Electronic Supplementary Information (ESI)

The Hy-MASS Concept: Hydrothermal Microwave Assisted Selective Scissoring of cellulose for in-situ production of (meso)porous nanocellulose fibrils and crystals †

Eduardo M. de Melo [a], James H. Clark [a], Avtar S. Matharu [a*]

[a] *Green Chemistry Centre of Excellence, Department of Chemistry, University of York, UK. *E-mail: avtar.matharu@york.ac.uk*

† Electronic Supplementary Information (ESI) available: Experimental data, ATR-IR, Py-GC-MS, HPLC sugar analysis, CHN and ICP-OES. See DOI: 10.1039/b000000x/

S1: INSTRUMENTAL EXPERIMENTAL DATA

I. Transmission Electron Microscopy (TEM)

TEM images of nanocellulose were acquired using a TEM Tecnai 12 BioTWIN (manufactured by FEI) coupled to a SIS Megaview 3 camera at acceleration voltage of 120 kV. Prior to the analysis, diluted samples (0.2% aqueous) were sonicated for 30 minutes using ice-cold ultrasound bath (output of 1200 W). Drops of the sample ((about 8 µL) were left on the grid for five minutes then negatively stained with 1% uranyl acetate and finally glow discharged. Copper grids with a formvar/carbon support film were used.

II. Solid State ^{13}C CP-MAS Nuclear Magnetic Resonance

Solid State ^{13}C CP-MAS NMR spectra were acquired using a 400 MHz Bruker Avance III HD spectrometer equipped with a Bruker 4mm H(F)/X/Y triple-resonance probe and 9.4T Ascend® superconducting magnet. The CP experiments employed a 1 ms linearly-ramped contact pulse, spinning rates of 12000 ± 2 Hz, optimized recycle delays of 5 seconds, and numbers of scans varying from 200-300. Chemical shifts were reported with respect to TMS, and were referenced using adamantine (29.5 ppm) as an external secondary reference.

III. Thermogravimetric Analysis (TGA)

TGA was carried out under a flow of nitrogen (100 mL min−1) using a NETZSCH Themishe Analyse STA 409 cell for nanocellulose, protopectin and hemicellulose analysis (25–700 °C at 10 °C min−1).

IV. X-ray Powder Diffraction (XRD)

XRD analysis was performed on a Bruker-AXS D8 Advance Diffractometer equipped with a Cu source producing a monochromatic K-α radiation at wavelength of 1.54184 Å and a PSD Lynxeye detector. Samples were ground to a fine powder prior to analysis. Samples were run with a rate of 0.05°/sec over a 2θ range of 5-38° (cellulose do not present any diffraction pattern after this angle) in a locked coupled theta-2θ scan mode. Generator voltage and current were set to 40 kV and 40 mA respectively. Samples background was subtracted.

The crystalline index (CrI) was calculated as:

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} * 100 \quad [\%]$$

Where:

I_{200} = intensity of the (200) peak (at ca. 2θ = 22°)

I_{am} = intensity of amorphous contributions (at 2θ = 18°)

V. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-IR)

ATR-IR was carried out using a Perkin Elmer Spectrometer (Spectrum 400). Spectra were taken from 4000 cm^{-1} to 600 cm^{-1} at 4 scans, with a spectral resolution of 4 cm^{-1} and a blank window for background.

VI. BET/BJH Porosimetry Analysis

The surface area and porosity of the Nanocellulose samples was analysed using a Micromeritics TriStar Surface Area and Porosity Analyser. A measured amount of dry (ca. 50 mg), powdered sample was put inside a clean, dry porosimetry tube and their mass was recorded. Next, degassing of the samples were performed at a temperature of 90 °C for 4-5 h. After degassing, the mass of the glassware and sample was re-measured and this value used for the analysis. All analyses were done in triplicates. The data was processed (using TriStar software). Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation. Desorption pore volume and pore size were calculated using Barrett-Joyner-Halenda (BJH) equations.

