

Supplementary material

Seasonal dynamics in structural characteristics within bark stems of cultivated willow (*Salix* sp.) by NMR and time-gated Raman spectroscopy

Dou Jinze^{1#}, Kögler Martin², Kesari Kavindra Kumar¹, Pitkänen Leena¹, Vuorinen Tapani¹

¹Department of Bioproducts and Biosystems, Aalto University, 02150 Espoo, Finland

²VTT Technical Research Centre of Finland, 90570 Oulu, Finland

#Corresponding author (and address of all authors):

Dr. Jinze Dou (jinze.dou@aalto.fi), +358413115001

Table S1. Mass balance (w/w %) of the willow bark that is harvested from five different seasons (02-17 to 12-04) and characteristics of the purified cellulose. Standard deviation is included inside the parenthesis. “a” denotes that this acid-insoluble lignin data is acquired from the sample after all pretreatments (N, **Fig. S1**).

		02-17	04-23	07-13	09-23	12-04
mass balance	DCM	3 (0)	3 (0.1)	3 (0.1)	2 (0.1)	4 (0)
	acetone	4 (0)	4 (0.8)	2 (0.1)	2 (2.0)	6 (0)
	water	5 (0)	7 (0.9)	10 (7.6)	9 (3.8)	6 (0)
	extracts (sum)	12 (0)	14 (1.8)	15 (7.9)	13 (1.7)	16 (0)
	crude pectin	3 (0)	4 (0.2)	4 (0.2)	4 (0.7)	3 (0.6)
	hemicellulose	1 (0)	3 (0)	2 (0)	3 (0)	2 (0)
	cellulose	17 (0)	31 (0)	32 (0)	27 (0)	24 (0)
	acid-insoluble “klason lignin” ^a	12.9 (0)	9.6 (0.6)	8.6 (0.2)	8.8 (0.4)	10.6 (0.04)
	overall sum	47	61	62	56	56
characteristic s of purified cellulose	Viscosity ([η] ml/g)	401 (0)	577 (5)	671 (9)	486 (4)	413 (5)
	Mn (kDa)	64 (2)	69 (2)	88 (2)	101 (50)	57 (0)
	Mw (kDa)	221 (2)	229 (1)	272 (3)	266 (94)	189 (2)
	Mw/Mn (degree of dispersion)	3.5 (0.06)	3.3 (0.08)	3.1 (0.02)	2.8 (0.43)	3.3 (0.02)

