Electronic Supplementary Material (ESI) for Green Chemistry.

Tuning the molar mass and substitution pattern of complex xylans from corn fibre using subcritical water extraction

Supplementary Material

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Supplementary material: Methods

Characterisation of starch fractions

Molar mass distributions of the whole branched starch molecules by SEC-MALLS

The molar mass distributions of the branched starch macromolecules were analysed by the SECcurity 1260 size-exclusion chromatography (Polymer Standard Services, Mainz, Germany) coupled to the SECcurity 1260 refractive index detector (Polymer Standard Services, Mainz, Germany) at 45 °C and the BIC-MwA7000 multiangle laser light scattering detector (MALLS; Brookhaven Instrument Corp., Holtsville, NY, USA) as previously reported.[1] The extracted starch fractions were dissolved directly in the SEC eluent consisting of HPLC grade dimethyl sulfoxide (DMSO; Scharlab, Barcelona, Spain) with 0.5 % (w/w) LiBr at 60 °C. SEC analyses were performed with a flow rate of 0.5 mL min^{-1} at 60 °C using a column set consisting of a GRAM PreColumn, 30 and 10000 analytical columns (Polymer Standard Services, Mainz, Germany).

Branch chain-length distributions of the debranched starch fractions by SEC-DRI

Debranching of starch was performed enzymatically using a isoamylase from *Pseudomonas sp.* (Megazyme, Wicklow, Ireland) as previously reported.[1] The debranched fractions were freeze-dried and finally re-dissolved in DMSO/LiBr 0.5% (w/w) prior to SEC analysis. The branch size distributions were analysed using the same SEC setup described for branched starch molecules. Calibration of the degree of polymerization of starch branches was performed by standard calibration using pullulan (Polymer Standard Services, Mainz, Germany).

X-ray diffraction (XRD) analysis of starch crystallinity

The fractions obtained from the destarching of the corn fibre material were analysed in the X'Pert PRO X-ray diffractometer (Malvern Panalytical, Malvern, UK) at environment temperatures. A monochromatic CuKα radiation (k = 1.54 A °) in the range of 2 θ varying from 10° to 60° was employed at a scan rate of 1°/min. X-ray diffraction data were processed and analysed using HighScore Plus 3.0 software (Malvern Panalytical, Malvern, UK).

Calculation for the GAX structure (Figure 4d in the main text)

The xylan backbone was first normalised to 100 % using the following equation, taking the 4-Xyl*p* as an example:

$$\%\ of\ 4\text{–}Xylp\ in\ backbone = \frac{\%mol\ 4\text{–}Xylp}{(\%mol\ 4\text{–}Xylp + \%mol\ 2{,}4\text{–}Xylp + \%mol\ 3{,}4\text{–}Xylp\ \%mol\ 2{,}3{,}4\text{–}Xylp)}\ x\ 100$$

Then choosing 20 xyloses for the figure, the amount of each xylose constituent (4-Xyl*p*, 2,4-Xyl*p*, 3,4-Xyl*p* and 2,3,4-Xyl*p*) was calculated. Other PMAAs constituting the GAX was normalised to the amount of xylose present in the backbone. This is so the ratio between the PMAAs remain the same in the whole GAX sample and in the model figure. For example, below is the calculation for determining the amount t-Ara*f* that should be present in the figure:

$$Amount\ of\ t\text{–}Araf = \frac{\%mol\ total\ amount\ of\ t\text{–}Araf}{\%mol\ total\ amount\ of\ backbone\ Xylp}\ x\ 20$$

The amount of substituting PMAAs (t-Ara*f*, t-Xyl*p*, t-Gal*p*, GalA, 2-Ara*f*, and 2-Xyl*p*) were then reconstructed on the xylan backbone based on possible positions previously reported in other studies. For simplicity, longer oligomeric substitutions containing the 3-Gal*p* were not included in the model figure. Table S6 summarises the possible substitution motifs previously reported for corn GAX.

Risks and hazards associated to the extraction processes

All the buffers used in the aqueous steeping of starch and subcritical water extraction of xylan are used in very diluted conditions and are food grade. Acetic acid is flammable and corrosive. Sodium bicarbonate causes irritation. Phosphate buffer has no risks associated.

None of the reagents contain components classified as persistent, bioaccumulative and toxic (PBT), or as very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

Table S1. Fractionation yields from the destarching process

Sample	**Corn fibre** (CF-0)	**Destarched corn fibre** (CF-1)	**Insoluble starch** (CF-2)	**Soluble starch** (CF-3)	**Global recovery**
Weight (g)	500	162.8	2.3	26.0	191.0
Dry content (%)	39.3				
Dry weight (g)	196.3				
Relative yield to dried CF (%)		82.9	1.1	13.3	97.3

Table S2. Composition of fractions after destarching of corn fibre

Sample	**Corn fibre** (CF-0)	**Destarched corn fibre** (CF-1)	**Insoluble starch** (CF-2)	**Soluble starch** (CF-3)
Carbohydrate (mg g^{-1}DW)[a]	792.0 (57.1)	805.6 (35.8)	477.8 (41.1)	743.3 (26.9)
Rha (%)	-	-	-	-
Fuc (%)	0.1 (0.03)	0.1 (0.01)	0.2 (0.01)	0.2 (0.01)
Ara (%)	17.3 (0.4)	19.4 (0.2)	3.0 (0.2)	5.2 (0.1)
Xyl (%)	36.5 (2.7)	37.6 (1.7)	4.2 (0.4)	3.8 (0.1)
Gal (%)	5.1 (0.4)	5.4 (0.1)	1.0 (0.1)	0.9 (0.1)
Glc (%)	35.1 (3.0)	31.9 (1.3)	89.2 (0.7)	83.9 (1.9)
Man (%)	2.4 (0.05)	2.7 (0.5)	0.7 (0.6)	-
GalA (%)	1.3 (0.3)	1.4 (0.2)	1.4 (0.4)	4.2 (1.2)
GlcA (%)	1.6 (0.1)	1.4 (0.1)	0.3 (0.1)	1.1 (0.1)
mGlcA (%)	0.3 (0.3)	-	-	0.9 (0.8)
GAX (%)	60.8 (3.8)	63.8 (2.1)	11.7 (1.1)	12.0 (1.2)
A/X[b]	0.47	0.51	0.71	1.37
Starch (mg g^{-1}DW)[c]	128.6 (3.7)	14.3 (3.7)	312.2 (38.0)	657.0 (22.2)

[a] Carbohydrate content was determined using H_2SO_4 hydrolysis followed by HPAEC-PAD analysis
[b] A/X is the ratio between Ara and Xyl
[c] Starch content was determined using the Total Starch Assay (Megazyme kit)

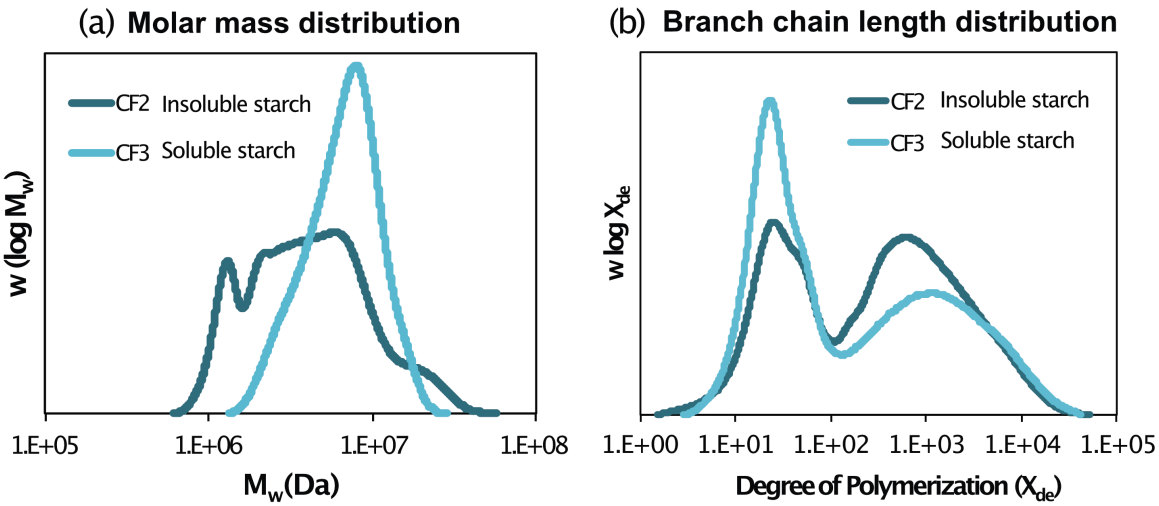

Figure S1. Molecular distributions by SEC for the starch fractions: (a) Molar mass distributions of the intact branched starch molecules; (b) Chain length distributions of the branches after enzymatic debranching