VII. High-performance Liquid Chromatography (HPLC) Analysis of sugars

Sugars (levoglucosan, glucose, fructose/xylose, cellobiose and rhamnose), sugar acids (glucuronic acid and galacturonic acid) and organic acids (lactic acid, formic acid and acetic acid) present in the aqueous filtrate where quantified by HPLC using the following conditions: Agilent Hi-Plex H (300 x 7.7mm, 8um particle size) column, 0.005M H_2SO_4 as mobile phase, isocratic mode, flow-rate at 0.4 mL/min., column temperature at 60 °C, Refractive Index Detector (55 °C), Injection Volume of 5 µl and total run time of 35 minutes.

VIII. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

A weighed sample was placed in a microwavable digestion tube, and reverse aqua-regia was added to it (9 mL of conc. HNO_3 and 3 mL of conc. HCl). The sample was then digested with the aid of a microwave digester (Mars Xpress). Once digestion was completed, the sample was diluted to 25 mL using deionised water and filtered. Samples were analysed on a axial Varian vista ICP-OES. Results w automatically corrected for dilution factor.

IX. Carbon, Hydrogen and Nitrogen Elemental Microanalysis (CHN)

CHN data was recorded with a CE-440 elemental analyser from Exeter Analytical, in conjunction with a Sartorius S2 analytical balance. Samples were combusted at 975 °C in an oxygen atmosphere, and the combustion products analysed by a series of thermal conductivity detectors.

X. Pyrolysis Gas Chromatography-Mass Spectroscopy (Py-GC-MS)

Py-GC-MS results were acquired using a CDS Analytical 5250-T Trapping Pyrolysis Autosampler (UK) was used as the pyrolysis unit, Agilent Technologies 7890B GC System (USA) as gas chromatography unit and Agilent Technologies 5977A MSD (USA) as mass spectrometer. The sample was loaded into the pyrolysis unit and pyrolyzed at 600 °C for 10 s. The volatile materials released were carried into the GC/MS unit by nitrogen for analysis. The following GC/MS parameters were applied: GC inlet temperature at 350 °C, initial temperature at 40 °C for 2 min, ramp rate at 10 K/min till 300 °C, holding at 300 °C for 30 min, split ratio with 50:1. Volatile compounds were identified by comparing the mass spectra with NIST Lab database. Analysis was performed in BDC, University of York.

XI. Water holding Capacity (WHC)

Water holding capacity (WHC) of samples were estimated by the method described by Matzain, 2014 [23]. Weighted mass of the sample (ca. 0.20g) is mixed with 20 mL of water, stirred for 20 minutes and then centrifuged (3500 rpm, 20°C, 20 minutes). After pouring down the supernatant

from the centrifuge tube, the WHC (g of water/g dry sample) of the sample can be calculated by the following equation:

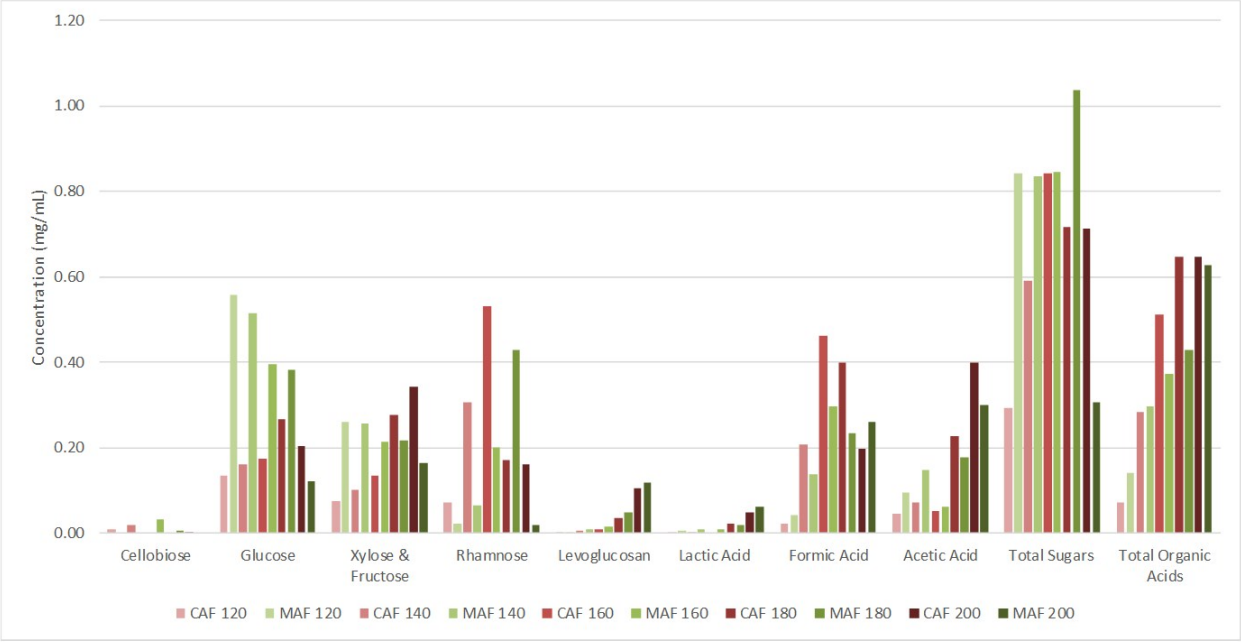
$$WHC = \frac{[(mass\ of\ tube + precipitate) - (mass\ of\ tube + sample\ mass)]}{mass of\ dry\ sample}$$

