

Supplementary materials

Development of a ^1H qNMR method for the identification and quantification of monosaccharides in dietary fibre fractions

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Supplementary Table 1. Percentage of β -D-fructofuranose anomers over time compared with weighing.

Level (ppm)	% after 1 h	% after 2 h	% after 3 h	% after 5 h	% after 12 h	% after 24 h
100 ppm	22.6	23.1	22.4	22.4	22.3	22.7
500 ppm	22.5	22.3	22.1	22.5	22.7	22.2
1000 ppm	22.7	22.7	23.6	23.1	22.6	22.6

Supplementary Table 2. Standard monosaccharide quantification at different relaxation delays (d1)

Compound	Real value (ppm)	D1=5s (ppm)	D1=8s (ppm)	D1=15s (ppm)
Glucose	504.9	559.1	561.4	557.2
Fructose	502.3	497.7	487.3	495.6
Galactose	505.5	526.9	526.1	521.4
Ribose	502.3	505.0	501.6	487.6
Arabinose	504.7	489.8	490.0	493.5
Rhamnose	505.2	502.8	507.0	503.3
Fucose	492.9	507.7	507.0	503.0
Mannose	504.0	519.2	519.2	517.0
Xylose	499.3	491.0	489.4	488.7
Galacturonic acid	457.8	446.6	445.6	444.8
Glucuronic acid	508.2	491.7	488.5	492.5
TSP (integral)	-	535	533	533

Supplementary Table 3. Monosaccharide quantification in SDF obtained from orange by products at different relaxation delays (d1).

Compound	D1=5s (ppm)	D1=8s (ppm)	D1=15s (ppm)	D1=20s (ppm)	D1=25s (ppm)	D1=30s (ppm)
Glucose	225.1	223.1	217.0	214.6	219.9	226.9
Fructose	ND	ND	ND	ND	ND	ND
Galactose	1030.9	1015.9	1020.0	1003.4	1007.4	1029.8
Ribose	56.1	54.5	56.5	54.3	55.1	58.3
Arabinose	1066.5	1068.0	1085.3	1065.9	1063.5	1069.0
Rhamnose	379.3	371.3	376.7	370.5	377.6	375.8
Fucose	22.6	20.9	23.9	21.7	22.3	22.6
Mannose	198.5	200.5	198.0	198.3	200.2	202.8
Xylose	59.5	54.4	61.4	54.7	57.8	54.8
Galacturonic acid	2012.3	2000.5	1993.7	2001.8	2019.3	2018.0
Glucuronic acid	109.7	109.5	110.4	110.3	109.7	109.7
Acetate	101.5	102.9	104.8	106.1	106.1	105.9
Methanol	37.2	38.1	39.5	40.7	40.7	40.6
Formic acid	80.4	85.1	94.7	100.9	100.9	101.2
Furfural	38.2	35.2	39.3	41.6	39.6	39.5
TSP (integral)	0.461	0.460	0.460	0.458	0.454	0.453

Supplementary Table 4. Inter-Day Repeatability (after 3, 10, 20 days) of the method, calculated on monosaccharide standard mixtures at different concentration levels.