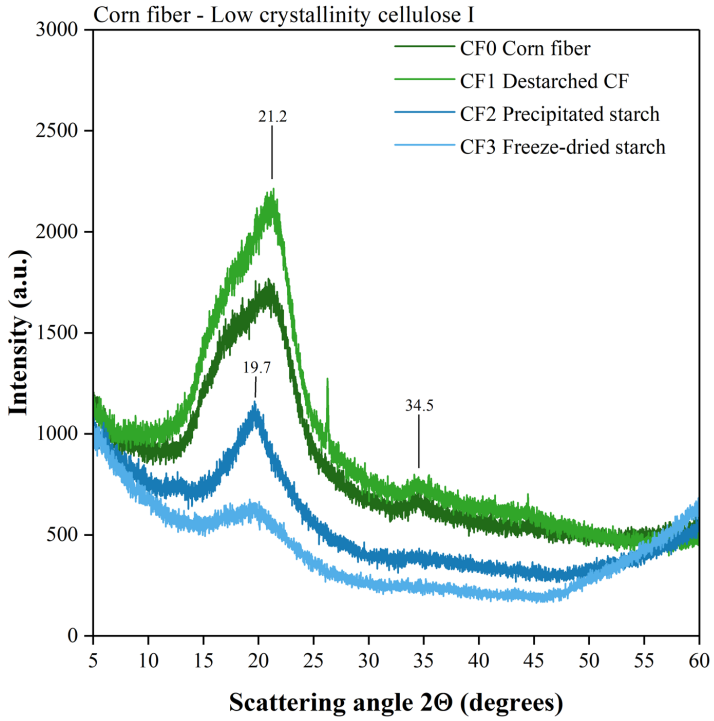

Figure S2. X-ray difractogram of fractions obtained during the destarching process of corn fibre

Table S3. General composition of destarched corn fibre

General composition	**Destarched Corn Fibre**
Moisture (%)[a]	8.5 (0.2)
Carbohydrate (mg g^{-1} DW)[b]	805.6 (36.2)
Rha (%)	-
Fuc (%)	0.1 (0.01)
Ara (%)	19.4 (0.2)
Xyl (%)	37.6 (1.7)
Gal (%)	5.4 (0.1)
Glc (%)	31.9 (1.3)
Man (%)	2.7 (0.5)
GalA (%)	1.4 (0.2)
GlcA (%)	1.4 (0.1)
mGlcA (%)	-
GAX (%)	57.0 (2.0)
A/X[c]	0.52
Starch (mg g^{-1} DW)[d]	14.3 (3.7)
Phenolic acid (mg g^{-1} DW)[e]	52.8 (6.3)
Caffeic (%)	-
p-Coumaric (%)	7.1 (0.9)
Ferulic (%)	79.2 (1.1)
Cinnamic (%)	9.2 (1.2)
5.5 DIFA (%)	4.5 (0.7)

[a] Moisture content was determined gravimetrically after lyophilisation

[b] Carbohydrate content was determined using H_2SO_4 hydrolysis followed by HPAEC-PAD analysis

[c] A/X is the ratio between Ara and Xyl

[d] Starch content was determined using the Total Starch Assay (Megazyme kit)

[e] Phenolic acid content was determined by saponification followed by HPLC analysis

Table S4. Detailed yields, composition and molecular characterisation of the extracts and residues (R) obtained from the temperature optimisation in the SWE

Composition	140 °C					160 °C					180 °C				
	5 min	**15 min**	**30 min**	**60 min**	**R**	**5 min**	**15 min**	**30 min**	**60 min**	**R**	**5 min**	**15 min**	**30 min**	**60 min**	**R**
Yield (% DW)[a]	4.1 (0.6)	2.5 (0.1)	3.2 (0.4)	6.6 (0.3)	81.5 (1.4)	5.0 (1.9)	8.4 (1.5)	12.2 (0.8)	18.5 (0.9)	51.2 (0.2)	12.8 (3.5)	20.8 (4.4)	18.3 (0.8)	11.5 (4.5)	31.8 (4.2)
Carbohydrate content (mg g^{-1})[b]	632.0 (61.3)	761.1 (39.9)	848.2 (33.9)	952.1 (192.3)	683.2 (40.7)	773.5 (50.2)	864.0 (62.7)	919.7 (32.8)	826.3 (94.9)	627.3 (53.4)	743.4 (61.2)	834.9 (20.9)	830.9 (47.1)	729.3 (57.8)	563.1 (213.7)
GAX (%)[c]	27.7 (0.3)	48.1 (1.1)	73.7 (0.5)	80.4 (0.3)	68.2 (1.0)	40.5 (1.1)	75.7 (0.3)	84.9 (0.5)	89.9 (0.7)	57.7 (2.0)	54.7 (0.9)	83.6 (0.8)	90.7 (1.0)	93.5 (0.5)	44.0 (13.8)
A/X[d]	2.10	2.96	2.35	1.68	0.22	2.24	1.48	0.99	0.66	0.14	1.63	0.98	0.66	0.47	0.11
Rha (%)[e]	0.6 (0.03)	1.0 (0.06)	1.1 (0.05)	1.4 (0.5)	-	0.9 (0.03)	1.2 (0.2)	1.7 (0.02)	1.4 (0.3)	-	1.0 (0.1)	1.2 (0.5)	0.7 (0.02)	0.5 (0.01)	-
Fuc (%)	-	-	0.2 (0.02)	-	0.08 (0.0)	-	-	-	-	0.05(0.01)	-	-	-	-	0.08(0.03)
Ara (%)	15.4 (0.1)	31.8 (0.7)	45.6 (0.2)	43.7 (0.2)	12.4 (0.6)	23.9 (0.2)	38.7 (0.1)	35.4 (0.2)	29.4 (0.2)	6.9 (0.4)	28.9 (0.5)	34.9 (0.5)	30.0 (0.2)	24.6(0.02)	4.5 (2.5)
Xyl (%)	7.3 (0.2)	10.7 (0.3)	19.4 (0.2)	26 (0.02)	55.8 (0.4)	10.7 (0.7)	26.2 (0.1)	35.9 (0.2)	44.6 (0.2)	50.7 (1.7)	17.8 (0.2)	35.5 (0.2)	45.1 (0.4)	52.1 (0.2)	39.6(11.3)
Gal (%)	3.4 (0.02)	3.9 (0.1)	5.7 (0.01)	6.5 (0.01)	4.1 (0.1)	4.0 (0.1)	6.6 (0.1)	7.9 (0.03)	9.2 (0.04)	3.7 (0.1)	5.1 (0.01)	7.9 (0.02)	9.1 (0.01)	10.2(0.01)	2.7 (1.0)
Glc (%)	65.0 (0.3)	42.9 (1.3)	15.2 (0.3)	9.6 (0.4)	20.1 (0.5)	50.9 (1.2)	15.7 (0.2)	8.3 (0.3)	5.6 (0.1)	29.3 (3.0)	36.7 (0.9)	9.8 (0.2)	5.4 (0.2)	3.9 (0.04)	45.0(14.9)
Man (%)	1.3 (0.1)	1.3 (0.02)	1.3 (0.02)	1.1 (0.1)	2.0 (0.5)	1.7 (0.1)	1.5 (0.1)	1.1 (0.1)	0.7 (0.02)	2.7 (0.5)	1.6 (0.2)	1.2 (0.1)	0.8 (0.03)	0.7 (0.03)	2.1 (0.5)
GalA (%)	5.4 (0.1)	6.7 (0.2)	8.4 (0.1)	7.5 (0.1)	3.4 (1.4)	6.0 (0.2)	5.9 (0.2)	4.1 (0.2)	2.5 (0.03)	3.0 (2.0)	6.0 (0.3)	4.2 (0.1)	2.4 (0.1)	1.4 (0.04)	3.0 (2.9)
GlcA (%)	1.6 (0.02)	1.7 (0.02)	2.9 (0.1)	4.0 (0.1)	2.2 (0.8)	1.9 (0.1)	4.1 (0.1)	5.5 (0.1)	6.5 (0.1)	2.7 (0.8)	2.9 (0.2)	5.2 (0.1	6.1 (0.4)	6.4 (0.2)	2.2 (1.2)
mGlcA (%)	-	0.1 (0.01)	0.2 (0.01)	0.2 (0.01)	0.1	0.04	0.2 (0.01)	0.2 (0.01)	0.2 (0.01)	0.8	-	0.2 (0.01)	0.2 (0.01)	0.2 (0.03)	0.9 (1.4)
Starch content (mg g^{-1})[f]	279.8 (27.7)	250.5 (54.6)	74.7 (4.2)	60.9 (10.4)	15.8 (2.2)	261.1 (11.4)	77.2 (6.2)	42.1 (12.0)	18.4 (3.0)	1.5 (0.3)	200.2 (17.2)	40.2 (1.5)	14.0 (2.4)	5.5 (0.2)	0.7 (0.5)
Protein content (mg g^{-1})[g]	13.5 (0.5)	35.5 (2.4)	23.6 (1.1)	10.5 (1.0)	N.D.	19.2 (2.7)	17.0 (2.9)	19.3 (3.6)	21.2 (3.7)	N.D.	15.8 (3.6)	20.0 (3.4)	20.7(3.4)	16.1 (2.7)	N.D.
Phenolic acid content (mg g^{-1})[g]	11.6 (1.2)	17.7 (1.3)	22.4 (1.5)	26.8 (3.2)	19.5 (0.4)	14.1 (0.2)	30.3 (1.8)	39.7 (0.2)	47.8 (1.4)	17.8 (2.0)	23.4 (2.5)	38.9 (1.0)	47.9 (2.4)	48.7 (2.0)	43.8 (1.2)
Caffeic (%)	4.8 (1.8)	4.6 (1.8)	2.3 (0.1)	1.5 (0.1)	-	3.3 (0.4)	1.5 (0.2)	0.6 (0.01)	0.4 (0.05)	-	2.2 (0.5)	0.8 (0.1)	0.5 (0.01)	0.6 (0.1)	-
p-Coumaric (%)	9.8 (1.1)	8.0 (0.1)	6.0 (1.2)	3.8 (0.4)	5.6 (0.9)	8.9 (0.2)	4.8 (0.5)	3.7 (0.02)	3.8 (0.2)	6.4 (1.3)	6.2 (0.1)	4.1 (0.2)	4.2 (0.5)	4.6 (0.6)	17.0 (1.1)
Ferulic (%)	46.6 (2.5)	50.7 (1.0)	84.3 (0.5)	85.8 (0.7)	88.8 (0.8)	84.9 (0.6)	85.7 (0.5)	79.6 (0.3)	76.8 (1.6)	87.0 (0.9)	84.5 (0.5)	80.6 (0.1)	76.8 (0.7)	73.6 (0.3)	71.1 (1.6)
Sinapic (%)	35.8 (0.1)	34.2 (3.5)	0.6	-	-	-	-	5.3 (0.4)	5.5 (0.6)	0.6	-	4.5 (0.2)	4.8 (0.7)	5.5 (0.9)	-
8-8’ diFA (%)	3.1 (0.3)	2.5 (0.6)	5.6 (0.4)	6.0 (0.2)	1.9 (0.4)	2.1 (0.2)	3.0 (0.9)	3.1 (0.04)	3.1 (0.7)	0.6	3.8 (0.9)	2.7 (0.2)	2.5 (0.7)	3.0 (0.6)	5.3 (0.4)
5-5’ diFA (%)	-	-	1.1 (0.4)	2.8 (0.02)	3.7 (0.5)	0.7(0.2)	5.0 (0.1)	7.7 (0.1)	10.3(0.01)	5.3 (2.2)	3.3 (0.2)	7.3 (0.3)	11.3 (1.0)	12.7 (1.0)	6.6 (0.1)
Acetyl (%)[j] **DSAc**	-	-	1.4 0.04	2.7 0.08	N.D.	-	2.7 0.08	6.0 0.20	7.7 0.26	N.D.	-	1.8 0.06	3.0 0.12	3.5 0.11	N.D.
pH of extract	6.5 (0.1)	6.1 (0.6)	6.2 (0.1)	5.2 (0.2)	N.D.	6.3 (0.2)	5.3 (0.2)	4.4 (0.1)	4.0 (0.01)	N.D.	5.3 (0.5)	4.2 (0.3)	4.0 (0.2)	4.2 (0.4)	N.D.
$\bar{M}$**n** (kDa)	6.2	6.5	13.6	15.6		11.6	12.9	11.7	9.3		12.5	10.1	8.9	6.4	
$\bar{M}$**w** (kDa)	205.9	333.0	171.1	105.8	N.D.	367.1	105.5	57.6	32.9	N.D.	211.3	61.7	32.5	18.9	N.D.
Dispersity (D)	33.5	51.2	12.6	6.8		31.6	8.2	4.9	3.5		16.9	6.1	3.6	3.0	

