SUPPLEMENTARY DATA

Fig. S1. MALDI-TOF MS of *endo*-glucanase-generated XyG fragments from (A) *S. lycopersicum* var. *Saint-Pierre*, (B) *S. lycopersicum* var. cerasiforme, (C) *S. pimpinellifolium* and (D) *S. peruvianum* leaves. Possible structures of XyG fragments are shown according to the one-letter nomenclature proposed by Fry *et al.*, (1993) and as described in Fig. 1. The structures in bold were characterized by York *et al.*, (1996), Jia *et al.*, (2005) and Hoffman *et al.*, (2005). Underlined structures indicate the presence of *O*-acetylated side chains on the XyG fragment. The black star represents unassigned fragment and the black square represents the sodiated adduct corresponding to $(Pent)_6GlcA_1OAc_1$ originating from glucuronoarabinoxylan. Pent. Pentose, GlcA. glucuronic acid, OAc. *O*-acetyl group.

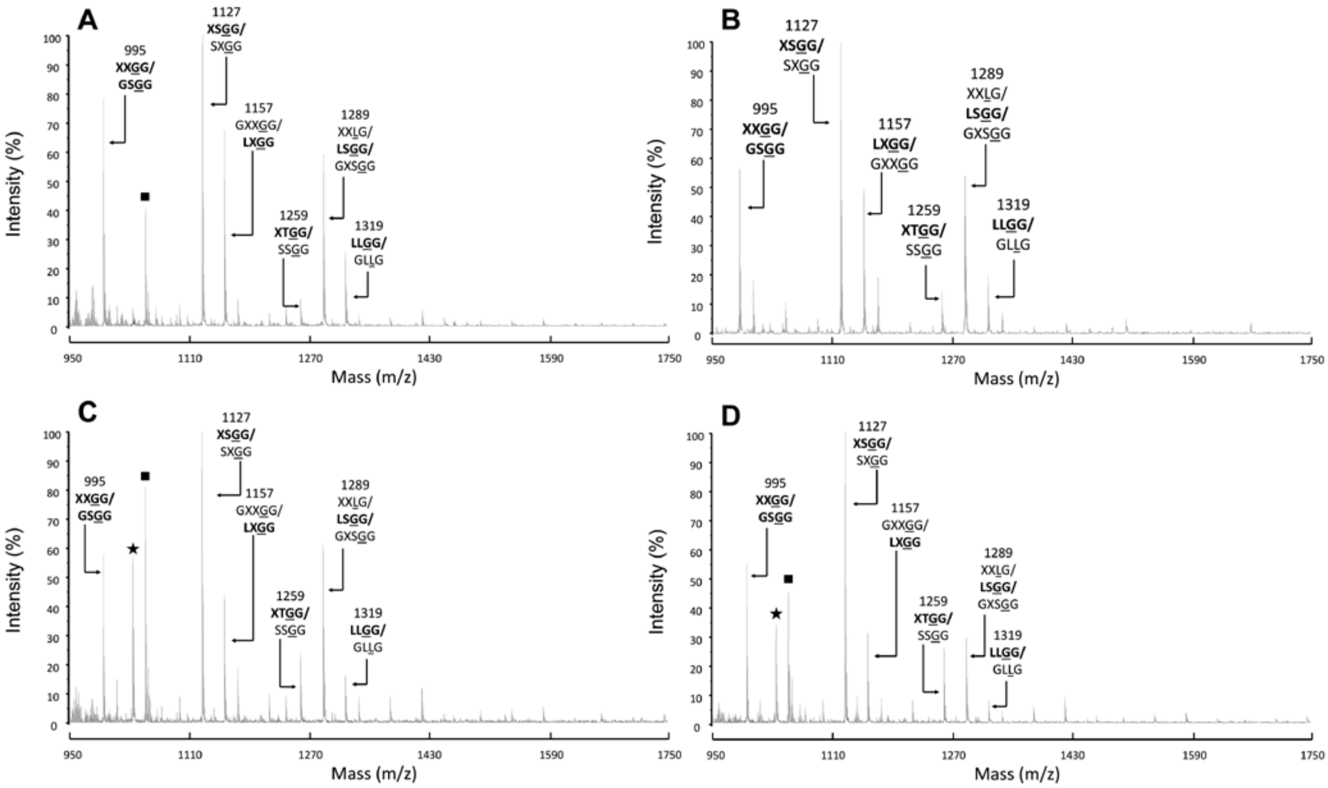