Compounds	Level (ppm)	interday repeatability (RSD %)			Horwitz ratio for interday repeatability		
		3 days	10 days	20 days	3 days	10 days	20 days
Glucose	100	4.0	4.1	2.8	0.8	0.8	0.5
	500	2.0	2.9	2.5	0.5	0.7	0.6
	1000	1.8	2.0	2.0	0.5	0.5	0.5
Fructose	100	3.7	4.8	2.6	0.7	0.9	0.5
	500	2.6	3.7	2.4	0.6	0.9	0.6
	1000	4.2	4.4	4.5	1.1	1.2	1.2
Galactose	100	3.8	3.9	3.5	0.7	0.7	0.7
	500	2.0	2.8	2.4	0.5	0.7	0.6
	1000	2.4	1.5	2.3	0.6	0.4	0.6
Ribose	100	3.9	4.0	5.0	0.7	0.8	0.9
	500	5.6	6.1	5.7	1.3	1.5	1.4
	1000	1.5	1.5	2.0	0.4	0.4	0.5
Arabinose	100	4.6	3.7	5.2	0.9	0.7	1.0
	500	1.2	1.3	0.9	0.3	0.3	0.2
	1000	1.7	1.5	1.9	0.5	0.4	0.5
Rhamnose	100	4.0	2.3	2.5	0.8	0.4	0.5
	500	1.4	1.9	1.5	0.3	0.5	0.4
	1000	0.8	1.3	2.0	0.2	0.4	0.5
Fucose	100	2.4	3.6	3.5	0.5	0.7	0.7
	500	1.5	1.5	1.5	0.4	0.4	0.4
	1000	1.2	1.5	1.1	0.3	0.4	0.3
Mannose	100	2.4	8.2	8.5	0.5	1.5	1.6
	500	1.2	1.7	1.5	0.3	0.4	0.4
	1000	0.6	1.8	2.6	0.1	0.5	0.7
Xylose	100	2.8	4.4	3.9	0.5	0.8	0.7
	500	3.1	3.7	4.3	0.8	0.9	1.0
	1000	2.6	2.8	2.3	0.7	0.7	0.6
Galacturonic acid	100	3.1	2.0	3.1	0.6	0.4	0.6
	500	1.5	2.0	1.7	0.4	0.5	0.4
	1000	1.8	2.0	2.2	0.5	0.5	0.6
Glucuronic acid	100	2.9	2.7	5.2	0.5	0.5	1.0
	500	5.6	4.6	5.3	1.4	1.1	1.3
	1000	6.0	5.8	5.8	1.6	1.6	1.5

Supplementary Table 5. Monosaccharide composition and yield (g 100⁻¹g DF) of DF fractions in orange by-products obtained by ¹H NMR and GC-MS.

	SDF		IDF (TFA)		IDF (H ₂ SO ₄)	
Monosaccharides	NMR	GC-MS	NMR	GC-MS	NMR	GC-MS
Glucose	4.0 ± 0.3	3.7 ± 0.6	10.8 ± 0.3	12.8 ± 1.8	77.5 ± 1.8	80.7 ± 4.9
Fructose	ND	ND	ND	ND	ND	1.9 ± 0.8
Galactose	16.7 ± 0.6	16.0 ± 1.1	18.6 ± 0.5	18.6 ± 0.6	2.0 ± 0.2	3.2 ± 1.2
Ribose	1.3 ± 0.1*	0.2 ± 0.2*	2.7 ± 0.3*	ND*	ND	ND
Arabinose	19.5 ± 0.8	20.5 ± 3.1	25.7 ± 1.3*	33.0 ± 2.6*	2.63 ± 0.03	5.2 ± 2.1
Rhamnose	8.1 ± 0.5*	2.3 ± 0.8*	10.4 ± 0.7*	13.2 ± 0.7*	ND*	3.1 ± 0.4*
Fucose	0.5 ± 0.1	0.51 ± 0.04	1.4 ± 0.2*	2.6 ± 0.5*	ND*	1.1 ± 0.1*
Mannose	3.39 ± 0.03	3.4 ± 0.7	3.5 ± 0.2*	9.6 ± 2.0*	4.9 ± 1.4	3.5 ± 0.5
Xylose	0.94 ± 0.01	1.0 ± 0.2	8.6 ± 0.3*	10.1 ± 0.7*	3.6 ± 0.8	1.2 ± 0.1
Galacturonic acid	40.5 ± 0.9*	51.4 ± 6.5*	14.9 ± 3.4*	ND*	9.2 ± 0.6*	ND*
Glucuronic acid	3.6 ± 0.9*	0.9 ± 1.2*	1.48 ± 0.02*	ND*	ND	ND
Degradation products	1.4 ± 0.1	ND	1.8 ± 0.1	ND	0.22 ± 0.02	ND
Yield	101.2 ± 0.1	51.22 ± 9.5	50.7 ± 1.9	38.7 ± 2.2	38.0 ± 1.1	44.8 ± 1.6

Data with * are significantly different according to t-test.

Supplementary Table 6. Monosaccharide composition and yield (g 100⁻¹g DF) of DF fractions in hazelnut shells obtained by ¹H NMR and GC-MS.

