

図 107. 種々の細胞における PI3K アイソフォームの発現

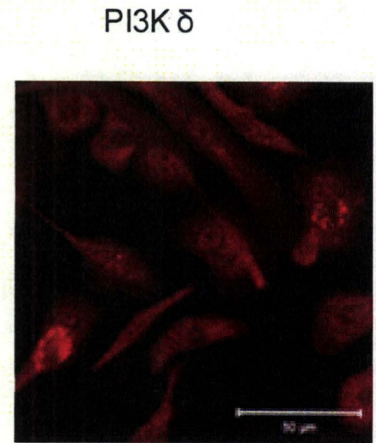


図 108. AC133 由来 Early EPC における p110 PI3K δ の発現

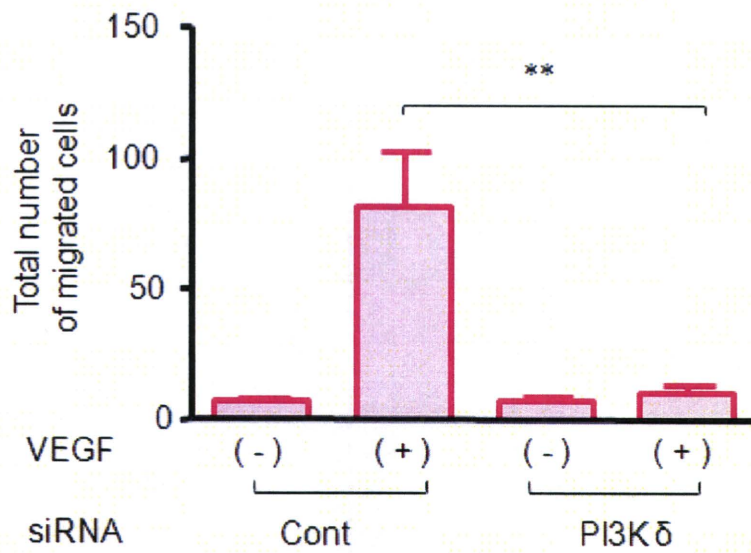
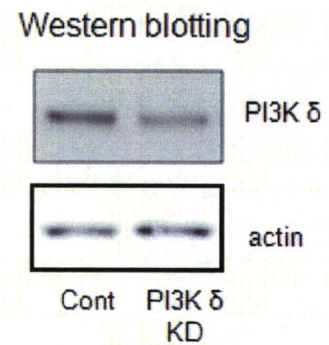


図 109. VEGF に誘導される Early EPC の遊走に対する p110 PI3K δ siRNA の効果



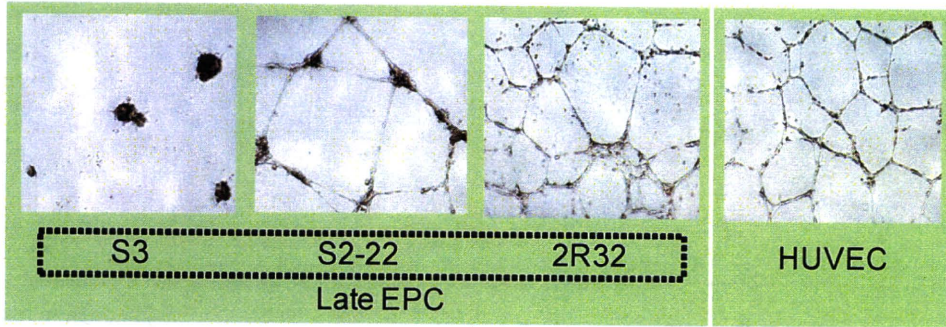


図 110. 種々の late EPC の *in vitro* 管腔形成能

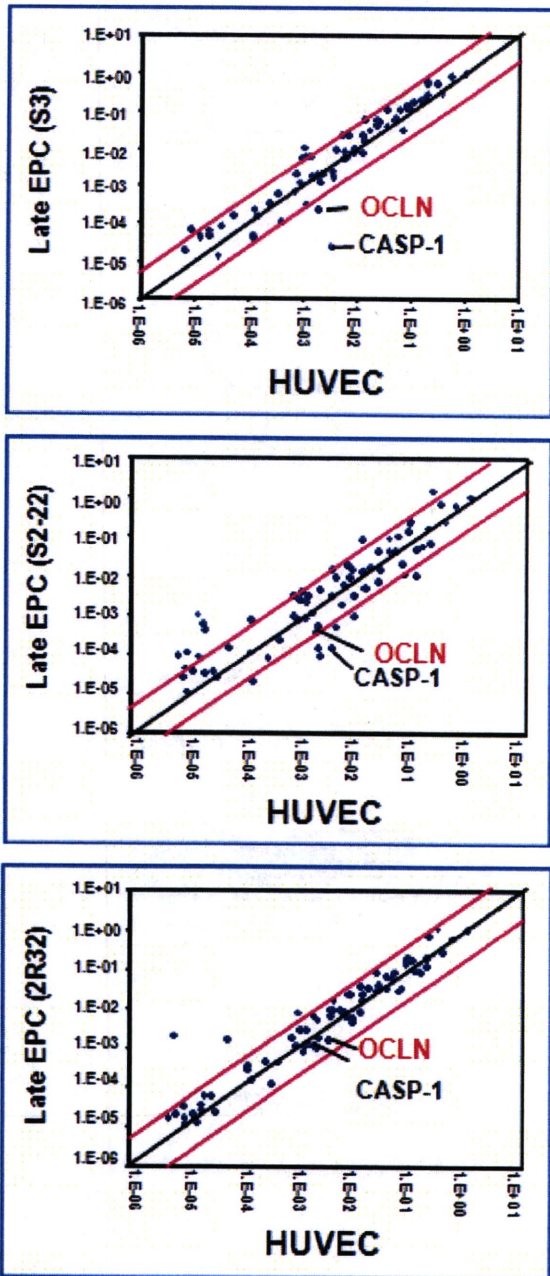


図 112. LateEPC と HUVEC における遺伝子発現プロファイル比較

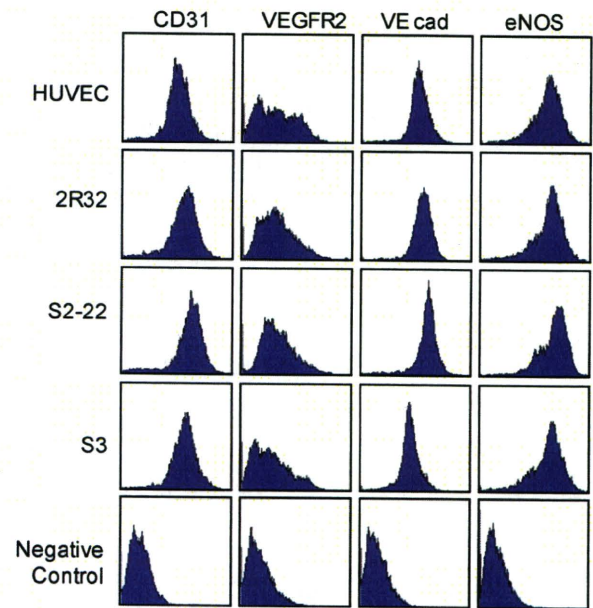
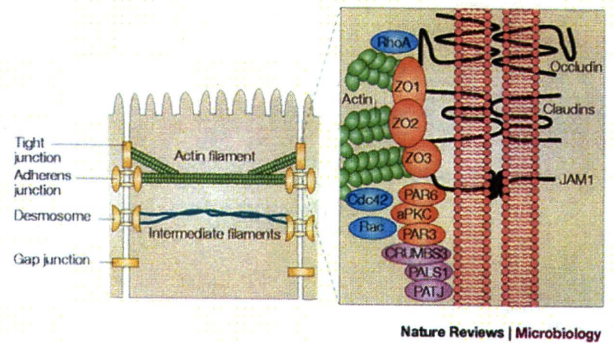