Fig. S2. MALDI-TOF MS of *endo*-glucanase-generated XyG fragments from *S. lycopersicum* cv. dombito cell-suspension. Possible structures of XyG fragments are shown according to the one-letter nomenclature proposed by Fry *et al.*, (1993) and shown in Fig. 1. The structures in bold were characterized by York *et al.*, (1996), Jia *et al.*, (2003) and Hoffman *et al.*, (2005). Underlined structures indicate the presence of *O*-acetylated side chains on the XyG fragment.

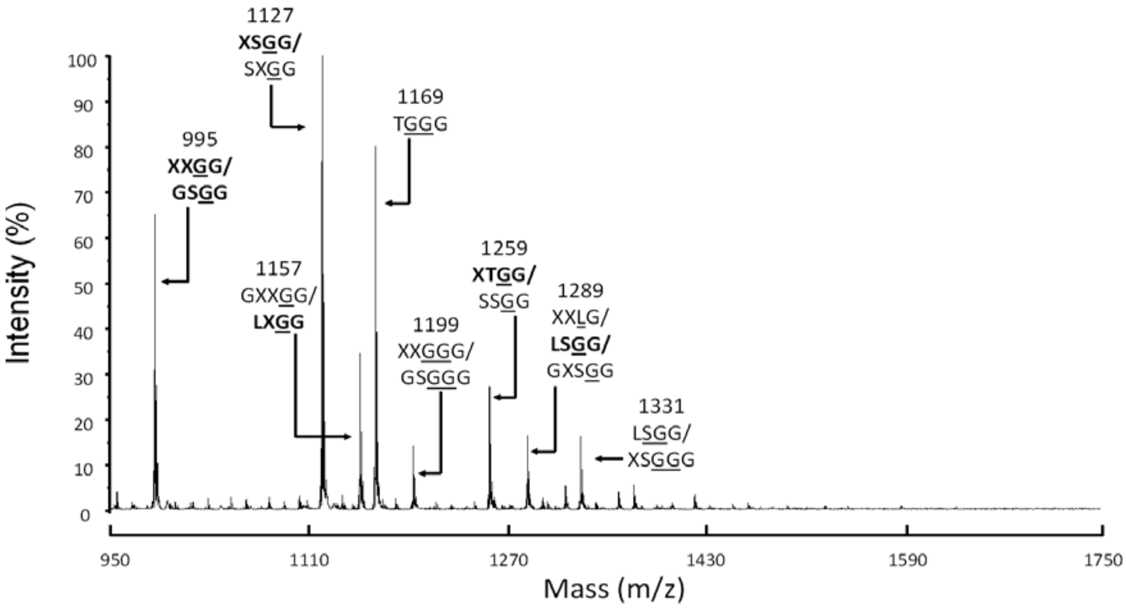

Fig. S3. Structural characterization of LSG/XXXG and LSGG/XXLG oligosaccharides from *S. peruvianum* pollen tubes. (A) MALDI-TOF/TOF MS of the precursor ion at *m/z* = 1365.7 ($[M+Na]^+$ adduct) of the permethylated Hex_4Pent_3 structures (LSG and XXXG) and the corresponding fragmentation pattern. (B) MALDI-TOF/TOF MS of the precursor ion at *m/z* = 1569.8 ($[M+Na]^+$ adduct) of the permethylated Hex_5Pent_3 structures (LSGG and XXLG) and the corresponding fragmentation pattern. Ara. arabinose, Fuc. Fucose, Gal. galactose, Glc. glucose, Xyl. xylose. *, double fragmentation ion. The MALDI-TOF MS of the permethylated oligosaccharides is shown in Fig. 6.

