

Figure S1: Phylogenetic tree calculated on the basis of aligned amino acid sequences of the GH70 catalytic domains of selected glucansucrases. Each protein is labelled with its Uniprot ID, if available. Branch lengths are measured in the number of substituted amino acids per site. Glucansucrases investigated in the current study are indicated in bold letters. Lc2135 and DsrE both feature two GH70 domains and are thus split into catalytic domain (CD) 1 and 2.

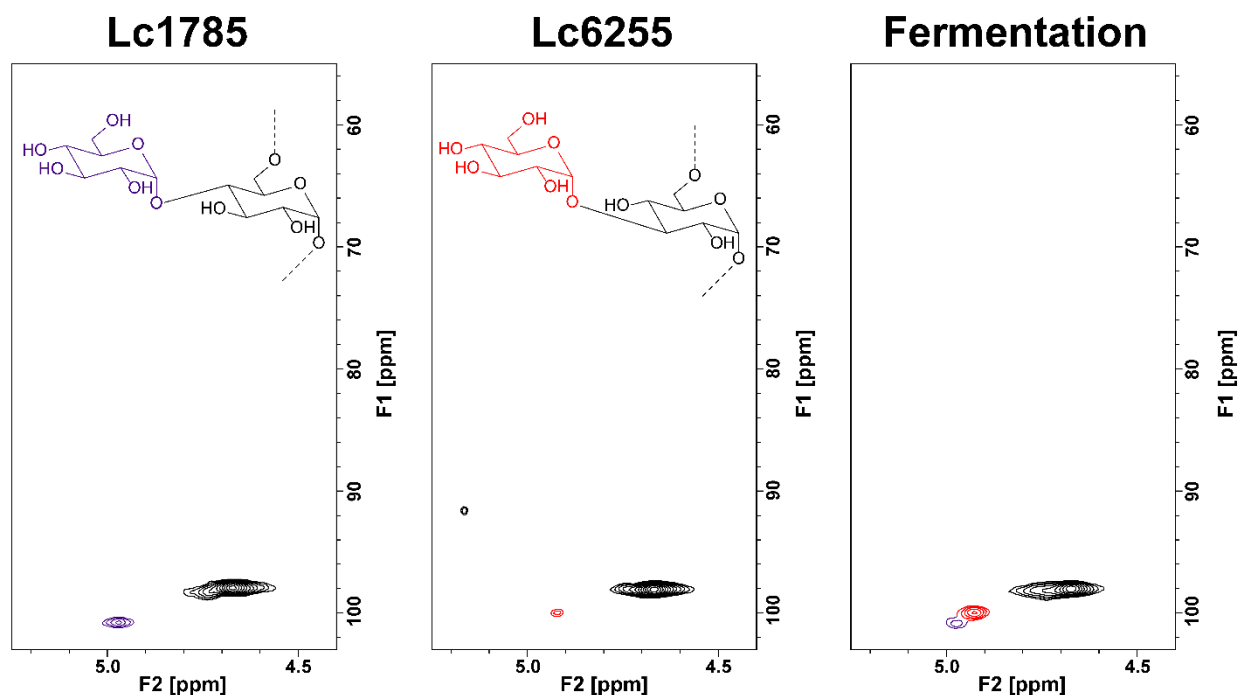


Figure S2: Anomeric HSQC signals of the dextrans produced by Lc1785, Lc6255, and by fermentation. Spectra were recorded in DMSO-*d*₆ / 50 mM LiBr. Signals which are characteristic for O3- and O4-bound side chains are colored accordingly (the black signals represents unsubstituted and substituted 1,6-linked glucose units, the signal at 5.17 / 91.6 ppm in the spectrum of Lc6255 dextrans is derived from residual sucrose).