図 111. 種々の late EPC における血管内皮細胞マーカー分子の発現



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図 113. Tight Junction タンパクとして働くオクルジン

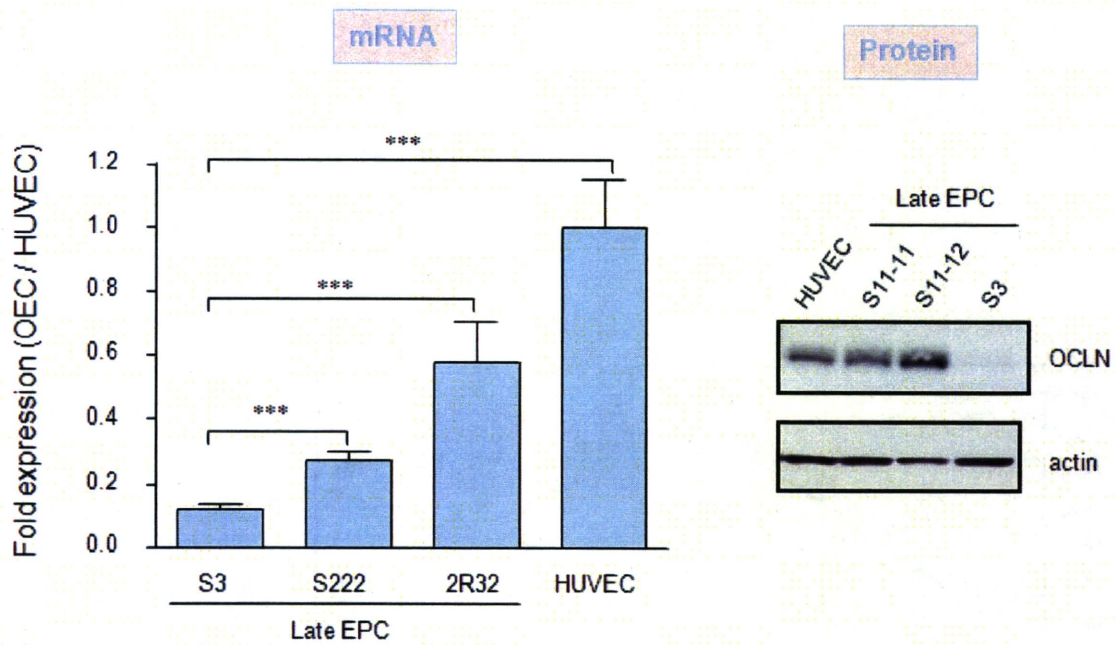


図 114. Late EPC におけるオクルディンの mRNA 及びタンパク質発現

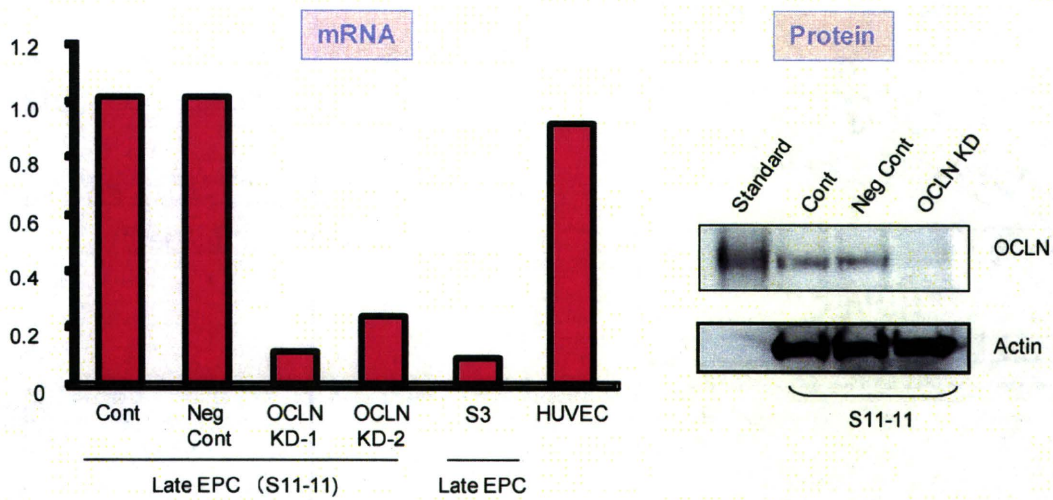


図 115. siRNA によるオクルディンの mRNA 及びタンパク質質量の変化

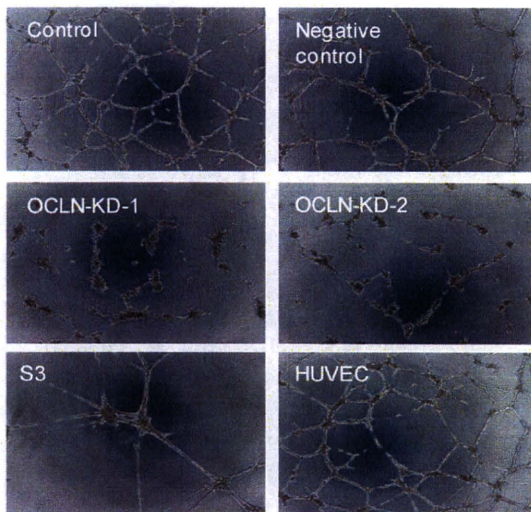


図 116. オクルディン siRNA による管腔形成の抑制

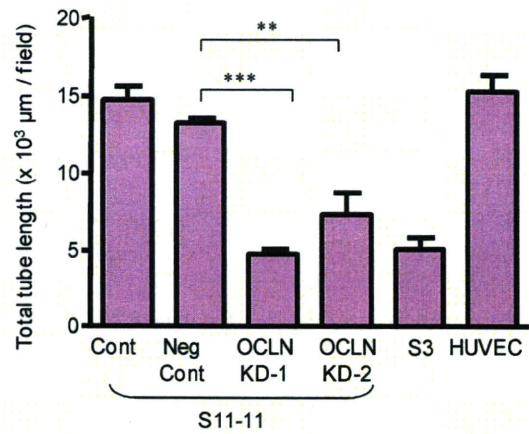


図 117. オクルディン siRNA による管腔形成抑制の定量評価

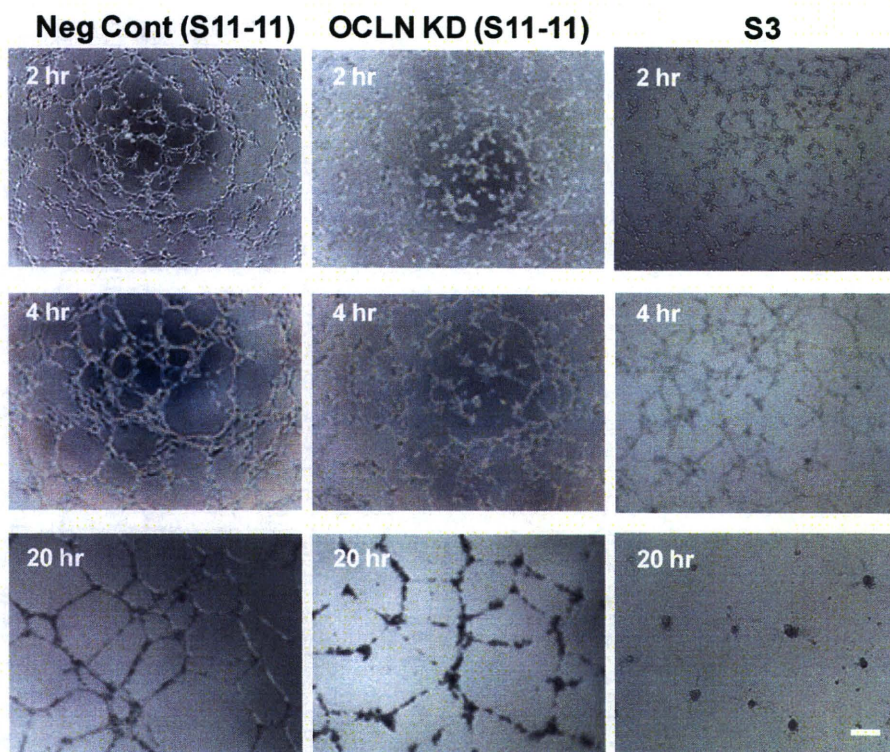


図 118. オクルディン siRNA の管腔形成への影響の経時的観察

Table 31. O-Glycans found in leukemia cell lines

Structure and monosaccharide compositions	Molecular ions	Peak ID	Relative abundance (%)		
			K562	U937	Jurkat HL-60
Asialo glycan					
Gal β 1-3(Gal β 1-4GlcNAc β 1-6)GalNAc-2AA ^{#A2}	869(+)	H-1			4.44
Monosialo glycans					
NeuAc α 2-3Gal β 1-3GalNAc-2AA ^{#MS1} (Sialyl T antigen)	795(+)	K-1, U1, J-1, H-4	32.3	36.6	20.5
NeuAc α 2-6GalNAc-2AA (Sialyl Tn antigen)	633(+)	H-7, J-2			28.9
NeuAc α 2-3Gal β 1-3(GlcNAc β 1-6)GalNAc-2AA ^{#MS2}	997(+)	H-3			1.16
Gal β 1-3(Gal β 1-4GlcNAc β 1-6)GalNAc-2AA + NeuAc α 1 ^{#MS3}	1159(-)	H-6			4.24
NeuAc α 2-3Gal β 1-3(GlcNAc β 1-6)GalNAc-2AA + Fuc	1143(-)	H-2			4.26
Gal β 1-3(Gal-(Fuc-)GlcNAc β 1-6)GalNAc-2AA + NeuAc α 1 ^{#MS4}	1305(-)	H-5			2.08
Disialo glycans					
NeuAc α 2-3Gal β 1-3(NeuAc α 2-6)GalNAc-2AA ^{#DS1} (Disialyl T antigen)	1085(-)	K-3, U-3, J-5, H-14	30.7	30.1	12.9
NeuAc α 2-3Gal β 1-3(NeuAc α 2-3Gal β 1-4GlcNAc β 1-6)GalNAc-2AA ^{#DS2}	1450(-)	J-4, H-13			10.7
NeuAc α 2-3Gal β 1-3(NeuAc α 2-3Gal β 1-4(Fuca1-3)GlcNAc β 1-6)GalNAc-2AA	1596(-)	H-12			0.14
NeuAc α 2-3Gal β 1-3(NeuAc α 2-3Gal β 1-4GlcNAc β 1-3Gal β 1-4GlcNAc β 1-6)GalNAc-2AA ^{#DS3}	1815(-)	H-10			1.49
NeuAc α 2-3Gal β 1-3(NeuAc α 2-3Gal β 1-4GlcNAc β 1-3Gal β 1-4(Fuca1-3)GlcNAc β 1-6)GalNAc-2AA ^{#DS4}	1961(-)	H-10			1.49
NeuAc-Gal β 1-3(NeuAc-(Gal-GlcNAc) $_2$ -Gal β 1-4GlcNAc β 1-6)GalNAc-2AA ^{#DS6}	2180(-)	H-9			1.11
NeuAc-Gal β 1-3(NeuAc-(Gal-GlcNAc) $_3$ -Gal β 1-4GlcNAc β 1-6)GalNAc-2AA ^{#DS9}	2545(-)	H-8			2.13
Degradation product					
NeuAc α 2-3Gal-2AA	592(+)	K-2, U-2, J-3, H-11	17.3	21.2	20.6