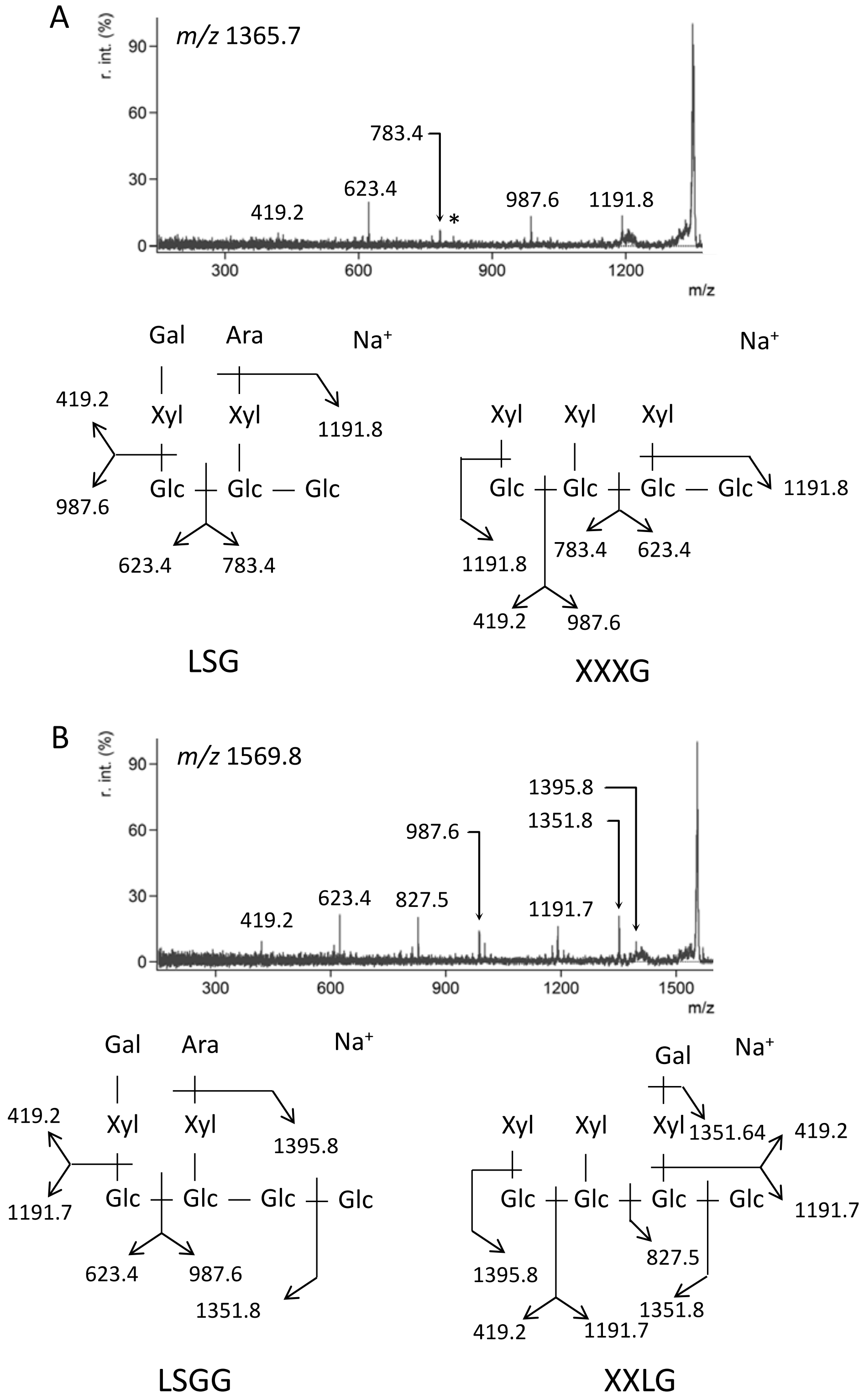

Fig. S4. MALDI-TOF MS of *endo*-glucanase-generated XyG fragments from the hemicellulose-enriched extract of *S. lycopersicum* var. cerasiforme pollen tubes. Possible structures of XyG fragments are shown according to the one-letter nomenclature proposed by Fry *et al.*, (1993) as described in Fig. 1. Underlined structures indicate *O*-acetylated side chains of XyG fragments. * indicates the shift of m/z = 16 of the potassium adducts which are present in addition to sodiated adducts.