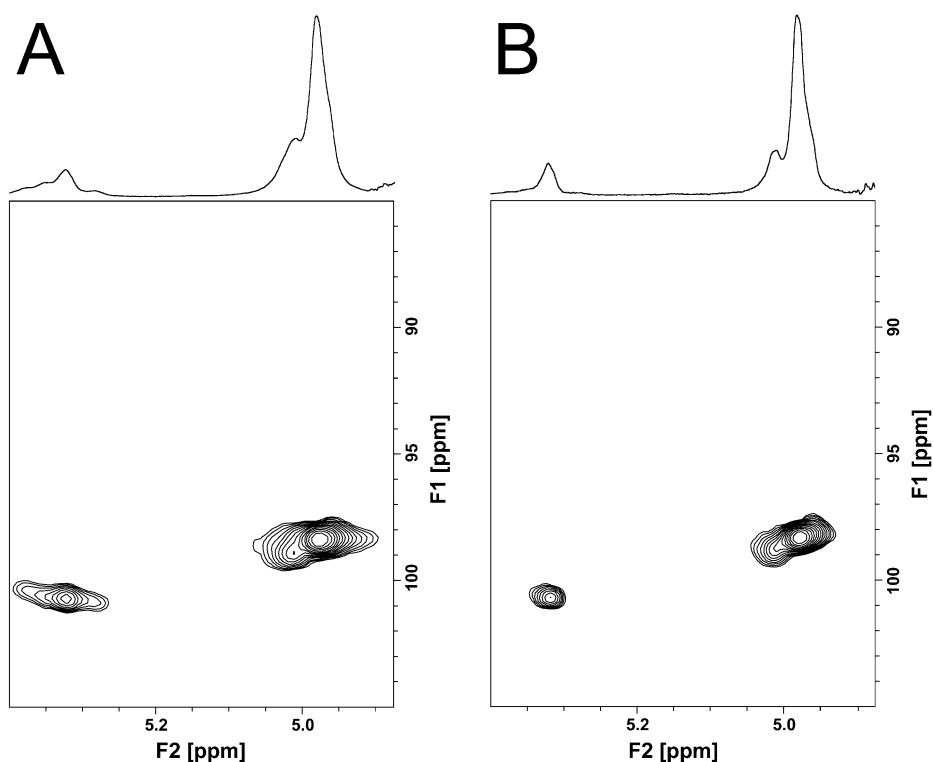


Figure S3: Anomeric HSQC signals of the dextrans produced by Lc1785 (A) and *L. reuteri* TMW 1.106 dextransucrase (B). Spectra were recorded in D₂O.