We showed ms/ms data for the glycan with # marks in supporting information. The information is available free of charge via the Internet at <http://pubs.acs.org>. The structures in blue are confirmed according to the analogous consideration on the structures of higher / lower series of O-glycans. The structures in red are not assigned in the present study, because we could not observe good MSⁿ data.

Table 32. O-Glycans found in pancreatic cancer cell lines

O-glycans observed in PANC1	Molecular ions	O-glycans observed in BxPC3	Molecular ions
<u>Asialo fraction(peak P-1): 0%</u>		<u>Asialo fraction (Peak B-1):6.0%</u> Galβ1-3GalNAc-2AA Galβ1-3(GlcNAcβ1-6)GalNAc-2AA#A1 Galβ1-3(Galβ1-4GlcNAcβ1-6)GalNAc-2AA#A2 Galβ1-3(GlcNAcβ1-3Galβ1-4GlcNAcβ1-6)GalNAc-2AA#A4 Galβ1-3(Gal-GlcNAc-Galβ1-4GlcNAcβ1-6)GalNAc-2AA#A5	504 (+) 707 (+) 869 (+) 1093(+) 1255(+)
<u>Monosialo fraction (Peak P2, P3): 63%</u> NeuAcc2-3Galβ1-3GalNAc-2AA#MS1 (Sialyl T antigen)	795(+)	<u>Monosialo fraction (Peak B-2): 70%</u> NeuAcc2-3Galβ1-3GalNAc-2AA#MS1 (Sialyl T antigen) Galβ1-3(Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc1#MS3 Galβ1-3(Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc1#MS5 Galβ1-3 (Gal-GlcNAc-Gal-(Fuc-) GlcNAcβ1-6) -GalNAc-2AA + NeuAc1#MS6 Galβ1-3((Gal-GlcNAc)2-Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc1#MS8 Galβ1-3((Gal-GlcNAc)2-Gal-(Fuc-)GlcNAcβ1-6) -GalNA-2AA + NeuAc1#MS9 Galβ1-3((Gal-GlcNAc)3-Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc1#MS10 Galβ1-3((Gal-GlcNAc)3-Gal-(Fuc-)GlcNAcβ1-6) GalNAc-2AA + NeuAc1#MS11 Galβ1-3((Gal-GlcNAc)4-Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc1#MS12 Galβ1-3((Gal-GlcNAc)4-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA + NeuAc1#MS13	795(+) 1159(-) 1524(-) 1670(-) 1889(-) 2035(-) 2254(-) 2400(-) 2619(-) 2765(-)
<u>Disialo fraction (Peak P4): 37%</u> NeuAcc2-3Galβ1-3(NeuAcc2-6)GalNAc-2AA#DS1 (Disialyl T antigen)	1085(-)	<u>Disialo fraction (Peak B3, B4, B5): 24%</u> NeuAcc2-3Galβ1-3(NeuAcc2-6)GalNAc-2AA#DS1 (Disialyl T antigen) NeuAc2Hex1HexNAcIdHex1-2AA NeuAc-Galβ1-3(NeuAc-Gal-GlcNAcβ1-6)GalNAc-2AA#DS2	1085(-) 1231(-) 1450(-)

