

## Supporting information

**Table S1**

List of the detected neutral oligosaccharides (unreduced neutral mass) from Jersey sample 1230. Abbreviations: expt: experimental, cal: calibrated, RT: retention time (minutes).

<sup>1</sup>Hex, Hexose; HexNAc, *N*-acetylhexosamine. <sup>2</sup>expt: Experimental mass values have been averaged.

<sup>3</sup> Oligosaccharide is not detected in sample 1230, but it is present in other milk samples.

OS ID	Neutral mass			Oligosaccharides <sup>1</sup>			RT	Abundance
	expt <sup>2</sup>	Cal	delta	Hex	HexNAc	Fucose		
1	504.169	504.169	0.860	3			9.03	4798365
1	504.169	504.169	0.463	3			11.14	2289054
1	504.169	504.169	0.298	3			12.43	10735273
1	504.168	504.169	1.785	3			14.24	2925245
2	545.195	545.196	1.022	2	1		11.54	12303374
5	666.221	666.222	1.261	4			11.02	119885
8	707.247	707.248	1.697	3	1		12.34	11536
8	707.248	707.248	1.273	3	1		13.82	801323
8	707.248	707.248	1.273	3	1		15.04	1155341
8	707.247	707.248	2.192	3	1		17.77	120617
9	748.273	748.275	2.539	2	2		10.53	11621
9	748.274	748.275	2.005	2	2		14.25	291627
9	748.274	748.275	1.604	2	2		16.20	66392
14	869.300	869.301	1.898	4	1		17.46	3715431
15	910.327	910.328	1.318	3	2		14.06	21244
15	910.328	910.328	0.275	3	2		15.82	2563958
18	990.327	990.327	0.942	6			11.81	101203
18	990.326	990.327	1.868	6			14.51	71083
21	1072.380	1072.381	0.187	4	2		18.51	814672
22	1113.408	1113.407	0.943	3	3		17.22	336513
23	1152.381	1152.380	0.477	7			15.57	24633
26	n/a <sup>3</sup>	1234.433	2.592	5	2		n/a	n/a
28	n/a <sup>3</sup>	1275.460	0.157	4	3		n/a	n/a
29	1316.484	1316.487	1.975	3	4		18.54	10383
32	n/a <sup>3</sup>	1396.486	n/a	6	2		n/a	n/a
36	n/a <sup>3</sup>	1462.545	n/a	3	4	1	n/a	n/a
37	n/a <sup>3</sup>	1478.539	n/a	4	4		n/a	n/a
38	1519.563	1519.566	2.106	3	5		13.54	4659
42	1624.597	1624.597	0.123	4	4	1	16.10	17353
43	1640.590	1640.592	1.585	5	4		14.79	7325
45	n/a <sup>3</sup>	1681.619	n/a	4	5		n/a	n/a
46	1722.642	1722.645	1.974	3	6		14.81	10328
47	1786.653	1786.650	1.455	5	4	1	16.46	43540
49	1827.678	1827.677	0.821	4	5	1	17.54	22882
52	1868.704	1868.703	0.428	3	6	1	17.50	169536

