Supporting Information

Experimental section:

Materials and Chemicals. Ovalbumin from chicken egg white (OVA), myoglobin (MYO), ammonium bicarbonate (ABC), dithiothreitol (DTT), iodoacetamide (IAA), sodium cyanoborohydrate (NaCNBH₃), dimethyl sulfoxide (DMSO), sodium deoxycholate (SDC), sodium lauroyl sarcosinate (SLS), 2, 5-dihydroxybenzoinic acid (DHB), trifluoro-acetic acid (TFA) were purchased from Sigma. Ethyl acetate (EtOAc) and sodium chloride (NaCl) were purchased from Sinopharm. PNGase F was obtained from New England Biolabs. Phosphate-buffered saline (PBS) and AminoLink Coupling Resin were purchased from Thermo Fisher Scientific. Acetonitrile (ACN) was obtained from Merck. Protease inhibitors (Complete tablets) was purchased from Roche Diagnostics. HILIC Martial was purchased from Welch. Sep-Pak C18 column was purchased from Waters. Exosome Purification Filter and Blood PureExo Solution were purchased from Umibio. Deionized water used for all experiments was obtained from a Milli-Q system (Millipore, Bedford, MA).

Isolation of Serum exosome. The Institutional Review Board of Zhongshan Hospital approved the use of human plasma samples. Exosome were separated from 0.5 mL of pooled serum from 6 HCC patient or healthy control by differential centrifugation. In brief, an initial spin was performed at 3,000 g at 4°C for 10 min and 10,000 g at 4 °C for 20 min to remove cells and debris, then the 0.5 mL of Blood PureExo Solution (BPS) were added to the sample, according to the manufacturer's instructions. Mixtures were vortexed and incubated at 4 °C for 2 h and then centrifuged at 10,000 g at 4 °C for 60 min to precipitate the exosome pellets. Pellets were resuspended with 400 μ L PBS and purified with Exosome Purification Filter. All exosomes were stored at -80 °C immediately after isolation until further analysis.

Characterization of exosome. The exosome was measured using transmission electron microscope (TEM). First, exosomes were fixed in 2% formaldehyde in PBS overnight at 4 °C for negative staining. Exosomes were added to mesh grids coated with Formvar in chloroform and carbon and were further fixed with 50 uL 1% glutaraldehyde in PBS for 5 min. Then the grids were transferred to eight successive drops of distilled water (2 min in total) to remove salts, with the following step that transferred to a drop of 1% uranyl acetate in 1% methyl cellulose for 5 min. In a second drop of negative stain solution, the grids were placed for 5 min. Excess stain was blotted off and grids were air dried (about 5-10 min). Finally, the grids were observed at 80 kV on a transmission electron microscope and photographed. The exosome particle size and concentration were measured using nanoparticle tracking analysis (NTA) with ZetaView PMX 110 (Particle Metrix, Meerbusch, Germany) and corresponding software ZetaView 8.04.02. First, isolated exosomes were diluted with PBS buffer. Then, NTA measurement was recorded and analyzed at 11 positions. For immunoblotting, proteins from exosomes were analyzed by SDS-PAGE and transferred to polyvinyledene fluoride membrane that were then blocked for 30 min with 5 % non-fat powered milk in Tris-buffered saline (TBS) with 0.1% Tween-20 (TBST). The following antibody was used: rabbit anti-CD9 (1:1000) (Abcam). Secondary antibody was goat antirabbit immunoglobulin G (IgG) coupled to HRP (1:10000). The membrane was washed with TBST and CD9 was analyzed in nonreducing conditions.

Exosome Lysis and Protein Digestion. The exosome lysis and digestion were performed according to phase transfer surfactant aided (PTS) digestion with modification.¹ The exosomes were

solubilized by lysis buffer that containing 12 mM SDC, 12 mM SLS, and protease inhibitors in 100 mM Tris-HCl at pH 8.5. After being measured the concentration by BCA protein determination method, the obtained proteins were reduced with 10 mM DTT for 45 min at 37 °C, and subsequently alkylated by 20 mM IAA for 30 min at 25 °C in the dark. The solution was then diluted to five-folds with 50 mM ABC and digested with Lys-C in a 1:50 (w/w) enzyme-to-protein ratio at 37 °C for 3 h. Then trypsin was added to a final 1:50 (w/w) enzyme-to-protein ratio for overnight digestion. After digestion, trifluoroacetic acid was added to a final concentration of 0.5% to acidify the sample and followed by adding of ethyl acetate with the same volume of the sample. The mixture was vortexed for 2 min, and then centrifuged at 15,000 g for 2 min to separate the sample to two phases. Upper layer was removed, and the lower aqueous phase was dried in speed vacuum. After dried, the sample was desalted with Sep-Pak C18 column and lyophilized in vacuum.

Reverse capture of N-glycans. AminoLink aldehyde-functionalized resin (50% slurry, Pierce) was pre-washed three times using PBS. Peptides were incubated overnight with resin in the presence of 50 mM NaCNBH₃ at 37 °C to immobilize all the peptides on the resin. Then the resin was washed three times with PBS and 1 M Tris-HCl solution (pH 7.4), respectively. Finally, the N-glycans were released by 1 μ L PNGase F at 37 °C overnight with shaking. The supernatant that contained N-glycans was collected and dried by vacuum for further use.