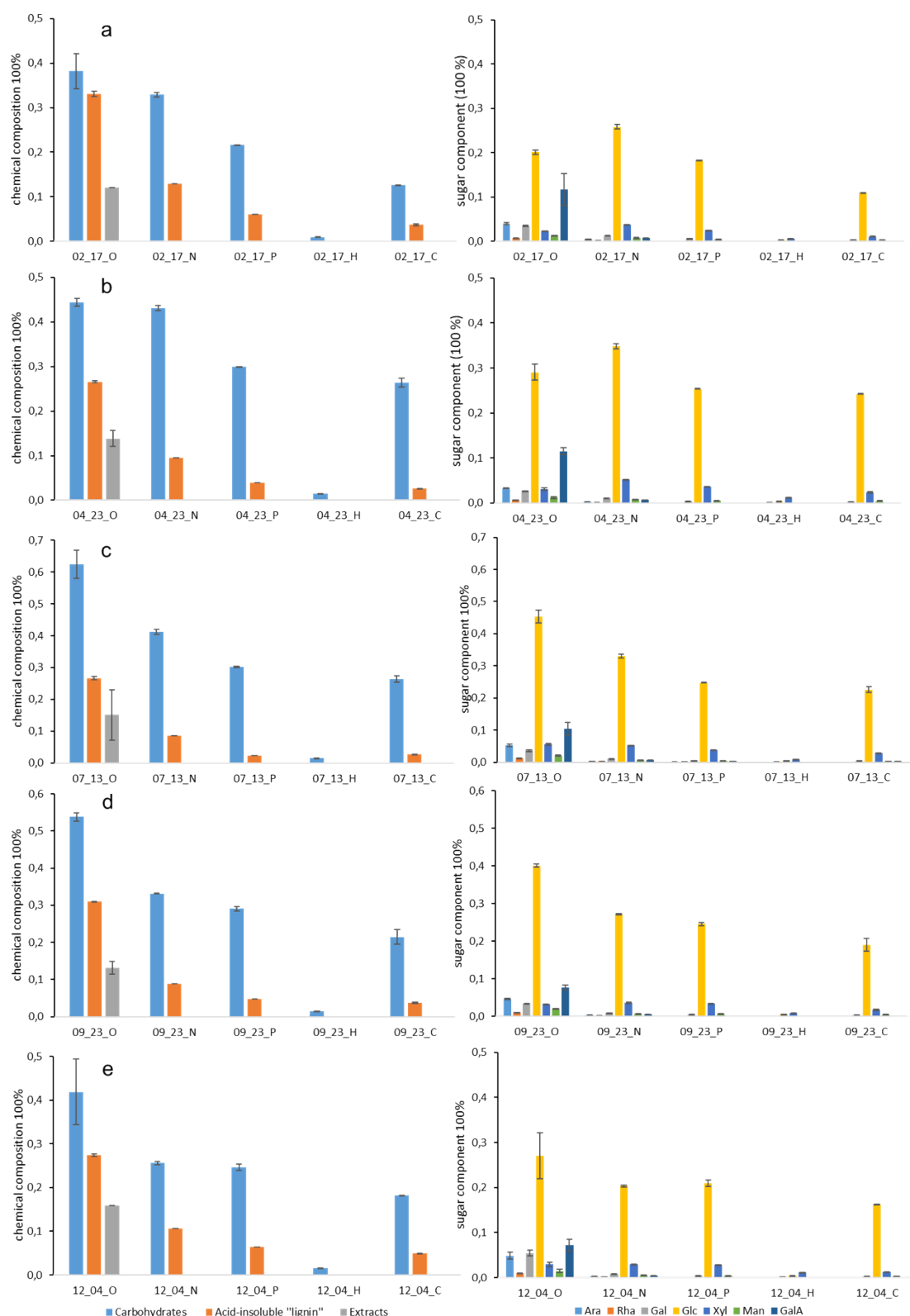


Fig. S1. Overall chemical composition (% of the accepted dry mass) (left) and carbohydrate composition (% of anhydro sugars in the monosaccharide (right) at the multiple solid residues that was processed throughout scheme Fig. 1. a 02-17. b 04-23. c 07-13. d 09-23. e 12-04. "O" refers to the original sample; "N" refers to the sample after treatment of solvent extraction, crude pectin removal, protein removal, and 0.1M NaOH treatment; "P" refers to the solid residue after the peracetic acid treatment; "H" refers to the recovered hemicellulose; "C" refers to the recovered cellulose. Abbreviations: arabinose (Ara), rhamnose (Rha), galactose (Gal), glucose (Glc), xylose (Xyl), mannose (Man), galacturonic acid (GalA).