Table S5. Detailed yields, composition and molecular characterisation of the extracts and residues (R) obtained from the pH optimisation in the SWE

Composition	pH 5.0					pH 7.0					pH 9.2				
	5 min	**15 min**	**30 min**	**60 min**	**R**	**5 min**	**15 min**	**30 min**	**60 min**	**R**	**5 min**	**15 min**	**30 min**	**60 min**	**R**
Yield (% DW)[a]	2.4 (0.6)	1.9 (0.4)	1.7 (0.1)	3.3 (0.2)	66.2(13.2)	3.6 (0.6)	2.8 (0.1)	3.0 (0.3)	6.2 (0.3)	69.3 (0.6)	3.6 (0.3)	4.5 (1.0)	14.5 (0.6)	16.2 (0.5)	54.4 (6.7)
Carbohydrate content (mg g^{-1})[b]	999.8 (53.1)	824.2 (215.7)	1006.1 (47.8)	745.2 (89.5)	906.5 (77.0)	1020.9 (160.5)	838.1 (99.5)	835.3 (95.8)	862.3 (50.3)	923.8 (150.2)	850.2 (49.7)	825.1 (42.0)	963.9 (89.3)	981.8 (85.3)	844.8 (155.9)
GAX (%)[c]	16.1 (2.3)	29.4 (2.6)	53.2 (1.9)	74.0 (5.3)	58.3 (1.6)	20.6 (1.6)	39.7 (3.4)	66.4 (4.4)	87.3 (2.4)	59.4 (1.4)	26.4 (1.6)	69.9 (1.5)	92.4 (2.6)	94.3 (3.2)	44.2 (8.1)
A/X[d]	1.36	1.22	0.99	0.70	0.43	0.83	0.82	0.70	0.55	0.47	1.08	0.72	0.56	0.53	0.45
Rha (%)[e]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fuc (%)	0.2 (0.01)	0.4 (0.2)	0.2 (0.01)	0.3 (0.1)	0.2 (0.04)	0.5 (0.4)	0.2 (0.02)	0.2 (0.02)	0.3 (0.1)	0.2 (0.05)	0.2 (0.01)	0.2 (0.1)	0.3 (0.01)	0.4 (0.2)	0.2 (0.1)
Ara (%)	7.3 (0.9)	12.0 (0.8)	22.7 (0.3)	23.5 (1.6)	15.0 (0.3)	7.6 (0.7)	14.1 (1.1)	21.7(0.04)	24.5 (0.3)	16.2 (0.4)	10.1 (0.5)	23.1 (0.1)	28.9 (1.0)	25.4 (0.2)	11.7 (1.8)
Xyl (%)	5.3 (0.6)	9.8 (0.9)	23.0 (0.7)	33.7 (1.4)	35.0 (1.0)	9.2 (0.6)	17.2 (1.7)	31.2 (3.1)	44.8 (0.9)	34.5 (0.8)	9.3 (0.2)	32.0 (0.7)	51.2 (0.6)	47.5 (1.4)	25.7 (5.3)
Gal (%)	2.0 (0.01)	3.1 (0.1)	4.7 (0.2)	6.3 (0.2)	7.0 (0.2)	9.0 (3.5)	5.1 (1.9)	6.4 (0.4)	7.8 (0.2)	7.2 (0.1)	3.0 (0.1)	5.8 (0.2)	8.3 (0.4)	8.4 (0.1)	5.4 (0.8)
Glc (%)	77.8 (0.4)	57.2 (8.3)	37.5 (0.9)	16.3 (2.9)	37.4 (0.3)	69.9 (4.7)	53.8 (4.0)	29.1 (2.2)	8.4 (0.3)	35.8 (0.8)	56.8 (2.3)	25.6 (0.9)	3.3 (0.3)	2.0 (0.2)	50.5 (7.5)
Man (%)	-	1.1 (1.0)	2.9 (0.1)	1.0 (1.5)	3.1 (0.9)	-	1.3 (0.04)	1.2 (0.1)	1.5 (0.1)	3.4 (0.5)	-	-	1.8 (0.5)	1.3 (0.3)	3.9 (0.8)
GalA (%)	5.9 (1.2)	11.9 (5.4)	7.2 (1.2)	8.3 (2.1)	1.1 (0.03)	9.0 (3.5)	5.1 (1.9)	3.2 (0.4)	2.6 (0.4)	1.2 (0.2)	16.6 (0.7)	4.2 (0.1)	2.2 (1.1)	2.0 (0.1)	1.2 (0.2)
GlcA (%)	1.3 (0.8)	4.5 (0.7)	1.4 (0.7)	10.5 (1.9)	1.2 (0.1)	0.6 (0.1)	3.3 (0.5)	6.9 (0.8)	10.1 (1.0)	1.4 (0.1)	4.0 (0.7)	9.0 (0.5)	3.5 (0.1)	12.8 (1.4)	1.3 (0.2)
mGlcA (%)	0.2 (0.01)	-	0.5 (0.1)	0.1 (0.1)	0.1 (0.01)	0.4 (0.1)	-	0.1 (0.02)	0.2 (0.03)	0.1 (0.01)	-	-	0.6 (0.5)	0.2 (0.1)	0.1 (0.02)
Starch content (mg g^{-1})[f]	372.8 (51.1)	238.2 (23.9)	181.1 (8.9)	122.6 (8.2)	5.4(0.7)	289.0 (49.8)	116.5 (22.3)	70.3 (11.2)	21.3 (4.4)	4.0 (1.3)	155.8 (16.6)	97.4 (14.1)	8.1 (1.9)	9.2 (1.2)	10.1 (3.7)
Protein content (mg g^{-1})[g]	24.8 (0.3)	50.1 (0.7)	50.8 (0.1)	27.5 (3.6)	N.D.	101.7 (16.1)	127.0 (6.7)	111.7 (12.4)	80.7 (0.7)	N.D.	97.9 (2.0)	123.3 (0.2)	60.5 (3.4)	61.7 (14.1)	N.D.
Phenolic acid content (mg g^{-1})[g]	3.9 (0.8)	7.1 (0.3)	11.9 (1.5)	20.2 (5.0)	27.1 (1.4)	4.0 (0.3)	5.1 (0.1)	3.9 (2.1)	2.5 (0.2)	6.4 (0.8)	5.4 (0.2)	7.8 (1.6)	4.0 (1.0)	1.4 (0.1)	11.0 (3.0)
Caffeic (%)	0.6 (0.03)	0.1 (0.04)	-	-	-	-	-	-	-	-	-	-	-	-	-
p-Coumaric (%)	4.6 (0.9)	4.5 (0.6)	3.9 (0.5)	3.9 (1.0)	7.1 (0.8)	4.5 (0.3)	8.8 (0.2)	12.2 (0.8)	15.5 (1.9)	12.0 (1.9)	5.4 (0.7)	7.5 (0.3)	10.5 (1.8)	3.6 (0.1)	9.1 (0.9)
Ferulic (%)	78.7(12.6)	72.3 (0.6)	70.3 (2.6)	74.8 (2.4)	84.6 (1.3)	83.1 (0.5)	80.9 (1.2)	71.3 (2.5)	54.5 (1.6)	82.6 (2.8)	84.7 (0.9)	74.0 (1.5)	35.7 (1.0)	21.1(0.03)	86.3 (1.1)
Sinapic (%)	-	-	-	-	-	-	-	-	8.4 (0.3)	-	-	4.2 (0.04)	2.8 (0.2)	4.6 (1.8)	-
8-8’ diFA (%)	16.1(11.6)	23.1 (0.1)	25.2 (3.6)	20.0 (1.6)	3.8 (0.5)	11.6 (0.7)	5.7 (0.8)	4.9 (3.0)	6.2 (0.4)	4.1 (0.2)	8.5 (0.1)	-	1.0 (0.8)	3.5 (1.5)	3.4 (0.4)
5-5’ diFA (%)	-	-	0.6 (0.5)	1.3 (0.1)	4.4 (0.01)	0.9 (0.1)	4.7 (0.2)	11.6 (1.3)	15.3 (0.2)	1.3 (0.8)	1.4 (0.01)	14.4 (1.2)	50.0 (3.9)	67.2 (3.0)	1.2 (0.6)
Acetyl (%)[i] **DSAc**	0.8 0.03	1.4 0.04	1.9 0.06	4.6 0.15	N.D.	-	0.7 0.02	0.7 0.02	1.5 0.05	N.D.	-	0.7 0.01	0.4 0.01	1.0 0.03	N.D.
pH of extract	4.9 (0.01)	5.0 (0.01)	5.0 (0.02)	4.9 (0.02)	N.D.	7.0 (0.04)	7.0 (0.08)	7.0 (0.05)	7.0 (0.04)	N.D.	8.6 (0.3)	9.1 (0.02)	9.3 (0.02)	9.4 (0.03)	N.D.
$\bar{M}$n (kDa) [j]	5.2	5.8	6.6	9.2	N.D.	4.1	3.8	6.7	15.4	N.D.	3.3	4.1	10.3	17.5	N.D.
$\bar{M}$w (kDa)	160.8	299.9	190.7	179.7		182.3	155.4	178.1	225.1		145.0	163.2	199.8	195.9	
Dispersity (D)	31.1	51.5	28.8	19.5		44.0	41.3	26.5	14.6		44.6	39.7	19.3	11.2	

