Supplementary mass spectrometric data to Figure 2

Fraction No.	$[M-H]^-_{obs}$	$[M-H]^-_{calc}$	Adduct	Assignment
1	**1508**	**1508**	**DHB**	**$Hex_5HexNAc_2$**
	1670	1670	DHB	$Hex_6HexNAc_2$
	1735	1736	DHB	$Fuc_1Hex_3HexNAc_4$
	1831	1832	DHB	$Hex_7HexNAc_2$
	1898	1898	DHB	$Fuc_1Hex_4HexNAc_4$
	1915	1914	DHB	$Hex_5HexNAc_4$
	1994	1994	DHB	$Hex_8HexNAc_2$
	2061	2060	DHB	$Fuc_1Hex_5HexNAc_4$
	2280	2279	DHB	$Hex_6HexNAc_5$
	2426	2425	DHB	$Fuc_1Hex_6HexNAc_5$
	2636	2636		$Fuc_1Hex_7HexNAc_6$
	3156	3155	DHB	$Fuc_1Hex_8HexNAc_7$
2	2050	2051		$NeuAc_1Hex_5HexNAc_4$
	2196	**2197**		**$NeuAc_1Fuc_1Hex_5HexNAc_4$ ***
	2212	2213		$NeuGc_1Fuc_1Hex_5HexNAc_4$
	2416	2416		$NeuAc_1Hex_6HexNAc_5$
	2562	2562		$NeuAc_1Fuc_1Hex_6HexNAc_5$
	2577	2578		$NeuGc_1Fuc_1Hex_6HexNAc_5$
	2781	2781		$NeuAc_1Hex_7HexNAc_6$
	2927	2927		$NeuAc_1Fuc_1Hex_7HexNAc_6$
	2944	2943		$NeuGc_1Fuc_1Hex_7HexNAc_6$
	3292	3292		$NeuAc_1Fuc_1Hex_8HexNAc_7$
3	2927	2927		$NeuAc_1Fuc_1Hex_7HexNAc_6$
	3072	3072		$NeuAc_2Hex_7HexNAc_6$
	3218	**3218**		**$NeuAc_2Fuc_1Hex_7HexNAc_6$ ***
	3234	3234		$NeuAc_1NeuGc_1Fuc_1Hex_7HexNAc_6$
	3583	3583		$NeuAc_2Fuc_1Hex_8HexNAc_7$
4	1595	1596		$Phos_1Hex_6HexNAc_2$ *
	2050	2051		$NeuAc_1Hex_5HexNAc_4$
	2342	2342		$NeuAc_2Hex_5HexNAc_4$ *
	2416	2416		$NeuAc_1Hex_6HexNAc_5$
	2488	2488		$NeuAc_2Fuc_1Hex_5HexNAc_4$ *
	2504	2504		$NeuAc_1NeuGc_1Fuc_1Hex_5HexNAc_4$
	2707	**2707**		**$NeuAc_2Hex_6HexNAc_5$ ***
	2853	2853		$NeuAc_2Fuc_1Hex_6HexNAc_5$
	2869	2869		$NeuGc_1NeuAc_1Fuc_1Hex_6HexNAc_5$
	3072	3072		$NeuAc_2Hex_7HexNAc_6$
	3218	3218		$NeuAc_2Fuc_1Hex_7HexNAc_6$ *
5	3584	3583		$NeuAc_2Fuc_1Hex_8HexNAc_7$
	3729	3728		$NeuAc_3Hex_8HexNAc_7$
	3875	**3874**		**$NeuAc_3Fuc_1Hex_8HexNAc_7$ ***
	3891	3890		$NeuGc_1NeuAc_2Fuc_1Hex_8HexNAc_7$
6	3218	3218		$NeuAc_2Fuc_1Hex_7HexNAc_6$
	3363	3363		$NeuAc_3Hex_7HexNAc_6$
	3509	**3509**		**$NeuAc_3Fuc_1Hex_7HexNAc_6$ ***
	3526	3525		$NeuGc_1NeuAc_2Fuc_1Hex_7HexNAc_6$
7	2707	2707		$NeuAc_2Hex_6HexNAc_5$
	2999	**2998**		**$NeuAc_3Hex_6HexNAc_5$ ***
	3145	3144		$NeuAc_3Fuc_1Hex_6HexNAc_5$
8	**2633**	**2633**		**$NeuAc_3Hex_5HexNAc_4$**
	2998	2998		$NeuAc_3Hex_6HexNAc_5$
	4531	4531		$NeuAc_4Fuc_1Hex_9HexNAc_8$
9	3000	2998		$NeuAc_3Hex_6HexNAc_5$
	4166	**4166**		**$NeuAc_4Fuc_1Hex_8HexNAc_7$ ***
10	3510	3509		$NeuAc_3Fuc_1Hex_7HexNAc_6$
	3654	3654		$NeuAc_4Hex_7HexNAc_6$
	3800	**3800**		**$NeuAc_4Fuc_1Hex_7HexNAc_6$ ***
	3816	3816		$NeuGc_1NeuAc_3Fuc_1Hex_7HexNAc_6$
11	2998	2998		$NeuAc_3Hex_6HexNAc_5$
	3289	**3289**		**$NeuAc_4Hex_6HexNAc_5$ ***
	3306	3305		$NeuGc_1NeuAc_3Hex_6HexNAc_5$

The peak fractions 1-11 collected from the ion exchange chromatography of 2-aminobenzamide-labeled N-glycans shown in **Fig. 2A** were analyzed by MALDI-TOF MS in negative polarity linear mode. The assignment of glycan compositions is based on comparison of the observed monoisotopic masses $[M-H]^-_{obs}$ with monoisotopic masses calculated from N-linked oligosaccharide structures commonly found on glycoproteins expressed in wild-type Chinese hamster ovary cells ($[M-H]^-_{calc}$; NeuAc, N-acetylneuraminic acid; NeuGc, N-glycolylneuraminic acid; Fuc, fucose; Hex, hexose; HexNAc, N-acetylhexosamine). The major glycan species present in each peak fraction as revealed by MALDI-TOF MS (which are schematically shown in **Fig. 2B**) are highlighted by bold letters and asterisks designate glycans whose number of terminal negatively charged substituents was confirmed by MALDI-TOF/TOF tandem mass spectrometry. Most of the neutral N-glycans contained in fraction No. 1 were found as negatively charged, non-covalent matrix (2,5-dihydrobenzoic acid; DHB) adducts of the type $[M+DHB-H]^-$ as frequently observed for neutral oligosaccharides composed of more than four monosaccharides with underivatized OH groups (Mele and Malpezzi, 2000).

Mele, A. and Malpezzi, L. (2000) Noncovalent association phenomena of 2,5-dihydroxybenzoic acid with cyclic and linear oligosaccharides. A matrix-assisted laser desorption/ionization time-of-flight mass spectrometric and X-ray crystallographic study. *J Am Soc Mass Spectrom*, **11**, 228-236.