NeuAc-Galβ1-3(NeuAc-Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA#DS3	1815(-)
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAc-Gal-(Fuc)GlcNAcβ1-6)GalNAc-2AA#DS4	1961(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₂ -Gal-GlcNAcβ1-6)GalNAc-2AA#DS6	2180(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₂ -Gal-(Fuc)GlcNAcβ1-6)GalNAc-2AA#DS7	2326(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₃ -Gal-GlcNAcβ1-6)GalNAc-2AA#DS9	2545(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₃ -Gal-(Fuc)GlcNAcβ1-6)GalNAc-2AA	2691(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₄ -Gal-GlcNAcβ1-6)GalNAc-2AA#DS10	2910(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₄ -Gal-(Fuc)GlcNAcβ1-6)GalNAc-2AA	3056(-)
<u>Degradation product</u> NeuAcα2-3Gal-2AA	592(+)

We showed ms/ms data for the glycan with # marks in supporting information. The information is available free of charge via the Internet at <http://pubs.acs.org>. The structures in blue are confirmed according to the analogous consideration on the structures of higher / lower series of *O*-glycans. The structures in red are not assigned in the present study, because we could not observe good MSⁿ data.

Table 33. O-Glycans found in colon cancer cell lines

O-glycans observed in LS174T	Molecular ions	O-glycans observed in HCT-15	Molecular ions
<u>Asialo fraction (peak L-1): 25.6%</u>		<u>Asialo fraction (Peak H-1): 13.8%</u>	
Galβ1-3GalNAc-2AA	504 (+)	GlcNAc-GalNAc-2AA	545 (+)
GlcNAc-GalNAc-2AA	545 (+)	Fuc-Galβ1-3GalNAc-2AA	649(+)
Galβ1-3(GlcNAcβ1-6)GalNAc-2AA ^{#A1}	707 (+)	Galβ1-3(GlcNAcβ1-6)GalNAc-2AA ^{#A1}	707 (+)
Galβ1-3(Gal-GlcNAcβ1-6)GalNAc-2AA ^{#A2}	869 (+)	Galβ1-3(Gal-GlcNAcβ1-6)GalNAc-2AA ^{#A2}	869 (+)
Galβ1-3(Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA ^{#A3}	1014(-)		
Galβ1-3(GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA ^{#A4}	1071(-)		
Galβ1-3(Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA ^{#A5}	1233(-)		
Galβ1-3(Gal-GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA ^{#A6}	1379(-)		
Galβ1-3(GlcNAc-Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA ^{#A7}	1436(-)		
Galβ1-3((Gal-GlcNAc) ₂ -Gal-GlcNAcβ1-6)GalNAc-2AA ^{#A8}	1598(-)		
Galβ1-3(((Gal-GlcNAc) ₂ -Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA ^{#A9}	1744(-)		
<u>Monosialo fraction (Peak L-2): 37.1%</u>		<u>Monosialo fraction (Peak H-2): 23.8%</u>	
Galβ1-3(Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ ^{#MS3}	1159(-)	NeuAc ₂ -3Galβ1-3GalNAc-2AA ^{#MS1} (Sialyl T antigen)	795(+)
Galβ1-3(Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ ^{#MS4}	1305(-)	Galβ1-3(GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ ^{#MS2}	997(-)
Galβ1-3(Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ + SO ₃	1385(-)	Galβ1-3(Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ ^{#MS3}	1159(-)
Galβ1-3((Gal-GlcNAc-Gal-(Fuc-)(SO ₃ -)GlcNAcβ1-6)GalNAc-2AA ^{#SU2}	1459(-)	Galβ1-3(Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA NeuAc ₁ ^{#MS4}	+ 1305(-)
Galβ1-3(Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ ^{#MS5}	1524(-)		
Galβ1-3(Gal-(Fuc-)GlcNAc-Gal-(Fuc-)(SO ₃ -)GlcNAcβ1-6) GalNAc-2AA ^{#SU3}	1604(-)		
Galβ1-3(Gal-GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ ^{#MS6}	1670(-)		
Galβ1-3(Gal-(Fuc-)GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ ^{#MS7}	1816(-)		
Galβ1-3(Gal-(Fuc-)GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ + SO ₃	1896(-)		
Galβ1-3((Gal-GlcNAc) ₂ -Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ + SO ₃	1969(-)		

Galβ1-3((Gal-GlcNAc) ₂ -Gal-(Fuc-)GlcNAcβ1-6)-GalNA-2AA + NeuAc ₁ ^{#MS9}	2035(-)
Galβ1-3(Gal-GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁	2181(-)
<u>Disialo fraction (Peak L-3, L-4, L-5): 37.1%</u>	
NeuAcα2-3Galβ1-3(NeuAcα2-6)GalNAc-2AA ^{#DS1} (Disialyl T antigen)	1085(-)
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAcβ1-6)GalNAc-2AA ^{#DS2}	1450(-)
NeuAc-Galβ1-3(NeuAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA	1596(-)
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA ^{#DS3}	1815(-)
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAc-Gal-(SO ₃ -)GlcNAcβ1-6)GalNAc-2AA ^{#SU4}	1895(-)
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA ^{#DS4}	1961(-)
NeuAc-Galβ1-3(NeuAc-Gal-(Fuc-)GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA ^{#DS5}	2107(-)
Galβ1-3((Gal-GlcNAc) ₂ -Gal-(Fuc-)(SO ₃ -)GlcNAcβ1-6)GalNA-2AA + NeuAc ₁ ^{#SU5}	2115(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₂ -Gal-GlcNAcβ1-6)GalNAc-2AA ^{#DS6}	2180(-)
Galβ1-3(Gal-GlcNAc-Gal-(Fuc-)(SO ₃ -)GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ ^{#SU6}	2260(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₂ -Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA ^{#DS7}	2326(-)
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAc-Gal-(Fuc-)GlcNAc-Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA ^{#DS8}	2472(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₃ -Gal-(Fuc-)GlcNAcβ1-6)GalNAc-2AA	2691(-)
<u>Degradation product</u> (Gal-GlcNAc) ₂ -Gal-2AA ^{#DP2}	
	1029(-)
<u>Disialo fraction (Peak H-3, H-4): 62.4%</u>	
NeuAcα2-3Galβ1-3(NeuAcα2-6)GalNAc-2AA ^{#DS1} (Disialyl T antigen)	1085(-)
Galβ1-3(Gal-GlcNAcβ1-6)GalNAc-2AA + SO ₃ + NeuAc ₁ ^{#SU1}	1238(-)
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAcβ1-6)GalNAc-2AA ^{#DS}	1450(-)
Galβ1-3(Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA + SO ₃ + NeuAc ₁	1604
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA ^{#DS3}	1815(-)
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₂ -Gal-GlcNAcβ1-6)GalNAc-2AA ^{#DS6}	2180(-)
<u>Degradation product</u> NeuAc-Gal-GlcNAc-Gal-2AA ^{#DP1}	
	956(+)

