Supplementary data

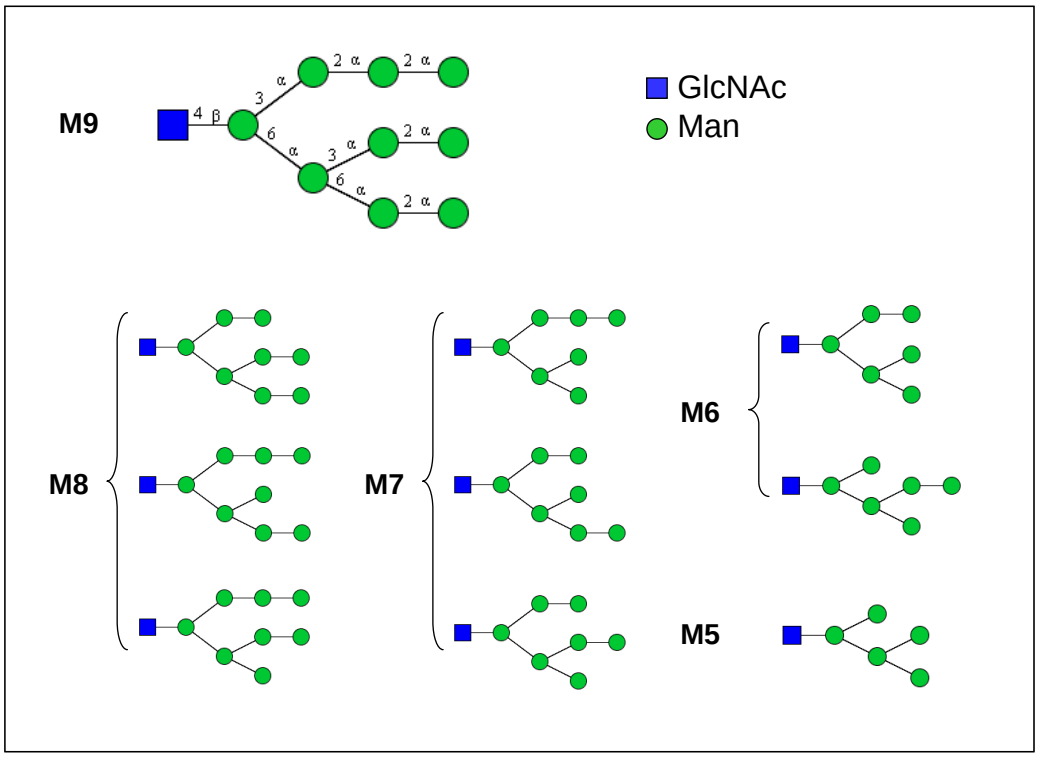


Fig. S-1 Structures of high mannose type *N*-linked glycans $Man_5GlcNAc$ (M5) to $Man_9GlcNAc$ (M9) and their structural isoforms, adapted from Mikami, K. *et al*., Glycobiology, 20, 310-321, 2010. Structures drawn with GlycoWorkbench v2.1.