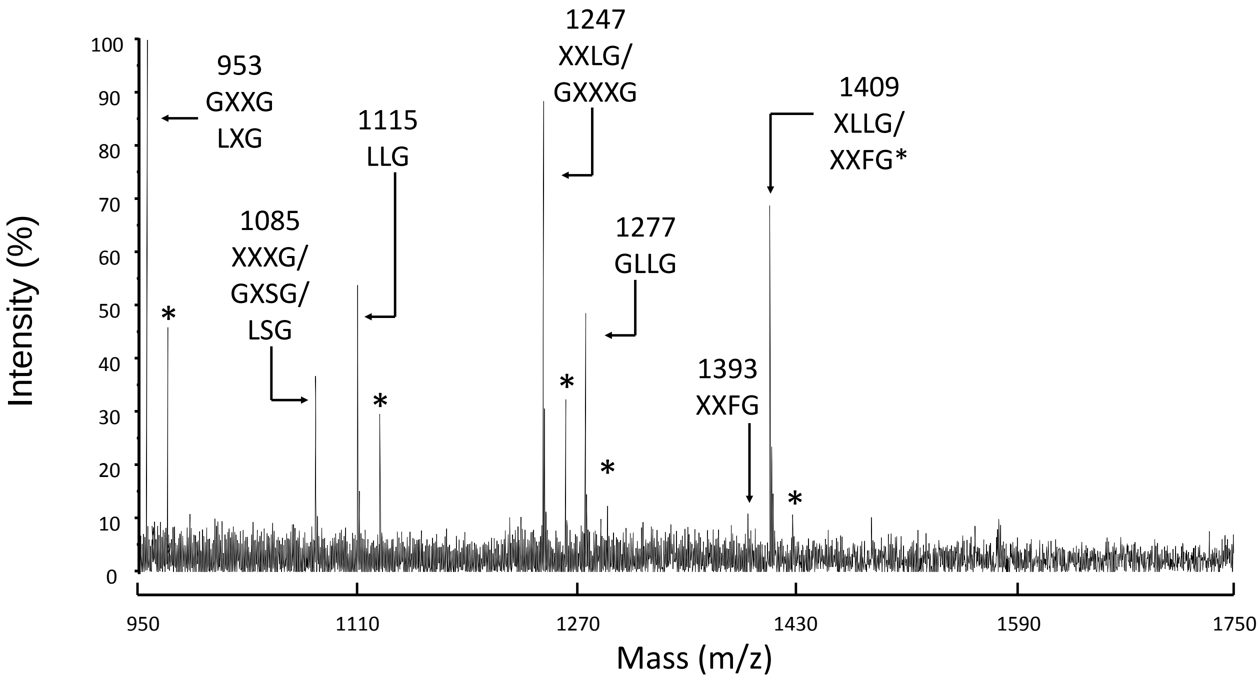

Fig. S5. MALDI-TOF MS of *endo*-glucanase-generated XyG fragments from (A) the cell wall extract and (B) the hemicellulose-enriched extract of *N. tabacum* pollen tubes. Possible structures of XyG fragments are shown according to the one-letter nomenclature proposed by Fry *et al.*, (1993) and shown in Fig. 1. The three structures in bold were characterized in *Nicotiana alata* pollen tubes by Lampugnani *et al.*, (2013). Underlined structures represent *O*-acetylated side chains. Black star represents unassigned fragment. * indicates the shift of m/z = 16 of the potassium adducts.