Protect the sialic acid. Methylamidation of sialyated N-glycans was performed according to the reported protocol.^{2, 3} Briefly, 45 μ L of 5 M methylamide chroloride in DMSO and 45 μ L of 1 M PyAOP in 30% N-methylmorpholine/DMSO were added to the N-glycans. The solution was incubated for 1.5 h in room temperature. After reaction, 2 mL 80% ACN, 1% TFA was added to quench the reaction.

Investigation the ratio of peptides to resin and the capacity of resin. 100 μ g of tryptic OVA peptides were incubated with different amounts of resin and proceeded with the reverse phase capture procedure, then the supernatants containing the released N-glycans were analyzed by MS. According to the number of glycans detected and the intensity of base peak, the appropriate ratio of glycoprotein to resin was estimated as 100 μ g peptides using 200 μ L resin (Figure S2). Next, the binding capacity was checked. 200 μ L of resin was incubated with 100 μ L of OVA tryptic peptides solutions at different concentration and the supernatants were analyzed. After the samples were loaded, the flow-through fractions were analyzed by MS. When the total amount of peptides was lower than the capacity of the resin, the peptides could not be detected. Once the signal of peptides was detected, it indicated that the material could not capture all the peptides at the concentration in question.

MALDI Sample Preparation and Analysis. DHB was dissolved in 50% ACN containing 0.1% TFA at a concentration of 10 mg/mL. 1 μ L of sample was loaded onto a MALDI target and mixed with 1 μ L of DHB solution, then the mixture was dried before MS analysis. The MALDI-TOF MS analysis was performed on a 5800 Proteomics Analyzer (Applied Biosystems, Framingham, MA, USA) equipped with a Nd:YAG laser (355 nm), an acceleration voltage of 20 kV, and a repetition rate of 400 Hz. The mass spectrometer was operated in positive mode. In addition, external mass calibration was performed using peptides from myoglobin digests.



Fig. S1. MALDI mass spectra of the mixture of standard peptide GGYTLVSGYPK and its dimethylated counterparts (with a molar ratio 10:1) (a) before and (b) after captured by resin.



Fig. S2 The number of detected N-glycans and the highest intensity of base peak from the same amount OVA enriched by a series of different volume of serum.



Fig. S3 Binding capacity analysis of the reverse capture method.



Fig. S4 MALDI mass spectra of the tryptic digest of 0.5 ng/ μ L OVA (a) after enrichment by the reverse phase capture protocol, and (b) after enrichment by HILIC tips (glycan peaks are labeled with Arabic numbers).



Fig. S5 Venn diagram of the number of N-glycans identified from serum exosomes of (a) HCC patients and (b) normal controls.



Fig. S6 MALDI mass spectrum of the N-glycans from serum of normal controls.



Fig. S7 MALDI mass spectrum of the N-glycans from serum of HCC patients.



Fig. S8. (a) Relative intensity of N-glycans from serums of normal controls and HCC patients, (b) Type distribution and monosaccharide composition distributions of the increased glycans of serum.

	Potontial	Detential Native		Detection		
No.	Structure*	mass** /Da	Peak***	m/z Da	Intensity (%)	CV
1	6 → 1 → 1	910.33	[M+Na] ⁺	933.22	0.25	0.42
2		1056.39	[M+Na] ⁺	1079.26	0.23	0.62
3		1072.38	[M+Na] ⁺	1095.26	0.29	0.52
4	•	1113.41	[M+Na] ⁺	1136.29	0.43	0.55
5	•••	1218.44	[M+Na] ⁺	1241.25	0.18	0.46
6		1234.43	[M+Na] ⁺	1257.30	3.22	0.21
7		1259.47	[M+Na] ⁺	1282.32	0.60	0.48
8		1275.46	[M+Na] ⁺	1298.30	0.52	0.54
9		1316.49	[M+Na] ⁺	1339.33	0.24	0.46
10		1380.49	[M+Na] ⁺	1403.25	0.19	0.21
11	<u>}</u>	1396.49	[M+Na] ⁺	1419.32	4.58	0.12
12		1421.52	[M+Na] ⁺	1444.33	0.52	0.34
13		1437.51	[M+Na] ⁺	1460.33	0.55	0.23
14		1462.54	[M+Na] ⁺	1485.36	3.51	0.07
15		1478.54	[M+Na] ⁺	1501.34	1.14	0.23
16		1519.57	[M+Na] ⁺	1542.35	0.22	0.36
17		1558.54	[M+Na] ⁺	1581.33	1.74	0.09
18	+	1566.56	[M+ma+Na] ⁺	1602.37	0.95	0.36

 Table S1 N-glycan compositions identified from exosomes in serum of HCC patients.

