96%), dichloromethane (99%), potassium hydroxide(85%), methyl tert-butyl ether (99.8%), calcium carbonate (98.5%) and glycerol (99%) were procured from Panreac Applichem. Ethanol (99.9%) was sourced from Davila Villalobos, Spain while phenol (99%) and chloroform (99%) were from Acros Organics. Sodium methoxide (95%), BSTFA (99%), anhydrous pyridine (99.8%), chlorotrimethylsilane (98%) and hexadecane (99.9%) were bought from Sigma Aldrich. Deionized water was used as the reaction medium. The HPLC standards (cellobiose, galacturonic acid, glucuronic acid, glucose, mannose, xylose, fructose, arabinose, glyceraldehyde, glycolaldehyde, lactic, formic, acetic and acrylic acids, furfural and 5-hydroxymethylfurfural (5-HMF)) were purchased from Sigma Aldrich.