[a] Solid yield was determined gravimetrically on the basis of dry weight
[b] Carbohydrate content was determined using acid methanolysis for the extracts and H_2SO_4 hydrolysis for the residues (R) followed by HPAEC-PAD analysis
[c] Glucuronorabinoxylan (GAX) content was calculated as the total arabinose (Ara), xylose (Xyl), galactose (Gal), glucuronic acid (GlcA) and 4-*O*-methyl-glucuronic acid (mGlcA) composition
[d] A/X is the ratio between Ara and Xyl
[e] Monosaccharide composition was determined by acid methanolysis for the extracts and H_2SO_4 hydrolysis followed by HPAEC-PAD analysis for the residues (R)
[f] Starch content was determined enzymatically using the Total Starch Assay (Megazyme kit)
[g] Soluble protein content was determined using the Bradford method
[h] Phenolic acid content was determined by saponification followed by HPLC analysis
[I] Acetyl content was determined by saponification followed by HPLC analysis
[J] Average molar mass values were determined using SEC-DRI-MALLS in DMSO/LiBr
N.D: Not determined
Description valid for Table S4

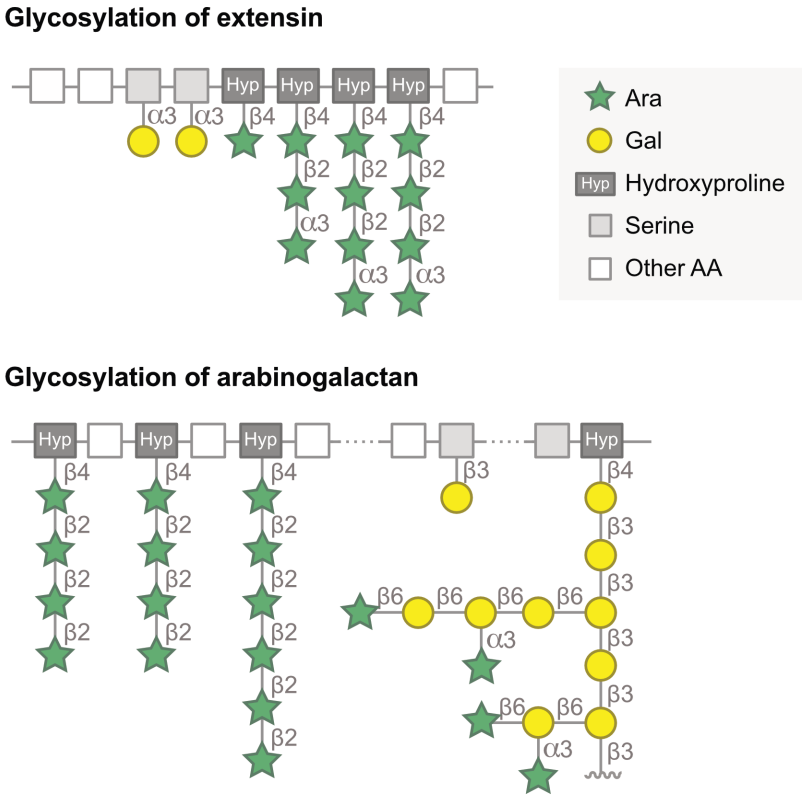

Figure S3. Glycosylation motif of hydroxyproline rich proteins in corn fibre. Graphical representation adapted from previous studies [2-5]

Table S6. Summary of substitution motifs in corn GAX based on previous studies

No.	Substitution	PMAA/ Component	Analysis method/ comment	Reference
1.		GlcA OMeGlcA	Reduction of carboxyl groups followed by methylation, analysis of alditol acetates	6
			Mentioned in text	7
2.		t-Araf	Linkage analysis of methylated alditol acetates from alkaline extracted GAX	8
3.		t-Araf	Linkage analysis of methylated alditol acetates from alkaline extracted GAX	8
4.		t-Xylp	Linkage analysis of methylated alditol acetates from alkaline extracted GAX	8
			Mentioned in text	7
5.		t-Araf Ferulic acid	Isolation of oligosaccharides, linkage analysis of methylated alditol acetates, NMR	9
			Mild acid hydrolysis of corn fibre, reduction of sidechains and analysis on LC-DAD/MS	10
6.		t-Araf *p*-coumaric acid	Mild acid hydrolysis of treated corn insoluble fibre, fractionation using gel permeation chromatography, analysis using 1D/2D NMR spectroscopy and HPLC-MS of methylated samples	11
7.		2-Araf t-Xylp Ferulic acid	Isolation of oligosaccharides from corn bran, linkage analysis of methylated alditol acetates, NMR	9
			Analysis of oligosaccharides from mild acid and enzymatic treatment of corn fibre using NMR and ESI-MS^n	12
			Mild acid hydrolysis of corn fibre, reduction of sidechains and analysis on LC-DAD/MS	10
8.		2-Araf 4-Xylp t-Galp Ferulic acid	Isolation of oligosaccharides from corn bran, linkage analysis of methylated alditol acetates, NMR	9
9.		2-Araf 2-Xylp t-Galp Ferulic acid	Analysis of oligosaccharides from mild acid and enzymatic treatment of corn fibre using NMR and ESI-MS^n	12

10.		2-Araf 2-Xylp 3-Galp t-Galp Ferulic acid	Mild acid hydrolysis of treated corn insoluble fibre, fractionation using gel permeation chromatography, analysis using 1D/2D NMR spectroscopy and HPLC-MS of methylated samples	11
11.		2-Araf 2-Xylp 3-Galp t-Xylp Ferulic acid	Mild acid hydrolysis of treated corn insoluble fibre, fractionation using gel permeation chromatography, analysis using 1D/2D NMR spectroscopy and HPLC-MS of methylated samples	11
12.		2-Araf 3-Araf	Part of oligomeric sidechains, linkage analysis of methylated alditol acetates	8
13.		3-Xylp	Part of oligomeric sidechains, linkage analysis of methylated alditol acetates	6
14.		Acetic acid	O2 link was confirmed using ESI-MS^n	12
			Xylans can be acetylated at both the O2 and O3 position	13