19		1583.57	[M+Na] ⁺	1606.37	0.30	0.15
20		1599.57	[M+Na] ⁺	1622.37	0.25	0.18
21		1608.60	[M+Na] ⁺	1631.38	0.21	0.24
22		1624.60	[M+Na] ⁺	1647.38	6.16	0.02
23		1640.59	[M+Na] ⁺	1663.36	1.77	0.11
24		1665.62	[M+Na] ⁺	1688.40	0.62	0.09
25		1681.62	[M+Na] ⁺	1704.38	0.37	0.19
26		1720.59	[M+Na] ⁺	1743.34	2.48	0.01
27	+	1712.61	[M+ma+Na] ⁺	1748.40	0.65	0.24
28	+	1728.61	[M+ma+Na] ⁺	1764.40	0.63	0.14
29		1769.63	[M+ma+Na] ⁺	1805.41	1.16	0.09
30		1786.65	[M+Na] ⁺	1809.40	4.59	0.07
31		1802.64	[M+Na] ⁺	1825.38	0.70	0.03
32		1827.68	[M+Na] ⁺	1850.42	1.94	0.04
33		1843.67	[M+Na] ⁺	1866.39	1.12	0.07
34		1882.64	[M+Na] ⁺	1905.36	2.33	0.06
35	••••••	1874.67	[M+ma+Na] ⁺	1910.41	0.25	0.58
36	• •	1890.66	[M+ma+Na] ⁺	1926.40	0.34	0.05
37	>	1925.72	[M+Na] ⁺	1948.44	0.38	0.33
38		1915.69	[M+ma+Na] ⁺	1951.45	0.98	0.07
39		1931.69	[M+ma+Na] ⁺	1967.43	9.74	0.07

40	I I	1957.74	[M+Na] ⁺	1980.41	0.69	0.02
41		1972.71	[M+ma+Na] ⁺	2008.43	0.24	0.18
42		1989.73	[M+Na] ⁺	2012.44	1.42	0.10
43		2005.72	[M+Na] ⁺	2028.44	0.52	0.10
44		2028.70	[M+Na] ⁺	2051.47	0.22	0.91
45		2030.76	[M+Na] ⁺	2053.42	0.34	0.13
46		2044.70	[M+Na] ⁺	2067.47	0.24	0.15
47	>- 1	2071.78	[M+Na] ⁺	2094.42	0.26	0.25
48	•	2087.78	[M+Na] ⁺	2110.41	0.44	0.18
49		2077.75	[M+ma+Na] ⁺	2113.47	7.62	0.13
50	***** >***	2093.74	[M+ma+Na] ⁺	2129.44	1.22	0.03
51	+	2118.77	[M+ma+Na] ⁺	2154.40	0.68	0.07
52		2134.77	[M+ma+Na] ⁺	2170.45	2.24	0.07
53		2151.78	[M+Na] ⁺	2174.44	0.92	0.24
54		2176.81	[M+Na] ⁺	2199.45	0.21	0.25
55		2192.81	[M+Na] ⁺	2215.44	0.25	0.58

56		2239.80	[M+ma+Na] ⁺	2256.00	0.50	0.21
57		2223.80	[M+ma+Na] ⁺	2259.52	0.23	0.12
58		2222.78	[M+2ma+Na] ⁺	2271.42	13.78	0.13
59		2264.83	[M+ma+Na] ⁺	2300.00	0.29	0.23
60		2280.82	[M+ma+Na] ⁺	2316.50	5.27	0.14
61		2296.82	[M+ma+Na] ⁺	2332.40	1.70	0.10
62		2321.85	[M+ma+Na] ⁺	2357.49	0.38	0.25
63		2337.85	[M+ma+Na] ⁺	2373.46	0.15	0.22
64		2352.81	[M+Na] ⁺	2375.47	0.19	0.39
65		2369.86	[M+ma+Na] ⁺	2405.54	0.17	0.18
66	····	2378.87	[M+ma+Na] ⁺	2414.62	0.17	0.58
67		2368.84	[M+2ma+Na] ⁺	2417.55	2.07	0.15
68		2411.88	[M+2ma+Na] ⁺	2433.54	0.21	0.02
69		2426.88	[M+ma+Na] ⁺	2462.53	0.14	0.24
70		2425.86	[M+2ma+Na] ⁺	2474.30	0.06	0.25

71	2442.88	[M+ma+Na] ⁺	2478.53	0.29	0.14
72	2571.92	[M+2ma+Na] ⁺	2620.59	0.87	0.22
73	2587.92	[M+2ma+Na] ⁺	2636.59	0.20	0.10
74	2645.96	[M+ma+Na] ⁺	2681.55	0.03	0.31
75	2733.97	[M+2ma+Na] ⁺	2782.51	0.04	0.07
76	2879.00	[M+3ma+Na] ⁺	2941.62	0.13	0.25
77	3025.07	[M+3ma+Na] ⁺	3087.62	0.05	0.13

Table S2 N-glycan compositions identified from exosomes in serum of normal controls.

