Table S1 *Composition of acyl sugars from* N. benthamiana

Peak				Major MS spectrum ions (relative intensity value)		Product ions in MS3 (m/z)	Predicted subunit substitution		Major FA observed	
Order	Rt (min)	MW	[M+18]+	(m/z)	Product ions in MS2 (m/z) for[a]	for [b]	Glucose	Fructose	(FAMES GC-FID)	Putative acyl groups[c]
1	6.66	580	598	598(100), 580(1), 563(11), 289(10), 275(84)[a], 209(5)	257(12), 239(8), 209(100), 113(18), 95(3)	-	C_7	C_8	-	[MeC6:0] [MeC7:0]
2	7.71	608	626	626(100), 608(4), 591(17), 289(38)[a], 223(3), 124(?)	271(5), 253(5), 223(100), 162(1), 127(14), 109(5), 97(2)	-	C_8	C_8, C_3	-	[MeC7:0][MeC7:0,C3]
3	9.47	594	612	612(100), 594(6), 577(10), 289(70)[a], 223(5)	271(5), 253(5), 223(100)[b], 162(1), 127(14), 109(5), 97(2)	127	C_8	C_8	5MeC7:0 > 6MeC7:0	[MeC7:0] [MeC7:0]
4	10.76	622	640	640(100), 622(4), 605(16), 289(82)[a], 223(6)	271(5), 253(5), 223(100)[b], 162(1), 127(14), 109(5), 97(2)	127	C_8	C_7, C_2	5MeC7:0 > 6MeC7:0	[MeC7:0] [MeC6:0,C2]
5	11.26	622	640	640(100), 622(3), 605(15), 275(35)[a], 209(3)	257(12), 239(8), 209(100), 113(18), 95(3)	-	C_7	C_8, C_2	-	[MeC6:0] [MeC7:0,C2]
6	15.76	636	654	654(100), 636(3), 619(15), 289(35)[a], 223(?)	271(5), 253(5), 223(100)[b], 162(1), 127(14), 109(5), 97(2)	127	C_8	C_8, C_2	6MeC7:0 > 5MeC7:0	[MeC7:0] [MeC7:0,C2]
7	32.62	762	780	780(100), 415(3),295(2)	397[b], 271, 253, 210, 144, 127	271, 253, 127	$2C_8$	C_8, C_2	6MeC7:0, 5MeC7:0	[2xMeC7:0] [MeC7:0,C2]
8	34	804	822	822(100), 415(4), 295(2)	-	-	$2C_8$	C_8, C_3	-	[2xMeC7:0] [MeC8:0,2MeC3:0]

Acyl sugars observed in the extracts of *N. benthamiana*, their APCI spectra and the corresponding aliphatic acid groups obtained by LC-MS. Peak and retention times (Rt) refer to major peaks from LC-MS analysis of leaf methanol extracts. Major peaks were collected and FAMES analysed by GC to corroborate model. [c] Putative acyl group composition shown for each monosaccharide subunit.