XII. Scanning Electron Microscopy (SEM)

Dried samples were sputter coated with Gold/Palladium, around 4nm and analysed in a JEOL JSM-7600F SEM equipment.

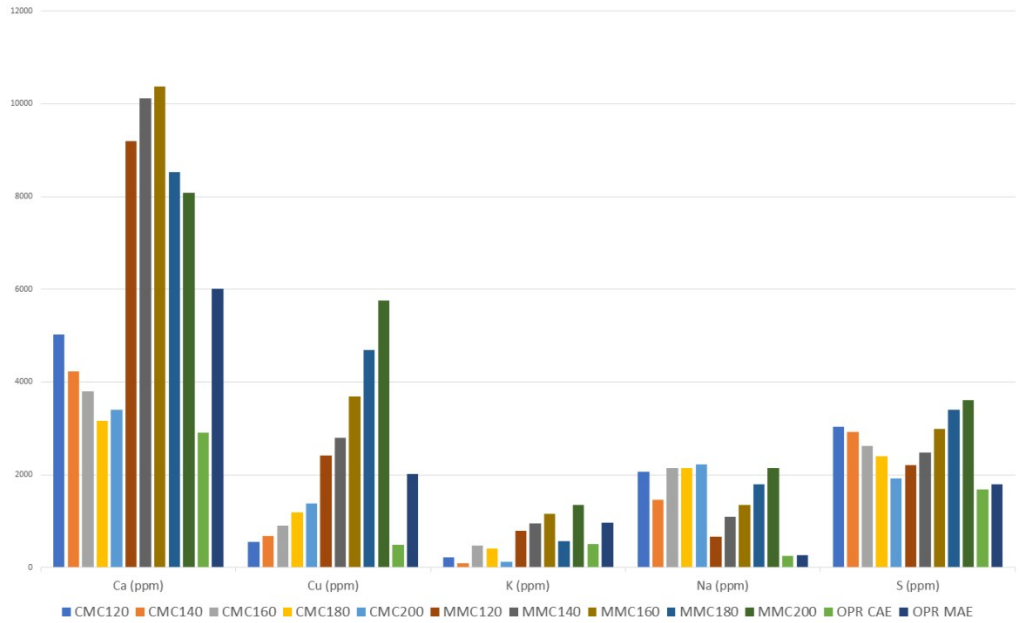
S2: HPLC SUGAR ANALYSIS

After microwave processing (MHT) of OPR-CAE and OPR-MAE, the products nanocellulose (CMC and MMC respectively) and aqueous filtrate (CAF and MAF respectively) were yielded. This HPLC analysis shows the concentration (mg/mL) of several sugars and sugar derivatives on the aqueous filtrates.