	Potential	Nativo –	Detect	ion	Relative	
No.	Structure*	mass** /Da	Peak***	m/z Da	Intensity (%)	CV
1		910.33	[M+Na] ⁺	933.25	0.28	0.33
2	der van Taalener van Stern	1056.39	[M+Na] ⁺	1079.29	0.33	0.28
3	Gattalan minawa tu dinakan ku	1072.38	[M+Na] ⁺	1095.28	0.43	0.30
4		1113.41	[M+Na] ⁺	1136.30	0.88	0.24
5	635255426999999999999999999999999999999999	1218.44	[M+Na] ⁺	1241.30	0.30	0.26

6		1234.43	[M+Na] ⁺	1257.31	5.01	0.13
7	ETT HAT HE FOLLOW THE THE STATE OF T	1259.47	[M+Na] ⁺	1282.34	0.49	0.22
8	THE TRACTICAL AND A CONTRACT OF	1275.46	[M+Na] ⁺	1298.33	0.97	0.20
9	6893688788898998999999999999999999999	1316.49	[M+Na] ⁺	1339.34	0.36	0.19
10	<u>an an a</u> gus an ann an	1380.49	[M+Na] ⁺	1403.34	0.28	0.23
11	dinaraa kanalaka ka dabada ka	1396.49	[M+Na] ⁺	1419.34	6.25	0.07
12	Of the subscription of the	1421.52	[M+Na] ⁺	1444.36	0.51	0.12
13	Pri stali i secondo pri stali se na seconda da seconda da seconda da seconda da seconda da seconda da seconda d	1437.51	[M+Na] ⁺	1460.35	1.09	0.07
14		1462.54	[M+Na] ⁺	1485.38	1.67	0.07
15	ที่ไปได้มาให้มาให้และสำนักแล้วมีการที่กับให้เหตุ และเกตราส	1478.54	[M+Na] ⁺	1501.36	0.95	0.13
16		1519.57	[M+Na] ⁺	1542.40	0.24	0.35
17	<u>}-1</u>	1542.54	[M+Na] ⁺	1565.00	0.23	0.15
18	and the second	1558.54	[M+Na] ⁺	1581.36	3.03	0.05
19	5	1566.56	[M+ma+Na] ⁺	1602.41	1.09	0.10
20		1583.57	[M+Na] ⁺	1606.39	0.56	0.02
21	alentalalen innen erannan den	1599.57	[M+Na] ⁺	1622.37	0.39	0.04
22		1608.60	[M+Na] ⁺	1631.40	0.20	0.58
23	n an	1624.60	[M+Na] ⁺	1647.41	2.33	0.04
24	galanten andres states and and					0.06
		1640.59	[M+Na] ⁺	1663.39	1.50	0.06
25	8500-80 ⁰ -001008-800209-00	1640.59 1665.62	[M+Na] ⁺ [M+Na] ⁺	1663.39 1688.44	0.30	0.00
25 26		1640.59 1665.62 1681.62	[M+Na] ⁺ [M+Na] ⁺ [M+Na] ⁺	1663.39 1688.44 1704.42	0.30	0.08

28		1712.61	[M+ma+Na] ⁺	1748.44	1.07	0.06
29	स्वित्वाराज्येनीयां १४ विद्यानस्वरण्डते प्रतिविध्यान्त्रव्यात्व	1728.61	[M+ma+Na] ⁺	1764.43	0.70	0.02
30	Genowed and a set of the set of t	1769.63	[M+ma+Na] ⁺	1805.45	1.62	0.03
31	Ranger Frankriker gester sin eine ster eine soner soner	1786.65	[M+Na] ⁺	1809.44	1.42	0.01
32	anden van de Konstantin (de Konstantin) (de Konstantin)	1802.64	[M+Na] ⁺	1825.42	0.52	0.06
33		1811.68	[M+Na] ⁺	1834.43	0.27	0.58
34	an fear ann an an ann an An	1827.68	[M+Na] ⁺	1850.46	2.47	0.03
35	ggo astronomicant strants and an and an	1843.67	[M+Na] ⁺	1866.43	1.85	0.06
36	<u>an an a</u>	1882.64	[M+Na] ⁺	1905.41	1.37	0.05
37	EULETOT, LATSICOLUSIONELOZI (LULI + + + + + + + + + + + + + + + + + + +	1874.67	[M+ma+Na] ⁺	1910.47	0.38	0.01
38	KATARANAN AT AT ANN BATA BASS A TANAN BOLLAN AN AN	1890.66	[M+ma+Na] ⁺	1926.45	0.38	0.02
39		1925.72	[M+Na] ⁺	1948.49	0.40	0.25
40	Galand Januar de la substantia de la encontracta de la seconda de la seconda de la seconda de la seconda de la	1915.69	[M+ma+Na] ⁺	1951.48	1.10	0.58
41	<u>๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛</u>	1931.69	[M+ma+Na] ⁺	1967.48	14.50	0.04
42		1957.74	[M+Na] ⁺	1980.42	0.87	0.25
43		1973.73	[M+Na] ⁺	1996.50	0.27	0.58
44	CHECTORY CONTRACTOR OF CONT	1972.71	[M+ma+Na] ⁺	2008.53	0.27	0.03
45	REFERENCE AND	1989.73	[M+Na] ⁺	2012.48	2.06	0.07
46		2005.72	[M+Na] ⁺	2028.49	1.14	0.03