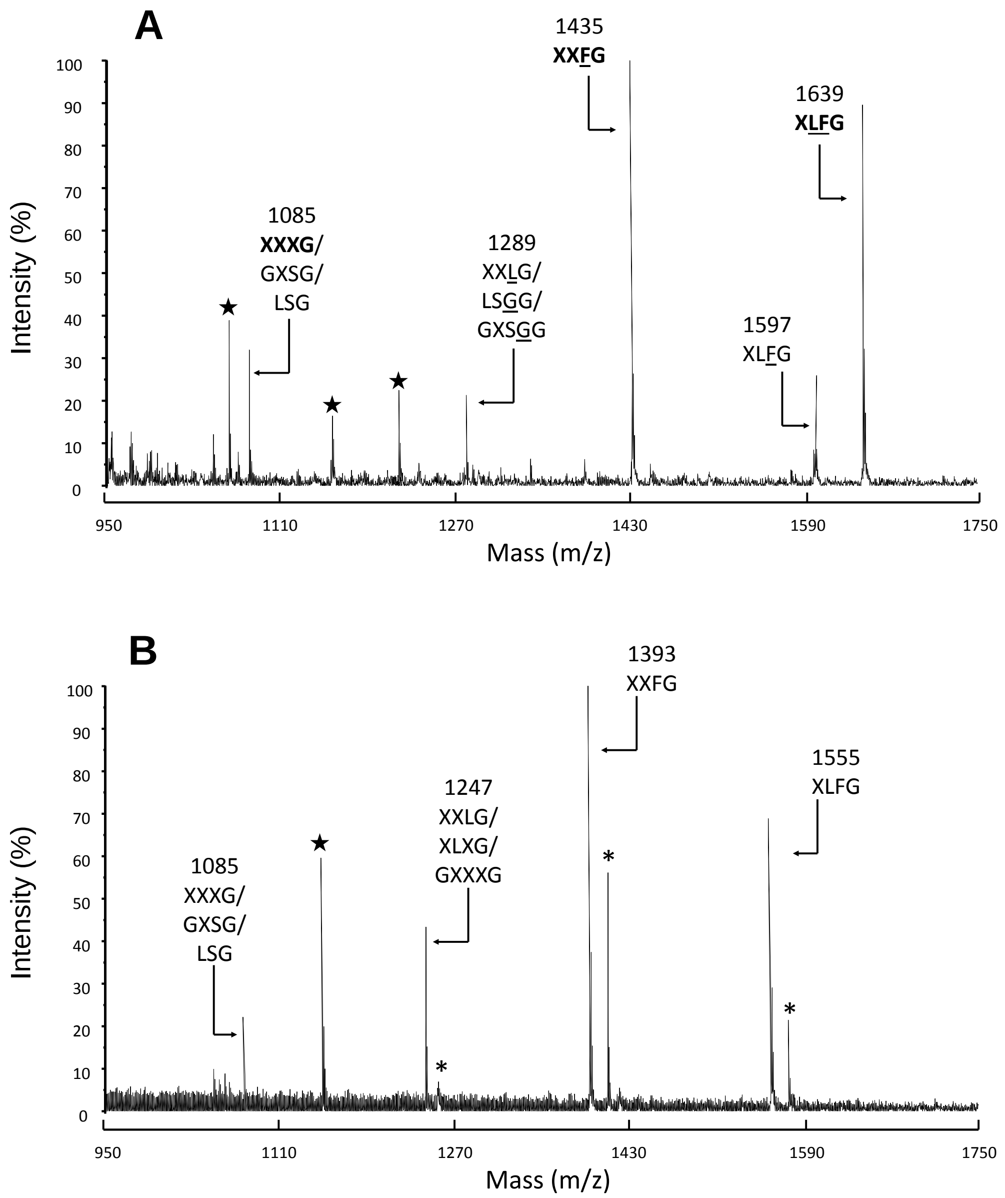

Table S1. Relative abundance of XyG oligosaccharides released after *endo*-glucanase digestion of the cell wall of *S. lycopersicum* cv. dombito cell suspension and *S. lycopersicum* var. cerasiforme leaves.

Mass [a]	Cells	Leaves	Composition[b]	Possible structure[c]
953	1 ± 0.1[d]	< 1	Hex$_4$Pent$_2$	GXXG
995	17.5 ± 0.1	15.5 ± 2.7[e]	Hex$_4$Pent$_2$OAc$_1$	**XXGG** / **GSGG**
1055	< 1	4 ± 0.7	Hex$_3$Pent$_4$	SSG
1085	< 1	< 1	Hex$_4$Pent$_3$	XXXG/**GXSG**/LSG
1127	26.1 ± 1.6	31 ± 1.5	Hex$_4$Pent$_3$OAc$_1$	**XSGG**/ SXGG
1157	9.8 ± 0.8	14.3 ± 1.8[e]	Hex$_5$Pent$_2$OAc$_1$	**LXGG** / GXXGG
1169	21.2 ± 0.4	- [f]	Hex$_4$Pent$_3$OAc$_2$	TGGG
1199	3.8 ± 0.1	< 1	Hex$_5$Pent$_2$OAc$_2$	GSGGG / XXGGG
1259	7.7 ± 0.5	4.6 ± 0.3	Hex$_4$Pent$_4$OAc$_1$	SSGG/**XTGG**
1289	4.5 ± 0.2	20.8 ± 3.1	Hex$_5$Pent$_3$OAc$_1$	XXLG/**LSGG**/ GXSGG
1319	1.5 ± 0.2	6.7 ± 1	Hex$_6$Pent$_2$OAc$_1$	**LLGG**/GLLG
1331	4.5 ± 0.2	< 1	Hex$_5$Pent$_3$OAc$_2$	LSGG/XSGGG
1421	< 1	1.6 ± 0.4	Hex$_5$Pent$_4$OAc$_1$	**LTGG**/GSSGG
Fucosylated	-	-		