Gal-GlcNAc-Gal-(Fuc-)GlcNAc-Gal-2AA#DP8	1176(-)
(Gal-GlcNAc) ₈ -Gal-2AA +Fuc	1541(-)
NeuAc-Gal-(Fuc-)GlcNAc-Gal-(Fuc-)(SO ₈)GlcNAc-Gal-2AA#DP6	1691(-)
NeuAc-(Gal-GlcNAc) ₂ -Gal-2AA +Fuc ₃	1758(-)

We showed ms/ms data for the glycan with # marks in supporting information. The information is available free of charge via the Internet at <http://pubs.acs.org>. The structures in blue are confirmed according to the analogous consideration on the structures of higher / lower series of *O*-glycans. The structures in red are not assigned in the present study, because we could not observe good MSⁿ data.

Table 34. O-Glycans found in gastric cancer cell lines

O-glycans observed in MKN45	Molecular ions	O-glycans observed in MKN7	Molecular ions
<u>Asialo fraction (Peak M-1): 5.0%</u>			
Galβ1-3GalNAc-2AA	504 (+)	<u>Asialo fraction (Peak M7-1): 0%</u>	
GlcNAc-GalNAc-2AA	545 (+)		
Galβ1-3(GlcNAcβ1-6)GalNAc-2AA#A1	707 (+)		
<u>Monosialo fraction (Peak M-2, M-3): 21.3%</u>			
NeuAcα2-6GalNAc-2AA + Na (Sialyl Tn antigen)	654(+)	<u>Monosialo fraction (Peak M7-3, M7-4): 74.6%</u>	
NeuAcα2-3Galβ1-3GalNAc-2AA#MS1 (Sialyl T antigen)	795(+)		
Galβ1-3(GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ #MS2	998(+)		
Galβ1-3(Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ #MS3	1159(-)		
Galβ1-3(Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ #MS5	1524(-)		
Galβ1-3((Gal-GlcNAc) ₂ -Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ #MS8	1889(-)		
Galβ1-3((Gal-GlcNAc) ₃ -Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ #MS10	2254(-)		
Galβ1-3((Gal-GlcNAc) ₄ -Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ #MS12	2619(-)		
Galβ1-3((Gal-GlcNAc) ₅ -Gal-GlcNAcβ1-6)GalNAc-2AA + NeuAc ₁ #MS14	2984(-)		
<u>Disialo fractions (Peak M-4, M-6): 61.4%</u>			
NeuAcα2-3Galβ1-3(NeuAcα2-6)GalNAc-2AA#DS1 (Disialyl T antigen)	1085(-)	<u>Disialo fractions (Peak M7-5): 25.4%</u>	
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAcβ1-6)GalNAc-2AA#DS2	1450(-)		
NeuAc-Galβ1-3(NeuAc-Gal-GlcNAc-Gal-GlcNAcβ1-6)GalNAc-2AA#DS3	1815(-)		
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₂ -Gal-GlcNAcβ1-6)GalNAc-2AA#DS6	2180(-)		
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₃ -Gal-GlcNAcβ1-6)GalNAc-2AA#DS9	2545(-)		
NeuAc-Galβ1-3(NeuAc-(Gal-GlcNAc) ₄ -Gal-GlcNAcβ1-6)GalNAc-2AA#DS12	2910(-)		
		NeuAcα2-3Galβ1-3(NeuAcα2-6)GalNAc-2AA#DS1 (Disialyl T antigen)	1085(-)
			1305

Ac-2AA #DS10			
NeuAc-Gal β 1-3(NeuAc-(Gal-GlcNAc) ₅ -Gal-GlcNAc β 1-6)GalN			3275(-)
Ac-2AA #DS11			
<u>Trisialo fraction (Peak M-5): 12.3%</u>			
NeuAc-Gal-GlcNAc-(NeuAc-Gal-GlcNAc)Galb1-3(NeuAca2-6)GalNAc-2AA#TS1			2106(-)
NeuAc-Gal-GlcNAc-(NeuAc-Gal-GlcNAc)Galb1-3(NeuAca2-6)GalNAc-2AA+Gal-GlcNAc#TS2			2471(-)
NeuAc-Gal-GlcNAc-(NeuAc-Gal-GlcNAc)Galb1-3(NeuAca2-6)GalNAc-2AA+(Gal-GlcNAc)#TS3			2836(-)
NeuAc-Gal-GlcNAc-(NeuAc-Gal-GlcNAc)Galb1-3(NeuAca2-6)GalNAc-2AA+(Gal-GlcNAc)#TS4			3201(-)
NeuAc-Gal-GlcNAc-(NeuAc-Gal-GlcNAc)Galb1-3(NeuAca2-6)GalNAc-2AA+(Gal-GlcNAc)#TS5			3566(-)
NeuAc-Gal-GlcNAc-(NeuAc-Gal-GlcNAc)Galb1-3(NeuAca2-6)GalNAc-2AA+(Gal-GlcNAc)#TS6			3931(-)
<u>Degradation product</u>			
NeuAca2-3Gal-2AA			592(+)
NeuAc-Gal-GlcNAc-Gal-2AA#DP1		NeuAca2-3Gal-2AA	957(+)
NeuAc-(Gal-GlcNAc) ₂ -Gal-2AA#DP4		NeuAc-Gal-GlcNAc-Gal-2AA#DP1	1321(-)
NeuAc-(Gal-GlcNAc) ₃ -Gal-2AA#DP5			1686(-)
NeuAc-(Gal-GlcNAc) ₄ -Gal-2AA#DP7			2051(-)
NeuAc-(Gal-GlcNAc) ₅ -Gal-2AA			2416(-)
NeuAc-(Gal-GlcNAc) ₆ -Gal-2AA#DP8			2781(-)

We showed ms/ms data for the glycan with # marks in supporting information. The information is available free of charge via the Internet at <http://pubs.acs.org>. The structures in blue are confirmed according to the analogous consideration on the structures of higher / lower series of O-glycans. The structures in red are not assigned in the present study, because we could not observe good MSⁿ data.

Table 35 Mucin-type O-glycans observed in HCT116 cell.