47	ander and and and and and and and and a	2028.70	[M+Na] ⁺	2051.50	0.34	0.06
48	NERSEN STORES	2030.76	[M+Na] ⁺	2053.45	0.52	0.10
49	an a	2044.70	[M+Na] ⁺	2067.44	0.30	0.03
50		2078.77	[M+Na] ⁺	2101.51	0.37	0.07
51		2087.78	[M+Na] ⁺	2110.48	0.43	0.06
52	Engen ander der Meinwerk of Britisher von Britisher von Britisher von Britisher von Britisher von Britisher von	2077.75	[M+ma+Na] ⁺	2113.51	4.64	0.09
53	Sanananan - Angertan Sanan Angertan Sanan	2093.74	[M+ma+Na] ⁺	2129.49	0.97	0.08
54	BATTETATEGRAFI GENTE BATTALENA-SUNAT ETARE	2118.77	[M+ma+Na] ⁺	2154.54	1.53	0.24
55		2134.77	[M+ma+Na] ⁺	2170.52	1.76	0.01
56	ณะมารถสารที่สุขารรูกอาสมารณคณะสายห	2151.78	[M+Na] ⁺	2174.52	0.56	0.02
57		2192.81	[M+Na] ⁺	2215.50	0.34	0.07
58		2239.80	[M+ma+Na] ⁺	2256.00	0.47	0.02
59	anna a dha anna a chuir anna anna an tharanna ann	2222.78	[M+2ma+Na] ⁺	2271.57	9.25	0.09
60		2280.82	[M+ma+Na] ⁺	2316.56	7.53	0.10
61	Sonething <u>and an an o</u> r an	2296.82	[M+ma+Na] ⁺	2332.55	2.01	0.07
62		2321.85	[M+ma+Na] ⁺	2357.54	0.21	0.18

63		2352.81	[M+Na] ⁺	2376.53	0.29	0.19
64		2379.89	[M+Na] ⁺	2402.53	0.16	0.58
65	<u>En En 2007 en 2009 en 2007 en 1000 en 2007</u>	2369.86	[M+ma+Na] ⁺	2405.57	0.14	0.03
66	ntalinaideuri deur sub <u>Conte</u>gna autorea en ar ess	2378.87	[M+ma+Na] ⁺	2414.61	0.16	0.58
67	ann sinn an far an far far an tha	2368.84	[M+2ma+Na] ⁺	2417.60	0.94	0.20
68		2411.88	[M+2ma+Na] ⁺	2434.56	0.13	0.58
69	Realistic and the second s	2426.88	[M+ma+Na] ⁺	2462.59	0.11	0.58
70	kane (Sentatika) ana <u>Long</u> unan eta Inaka	2442.88	[M+ma+Na] ⁺	2478.58	0.19	0.18
71	2951103255522205943103995799579957955222078	2571.92	[M+2ma+Na] ⁺	2620.63	0.81	0.14
72	anna an	2587.92	[M+2ma+Na] ⁺	2636.61	0.15	0.10
73	din kanafarika katalan katalan juli ya unaka katalan katalan katalan katalan katalan katalan katalan katalan k	2645.96	[M+ma+Na] ⁺	2681.67	0.03	0.59
74		2879.00	[M+3ma+Na] ⁺	2941.62	0.06	0.12

	Potential	Native	Detecti	Detection		
No.	Structure*	mass** /Da	Peak***	m/z Da	Intensity (%)	CV
1		910.33	[M+Na] ⁺	933.49	0.45	0.49
2	alernaad Tasalamason aasta	1056.39	[M+Na] ⁺	1079.22	0.26	0.58
3	Englisheannan ann an ann ann ann ann ann ann an	1072.38	[M+Na] ⁺	1095.25	0.43	0.69
4	<u>বিশ্বব</u> িদ্যালয়ীয়ে এই প্ৰথম কৰিছে বিশ্ববিদ্যালয়	1113.41	[M+Na] ⁺	1136.24	0.31	0.57
5	and the state of the second	1234.43	[M+Na] ⁺	1257.24	2.16	0.10
6		1259.47	[M+Na] ⁺	1282.28	0.26	0.46
7	San Carlo and Tang and an and Alexandra and Alexandra	1275.46	[M+Na] ⁺	1298.25	0.34	0.39
8	and The Transform and the second second second second	1316.49	[M+Na] ⁺	1339.29	0.23	0.37
9	Energia Petra alta dan mendebadan	1396.49	[M+Na] ⁺	1419.27	4.29	0.05
10	22237322222,7899387932773279349894879387287	1421.52	[M+Na] ⁺	1444.30	0.23	0.41
11	PARTAN SECOND AND SECOND AND AND AND AND AND AND AND AND AND A	1437.51	[M+Na] ⁺	1460.29	0.39	0.15
12	alter verk brachten alter Kahnen Französen w	1462.54	[M+Na] ⁺	1485.32	3.69	0.03
13	สรรรณีที่สามสองสาราชสารสาราชสารสารสารสารสารสารสารสารสาร	1478.54	[M+Na] ⁺	1501.30	0.89	0.18
14		1519.57	[M+Na] ⁺	1542.32	0.23	0.19
15	an a	1558.54	[M+Na] ⁺	1581.29	1.40	0.02
16	Stand 200 (200) 1222222 - 549 (1996) 1996	1566.56	[M+ma+Na] ⁺	1602.33	0.99	0.28
17		1583.57	[M+Na] ⁺	1606.32	0.18	0.59
18	a gang sang gang pang kang kang kang kang kang kang kang k	1599.57	[M+Na] ⁺	1622.29	0.22	0.16

 Table S3 N-glycan compositions identified from serum of HCC patients.