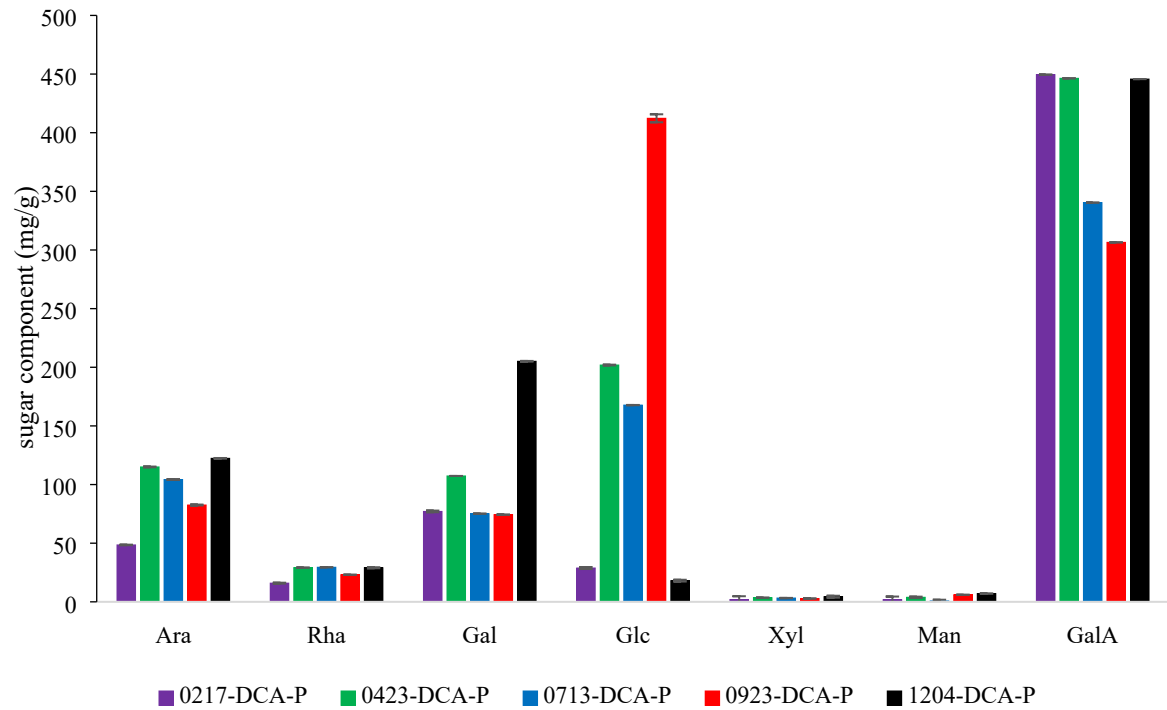


Fig. S2. Chemical compositional analysis of the dialyzed pectin (DCA-P) from five different seasoned willow bark (02-17; 04-23; 07-13; 09-23; 12-04) that is harvested throughout one calendar year.

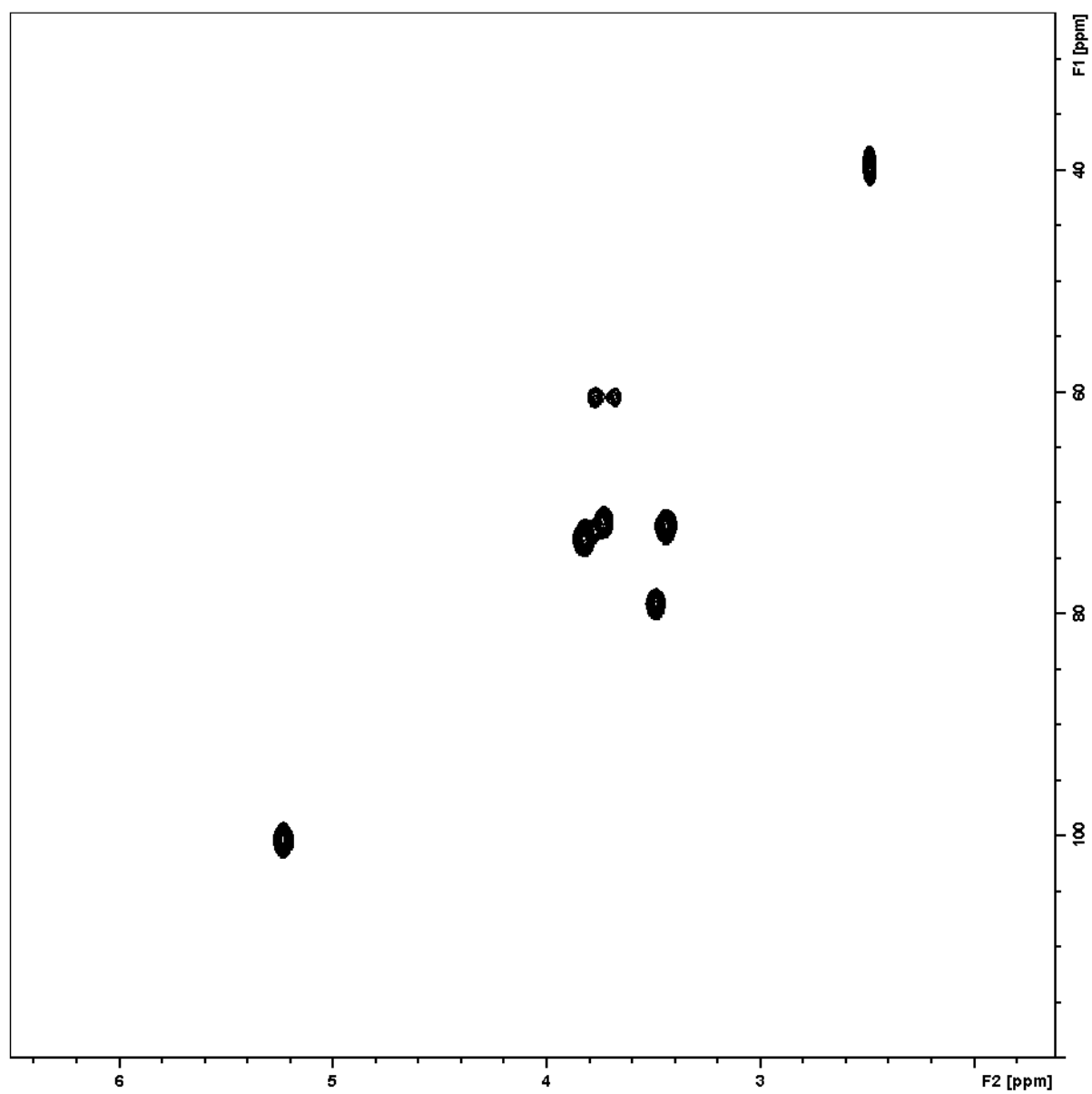


Fig. S3. HSQC NMR spectrum of the authentic starch in DMSO-*d*₆/pyridine-*d*₅ (v/v 4/1).