Table S7. Glycosidic linkage analysis of temperature optimised extracts at 160 °C

		Linkage composition (% mol)[a]							
		160 °C 5 min		160 °C 15 min		160 °C 30 min		160 °C 60 min	
		AVG	STD	AVG	STD	AVG	STD	AVG	STD
t-Ara*f*	Ara*f*-(1→	9.8	0.07	14.8	0.02	14.5	0.07	11.1	0.10
t-Ara*p*	Ara*p*-(1→	1.7	0.01	5.1	0.02	3.0	0.04	2.7	0.04
2-Ara*f*	→2)-Ara*f*(1→	1.8	0.01	4.4	<0.01	5.8	0.01	6.6	<0.01
3-Ara*f*[a]	→3)-Ara*f*-(1→	1.8	0.02	3.8	<0.01	4.6	<0.01	4.3	0.02
5-Ara*f*	→5)-Ara*f*-(1→	8.0	0.07	8.3	<0.01	5.4	<0.01	3.3	0.01
3-Xyl*p*/3-Ara*p*	→3)-Ara*p*(1→	1.0	<0.01	2.5	0.01	2.5	<0.01	1.6	0.03
3,5-Ara*f*	→3,5)-Ara*f*-(1→	1.9	0.04	1.7	<0.01	0.8	<0.01	0.4	<0.01
2,5-Ara*f*	→2,5)-Ara*f*-(1→	0.9	0.01	0.6	<0.01	0.4	<0.01	0.5	0.01
2,3,5-Ara*f*	→2,3,5)-Ara*f*-(1→	0.2	<0.01	0.1	<0.01	0.3	<0.01	0.1	<0.01
Total Ara		**27.0**	**0.2**	**41.4**	**0.1**	**37.3**	**0.1**	**30.8**	**0.2**
t-Xyl*p*	Xyl*p*-(1→	1.1	0.03	4.1	0.01	7.1	0.07	9.1	0.04
2-Xyl*f*	→2)-Xyl*f*(1→	0.1	0.01	0.2	0.01	0.3	0.01	0.2	0.01
2-Xyl*p*/2-Ara*p*	→2)-Xyl*p*(1→	0.0	0.00	0.1	0.00	0.1	<0.01	0.1	<0.01
4-Xyl*p*	→4)-Xyl*p*(1→	3.2	0.19	8.9	0.04	13.4	0.03	19.2	0.08
2,4-Xyl*p*	→2,4)-Xyl*p*(1→	2.3	0.12	4.6	0.02	4.7	0.03	5.5	0.03
3,4-Xyl*p*	→3,4)-Xyl*p*(1→	2.9	0.21	6.2	0.02	8.3	0.05	9.7	0.02
2,3,4-Xyl*p*	→2,3,4)-Xyl*p*(1→	2.4	0.17	3.9	0.01	4.0	0.02	3.0	0.02
Total Xyl		**12.1**	**0.7**	**28.0**	**0.1**	**37.9**	**0.2**	**46.8**	**0.2**
t-Glc*p*	Glc*p*-(1→	4.4	0.24	1.3	0.01	0.5	0.01	0.4	0.01
3-Glc*p*	→3)-Glc*p*(1→	0.8	0.01	0.5	0.01	0.5	0.01	0.5	0.01
4-Glc*p*	→4)-Glc*p*(1→	40.4	0.92	11.4	0.16	5.8	0.22	3.7	0.04
3,6-Glc*p*	→3,6)-Glc*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4,6-Glc*p*	→4,6)-Glc*p*(1→	2.2	0.01	0.8	0.02	0.5	0.01	0.3	0.01
Total Glc		**47.8**	**1.2**	**14.0**	**0.2**	**7.3**	**0.3**	**4.9**	**0.1**
t-Gal*p*	Gal*p*-(1→	0.9	0.02	2.5	0.01	3.0	0.01	3.8	0.02
3-Gal*p*	→3)-Gal*p*(1→	0.5	0.02	1.1	0.01	1.6	0.01	2.1	0.01
2-Gal*p*	→2)-Gal*p*(1→	0.0	0.00	0.2	<0.01	0.2	<0.01	0.2	<0.01
4-Gal*p*	→4)-Gal*p*(1→	1.3	0.01	1.1	0.01	1.0	0.01	0.8	<0.01
6-Gal*p*	→6)-Gal*p*(1→	0.2	<0.01	0.6	0.01	0.7	<0.01	0.9	<0.01
2,4-Gal*p*	→2,4)-Gal*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
3,6-Gal*p*	→4,6)-Gal*p*(1→	0.8	0.02	0.4	0.02	0.6	<0.01	0.3	<0.01
Total Gal		**3.7**	**0.1**	**5.8**	**0.1**	**7.0**	**0.03**	**8.1**	**0.04**
t-Man*p*	Man*p*-(1→	0.1	<0.01	0.08	<0.01	0.1	<0.01	0.1	0.01
4-Man*p*	→4)-Man*p*(1→	0.9	0.03	1.05	0.04	0.8	0.04	0.5	<0.01
3,4-Man*p*	→3,4)-Man*p*(1→	0.3	0.01	0.09	0.01	0.1	<0.01	0.03	<0.01
2,4-Man*p*	→2,4)-Man*p*(1→	0.1	0.01	0.05	<0.01	0.0	0.00	0.0	0.00
4,6-Man*p*	→4,6)-Man*p*(1→	0.1	0.01	0.06	<0.01	0.0	0.00	0.0	0.00
Total Man		**1.6**	**0.1**	**1.33**	**0.1**	**1.0**	**0.1**	**0.6**	**0.02**
2-Rha*p*	→2)-Rha*p*(1→	0.0	0.00	0.0	0.00	0.0	0.0	0.0	0.0
3-Rha*p*	→3)-Rha*p*(1→	0.2	0.00	0.2	0.04	0.0	0.0	0.0	0.0
2,4-Rha*p*	→2,4)-Rha*p*(1→	0.7	0.06	0.9	0.19	0.0	0.0	0.0	0.0
Total Rha		**0.9**	**0.06**	**1.14**	**0.2**	**0.0**	**0.0**	**0.0**	**0.0**

[a] % mol was corrected to the monosaccharide content of the sample

Table S8. Glycosidic linkage analysis of temperature optimised extracts at 180 °C

		Linkage composition (% mol)[a]							
		180 °C 5 min		180 °C 15 min		180 °C 30 min		180 °C 60 min	
		AVG	STD	AVG	STD	AVG	STD	AVG	STD
t-Ara*f*	Ara*f*-(1→	8.1	0.24	10.0	0.21	7.5	0.09	3.0	0.01
t-Ara*p*	Ara*p*-(1→	2.0	0.04	2.7	0.09	2.5	0.02	1.5	<0.01
2-Ara*f*	→2)-Ara*f*(1→	3.0	0.04	6.5	0.10	7.7	0.02	8.1	<0.01
3-Ara*f*[a]	→3)-Ara*f*-(1→	2.9	0.03	5.0	0.03	5.3	0.02	4.6	<0.01
5-Ara*f*	→5)-Ara*f*-(1→	10.3	0.12	7.3	0.01	4.6	0.01	4.5	<0.01
3-Xyl*p*/3-Ara*p*	→3)-Ara*p*(1→	2.5	0.02	3.1	0.06	2.9	<0.01	3.1	<0.01
3,5-Ara*f*	→3,5)-Ara*f*-(1→	2.3	0.01	1.3	<0.01	0.5	<0.01	0.4	<0.01
2,5-Ara*f*	→2,5)-Ara*f*-(1→	0.8	0.03	0.7	0.01	0.4	<0.01	0.6	<0.01
2,3,5-Ara*f*	→2,3,5)-Ara*f*-(1→	0.3	0.02	0.2	0.00	0.1	<0.01	0.2	<0.01
Total Ara		**31.9**	**0.5**	**36.9**	**0.5**	**31.5**	**0.2**	**25.7**	**0.02**
t-Xyl*p*	Xyl*p*-(1→	2.1	0.05	5.4	0.04	7.3	0.19	5.5	0.06
2-Xyl*f*	→2)-Xyl*f*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
2-Xyl*p*/2-Ara*p*	→2)-Xyl*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4-Xyl*p*	→4)-Xyl*p*(1→	6.3	0.05	14.5	0.04	20.0	0.07	26.4	0.05
2,4-Xyl*p*	→2,4)-Xyl*p*(1→	3.3	0.01	5.6	0.04	6.2	0.05	6.7	0.03
3,4-Xyl*p*	→3,4)-Xyl*p*(1→	5.0	0.02	8.8	0.04	10.9	0.07	13.4	0.04
2,3,4-Xyl*p*	→2,3,4)-Xyl*p*(1→	2.9	0.01	3.2	0.02	2.9	0.03	2.4	0.04
Total Xyl		**19.6**	**0.1**	**37.5**	**0.2**	**47.3**	**0.4**	**54.4**	**0.2**
t-Glc*p*	Glc*p*-(1→	2.2	0.04	0.6	0.04	0.4	0.01	0.3	0.00
3-Glc*p*	→3)-Glc*p*(1→	0.6	0.01	0.5	0.02	0.5	0.02	0.5	0.01
4-Glc*p*	→4)-Glc*p*(1→	29.1	0.80	7.1	0.12	3.7	0.16	2.4	0.02
3,6-Glc*p*	→3,6)-Glc*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4,6-Glc*p*	→4,6)-Glc*p*(1→	1.8	0.04	0.5	<0.01	0.3	0.01	0.2	<0.01
Total Glc		**33.8**	**0.9**	**8.6**	**0.2**	**4.8**	**0.2**	**3.4**	**0.04**
t-Gal*p*	Gal*p*-(1→	1.4	<0.01	5.0	0.01	6.1	0.01	6.7	0.01
3-Gal*p*	→3)-Gal*p*(1→	0.7	<0.01	0.8	<0.01	1.0	<0.01	1.1	<0.01
2-Gal*p*	→2)-Gal*p*(1→	0.1	<0.01	0.1	<0.01	0.1	<0.01	0.1	<0.01
4-Gal*p*	→4)-Gal*p*(1→	1.3	0.01	0.5	<0.01	0.3	<0.01	0.3	<0.01
6-Gal*p*	→6)-Gal*p*(1→	0.3	<0.01	0.3	<0.01	0.4	<0.01	0.5	<0.01
2,4-Gal*p*	→2,4)-Gal*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
3,6-Gal*p*	→4,6)-Gal*p*(1→	0.8	<0.01	0.2	<0.01	0.2	<0.01	0.1	<0.01
Total Gal		**4.6**	**0.01**	**6.9**	**0.0**	**8.0**	**0.02**	**8.9**	**0.02**
t-Man*p*	Man*p*-(1→	0.1	<0.01	0.1	0.01	0.1	0.00	0.1	0.01
4-Man*p*	→4)-Man*p*(1→	1.1	0.11	0.9	0.05	0.6	0.02	0.5	0.01
3,4-Man*p*	→3,4)-Man*p*(1→	0.2	0.04	0.0	0.00	0.0	0.00	0.0	0.00
2,4-Man*p*	→2,4)-Man*p*(1→	0.1	0.01	0.0	0.00	0.0	0.00	0.0	0.00
4,6-Man*p*	→4,6)-Man*p*(1→	0.1	0.01	0.0	0.00	0.0	0.00	0.02	0.01
Total Man		**1.5**	**0.2**	**1.10**	**0.1**	**0.7**	**0.0**	**0.6**	**0.03**
2-Rha*p*	→2)-Rha*p*(1→	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-Rha*p*	→3)-Rha*p*(1→	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,4-Rha*p*	→2,4)-Rha*p*(1→	0.0	0.0	0.0	0.0	0.6	0.02	0.5	0.01
Total Rha		**0.0**	**0.0**	**0.0**	**0.0**	**0.6**	**0.02**	**0.5**	**0.01**