19	<u>Gannen in Transmarken Andrew er nur an Film († 1986 aug</u>	1608.60	[M+Na] ⁺	1631.33	0.20	0.19
20	States I second frances and a support of the support of the support	1624.60	[M+Na] ⁺	1647.34	5.98	0.04
21	gunde inden av-dinnen enden anden andere andere	1640.59	[M+Na] ⁺	1663.32	1.24	0.11
22		1665.62	[M+Na] ⁺	1688.36	0.73	0.09
23	an a	1681.62	[M+Na] ⁺	1704.34	0.31	0.17
24	ggeralkonsken och att skände som	1720.59	[M+Na] ⁺	1743.32	1.84	0.01
25		1712.61	[M+ma+Na] ⁺	1748.37	0.36	0.21
26	Ananovérski klad konstantova kladnoverska se	1728.61	[M+ma+Na] ⁺	1764.37	0.42	0.19
27	guruun databalari di tarte da ang kang kang kang kang kang kang kang	1769.63	[M+ma+Na] ⁺	1805.37	0.51	0.15
28	n an	1786.65	[M+Na] ⁺	1809.37	3.61	0.04
29	allandan kan kan kan kan kan kan kan kan kan k	1802.64	[M+Na] ⁺	1825.34	0.47	0.10
30		1811.68	[M+Na] ⁺	1834.35	0.15	0.63
	-					
31	And Hard Sector Sector Distributions	1827.68	[M+Na] ⁺	1850.39	1.56	0.06
31		1827.68 1843.67	[M+Na] ⁺ [M+Na] ⁺	1850.39 1866.36	1.56 0.80	0.06
31 32 33		1827.68 1843.67 1882.64	[M+Na] ⁺ [M+Na] ⁺ [M+Na] ⁺	1850.39 1866.36 1905.34	1.56 0.80 0.86	0.06 0.16 0.10
31 32 33 34		1827.68 1843.67 1882.64 1874.67	[M+Na] ⁺ [M+Na] ⁺ [M+Na] ⁺ [M+ma+Na] ⁺	1850.39 1866.36 1905.34 1910.39	1.56 0.80 0.86 0.16	0.06 0.16 0.10 0.24
31 32 33 34 35		1827.68 1843.67 1882.64 1874.67 1890.66	[M+Na] ⁺ [M+Na] ⁺ [M+Na] ⁺ [M+ma+Na] ⁺ [M+ma+Na] ⁺	1850.39 1866.36 1905.34 1910.39 1926.40	1.56 0.80 0.86 0.16 0.34	0.06 0.16 0.10 0.24 0.10
31 32 33 34 35 36		1827.68 1843.67 1882.64 1874.67 1890.66 1915.69	[M+Na] ⁺ [M+Na] ⁺ [M+Na] ⁺ [M+ma+Na] ⁺ [M+ma+Na] ⁺	1850.39 1866.36 1905.34 1910.39 1926.40 1951.41	1.56 0.80 0.86 0.16 0.34 0.77	0.06 0.16 0.10 0.24 0.10 0.14
31 32 33 34 35 36 37		1827.68 1843.67 1882.64 1874.67 1890.66 1915.69 1931.69	[M+Na] ⁺ [M+Na] ⁺ [M+Na] ⁺ [M+ma+Na] ⁺ [M+ma+Na] ⁺ [M+ma+Na] ⁺	1850.39 1866.36 1905.34 1910.39 1926.40 1951.41 1967.40	1.56 0.80 0.86 0.16 0.34 0.77 7.57	0.06 0.16 0.10 0.24 0.10 0.14 0.03
31 32 33 34 35 36 37 38		1827.68 1843.67 1882.64 1874.67 1890.66 1915.69 1931.69 1957.74	[M+Na] ⁺ [M+Na] ⁺ [M+Na] ⁺ [M+ma+Na] ⁺ [M+ma+Na] ⁺ [M+ma+Na] ⁺ [M+ma+Na] ⁺	1850.39 1866.36 1905.34 1910.39 1926.40 1951.41 1967.40 1980.46	1.56 0.80 0.86 0.16 0.34 0.77 7.57 0.19	0.06 0.16 0.10 0.24 0.10 0.14 0.03 0.08