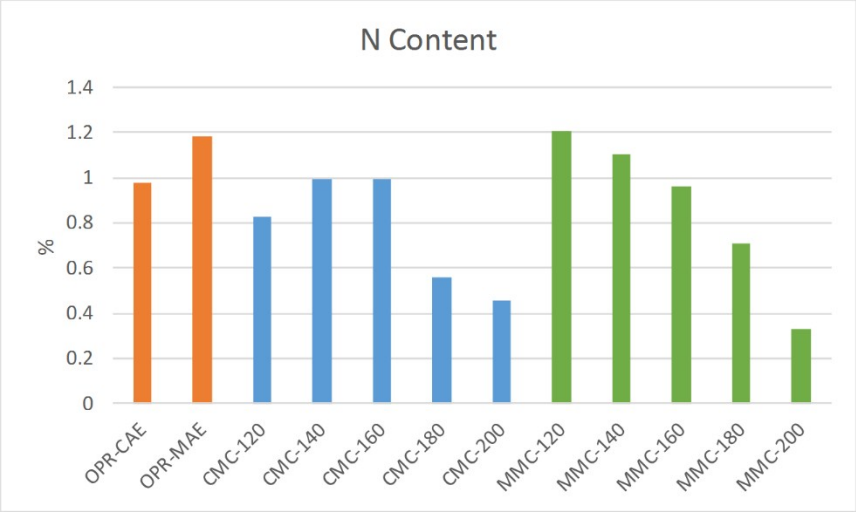
S3: ICP-OES

Summary results from ICP-OES analysis of nanocelluloses and their precursors (OPR-CAE and OPR-MAE). Only the top 5 inorganic elements are shown.



S4: CHN

This graph just shows the nitrogen (N) content of the samples.