[a] % mol was corrected to the monosaccharide content of the sample

Table S9. Glycosidic linkage analysis of pH optimised extracts at pH 7.0

		Linkage composition (% mol)[a]							
		pH 7.0 5 min		pH 7.0 15 min		pH 7.0 30 min		pH 7.0 60 min	
		AVG	STD	AVG	STD	AVG	STD	AVG	STD
t-Ara*f*	Ara*f*-(1→	5.2	0.32	8.6	0.005	14.8	0.09	14.0	0.04
t-Ara*p*	Ara*p*-(1→	0.1	<0.01	0.2	0.06	0.4	<0.01	0.3	0.01
2-Ara*f*	→2)-Ara*f*(1→	0.5	0.03	1.0	0.06	2.0	<0.01	3.8	0.01
3-Ara*f*[a]	→3)-Ara*f*-(1→	0.4	0.03	0.4	0.02	0.8	0.01	2.9	0.02
5-Ara*f*	→5)-Ara*f*-(1→	1.9	0.13	3.9	0.07	4.8	0.04	4.2	0.12
3-Xyl*p*/3-Ara*p*	→3)-Ara*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
3,5-Ara*f*	→3,5)-Ara*f*-(1→	0.4	0.02	0.4	0.07	0.4	0.01	0.7	0.03
2,5-Ara*f*	→2,5)-Ara*f*-(1→	0.2	0.03	1.2	0.90	0.4	<0.01	0.2	<0.01
2,3,5-Ara*f*	→2,3,5)-Ara*f*-(1→	0.1	0.03	0.2	0.01	0.3	<0.01	0.1	<0.01
Total Ara		**8.8**	**0.6**	**16.0**	**1.2**	**23.8**	**0.2**	**26.0**	**0.2**
t-Xyl*p*	Xyl*p*-(1→	0.8	0.11	4.2	0.59	9.2	0.69	10.1	0.01
2-Xyl*f*	→2)-Xyl*f*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
2-Xyl*p*/2-Ara*p*	→2)-Xyl*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4-Xyl*p*	→4)-Xyl*p*(1→	3.4	0.20	3.5	0.32	5.3	0.85	8.6	0.10
2,4-Xyl*p*	→2,4)-Xyl*p*(1→	1.6	0.14	2.2	0.58	3.6	0.69	5.5	0.18
3,4-Xyl*p*	→3,4)-Xyl*p*(1→	2.9	0.04	5.9	0.02	9.7	0.01	13.1	0.29
2,3,4-Xyl*p*	→2,3,4)-Xyl*p*(1→	2.0	0.06	3.7	0.29	6.4	0.95	10.2	0.20
Total Xyl		**10.7**	**0.5**	**19.5**	**1.8**	**34.1**	**3.2**	**47.6**	**0.8**
t-Glc*p*	Glc*p*-(1→	4.1	0.88	17.8	1.47	9.1	0.13	0.6	0.01
3-Glc*p*	→3)-Glc*p*(1→	1.0	0.14	1.8	0.32	1.4	0.19	0.3	0.01
4-Glc*p*	→4)-Glc*p*(1→	59.0	1.52	29.0	2.07	14.7	1.71	6.0	0.20
3,6-Glc*p*	→3,6)-Glc*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4,6-Glc*p*	→4,6)-Glc*p*(1→	4.0	0.65	2.3	0.08	1.3	0.12	0.5	0.02
Total Glc		**68.1**	**3.2**	**50.9**	**4.0**	**26.5**	**2.1**	**7.4**	**0.2**
t-Gal*p*	Gal*p*-(1→	0.4	<0.01	1.6	0.00	1.3	0.01	2.8	0.02
3-Gal*p*	→3)-Gal*p*(1→	0.4	<0.01	0.6	0.02	0.4	0.00	1.5	0.02
2-Gal*p*	→2)-Gal*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4-Gal*p*	→4)-Gal*p*(1→	1.0	0.01	1.2	0.03	1.6	0.04	0.9	0.04
6-Gal*p*	→6)-Gal*p*(1→	0.1	<0.01	0.7	0.02	0.4	<0.01	0.6	0.03
2,4-Gal*p*	→2,4)-Gal*p*(1→	0.0	0.00	0.0	0.00	1.7	0.33	0.0	0.00
3,6-Gal*p*	→4,6)-Gal*p*(1→	0.8	0.01	0.6	0.09	0.4	0.01	1.1	0.03
Total Gal		**2.7**	**0.02**	**4.7**	**0.2**	**5.9**	**0.4**	**6.9**	**0.1**
t-Man*p*	Man*p*-(1→	0.0	0.00	0.0	0.00	0.0	0.01	0.3	0.01
4-Man*p*	→4)-Man*p*(1→	0.0	0.00	1.1	0.04	1.0	0.08	0.7	0.05
3,4-Man*p*	→3,4)-Man*p*(1→	0.0	0.00	0.1	0.01	0.02	0.01	0.2	0.01
2,4-Man*p*	→2,4)-Man*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4,6-Man*p*	→4,6)-Man*p*(1→	0.0	0.00	0.1	<0.01	0.04	0.04	0.03	0.01
Total Man		**0.0**	**0.0**	**1.2**	**0.0**	**1.1**	**0.1**	**1.3**	**0.1**
2-Rha*p*	→2)-Rha*p*(1→	-							
3-Rha*p*	→3)-Rha*p*(1→								
2,4-Rha*p*	→2,4)-Rha*p*(1→								
Total Rha									