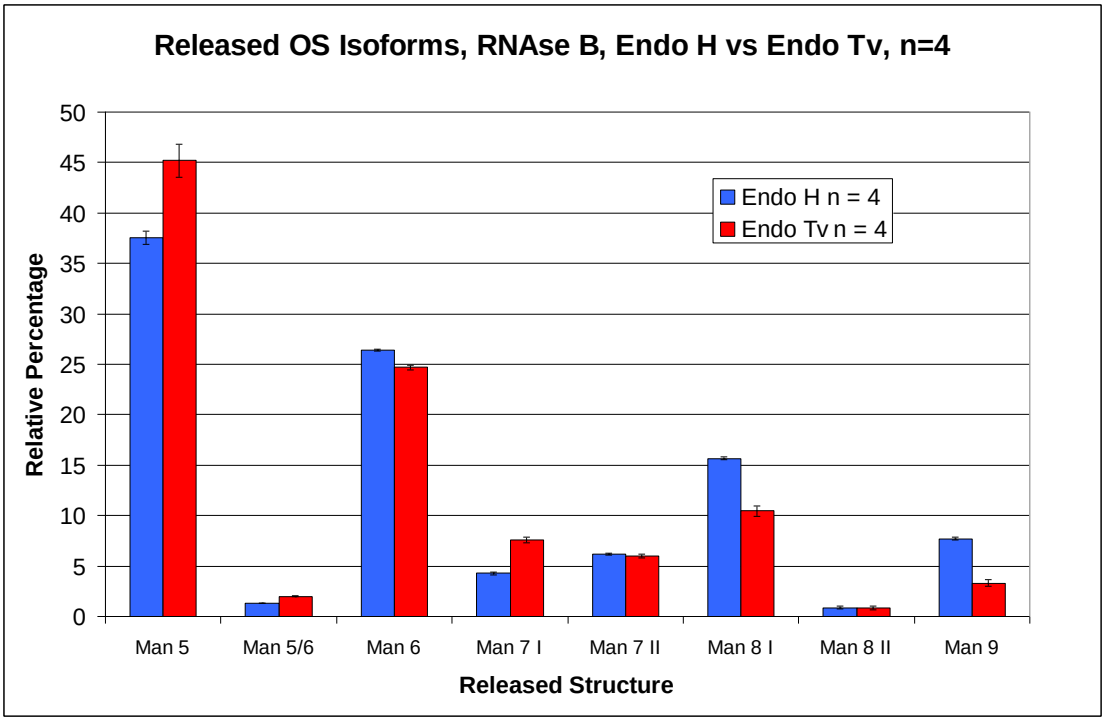


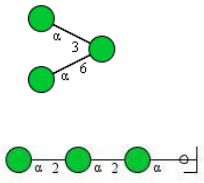
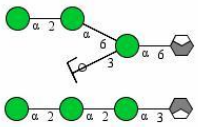
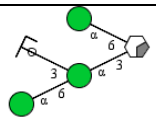
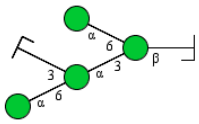
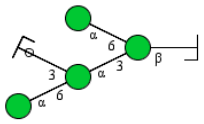
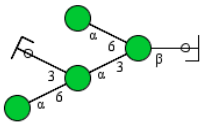
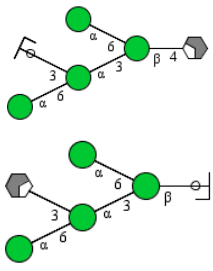
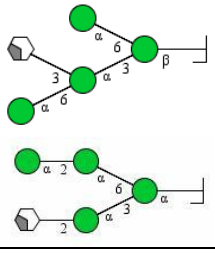
Fig. S-2 Relative percentages of individual high mannose glycoforms ($Man_5GlcNAc$ to $Man_9GlcNAc$) released by purified Endo Tv and Endo H as quantified by HPAEC-PAD. Data is mean of four replicates, error bars represent standard deviation.