M1		M4	
504	Gal-GalNAc-2AA	1815	NeuAc α 2-3Gal β 1-3 { NeuAc α 2-6(Gal-GlcNAc) $_2$ β 1-6}GalNAc-2AA
546	GlcNAc-GalNAc-2AA	1969	Gal β 1-3 {(Gal-GlcNAc) $_3$ β 1-6}GalNAc-2AA + NeuAc + SO₃
625	GlcNAc-GalNAc-2AA + SO₃	2180	NeuAc α 2-3Gal β 1-3 { NeuAc α 2-6(Gal-GlcNAc) $_3$ β 1-6}GalNAc-2AA
706	Gal β 1-3(GlcNAc β 1-6)GalNAc-2AA	2335	Gal β 1-3 {(Gal-GlcNAc) $_4$ β 1-6}GalNAc-2AA + NeuAc + SO₃
786	Gal β 1-3(GlcNAc β 1-6)GalNAc-2AA + SO₃	2546	NeuAc α 2-3Gal β 1-3 { NeuAc α 2-6(Gal-GlcNAc) $_4$ β 1-6}GalNAc-2AA
868	Gal β 1-3 (Gal-GlcNAc β 1-6)GalNAc-2AA	M5	
949	Gal β 1-3 (Gal-GlcNAc β 1-6)GalNAc-2AA + SO₃	1450	NeuAc α 2-3Gal β 1-3 (NeuAc α 2-6Gal-GlcNAc β 1-6)GalNAc-2AA
1234	Gal β 1-3 {(Gal-GlcNAc) $_2$ β 1-6}GalNAc-2AA	1815	NeuAc α 2-3Gal β 1-3 { NeuAc α 2-6(Gal-GlcNAc) $_2$ β 1-6}GalNAc-2AA
M2		M6	
1158	Gal β 1-3 (Gal-GlcNAc β 1-6)GalNAc-2AA + NeuAc	1085	NeuAc α 2-3Gal β 1-3(NeuAc α 2-6)GalNAc-2AA
1361	Gal β 1-3 (GlcNAc-Gal-GlcNAc β 1-6)GalNAc-2AA + NeuAc	1238	Gal β 1-3 (Gal-GlcNAc β 1-6)GalNAc-2AA + NeuAc + SO₃
1523	Gal β 1-3 {(Gal-GlcNAc) $_2$ β 1-6}GalNAc-2AA + NeuAc	1440	Gal β 1-3 (GlcNAc-Gal-GlcNAc β 1-6)GalNAc-2AA + NeuAc + SO₃
1888	Gal β 1-3 {(Gal-GlcNAc) $_3$ β 1-6}GalNAc-2AA + NeuAc	1450	NeuAc α 2-3Gal β 1-3 (NeuAc α 2-6Gal-GlcNAc β 1-6)GalNAc-2AA
2253	Gal β 1-3 {(Gal-GlcNAc) $_4$ β 1-6}GalNAc-2AA + NeuAc	1604	Gal β 1-3 {(Gal-GlcNAc) $_2$ β 1-6}GalNAc-2AA + NeuAc + SO₃
2618	Gal β 1-3 {(Gal-GlcNAc) $_3$ β 1-6}GalNAc-2AA + NeuAc	1684	Gal β 1-3 {(Gal-GlcNAc) $_3$ β 1-6}GalNAc-2AA + NeuAc + 2SO₃
M3		1764	Gal β 1-3 {(Gal-GlcNAc) $_2$ β 1-6}GalNAc-2AA + NeuAc + 3SO₃
633	NeuAc α 2-6GalNAc-2AA	2260	NeuAc α 2-3Gal β 1-3 { NeuAc α 2-6(Gal-GlcNAc) $_3$ β 1-6}GalNAc-2AA + SO₃
795	NeuAc α 2-3Gal β 1-3GalNAc-2AA	2626	NeuAc α 2-3Gal β 1-3 { NeuAc α 2-6(Gal-GlcNAc) $_4$ β 1-6}GalNAc-2AA + SO₃
998	NeuAc α 2-3Gal β 1-3(GlcNAc β 1-6)GalNAc-2AA	2106	NeuAc α 2-3Gal β 1-3 { NeuAc α 2-6(Gal-GlcNAc) $_2$ β 1-6}GalNAc-2AA + NeuAc
1160	Gal β 1-3 (Gal-GlcNAc β 1-6)GalNAc-2AA + NeuAc	2471	NeuAc α 2-3Gal β 1-3 { NeuAc α 2-6(Gal-GlcNAc) $_3$ β 1-6}GalNAc-2AA + NeuAc