40	na sening of the following formation of the following form	1989.73	[M+Na] ⁺	2012.41	1.27	0.06
41		2005.72	[M+Na] ⁺	2028.40	0.20	0.23
42		2028.70	[M+Na] ⁺	2051.43	0.34	0.21
43	Decision of the second s	2030.76	[M+Na]+	2053.44	0.18	0.58
44	at III and a state of the second s	2044.70	[M+Na]+	2067.35	0.19	0.27
45		2071.78	[M+Na] ⁺	2094.45	0.18	0.58
46		2087.78	[M+Na] ⁺	2110.50	0.58	0.58
47	<u>ann a</u> dharan an ann an	2077.75	[M+ma+Na] ⁺	2113.44	5.47	0.06
48	galanda a kananga ka dalaman kananga ka	2093.74	[M+ma+Na] ⁺	2129.42	0.96	0.05
49		2110.76	[M+Na]+	2133.46	0.17	0.58
50	RECEIPTION OF THE RECEIPTION	2118.77	[M+ma+Na]+	2154.45	0.46	0.09
51		2135.79	[M+Na] ⁺	2158.41	0.17	0.58
52		2134.77	[M+ma+Na] ⁺	2170.44	3.87	0.04
53		2151.78	[M+Na]+	2174.46	0.28	0.58
54		2175.79	[M+ma+Na]+	2211.48	0.32	0.46
55		2192.81	[M+Na] ⁺	2215.47	0.25	0.58

56	@300003280022293990039-34920703289899	2223.80	[M+ma+Na] ⁺	2259.41	0.18	0.24
57		2222.78	[M+2ma+Na] ⁺	2271.48	26.55	0.09
58		2256.81	[M+Na] ⁺	2279.56	0.55	0.58
59		2264.83	[M+ma+Na] ⁺	2300.36	0.25	0.18
60	<u>Gen ya ana</u> araa kata kata kata kata kata kata kata	2280.82	[M+ma+Na] ⁺	2316.49	5.37	0.09
61	Antonin <u>taaan Ing</u> elekansekenekendenta	2296.82	[M+ma+Na] ⁺	2332.46	0.95	0.04
62		2321.85	[M+ma+Na] ⁺	2357.44	0.20	0.11
63	LETTELESS STATEMENT LETTELESSE	2352.81	[M+Na] ⁺	2375.46	0.12	0.58
64	มีแต่สำนัญของสามารถเหตุสุของสมอัญชีวิธาติสุของของสามารถอายา	2368.84	[M+2ma+Na] ⁺	2417.33	3.15	0.08
65		2411.88	[M+2ma+Na]+	2433.21	0.26	0.11
66	Roment (1975) (1969) and 1 <u>803</u> 0,000 (1976)	2442.88	[M+ma+Na] ⁺	2478.40	0.15	0.11
67	dennad stategy a constant worked canon	2571.92	[M+2ma+Na] ⁺	2620.38	1.04	0.06
68	nersan kana an	2587.92	[M+2ma+Na] ⁺	2636.34	0.42	0.03
69		2733.97	[M+2ma+Na]+	2782.39	0.11	0.17
70		2790.99	[M+2ma+Na]+	2839.40	0.08	0.61

71		2879.00	[M+3ma+Na] ⁺	2941.35	1.48	0.12
72	(non-sector sector) in the construction of the sector of the	3025.07	[M+3ma+Na] ⁺	3087.39	0.84	0.17

Table S4 N-glycan compositions identified from serum of normal controls.

	Potential	Native -	Detection		Relative	
No.	Structure*	mass** /Da	Peak***	m/z Da	Intensity (%)	CV
1		910.33	[M+Na] ⁺	933.85	0.95	0.18
2	686 (1992) (C. 2006) (C. 2007)	1056.39	[M+Na] ⁺	1079.24	0.42	0.62
3		1072.38	[M+Na] ⁺	1095.13	1.26	0.58
4	<u>and an ann an an ann an ann ann ann ann </u>	1113.41	[M+Na] ⁺	1136.26	0.54	0.37
5	เมื่อไขไขไข้สุดที่มายในการที่เข้าไขไขไขไขไขไขไขไขไขไขไขไขไขไขไขไขไขไขไ	1234.43	[M+Na] ⁺	1257.23	0.78	0.25
6	CANALONG COLLEGE OF ANY	1259.47	[M+Na] ⁺	1282.28	0.39	0.58
7		1275.46	[M+Na] ⁺	1298.24	0.45	0.31
8	Geological Constraints (Constraints)	1316.49	[M+Na] ⁺	1339.28	0.62	0.25
9		1396.49	[M+Na] ⁺	1419.28	1.06	0.19
10	CREATECOUR AND	1421.52	[M+Na] ⁺	1444.32	0.40	0.58
11		1462.54	[M+Na] ⁺	1485.32	2.63	0.14
12	9003 Mar A 60 A 67 2002 (97 0 M 4 7 10 M 4 6 A 6 M 4 7 10 M 4 6 A 6 M 4 7 10 M 4 6 M 4 7 10 M 4 6 M 4 7 10 M 4	1478.54	[M+Na] ⁺	1501.31	1.18	0.29
13	Example Contraction and a second s	1519.57	[M+Na] ⁺	1542.32	0.37	0.29