[a]Mass (*m/z*) of the [M+Na]$^+$ adducts. [b]Hex, hexose; Pent, pentose; OAc, *O*-acetyl substituent. [c]Possible structures of XyG fragments are shown according to the one-letter nomenclature proposed by Fry *et al.*, (1993) and as shown in Fig. 1. The structures in bold were characterized by York *et al.*, (1996), Jia *et al.*, (2003), Jia et al., (2005) and Hoffman *et al.*, (2005). Underlined structures represent *O*-acetylated side chains. [d]Values are expressed as relative percentage and are the means ± SD from MALDI spectra obtained after *endo*-glucanase digestion from three independent cell wall extractions. The five most abundant fragments are highlighted in yellow. [e]Relative abundance of these fragments corresponds to the total of the [M+K]$^+$ and [M+Na]$^+$ adducts. [f] not detected above the signal to noise ratio.

Table S2. Relative abundance of XyG oligosaccharides released after *endo*-glucanase digestion of the cell wall residue and the hemicellulose-enriched extract from tomato pollen tubes.

Mass (*m/z*)	*S. lycopersicum* var. *cerasiforme* Cell Wall	*S. lycopersicum* var. *cerasiforme* KOH	*S. lycopersicum* var. *St-Pierre* Cell Wall	*S. pimpinellifolium* Cell Wall	*S. peruvianum* Cell Wall	Composition	Possible structure
953	4.6 ± 0.7	29.9 ± 2.8[f]	7.1 ± 0.3	15.8 ± 2.6	6.2 ± 0.5	Hex_4Pent_2	GXXG
995	15.7 ± 1.7	1.2 ± 0.5	20.8 ± 5.8	15.8 ± 2.2	15.7 ± 2.4	$Hex_4Pent_2OAc_1$	XX<u>G</u>G/GS<u>G</u>G
1037	-[e]	-	1.1 ± 0.6	-	-	$Hex_4Pent_2OAc_2$	S<u>GG</u>G
1055	2.6 ± 0.3	-	5.0 ± 1.4	2.6 ± 1.6	-	Hex_3Pent_4	SSG
1085	3.1 ± 1.4	5.1 ± 0.5	4.8 ± 0.1	4.2 ± 0.4	13.0 ± 1.5	Hex_4Pent_3	**XXXG/LSG**/GXSG
1097	1.8 ± 0.9	-	3.5 ± 0.3	2.1 ± 1.0	2.1 ± 0.6	$Hex_3Pent_4OAc_1$	S<u>S</u>G
1115	2.2 ± 0.8	11.8 ± 0.0[f]	1.9 ± 0.4	5.7 ± 0.6	2.5 ± 0.2	Hex_5Pent_2	LLG
1127	6.1 ± 1.8	-	3.6 ± 0.1	1.5 ± 0.2	2.8 ± 0.2	$Hex_4Pent_3OAc_1$	XS<u>G</u>G/SX<u>G</u>G
1157	11.0 ± 1.9	-	11.1 ± 1.9	8.8 ± 0.5	10.0 ± 1.8	$Hex_5Pent_2OAc_1$	GXX<u>G</u>G/LX<u>G</u>G
1199	1.9 ± 0.1	-	1.9 ± 0.4	1.4 ± 0.3	1.5 ± 0.9	$Hex_5Pent_2OAc_2$	GS<u>GG</u>G/XX<u>GG</u>G
1217	1.1 ± 0.3	-	1.1 ± 1.3	< 1	< 1	Hex_4Pent_4	GSSG/GXTG
1247	2.5 ± 0.6	24.2 ± 1[f]	2.8 ± 0.7	3.7 ± 0.5	4.4 ± 0.8	Hex_5Pent_3	**XXLG**/GXXXG