[a] % mol was corrected to the monosaccharide content of the sample

Table S10. Glycosidic linkage analysis of pH optimised extracts at pH 9.2

		Linkage composition (% mol)[a]							
		pH 9.2 5 min		pH 9.2 15 min		pH 9.2 30 min		pH 9.2 60 min	
		AVG	STD	AVG	STD	AVG	STD	AVG	STD
t-Ara*f*	Ara*f*-(1→	7.5	0.16	15.2	0.06	17.7	0.43	14.2	0.08
t-Ara*p*	Ara*p*-(1→	0.1	0.03	0.2	<0.01	0.9	0.08	0.2	<0.01
2-Ara*f*	→2)-Ara*f*(1→	0.8	0.10	3.1	<0.01	4.9	0.12	4.6	0.04
3-Ara*f*[a]	→3)-Ara*f*-(1→	0.5	0.01	2.4	0.01	2.1	0.05	4.7	0.02
5-Ara*f*	→5)-Ara*f*-(1→	2.2	0.09	3.4	0.01	3.9	0.06	2.6	0.01
3-Xyl*p*/3-Ara*p*	→3)-Ara*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
3,5-Ara*f*	→3,5)-Ara*f*-(1→	0.4	0.01	0.6	<0.01	0.2	0.05	0.3	<0.01
2,5-Ara*f*	→2,5)-Ara*f*-(1→	0.2	0.08	0.2	<0.01	0.2	0.04	0.1	<0.01
2,3,5-Ara*f*	→2,3,5)-Ara*f*-(1→	0.1	0.16	0.1	<0.01	0.1	0.03	0.1	<0.01
Total Ara		**11.8**	**0.6**	**25.2**	**0.1**	**30.0**	**0.9**	**26.8**	**0.2**
t-Xyl*p*	Xyl*p*-(1→	0.8	0.03	6.5	0.11	18.5	0.16	10.3	0.37
2-Xyl*f*	→2)-Xyl*f*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
2-Xyl*p*/2-Ara*p*	→2)-Xyl*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4-Xyl*p*	→4)-Xyl*p*(1→	3.1	0.08	6.5	0.12	7.2	0.04	8.8	0.01
2,4-Xyl*p*	→2,4)-Xyl*p*(1→	1.6	0.04	4.1	0.20	4.6	0.07	4.9	0.09
3,4-Xyl*p*	→3,4)-Xyl*p*(1→	3.3	0.03	10.2	0.06	13.2	0.06	15.2	0.44
2,3,4-Xyl*p*	→2,3,4)-Xyl*p*(1→	2.2	0.05	7.5	0.18	9.7	0.07	11.0	0.39
Total Xyl		**10.9**	**0.2**	**34.8**	**0.7**	**53.2**	**0.4**	**50.2**	**1.3**
t-Glc*p*	Glc*p*-(1→	4.2	0.51	1.8	0.09	0.4	0.03	0.1	0.01
3-Glc*p*	→3)-Glc*p*(1→	1.1	0.06	0.6	0.03	0.2	0.01	0.0	0.00
4-Glc*p*	→4)-Glc*p*(1→	47.4	1.54	19.6	0.68	2.2	0.18	1.5	0.10
3,6-Glc*p*	→3,6)-Glc*p*(1→	0.04	0.02	0.0	0.00	0.0	0.00	0.0	0.00
4,6-Glc*p*	→4,6)-Glc*p*(1→	2.7	0.16	1.4	0.06	0.1	0.01	0.2	0.06
Total Glc		**55.4**	**2.3**	**23.3**	**0.9**	**2.9**	**0.2**	**1.8**	**0.2**
t-Gal*p*	Gal*p*-(1→	1.1	0.08	1.9	0.06	6.3	0.18	5.2	0.04
3-Gal*p*	→3)-Gal*p*(1→	0.2	0.02	1.1	0.05	0.3	0.05	1.3	0.02
2-Gal*p*	→2)-Gal*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4-Gal*p*	→4)-Gal*p*(1→	0.9	0.02	0.8	0.03	0.2	0.04	0.2	0.001
6-Gal*p*	→6)-Gal*p*(1→	0.2	<0.01	0.5	0.02	0.3	0.06	0.4	0.01
2,4-Gal*p*	→2,4)-Gal*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
3,6-Gal*p*	→4,6)-Gal*p*(1→	0.6	0.01	1.0	0.06	0.1	0.02	0.2	0.01
Total Gal		**3.0**	**0.1**	**5.3**	**0.2**	**7.2**	**0.35**	**7.4**	**0.1**
t-Man*p*	Man*p*-(1→	0.0	0.00	0.0	0.00	0.3	0.09	1.1	0.22
4-Man*p*	→4)-Man*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
3,4-Man*p*	→3,4)-Man*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
2,4-Man*p*	→2,4)-Man*p*(1→	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
4,6-Man*p*	→4,6)-Man*p*(1→	0.0	0.00	0.0	0.00	1.3	0.36	0.0	0.00
Total Man		**0.0**	**0.0**	**0.00**	**0.0**	**1.6**	**0.4**	**1.1**	**0.2**
2-Rha*p*	→2)-Rha*p*(1→	-							
3-Rha*p*	→3)-Rha*p*(1→								
2,4-Rha*p*	→2,4)-Rha*p*(1→								
Total Rha									

[a] % mol was corrected to the monosaccharide content of the sample

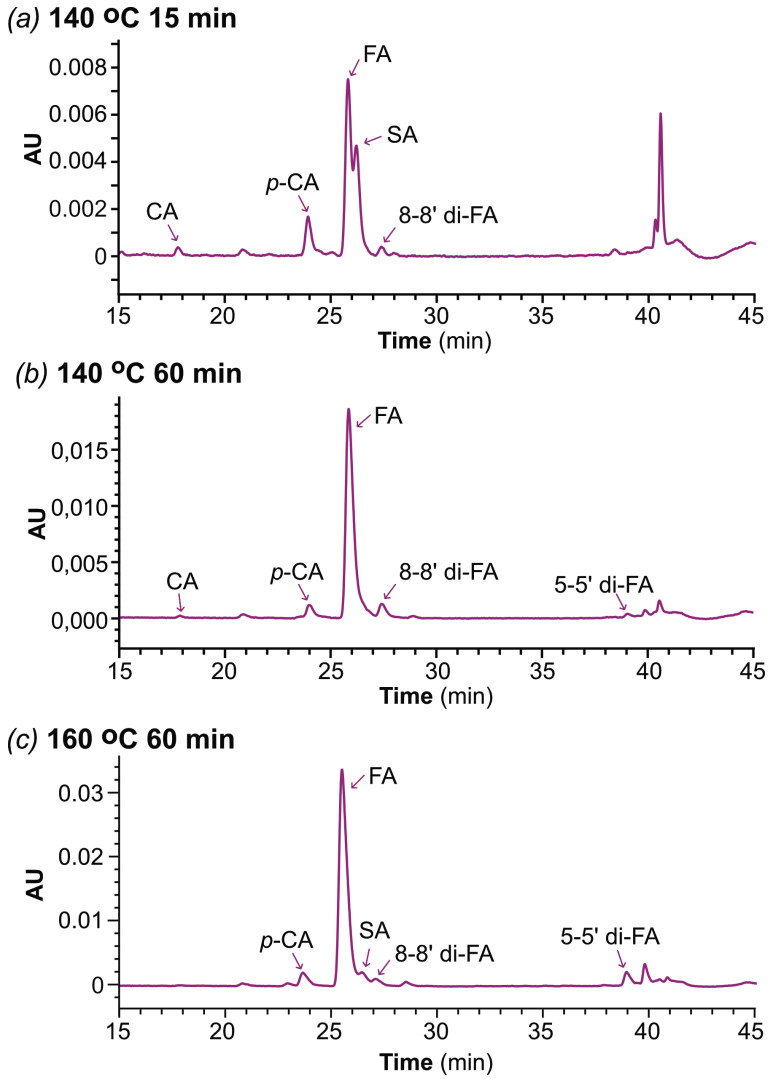

Figure S4. HPLC chromatograms of phenolic acids from the temperature optimised extracts. (a) Chromatograms from the (a) 140 ºC 5 min, (b) 140 ºC 60 min, (c) 160 ºC 60 min extracts obtained at 325 nm. Unassigned peaks eluting after 5-5' di-FA (39.0 – 42.0 min) at 325 nm are presumably other forms of ferulic acid dehydrodimers. Analysis was referenced to standards of caffeic acid, *p*-coumaric acid, ferulic acid, 8-8'-diFA, 5-5' di-FA and cinnamic acid. Wavelength used was 325 nm. Cinnamic showed the highest absorbance at 270 nm.