	SDF		IDF (TFA)		IDF (H₂SO₄)	
Monosaccharides	NMR	GC-MS	NMR	GC-MS	NMR	GC-MS
Glucose	3.5 ± 0.5	3.0 ± 0.6	2.6 ± 0.1	2.4 ± 0.1	89.7 ± 0.3	88.3 ± 1.9
Fructose	ND	ND	ND	ND	ND	ND
Galactose	4.5 ± 0.1*	0.7 ± 0.1*	5.3 ± 0.5	5.2 ± 0.8	ND	ND
Ribose	0.9 ± 0.2	0.17 ± 0.02	0.16 ± 0.02*	ND*	ND	ND
Arabinose	3.3 ± 0.2*	1.1 ± 0.2*	1.9 ± 0.1*	4.6 ± 0.8*	ND	ND
Rhamnose	2.4 ± 0.3*	1.1 ± 0.1*	2.8 ± 0.1*	5.5 ± 0.6*	ND	ND
Fucose	0.12 ± 0.02	0.11 ± 0.02	1.6 ± 0.1*	ND*	ND	ND
Mannose	19.5 ± 2.1	21.5 ± 4.6	0.1 ± 0.1	0.9 ± 0.4	ND*	1.1 ± 0.6*
Xylose	3.2 ± 0.9	0.5 ± 0.2	71.5 ± 0.1*	78.3 ± 0.8*	10.3 ± 0.3	10.6 ± 0.6
Galacturonic acid	55.8 ± 0.5	71.7 ± 5.9	5.9 ± 1.0	3.2 ± 1.0	ND	ND
Glucuronic acid	3.0 ± 0.4*	ND*	1.2 ± 0.2*	ND*	ND	ND
Degradation products	3.7 ± 0.1	-	7.0 ± 1.3	-	ND	-
Yield	80.1 ± 0.2	70.7 ± 6.4	28.1 ± 0.1	25.0 ± 1.4	22.0 ± 0.2	28.2 ± 1.4

Data with * are significantly different according to t-test.

Supplementary Table 7. Monosaccharide composition and yield (g 100⁻¹g DF) of DF fractions in Ulva obtained by ¹H NMR and GC-MS.

	SDF		IDF (TFA)		IDF (H₂SO₄)	
Monosaccharides	NMR	GC-MS	NMR	GC-MS	NMR	GC-MS
Glucose	2.8 ± 0.1	2.4 ± 0.9	34.5 ± 2.1*	46.5 ± 0.6*	88.2 ± 2.1*	100 ± 0.0*
Fructose	ND	ND	ND	ND	ND	ND
Galactose	1.4 ± 0.1*	0.6 ± 0.2*	1.0 ± 0.1	0.8 ± 0.1	ND	ND
Ribose	5.2 ± 0.4*	ND*	3.1 ± 0.1*	ND*	ND	ND
Arabinose	ND	ND	ND	ND	ND	ND
Rhamnose	50.3 ± 1.1	52.0 ± 6.7	26.8 ± 2.4	26.1 ± 3.1	ND	ND
Fucose	1.4 ± 0.1*	ND*	ND	ND	ND	ND
Mannose	6.1 ± 0.4	7.0 ± 0.8	ND	ND	ND	ND
Xylose	5.6 ± 0.1	6.1 ± 0.2	20.9 ± 1.4	19.4 ± 2.2	11.8 ± 2.1*	ND*
Galacturonic acid	0.6 ± 0.1*	ND*	ND	ND	ND	ND
Glucuronic acid	11.6 ± 1.6*	2.8 ± 0.8*	5.0 ± 0.7*	ND*	ND	ND
Unknown compounds	13.5 ± 1.6	29.0 ± 11.2	6.1 ± 1.5	7.3 ± 1.6	ND	ND
Degradation products	1.7 ± 0.2	-	2.6 ± 0.2	-	ND	ND
Yield	98.5 ± 1.8	60.1 ± 2.5	47.1 ± 1.3	21.7 ± 0.9	21.1 ± 0.1	26.0 ± 6.4

Data with * are significantly different according to t-test.

Supplementary Fig. 1. ^1H NMR spectrum (600 MHz) of hydrolysed pectin. The region between 5.08 and 5.16 ppm, corresponding to the H1 and H5 signals of the non-hydrolysed pectin backbone, can be integrated to estimate the degree of polysaccharide degradation.