**Table S2**

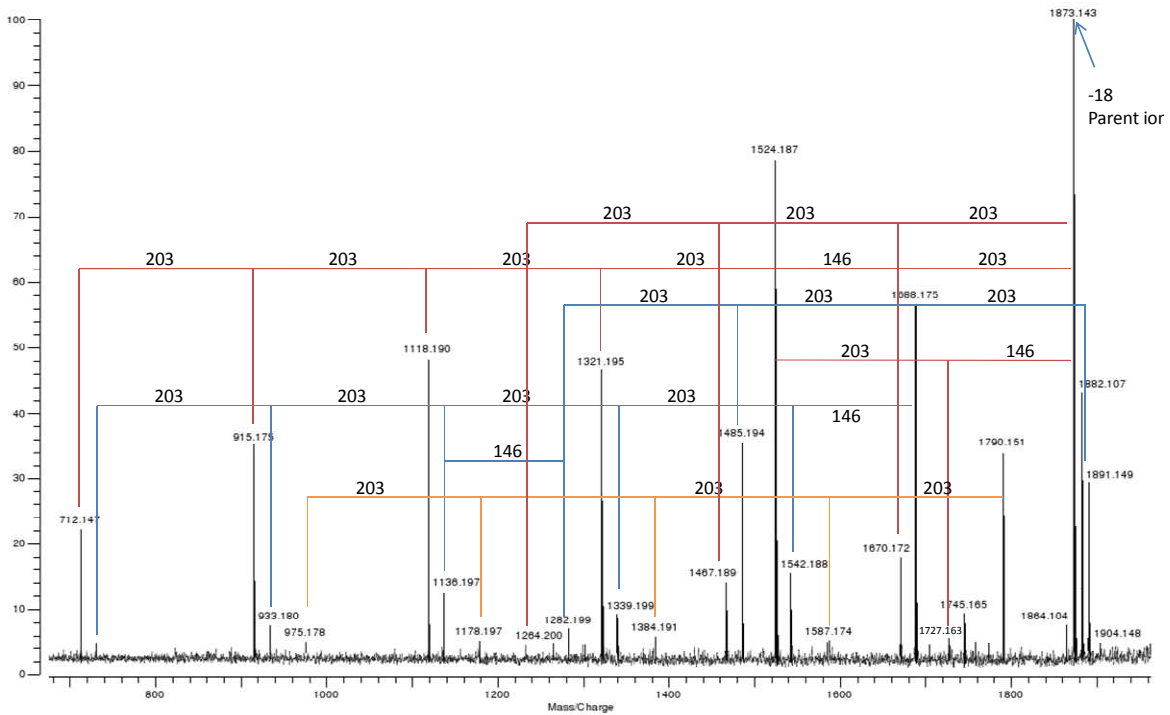
List of the detected acidic oligosaccharides (unreduced neutral mass) from Jersey sample 1230. Abbreviations: expt: experimental, cal: calibrated, RT: retention time (minutes).

<sup>1</sup>Hex, Hexose; HexNAc, *N*-acetylhexosamine; NeuAc, *N*-acetyl neuraminic acid; NeuGc, *N*-glycolyl neuraminic acid. <sup>2</sup>expt: Experimental mass values have been averaged. <sup>3</sup>Oligosaccharide is not detected in sample 1230, but it is present in other milk samples.

OS ID	Neutral mass			Oligosaccharides <sup>1</sup>				RT	Abundance
	expt <sup>2</sup>	Cal	delta (ppm)	Hex	HexNAc	NeuAc	NeuGc		
3	633.211	633.212	1.369	2		1		15.96	7764487
3	633.210	633.212	2.000	2		1		21.58	16195508
4	n/a <sup>3</sup>	649.206	n/a	2			1	n/a	n/a
6	n/a <sup>3</sup>	674.238	n/a	1	1	1		n/a	n/a
7	n/a <sup>3</sup>	690.233	n/a	1	1		1	n/a	n/a
7	n/a <sup>3</sup>	690.233	n/a	1	1		1	n/a	n/a
10	795.264	795.264	0.503	3		1		16.70	13683
10	795.263	795.264	1.886	3		1		23.49	1331060
12	836.290	836.291	0.957	2	1	1		15.31	20175
19	n/a <sup>3</sup>	998.344	n/a	3	1	1		n/a	n/a
24	1160.395	1160.397	1.724	4	1	1		24.96	472111
25	1201.426	1201.423	2.580	3	2	1		24.59	11694
39	n/a <sup>3</sup>	1525.529	1.901	5	2	1		n/a	n/a

**Figure S1:** (A) MALDI FTICR tandem MS of (A) ion at  $m/z$  1891.748 (corresponding to 1868.70 in HPLC Chip/TOF MS) and (B) ion at  $m/z$  1809.63 (corresponding to 1786.65 in HPLC Chip/TOF MS).

**A**



**B**