1259	1.2 ± 0.1	-	2.0 ± 0.5	1.1 ± 0.5	< 1	$Hex_4Pent_4OAc_1$	SS<u>G</u>G/XT<u>G</u>G
1277	< 1	10 ± 0.6[f]	< 1	3.4 ± 0.4	< 1	Hex_6Pent_2	GLLG
1289	7.3 ± 1.5	-	5.4 ± 0.3	3.4 ± 0.4	4.4 ± 0.0	$Hex_5Pent_3OAc_1$	XX<u>L</u>G/LS<u>G</u>G/GXS<u>G</u>G
1319	11.5 ± 1.8	-	7.9 ± 1.3	6.8 ± 0.9	7.3 ± 2.1	$Hex_6Pent_2OAc_1$	LL<u>G</u>G/GL<u>L</u>G
1331	1.0 ± 1.5	-	-	-	-	$Hex_5Pent_3OAc_2$	**L<u>SG</u>G**
1361	2.1 ± 0.3	-	1.4 ± 0.2	1.7 ± 0.5	1.1 ± 0.3	$Hex_6Pent_2OAc_2$	XL<u>GG</u>G
1379	< 1	-	1.2 ± 1.3	< 1	-	Hex_5Pent_4	XLSG
1393	< 1	1.8 ± 0.5	1.1 ± 0.4	2.9 ± 0.7	5.6 ± 1.4	$Hex_5Pent_3Dox_1$	**XXFG**
1409	1.2 ± 0.8	15.1 ± 1.6[f]	< 1	1.2 ± 0.2	1.1 ± 0.2	Hex_6Pent_3	XLLG/XXFG*
1421	1.2 ± 0.4	-	1.4 ± 0.6	< 1	< 1	$Hex_5Pent_4OAc_1$	GSS<u>G</u>G
1435	2.9 ± 0.9	-	2.1 ± 0.6	3.4 ± 0.9	6.8 ± 2.0	$Hex_5Pent_3Dox_1OAc_1$	XX<u>F</u>G
1451	1.0 ± 0.3		1.2 ± 0.3	1.3 ± 0.5	1.2 ± 0.2	$Hex_6Pent_3OAc_1$	XXL<u>G</u>G
1463	-	-	1.0 ± 0.2	< 1	1.2 ± 0.2	$Hex_5Pent_4OAc_2$	XX<u>SG</u>G
1481	6.4 ± 2.3	-	3.7 ± 0.6	2.1 ± 0.8	3.0 ± 1.3	$Hex_6Pent_2OAc_1$	GLL<u>G</u>G
1493	2.0 ± 0.5	-	1.1 ± 0.2	< 1	< 1	$Hex_6Pent_3OAc_2$	GXS<u>GG</u>G
1555	-	-	< 1	2.0 ± 0.6	2.1 ± 0.7	$Hex_6Pent_3Dox_1$	**XLFG**
1597	1.3 ± 0.1	-	1.0 ± 0.6	2.8 ± 0.9	2.8 ± 1.0	$Hex_6Pent_3Dox_1OAc_1$	X<u>L</u>FG/XL<u>F</u>G
1639	2.3 ± 0.7	-	1.1 ± 0.4	1.8 ± 0.4	2.1 ± 0.7	$Hex_6Pent_3Dox_1OAc_2$	X<u>LF</u>G
Fucosylated	6.5 ± 1.4	-	5.3 ± 1.0	12.9 ± 1.7	19.4 ± 2.6		
O-acetylated	73.9 ± 6.2		91.1 ± 8.4	55.3 ± 6.1	63.5 ± 8.3		

[a]Mass of the $[M+Na]^+$ adducts. [b]Hex, hexose; Pent, pentose; Dox, deoxyhexose; OAc, *O*-acetyl substituent. [c]Possible structures of XyG fragments are shown according to the one-letter nomenclature proposed by Fry *et al.*, (1993) and described in Fig. 1. Underlined structures represent *O*-acetylated side chains. [d]Values are expressed as relative percentage and are the means ± SD from MALDI-TOF mass spectra obtained after *endo*-glucanase digestion from three independent pollen tube cell wall extractions. The five most abundant fragments are highlighted in yellow. [e]not detected above the signal to noise ratio. [f]Relative abundance of these fragments corresponds to the total of the $[M+K]^+$ and $[M+Na]^+$ adducts. * adduct $[M+K]^+$. Structures in bold were characterized in *S. peruvianum* pollen tubes.