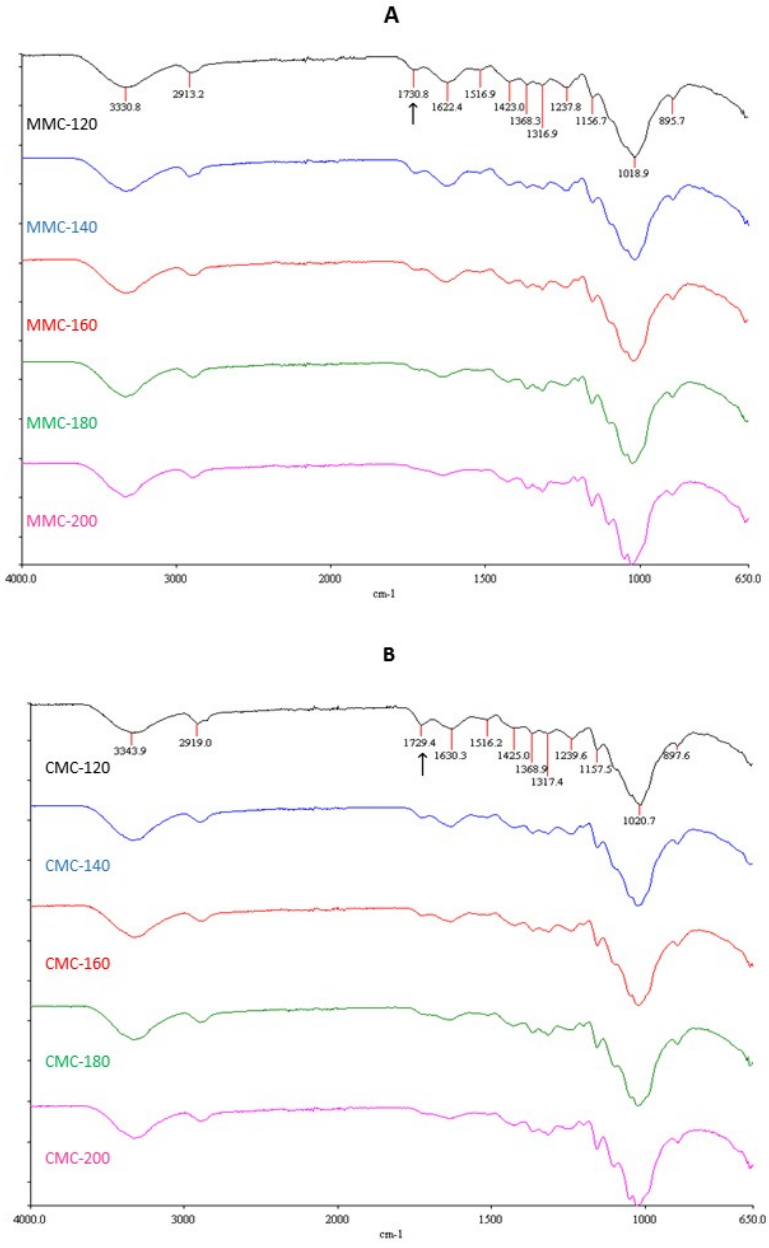


S5: ATR-IR

I. Table: Overall assignment of ATR-IR spectra of MNC samples. C = cellulose, P = pectins and H = hemicelluloses, CaC_2O_4 = calcium oxalate and lignin

Absorption Band (cm^{-1})	Group Assignment	Compound(s)
3570-3200	ν(O-H)	C, P, H
2980-2850	ν (C-H)	C, P, H
1740-1710	ν (C=O)	P, H, L
1645-1630	δ (H_2O)	All
1630-1610	ν (COO^-)	P, H, L, CaC_2O_4
1515-1520	ν (C-C, C-H)$_{arom.}$	L
1440-1420	δ (CH_2, CH_3) and ν (C-O)	All
1400-1300	ν, δ (C-H, C-O, C-C)	All
1230-1240	ν (C-O-H, C-O)$_{arom}$.	L
1200-1000	ν (C-C, C-O-C, C-O)	C, P, H
990-896	ν (C-O-C ring)	C, P, H

II. ATR-IR spectra of MMC (A) and CMC (B) samples. Arrows emphasise the removal of pectins/hemicellulose from nanocellulose fibrils with increasing microwave processing (MHT) temperature.



S6: PY-GC-MS

This table shows the Py-GC-MS result of sample CMC-120. All samples presented similar products.

Cpd	Name	Formula	Score	Mass (DB)	RT	Area	Relative%
1	2-Propanamine, 1-methoxy-	C4H11NO	70.71	89.1	1.75	663939	0.19
2	Methyl glyoxal	C3H4O2	90.24	72	1.898	20365075	5.73
3	6-exo-Methyl-5-endo-norbornenol	C8H12O	68.92	124.1	2.047	539640	0.15
4	4-Acetoxy-2-azetidinone	C5H7NO3	76.3	129	2.173	6570818	1.85
5	2-Butanone, 3-methyl-	C5H10O	79.85	86.1	2.253	5369585	1.51
6	Propanoic acid, 2-oxo-	C3H4O3	71.33	88	2.344	5566149	1.57
7	Acetic acid	C2H4O2	94.83	60	2.55	15314676	4.31
8	Methacrolein	C4H6O	87.6	70	2.71	1826976	0.51
9	2-Propanone, 1-hydroxy-	C3H6O2	81.51	74	2.813	11386274	3.20
10	3-Buten-2-one, 3-methyl-	C5H8O	87.25	84.1	2.904	1091195	0.31
11	Isoxazolidine, 4-ethyl-2,5-dimethyl-, cis-	C7H15NO	75.08	129.1	2.984	1314246	0.37
12	Hydroxylamine, O-(2-methylpropyl)-	C4H11NO	81.21	89.1	3.121	787905	0.22