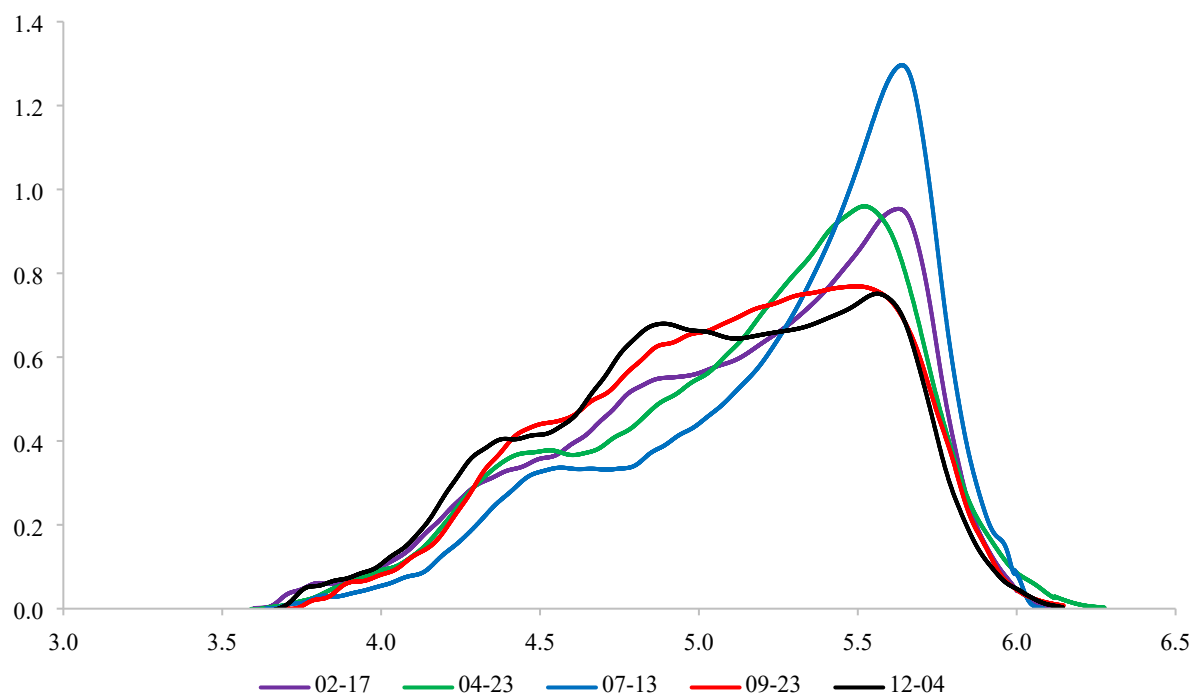


Fig. S4. The molar mass distribution of recovered cellulose from five different seasoned willow bark (02-17; 04-23; 07-13; 09-23; 12-04) that is harvested throughout one calendar year.