Table S3. Relative abundance of XyG oligosaccharides released after *endo*-glucanase digestion of the cell wall residue and the hemicellulose-enriched extract from *N. tabacum* pollen tubes.

Mass [a]	Cell wall	KOH	Composition[b]	Possible structure[c]
953	4.9 ±1.6[d]	1.0 ± 0.8	Hex_4Pent_2	GXXG
995	3.6 ± 3.4	- [e]	$Hex_4Pent_2OAc_1$	XXGG/GSGG
1085	11.7 ± 2.7	5.2 ± 1.2	Hex_4Pent_3	**XXXG**
1157	3.1 ± 0.4	-	$Hex_5Pent_2OAc_1$	LXGG
1247	4.5 ± 2	16.8 ± 2.7[f]	Hex_5Pent_3	XXLG/XLXG
1289	8.8 ± 1	-	$Hex_5Pent_3OAc_1$	XXLG/XLXG
1393	3.0 ± 0.6	50.4 ± 1.4[f]	$Hex_5Pent_3Dox_1$	XXFG
1435	29.7 ± 1.9	-	$Hex_5Pent_3Dox_1OAc_1$	**XXFG**
1555	< 1	26.6 ± 3.3[f]	$Hex_6Pent_3Dox_1$	XLFG
1597	6.2 ± 1.6	-	$Hex_6Pent_3Dox_1OAc_1$	XLFG/XLFG
1639	23.0 ± 3.5	-	$Hex_6Pent_3Dox_1OAc_2$	**XLFG**
Fucosylated	61.9 ± 4.4	77 ± 4.7		
O-acetylated	71.9 ± 7.2	-		

[a]Mass (*m/z*) of the $[M+Na]^+$ adducts. [b]Hex, hexose; Pent, pentose; Dox, deoxyhexose; OAc, *O*-acetyl substituent. [c]Possible structures of XyG fragments are shown according to the one-letter nomenclature proposed by Fry *et al.*, (1993) and as described in Fig. 1. Underlined structures represent *O*-acetylated side chains. [d]Values are expressed as relative percentage and are the means ± SD from MALDI-TOF mass spectra obtained after *endo*-glucanase digestion from three independent pollen tube cell wall extractions. The five most abundant fragments are highlighted in yellow. [e]not detected above the signal to noise ratio. [f]Relative abundance of these fragments corresponds to the total of the $[M+K]^+$ and $[M+Na]^+$ adducts. Structures in bold were characterized in *Nicotiana alata* pollen tubes by Lampugnani *et al.*, (2013).

Table S4. Monosaccharide composition and glycosyl-linkage analysis of *N. tabacum* hemicellulose-enriched pollen tube extract.

Monosaccharide composition[a] (mol%)	
Glc	27.9
Xyl	11.1
Gal	25
Ara	21.2
Fuc	1.4
GalA	4.3
Rha	2.4
Man	6.8
Detected glycosyl-linkage[b]	
	3-Glc*p* (callose)
	4-Glc*p* (XyG)
	4,6-Glc*p* (XyG)
	t-Xyl*p* (XyG)
	2-Xyl*p* (XyG)
	t-Gal*p* (XyG, RG-I, AGP)
	2-Gal*p* (XyG)
	4-Gal*p* (RG-I)
	6-Gal*p* (RG-I, AGP)
	t-Ara*f* (RG-I, AGP)
	5-Ara*f* (RG-I)
	t-Fuc*p* (XyG)

[a]Determined by GC and expressed as mol%. Ara, arabinose; Fuc, fucose; Gal, galactose; Glc, glucose; GalA, galacturonic acid; Rha, rhamnose; Man, mannose; Xyl, xylose. [b]Determined by GC-MS of partially methylated alditol acetates. t-Ara*f* denotes 1,4-di-*O*-acetyl-1-deuterio-2,3,5-tri-*O*-methyl-D-arabinitol, etc... Polymers that contain these glycosyl-linkages are indicated in brackets. XyG, Xyloglucan, RG-I, rhamnogalacturonan-I, AGP, arabinogalactan proteins. In bold are the glycosyl-linkages found in XyG. nd. not detected.