13	5-Hexen-2-ol, 5-methyl-	C7H14O	73.83	114.1	3.281	2926536	0.82
14	Propanoic acid, 2-oxo-, methyl ester	C4H6O3	77.59	102	3.567	480400	0.14
15	3-Buten-2-one, 3-methyl-	C5H8O	78.44	84.1	3.704	1011228	0.28
16	1-Cyclohexene-1-methanol	C7H12O	75.27	112.1	3.773	486257	0.14
17	2H-Pyran, 3,4-dihydro-	C5H8O	77.78	84.1	3.853	1261355	0.35
18	1-Hexyne	C6H10	81.58	82.1	3.944	845226	0.24
19	1-Phenyl-2-propanone	C9H10O	66.26	134.1	4.127	8524981	2.40
20	2-Hexene, (Z)-	C6H12	77.08	84.1	4.207	631583	0.18
21	Succindialdehyde	C4H6O2	84.79	86	4.299	2575625	0.72
22	Propanoic acid, 2-oxo-, methyl ester	C4H6O3	83.34	102	4.447	7221905	2.03
23	2H-Pyran, 3,4-dihydro-	C5H8O	78.23	84.1	4.562	2911089	0.82
24	Furfural	C5H4O2	79.47	96	4.813	1052802	0.30
25	Furfural	C5H4O2	89.41	96	5.156	11735314	3.30
26	Cyclopropanecarboxylic acid, cyclohexylmethyl ester	C11H18O2	79.21	182.1	5.259	1373519	0.39
27	2-Nonynoic acid	C9H14O2	74.48	154.1	5.373	651726	0.18
28	2,3-Dihydrooxazole, 2-t-butyl-4-(1-hydroxy-1-methylethyl)-3-methoxycarbonyl-5-methyl-	C6H10O	80.92	98.1	5.556	3839272	1.08
29	4-Penten-2-one, 3-methyl-	C6H10O	72.38	98.1	5.762	3470771	0.98
30	9-Oxabicyclo[6.1.0]nonan-4-one	C8H12O2	77.91	140.1	6.036	970882	0.27
31	Hexanoic acid, 2-phenylethyl ester	C14H20O2	75.69	220.1	6.15	732611	0.21
32	2-Nonynoic acid	C9H14O2	82.56	154.1	6.402	1576539	0.44
33	2H-Pyran, 3,4-dihydro-	C5H8O	78.36	84.1	6.562	3710984	1.04
34	1,3-Butadiene-1-carboxylic acid	C5H6O2	81.28	98	6.665	1431305	0.40
35	6-Oxa-bicyclo[3.1.0]hexan-3-one	C5H6O2	91.58	98	6.768	8937375	2.51
36	2,5-Furandione, dihydro-3-methylene-	C5H4O3	78.39	112	7.053	1533264	0.43
37	1-Octyn-3-ol	C8H14O	75.47	126.1	7.282	619188	0.17
38	2-Decen-1-ol	C10H20O	74.74	156.2	7.408	5479039	1.54