14		1558.54	$[M+Na]^+$	1581.30	0.42	0.20
15	an a	1566.56	[M+ma+Na] ⁺	1602.34	1.85	0.08
16	A CONTRACTOR OF THE AND A CONTRACTOR OF	1599.57	[M+Na] ⁺	1622.35	0.33	0.58
17	<u>Alement of Alements Annotations (Trades)</u>	1608.60	[M+Na] ⁺	1631.32	0.34	0.61
18	Ballounoode and Cherry Cherry and	1624.60	[M+Na] ⁺	1647.35	4.53	0.07
19	gantrick in date date and an and an and	1640.59	[M+Na] ⁺	1663.33	1.34	0.24
20		1665.62	[M+Na] ⁺	1688.36	0.47	0.23
21	ante ante a su a s	1681.62	[M+Na] ⁺	1704.35	0.50	0.28
22	a generalitet en de la desta de la dest	1720.59	[M+Na] ⁺	1743.33	0.62	0.31
23	<u>alan</u> an kanan ka	1712.61	[M+ma+Na] ⁺	1748.38	0.36	0.58
24	Nacione - Andrea de California da Sector de California de California de California de California de California	1728.61	[M+ma+Na] ⁺	1764.37	0.47	0.16
25	Gerver de Door in Constelle anna dha ann	1769.63	[M+ma+Na] ⁺	1805.39	0.91	0.12
26	n an	1786.65	[M+Na] ⁺	1809.38	1.99	0.16
27		1802.64	[M+Na] ⁺	1825.35	0.45	0.07
28		1827.68	[M+Na] ⁺	1850.40	0.87	0.24
29	an a	1843.67	[M+Na] ⁺	1866.38	0.99	0.27
30		1882.64	[M+Na] ⁺	1905.36	0.47	0.26
31	NATARA AN	1890.66	[M+ma+Na] ⁺	1926.39	0.40	0.08
32	<u>></u>	1925.72	[M+Na]+	1948.39	0.51	0.58
33	Guine (1979) and (1990)	1915.69	[M+ma+Na] ⁺	1951.44	0.83	0.24
34	Reference and a second s	1931.69	[M+ma+Na] ⁺	1967.41	12.24	0.03

35		1957.74	[M+Na] ⁺	1980.47	0.38	0.10
36		1973.73	[M+Na] ⁺	1996.41	0.25	0.58
37	Colores in consistent properties the second and a	1972.71	[M+ma+Na] ⁺	2008.57	0.49	0.58
38		1989.73	[M+Na] ⁺	2012.41	0.59	0.15
39	an a	2028.70	[M+Na] ⁺	2051.42	0.57	0.14
40	or and other and the second second	2044.70	[M+Na] ⁺	2067.46	0.33	0.25
41		2087.78	[M+Na] ⁺	2110.44	0.58	0.60
42		2077.75	[M+ma+Na] ⁺	2113.45	3.84	0.05
43	Sind and a second s	2093.74	[M+ma+Na] ⁺	2129.44	1.06	0.58
44	ng kan kanadar kan	2110.76	[M+Na] ⁺	2133.47	0.55	0.15
45	partition di trazilari di Angoli di Challoni di Challoni	2135.79	[M+Na] ⁺	2158.58	0.45	0.58
46	2000020-2009-2009-00-00-00-00-00-00-00-00-00-00-00-00-	2134.77	[M+ma+Na] ⁺	2170.45	4.88	0.07
47		2190.76	[M+ma+Na] ⁺	2213.48	0.36	0.23
48		2206.75	[M+Na] ⁺	2229.45	0.21	0.58
49		2217.84	[M+Na] ⁺	2240.47	0.24	0.29
50	1.577.582.4727.537.637.637.637.657.657.657.657.657.657.657.657.657.65	2223.80	[M+Na] ⁺	2256.43	0.57	0.58

51		2222.78	[M+2ma+Na] ⁺	2271.49	34.88	0.17
52		2255.79	[M+ma+Na] ⁺	2291.73	0.41	0.58
53		2264.83	[M+ma+Na] ⁺	2300.52	0.57	0.03
54	GUT THE COLOR OF THE	2280.82	[M+ma+Na] ⁺	2316.58	1.46	0.13
55	Spectraphing and an and a second strategy work of the	2296.82	[M+ma+Na] ⁺	2332.47	0.65	0.15
56	annan (an airs a' an airs an an ann an ann ann ann ann ann ann a	2321.85	[M+ma+Na] ⁺	2357.46	0.28	0.25
57		2352.81	[M+Na] ⁺	2375.45	0.21	0.58
58	00030004003607802820088000040478787008	2368.84	[M+2ma+Na] ⁺	2417.53	3.21	0.10
59	ADARTIN'S ALTRONOMIC AND	2411.88	[M+2ma+Na]+	2433.58	0.34	0.18
60	and an	2425.86	[M+2ma+Na]+	2474.53	0.16	0.58
61		2571.92	[M+2ma+Na] ⁺	2620.58	0.79	0.25
62		2587.92	[M+2ma+Na] ⁺	2636.57	0.77	0.06
63	Landerner og som samerar for ander	2733.97	[M+2ma+Na] ⁺	2782.63	0.17	0.09
64		2879.00	[M+3ma+Na]+	2941.67	2.49	0.06
65		3025.07	[M+3ma+Na] ⁺	3087.69	0.47	0.05

*: One potential structure corresponding to the glycan mass was displayed.

**: The monoisotopic molecular mass of the glycan with free reducing end.

***: "M" refers to the native molecule and "+(n) ma" means that (n) sialic acid units were converted into methylamidated ones, with mass shift of 13.03*n Da.

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