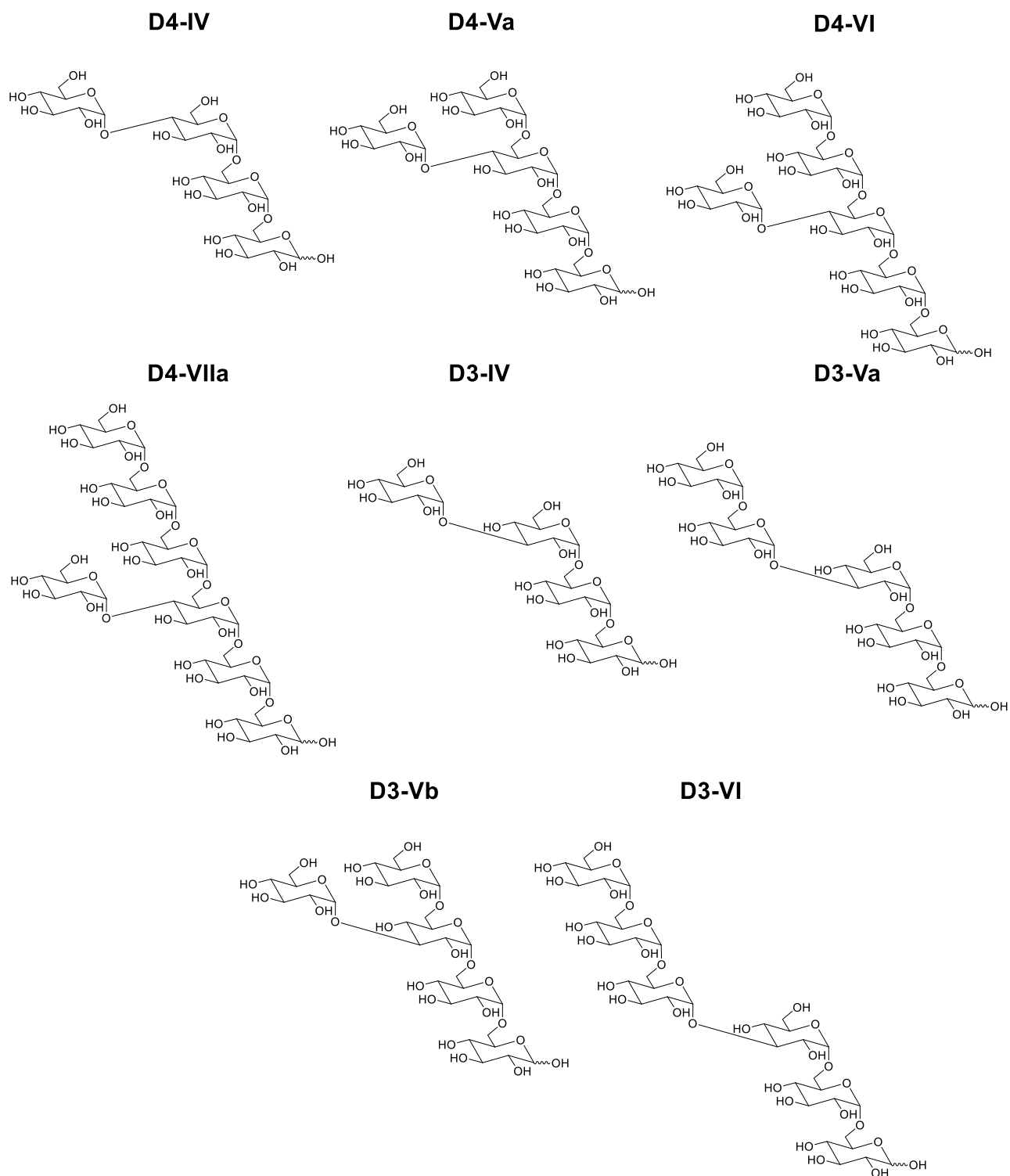


Figure S4: Structures of the previously isolated isomalto-oligosaccharides.

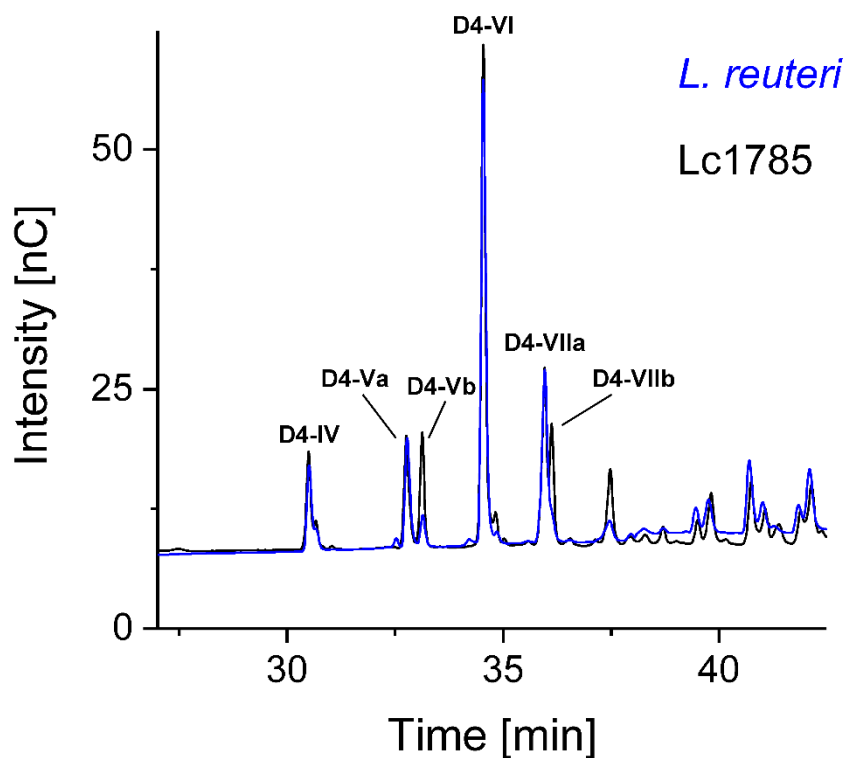


Figure S5: HPAEC-PAD chromatograms of the endo-dextranase hydrolysates of dextrans produced by *L. reuteri* TMW 1.106 dextransucrase (blue) and Lc1785 (black).