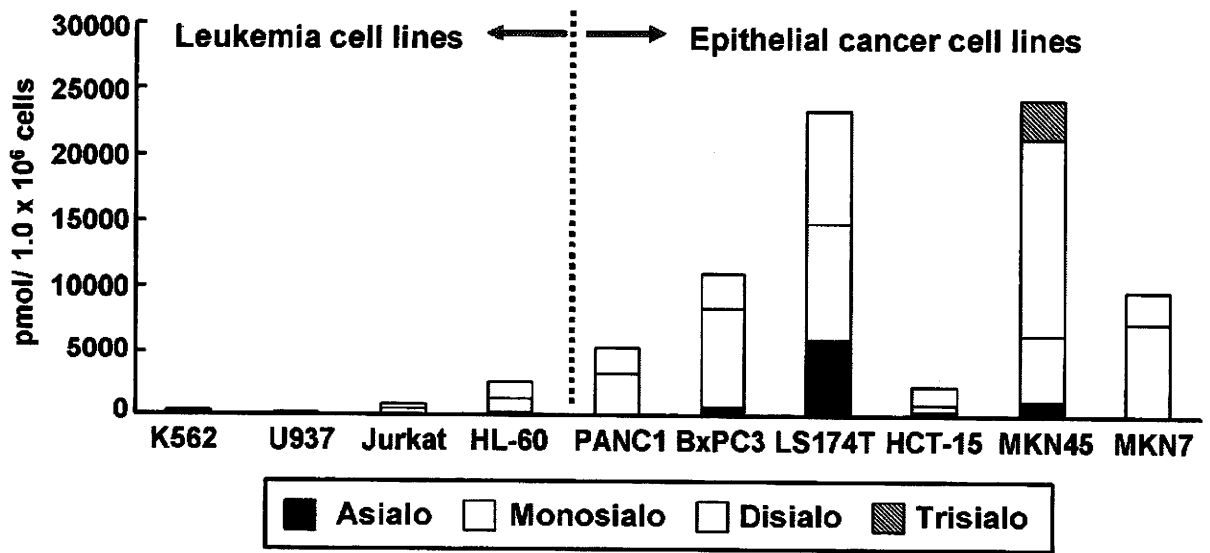


Fig.119 Comparison of the amounts of O-glycans expressed on cancer cells

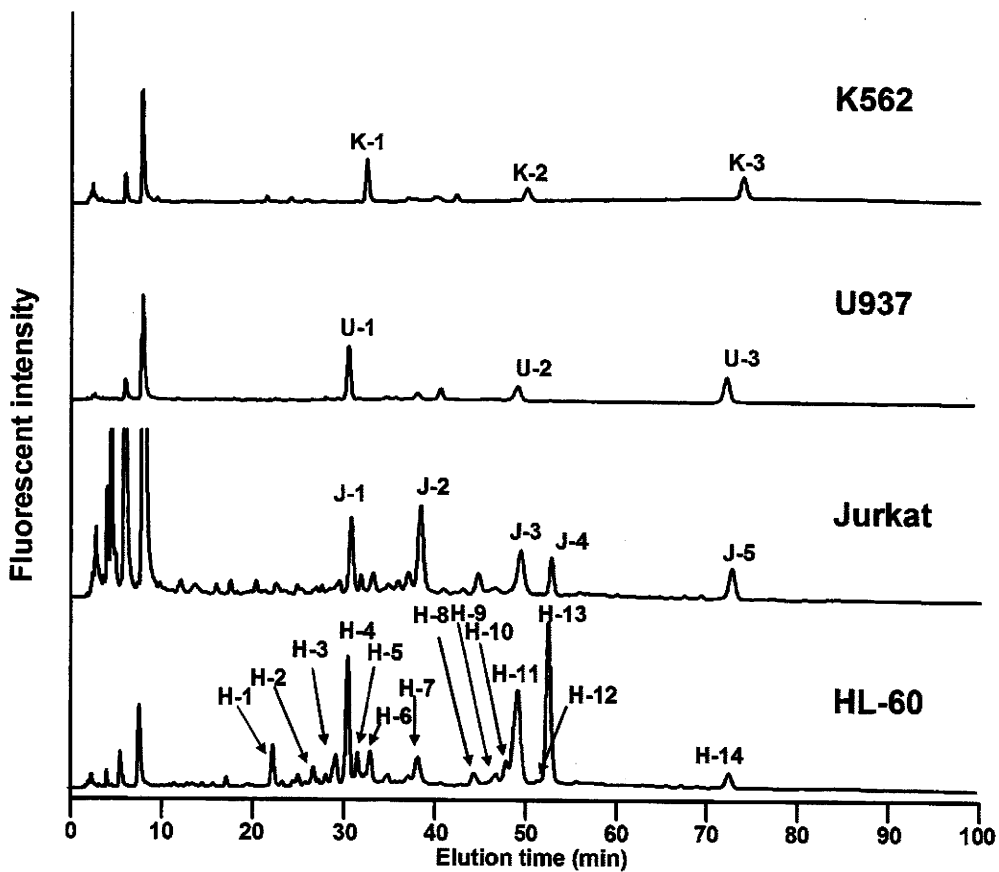


Fig.120 NP-HPLC analysis of O-glycans derived from leukemia cells

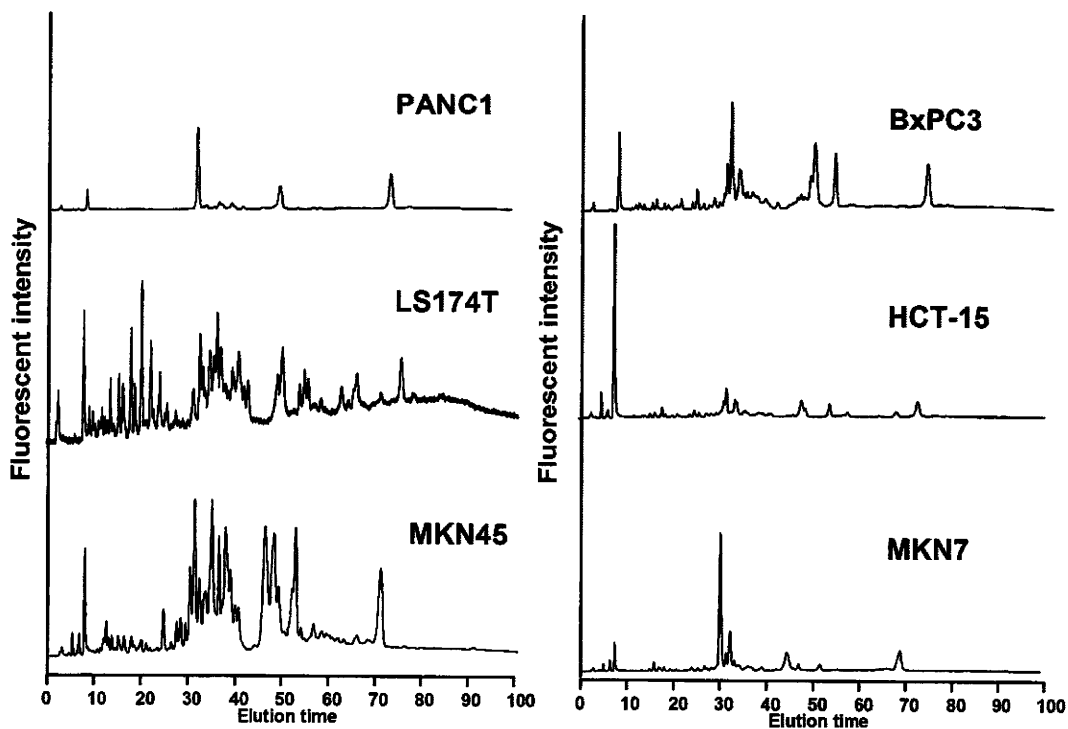


Fig.121 NP-HPLC analysis of O-glycans derived from epithelial cancer cells

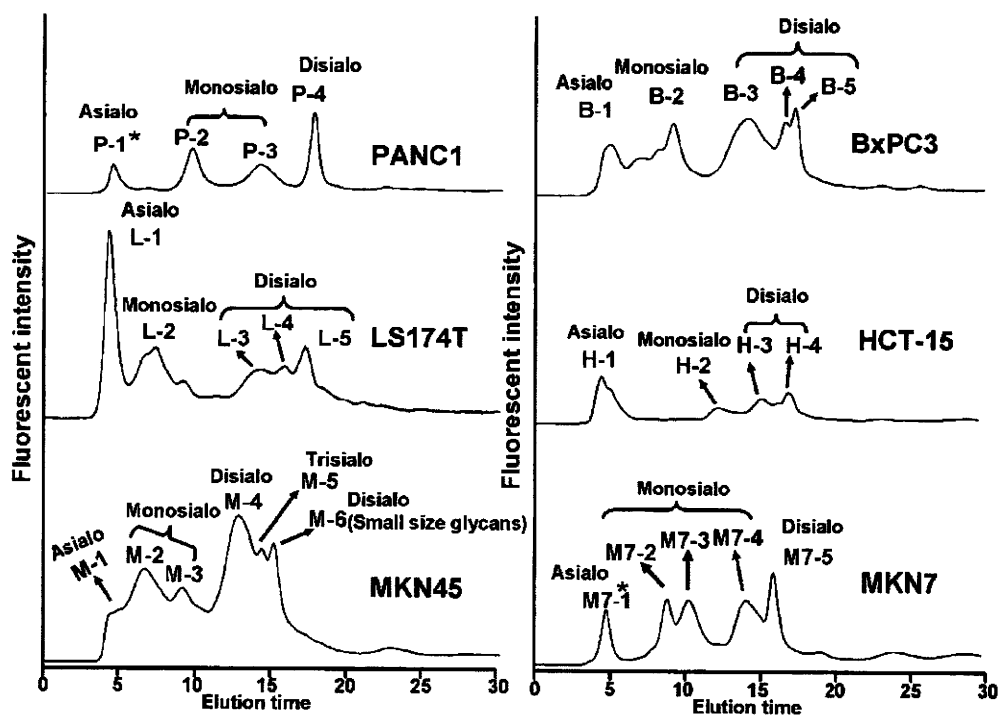


Fig.122 Separation of O-glycan pool derived from epithelial cancer cells by serotonin affinity chromatography