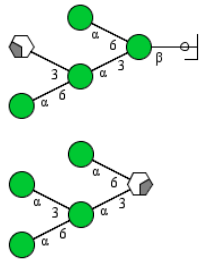
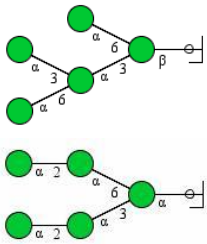
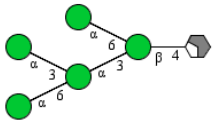
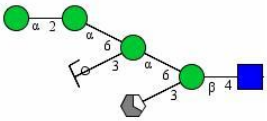
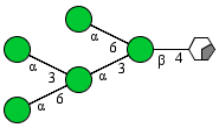
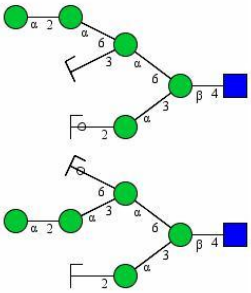
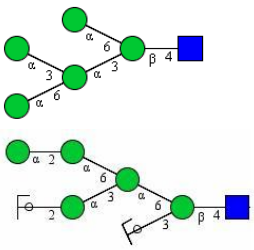
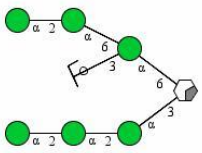
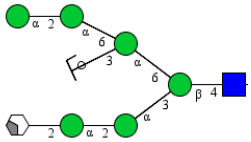
Table S-1 Expected and observed m/z values of PNGase F released structures from RNase B by ESI-MS in negative ion mode (+/- 0.5 Da calibration).

	Expected m/z		**Observed m/z**	
Structures	**$[M-H]^-$**	**$[M-2H]^{2-}$**	**$[M-H]^-$**	**$[M-2H]^{2-}$**
$Man_5GlcNAc_2$	1233.43	616.215	1233.6	616.8
$Man_6GlcNAc_2$	1397.48	698.24	1395.7	698
$Man_7GlcNAc_2$	1557.53	778.265	-	778.9
$Man_8GlcNAc_2$	1719.58	859.29	-	859.7
$Man_9GlcNAc_2$	1881.63	940.315	-	940.5

- not observed.

Table S-2 Deprotonated fragment ions from ESI-LC-MS of bacterial ENGase, Endo F1, and fungal WChTv-released native high mannose structures from RNase B. Fragment structures were made in GlycoWorkbench v2.1 and residues are as in Fig. S-1.

Fragment ion	Type	Expected m/z	Observed m/z	Bacterial	Fungal
	C	503.16	503.0	Y	Y
	$^{0,4}A_{Man}Y$ $^{1,3}A_{Man}$	545.17	545.1	Y	Y
	$^{0,2}A_{Man}Y$	605.19	605.1	Y	Y
	BZ	629.19	629.1	Y	Y
	BY	647.2	647.1	Y	Y
	CY	665.21	665.2	Y	Y
	$^{2,4}A_{GlcNAc}Y$ $C^{0,2}X_{Man}$	707.22	707.2	Y	Y
	$B^{2,4}X_{Man}$	749.24	749.2	Y	Y

	$C^{2,4}X_{Man}$ $^{0,2}A_{Man}$	767.25	767.2	Y	Y
	C	827.27	827.2	Y	Y
	$^{2,4}A_{GlcNAc}$	869.28	869.3	Y	Y
	$^{1,5}X_{Man}Y$	896.29	896.3	N	Y
	$^{0,2}A_{GlcNAc}$	929.3	929.3	Y	Y
	YZ ZY	1012.34	1012.3	Y	Y
	$[M-H]^-$ YY	1030.35	1030.4	Y	Y
	$^{0,2}A_{Man}Y$	1091.35	1091.4	Y	N
	$^{2,4}X_{Man}Y$	1294.43	1294.6	Y	Y

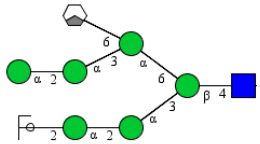
	$Y^{1,3}X_{Man}$				

Table S-3. Glycoproteins tested with WChTv and their *N*-linked oligosaccharide structures.

Glycoprotein	**Source Organism**	**Most Prevalent *N*-linked Oligosaccharides**
Fetuin	*B. taurus*	Bi-, tri- and tetra-antennary complex
RNase B	*B. taurus*	High mannose
Ovalbumin	*G. gallus*	High mannose, hybrid, bisecting GlcNAc
IgG	*B. taurus*	Biantennary complex, bisecting GlcNAc, α(1,6)-linked fucose
Invertase	*S. cerevisiae*	High mannose, yeast-type oligomannose