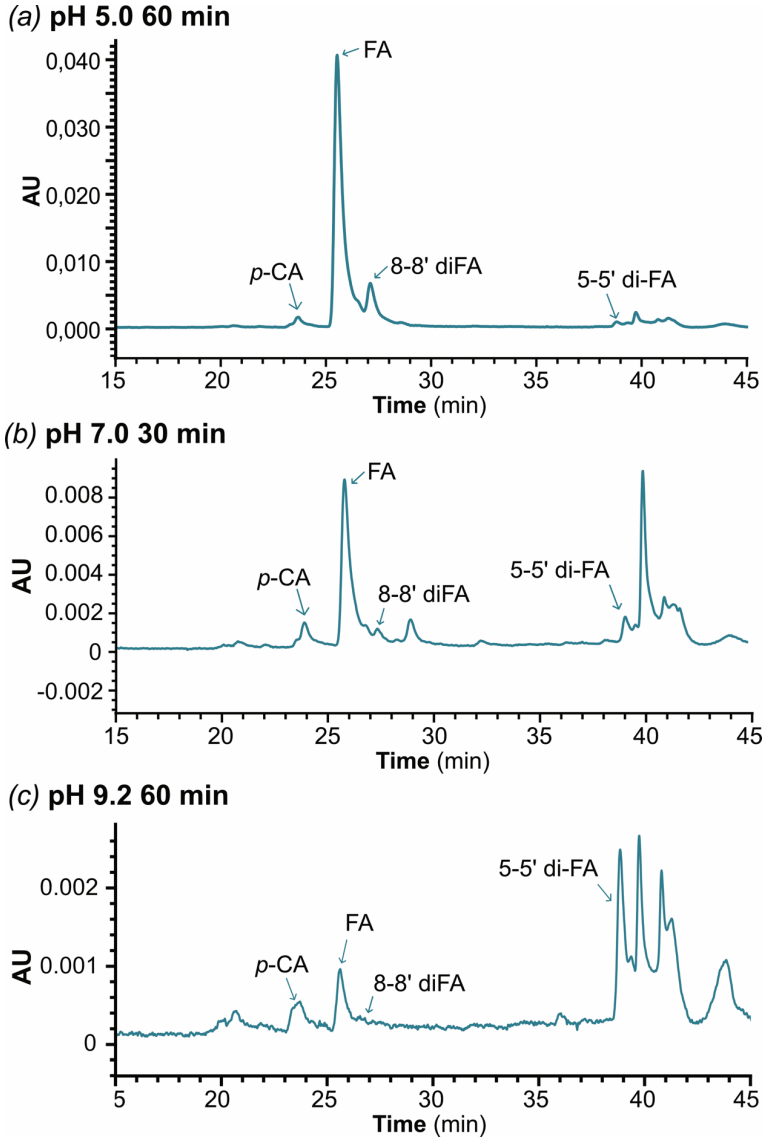

Figure S5. HPLC chromatograms of phenolic acids from the pH optimised extracts. Chromatograms from the (a) pH 5 60 min, (b) pH 7.0 30 min and (c) pH 9.2 60 min extracts obtained at 325 nm. Unassigned peaks eluting after 5-5' di-FA (39.0 – 42.0 min) at 325 nm are presumably other forms of ferulic acid dehydrodimers. Analysis was referenced to standards of caffeic acid, *p*-coumaric acid, ferulic acid, 8-8'-diFA, 5-5' di-FA and cinnamic acid. Wavelength used was 325 nm. Cinnamic showed the highest absorbance at 270 nm.

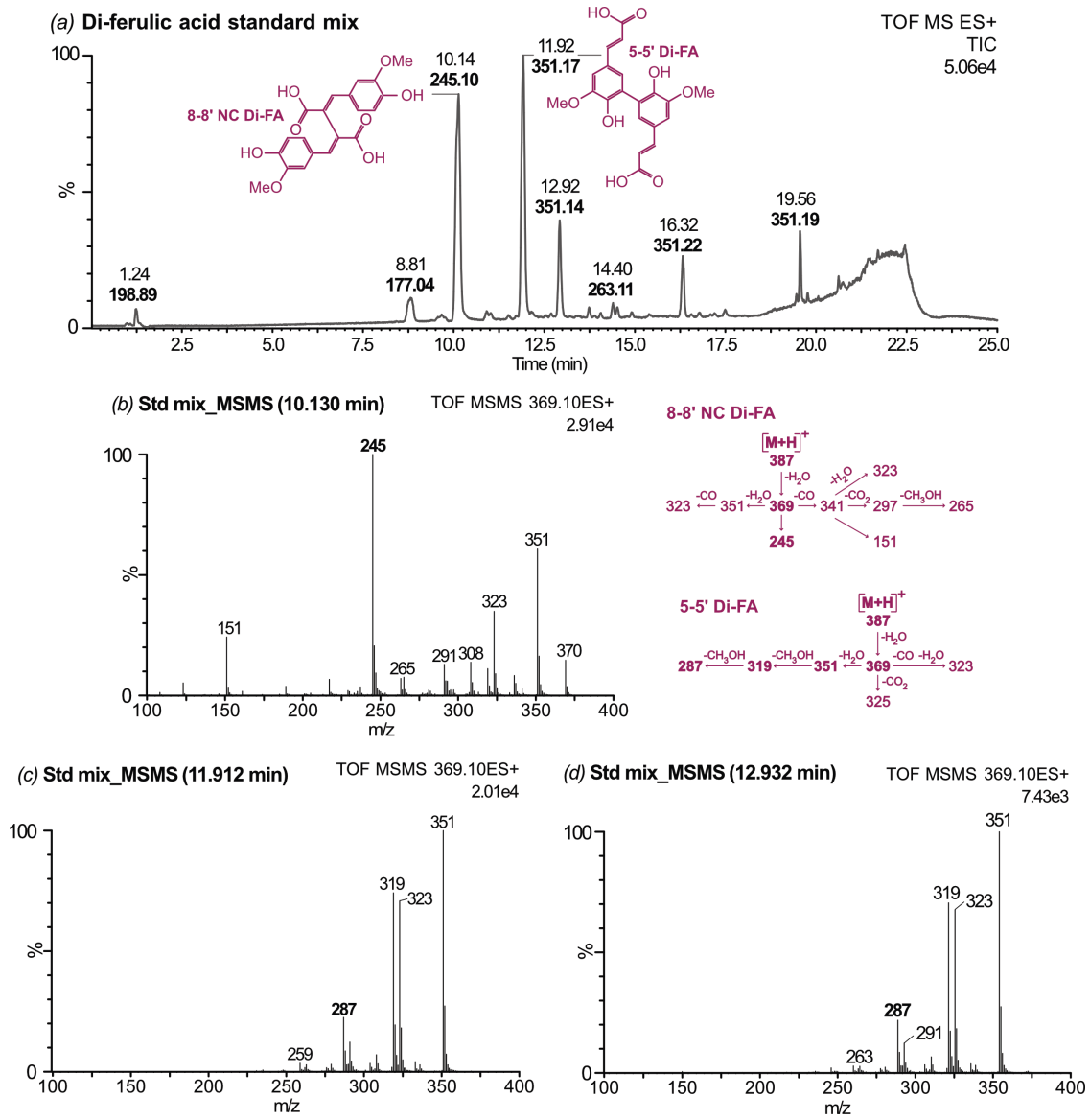

Figure S6. (a) HPLC-ESI-MS chromatogram of ferulic acid standard mixture containing monomeric ferulic acid (8.81 min), 8-8’ non-cyclic di-ferulic acid (10.14 min) and 5-5’ di-ferulic acid (11.92 min). Mass of analyte is shown in bold. Other peaks in the chromatogram mostly likely correspond to isomers that were co-produced during the synthesis of the ferulic acid dehydrodimers. CID MS^2 spectra of (b) 8-8’ non-cyclic ferulic acid dehydrodimer standard, (c) 5-5’ ferulic acid dehydrodimer and (d) 5-5’ ferulic acid dehydrodimer isomer (eluting at 12.92 min). Proposed fragmentation pathway and isomer-specific fragments (highlighted in bold in the spectra) are in accordance with a previous study.[14]

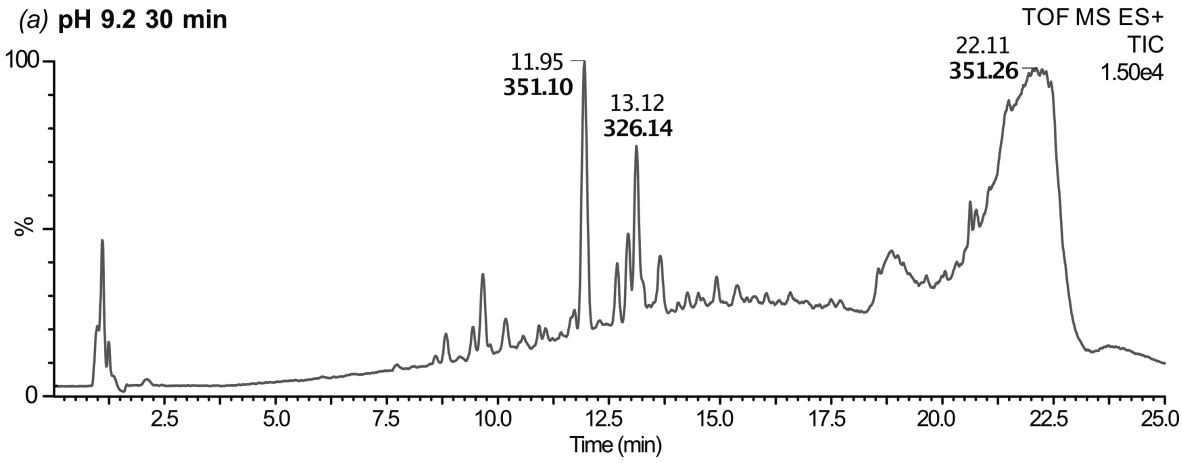

Figure S7. HPLC-ESI-MS chromatogram of the pH 9.2 30 min extract containing ions of di-FAs. The 351.1 m/z ion correspond to a dehydrated di-FA in adduct with a proton $[M - 2H_2O + H]^+$

Table S11. EC_{50} values of DPPH radical scavenging activity from temperature and pH optimised extracts

Sample	Extraction time (min)	EC_{50}[a] (mg extract/mg DPPH)
Temperature optimised extracts		
140 °C	5	5.37
	15	3.94
	30	4.46
	60	5.14
160 °C	5	5.79
	15	5.33
	30	4.63
	60	4.23
180 °C	5	4.87
	15	4.38
	30	3.89
	60	3.86
pH optimised extracts		
pH 5.0	5	-
	15	-
	30	8.84
	60	6.79
pH 7.0	5	10.43
	15	7.22
	30	6.11
	60	6.23
pH 9.2	5	10.12
	15	3.35
	30	4.95
	60	6.79
Free antioxidants		
Ferulic acid		0.19
Ascorbic acid		0.15

[a] EC_{50} is the effective concentration that resulted in 50 % of DPPH scavenging activity

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