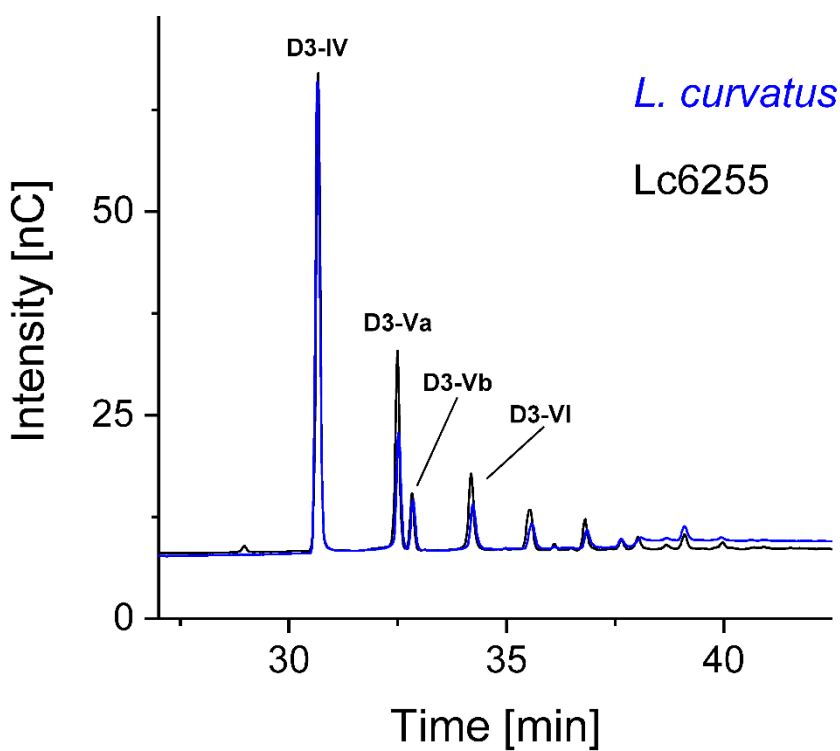


Figure S6: HPAEC-PAD chromatograms of the endo-dextranase hydrolysates of dextrans produced by *L. curvatus* TMW 1.624 dextransucrase (blue) and Lc6255 (black).

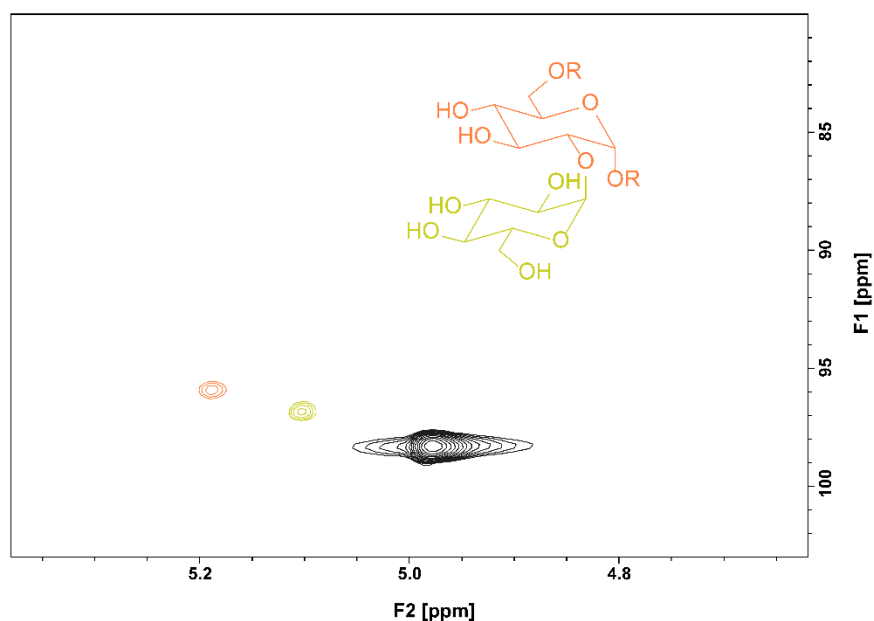


Figure S7: Anomeric HSQC signals of the water soluble fraction of Lc2135 glucans. The signals are colored according to the structural elements they represent (the black signal represents unsubstituted and substituted 1,6-linked glucose units).