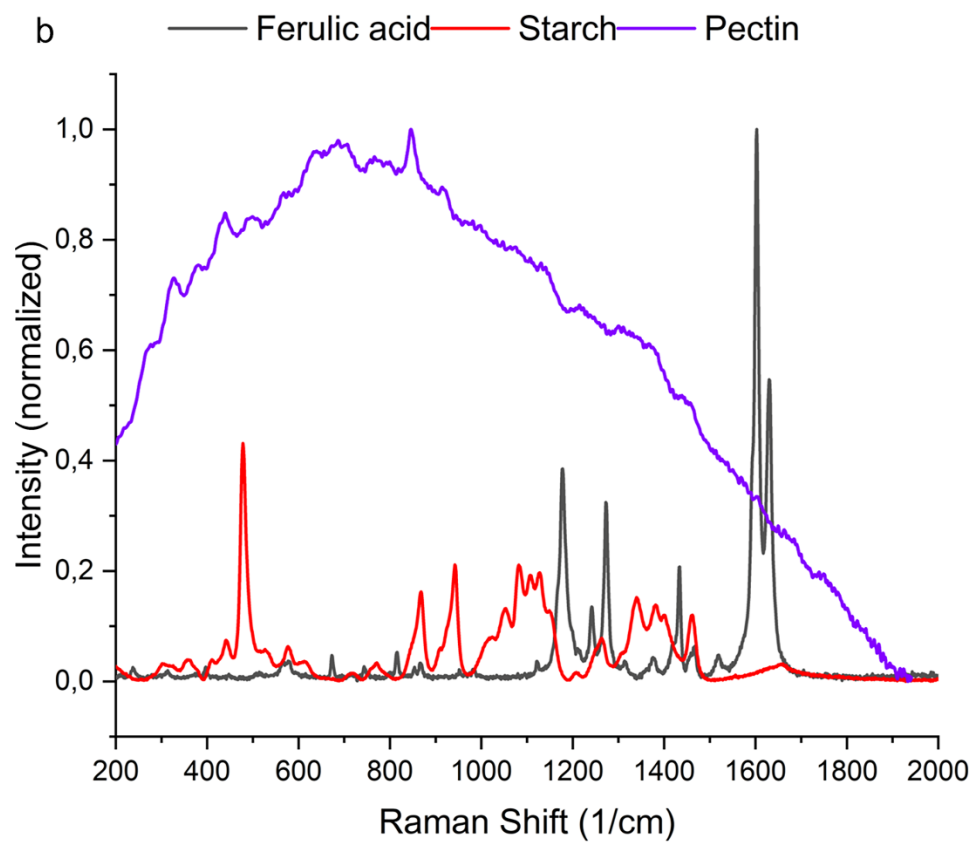
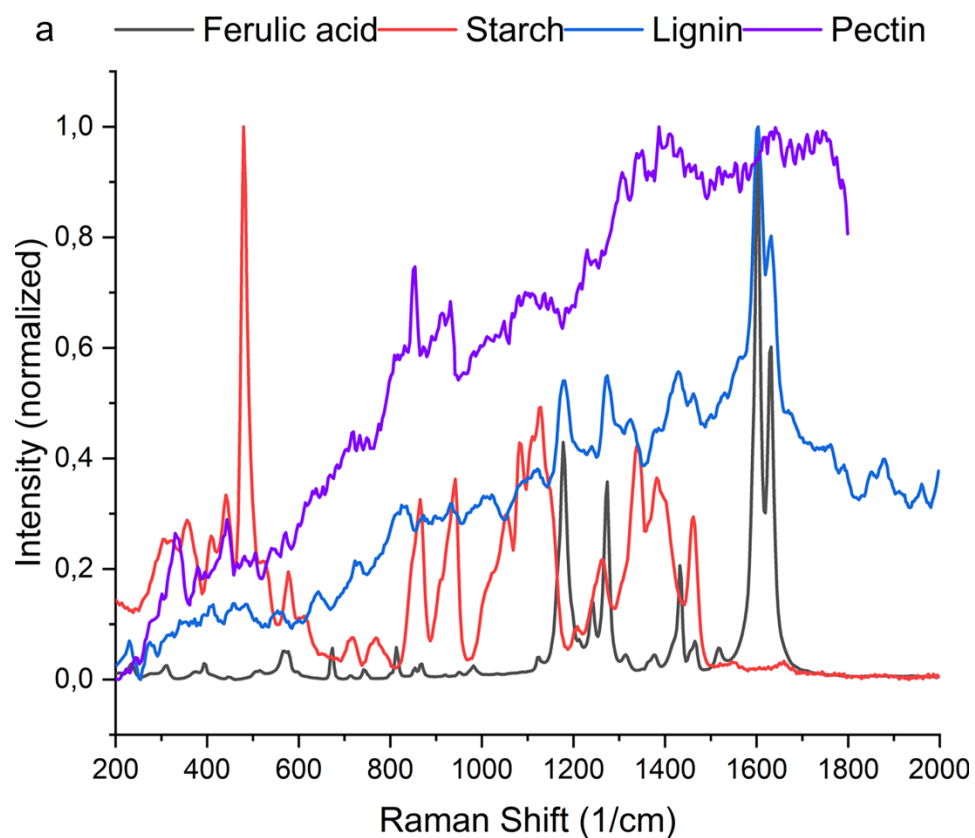


Fig. S5. Raman analysis of authentic ferulic acid, starch, kraft lignin and pectin for reference. a Time-gated Raman (TG). **b** Continuous wave (CW) Raman. No lignin results were acquired from CW Raman due to the excessive fluorescence.