39	2-Cyclohexen-1-one, 2-methyl-	C7H10O	76.38	110.1	7.659	2577127	0.72
40	Carbamic acid, phenyl ester	C7H7NO2	79.2	137	7.716	748146	0.21
41	Oxazolidine, 2,2-diethyl-3-methyl-	C8H17NO	77.84	143.1	8.025	9600193	2.70
42	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	C6H8O2	83.73	112.1	8.276	1605795	0.45
43	9-Oxabicyclo[6.1.0]nonan-4-one	C8H12O2	77.88	140.1	8.391	621223	0.17
44	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	C6H8O2	94.28	112.1	8.516	5167990	1.45
45	6,7-Dioxabicyclo[3.2.1]octane, 1-methyl-	C7H12O2	78.42	128.1	8.733	2167130	0.61
46	2-Octanone, 1-nitro-	C8H15NO3	73.24	173.1	8.779	3462517	0.97
47	1,2,6-Hexanetriol	C6H14O3	71.52	134.1	8.951	1712921	0.48
48	1,2,6-Hexanetriol	C6H14O3	73.48	134.1	9.076	915437	0.26
49	3-Nonynoic acid	C9H14O2	76.93	154.1	9.259	3716694	1.05
50	cis-2-Ethyl-2-hexen-1-ol	C8H16O	72.8	128.1	9.454	2582022	0.73
51	1-Octyn-3-ol, 4-ethyl-	C10H18O	80.61	154.1	9.625	2744450	0.77
52	3-Nonynoic acid	C9H14O2	79.69	154.1	9.716	641780	0.18
53	2-Hexenal, 2-ethyl-	C8H14O	79.98	126.1	9.899	3257874	0.92
54	Furan-2-carbohydrazide, N2-(1-methylhexylideno)-	C12H18N2O2	77.44	222.1	9.991	1819653	0.51
55	9-Oxabicyclo[6.1.0]nonan-4-one	C8H12O2	74.49	140.1	10.048	2581440	0.73
56	Bicyclo[2.2.1]heptan-2-ol, 7,7-dimethyl-, acetate	C11H18O2	75.3	182.1	10.414	499887	0.14
57	9-Oxabicyclo[6.1.0]nonan-4-one	C8H12O2	71.64	140.1	10.494	2270428	0.64
58	R-Limonene	C10H16O3	78.9	184.1	10.711	1390987	0.39
59	6-Hydroxyhexahydrocyclopenta[b]furan-2-one	C7H10O3	83.15	142.1	11.065	11111355	3.12
60	cis-2-Ethyl-2-hexen-1-ol	C8H16O	78.05	128.1	11.225	2676448	0.75
61	4-Cyclopropylcarbonyloxytridecane	C17H32O2	75.93	268.2	11.419	3273802	0.92
62	3-Trifluoroacetoxydodecane	C14H25F3O2	79.7	282.2	11.568	1413548	0.40
63	5-Hydroxymethylfurfural	C6H6O3	81.7	126	11.671	8963395	2.52
64	2-Dodecenoic acid	C12H22O2	80.39	198.2	11.991	1438101	0.40
65	4H,5H-Pyrano[4,3-d]-1,3-dioxin, tetrahydro-8a-methyl-	C8H14O3	79.31	158.1	12.254	7496246	2.11
66	3-Decenoic acid	C10H18O2	79.64	170.1	12.357	7184763	2.02
67	R-Limonene	C10H16O3	78.62	184.1	12.597	500798	0.14
68	R-Limonene	C10H16O3	80.2	184.1	12.665	662066	0.19
69	Melezitose	C18H32O16	76.54	504.2	12.768	3542444	1.00
70	3,5-Heptadienal, 2-ethylidene-6-methyl-	C10H14O	83.47	150.1	12.86	3267673	0.92
71	R-Limonene	C10H16O3	80.87	184.1	13.077	1354880	0.38
72	R-Limonene	C10H16O3	84.7	184.1	13.397	949173	0.27
73	R-Limonene	C10H16O3	83.45	184.1	13.465	492462	0.14
74	Melezitose	C18H32O16	83.98	504.2	14.014	6905044	1.94
75	R-Limonene	C10H16O3	81.21	184.1	14.414	559756	0.16
76	R-Limonene	C10H16O3	83.38	184.1	14.574	677423	0.19
77	10-Heptadecen-8-ynoic acid, methyl ester, (E)-	C18H30O2	81.48	278.2	14.654	565674	0.16
78	R-Limonene	C10H16O3	81.2	184.1	14.86	2422261	0.68
79	R-Limonene	C10H16O3	79.62	184.1	15.191	844282	0.24
80	.beta.-D-Glucopyranose, 1,6-anhydro-	C6H10O5	90.23	162.1	15.877	47743009	13.42
81	.beta.-D-Glucopyranose, 1,6-anhydro-	C6H10O5	91.5	162.1	16.003	29409924	8.27
82	Melezitose	C18H32O16	79.01	504.2	16.506	2607895	0.73

83	Dodecanoic acid, 3-hydroxy-	C12H24O3	79.89	216.2	16.951	3434737	0.97
84	Acetamide, N-methyl-N-[4-(3-hydroxypyrrolidinyl)-2-butynyl]-	C11H18N2O2	80.81	210.1	17.169	492109	0.14
85	3H-Cyclodeca[b]furan-2-one, 4,9-dihydroxy-6-methyl-3,10-dimethylene-3a,4,7,8,9,10,11,11a-octahydro-	C15H20O4	83.58	264.1	20.037	530979	0.15
86	n-Hexadecanoic acid	C16H32O2	89.08	256.2	20.243	3143476	0.88
87	Oleic Acid	C18H34O2	81.53	282.3	21.9	484547	0.14
88	Octadecanoic acid	C18H36O2	81.89	284.3	22.118	1097852	0.31
89	9-Hexadecenoic acid	C16H30O2	79.95	254.2	23.489	557084	0.16
90	Oleic Acid	C18H34O2	74.2	282.3	23.683	483251	0.14
91	13-Docosenamide, (Z)-	C22H43NO	77.81	337.3	27.055	2505397	0.70