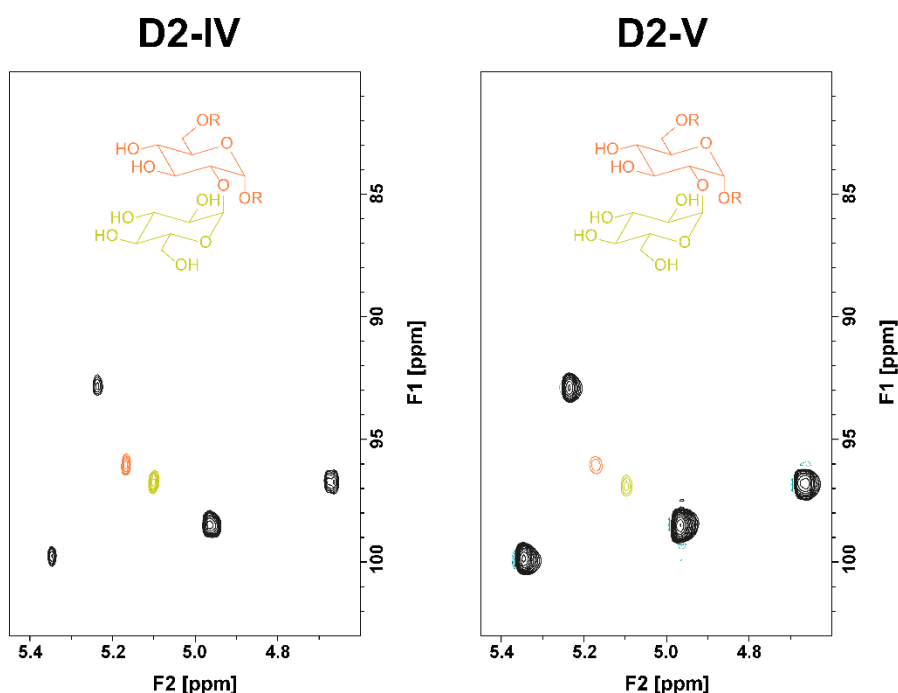


Figure S8: Anomeric HSQC signals of the oligosaccharides isolated from the endo-dextranase hydrolysates of Lc2135 glucans. The signals are colored according to the structural elements they represent (the black signals are mainly derived from the *O*3-branched oligosaccharide **D3-IV** which was also present in the mixtures).

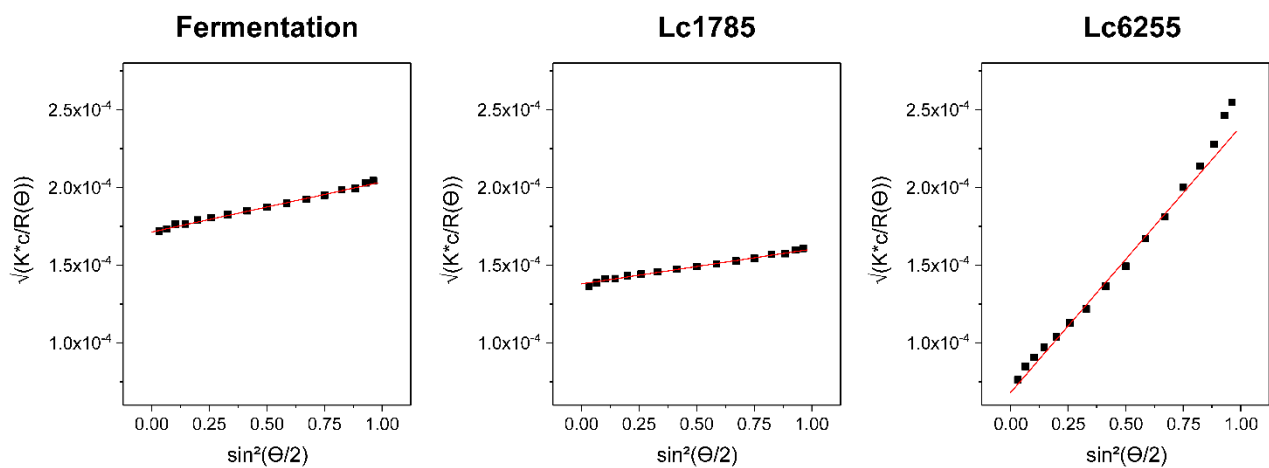


Figure S9: Debye plots of glucans produced by fermentation, Lc1785 and Lc6255 using the Berry fit (order 1) as a function of 16 scattering angles.

Tab. S1. Primer sequences used for gene cloning.

Gene	Orientation	Sequence
Lc1215	Forward	5'-TACTTCCAATCCAGCAGTAGTGATAATGATAGCAAAA CACAAACTATTTC-3'
	Reverse	5'-TATCCACCTTTACTGGTATGTTATTTTTTTCATTTACC ACTGTCTTTATCCATC-3'
Lc1785	Forward	5'-TACTTCCAATCCGATACACAAACGCCGGTTGGTACAA C-3'
	Reverse	5'-TATCCACCTTTACTGAGCTTGCAAAGCACGCTTATCA ATCC-3'
Lc2135	Forward	5'-TACTTCCAATCCAGTGCAAATACGATTGCAGTTGACA CG-3'
	Reverse	5'-TATCCACCTTTACTGAATTTGAGGTAATGTTGATTTAT CACCATCAAGCTTG-3'
Lc6255	Forward	5'-TACTTCCAATCCATGCTGTCTATGACCGCTACTTCACA AAATG-3'
	Reverse	5'-TATCCACCTTTACTGAGCGACTGAGACAAAGTAACCT TGGTC-3'

Table S2. ^1H and ^{13}C chemical shifts of the structural units of oligosaccharide **D4-Vb** isolated from the endo-dextranase hydrolysate of Lc1785 dextran. The structure of **D4-Vb** is shown in Figure 2.

Compound / Structural unit	1	2	3	4	5	6-1	6-2
	D4-Vb						
R-α	5.24	3.53	3.70	3.51	4.01	3.70	4.01
	92.8	72.1	73.6	70.1	70.6	66.5	66.5
R-β	4.67	3.25	3.48	3.51	3.63	3.76	3.98
	96.7	74.7	76.6	70.2	74.8	66.5	66.5
A	4.96	3.58	3.71	3.50	3.92	3.76	3.96
	98.4	72.2	73.8	70.2	70.9	66.4	66.4
B	4.96	3.58	3.99	3.65	3.86	3.85	3.85
	98.4	72.1	74.1	78.1	71.0	61.1	61.1
a	5.38	3.60	3.69	3.50	3.92	3.73	3.98
	100.6	72.1	73.8	70.2	72.1	66.5	66.5
b	4.96	3.55	3.71	3.42	3.71	3.76	3.86
	98.6	72.1	73.8	70.2	72.5	61.1	61.1

Table S3. ^1H and ^{13}C chemical shifts of the structural units of oligosaccharide **D4-VIIb** isolated from the endo-dextranase hydrolysate of Lc1785 dextran. The structure of **D4-VIIb** is shown in Figure 2.

Compound / Structural unit	1	2	3	4	5	6-1	6-2
D4-VIIb							
R-α	5.24	3.53	3.70	3.51	4.01	3.70	4.01
	92.9	72.2	73.8	70.2	70.6	66.4	66.4
R-β	4.67	3.25	3.48	3.51	3.63	3.76	3.98
	96.8	74.8	76.7	70.2	74.9	66.4	66.4
A	4.96	3.58	3.71	3.50	3.93	3.76	3.96
	98.5	72.2	73.9	70.2	71.0	66.3	66.3
B	4.96	3.62	4.01	3.66	4.03	3.87	3.95
	98.5	71.9	73.9	79.1	69.6	67.4	67.4
C	5.01	3.55	3.73	3.57	3.92	3.70	4.04
	99.1	72.2	73.9	69.9	71.0	66.0	66.0
T	4.96	3.55	3.71	3.43	3.70	3.77	3.84
	98.5	72.2	73.9	70.1	72.6	61.1	61.1
a	5.34	3.61	3.68	3.57	3.91	3.70	4.04
	100.7	72.2	73.9	69.9	72.1	66.0	66.0
b	4.98	3.55	3.71	3.43	3.70	3.77	3.84
	98.5	72.2	73.9	70.1	72.6	61.1	61.1

Table S4. Glycosidic linkages (mol%) of the dextrans produced by fermentation of *Lc. citreum* TMW 2.1194 as determined by methylation analysis.

Glycosidic linkage	<i>Lc. citreum</i> TMW 2.1194
t-Glcp	27.3
1,3-Glcp	-
1,4-Glcp	-
1,6-Glcp	52.9
1,2,6-Glcp	-
1,3,6-Glcp	7.0
1,4,6-Glcp	12.8

All analyses were performed in duplicate and relative half range uncertainties were mostly < 5 %. t = terminal, Glc = glucose, p = pyranose. Numbers indicate the substituted positions of a sugar unit.