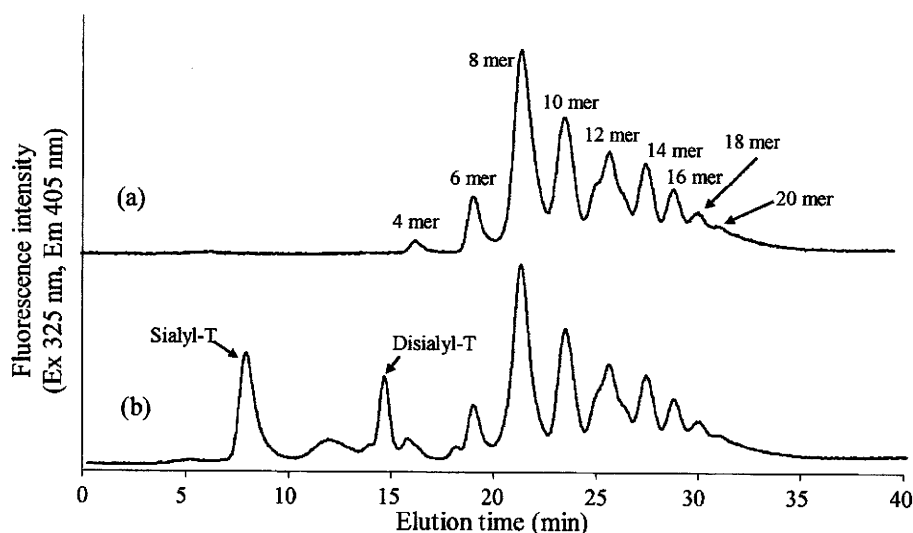


Fig.123 Serotonin affinity chromatography of HA oligosaccharides and mucin-type O-glycans. (a) 2AA-labeled HA oligosaccharides (4-20 mer) and (b) a mixture of mucin-type O-glycans from bovine fetuin and HA oligosaccharides. Analytical conditions; column, LA-serotonin (4.6 x 150 mm). flow rate, 0.5 mL/min. eluent; solvent A, water. solvent B, 50 mM Ammonium acetate in water. gradient conditions, a linear gradient (5-75 % solvent B) from 2 to 45 min and 75% solvent B from 37 to 45 min.

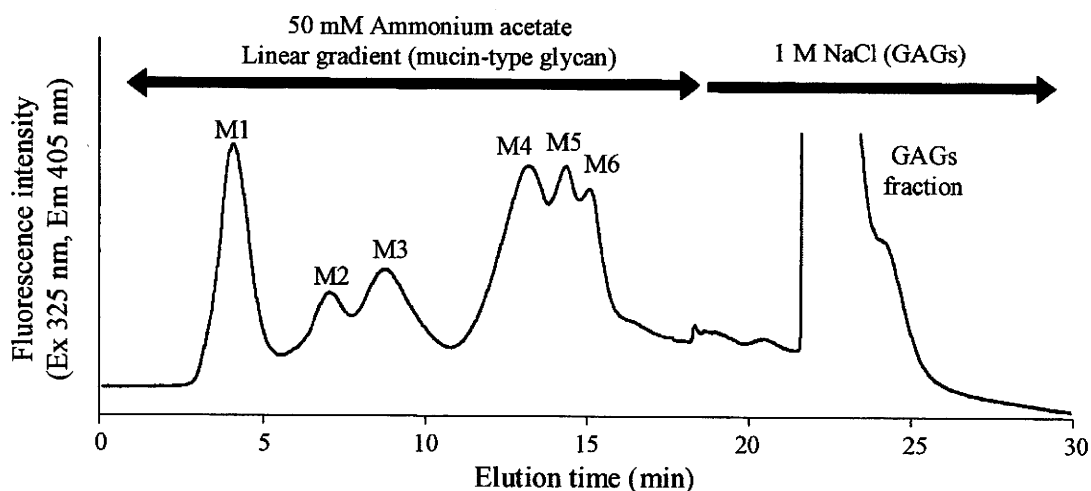


Fig.124 Serotonin affinity chromatography of O-linked glycans derived from HCT116 cell. Analytical conditions; column, LA-serotonin (4.6 x 150 mm). flow rate, 0.5 mL/min. eluent; solvent A, water. solvent B, 50 mM Ammonium acetate in water. gradient conditions, a linear gradient (5-40 % solvent B) from 2 to 20 min and 1 M NaCl from 20 to 45 min.

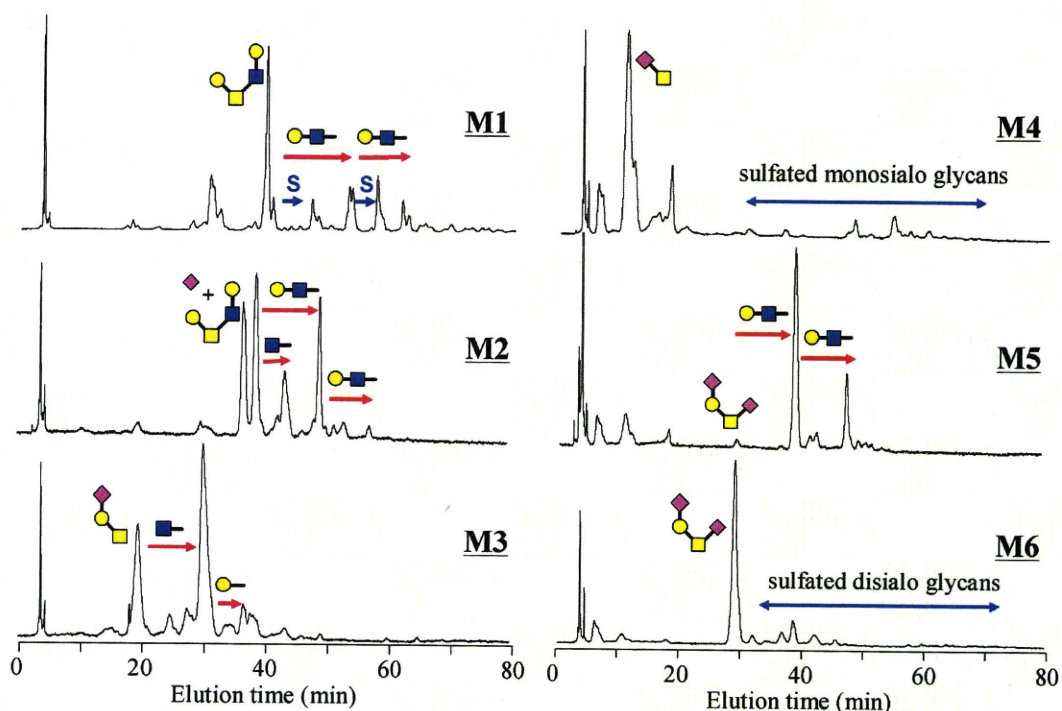


Fig.125 NP-HPLC analysis of mucin-type O-glycans from HCT116 cell. Analytical conditions: column, TSK-GEL Amide-80 (4.6 x 250 mm). flow rate, 0.8 mL/min. eluent, solvent A, 0.1% CH₃COOH in MeCN. solvent B, 0.2% CH₃COOH/0.2% triethylamine in water. gradient conditions: a linear gradient (15-50 % solvent B) from 5 to 85 min.

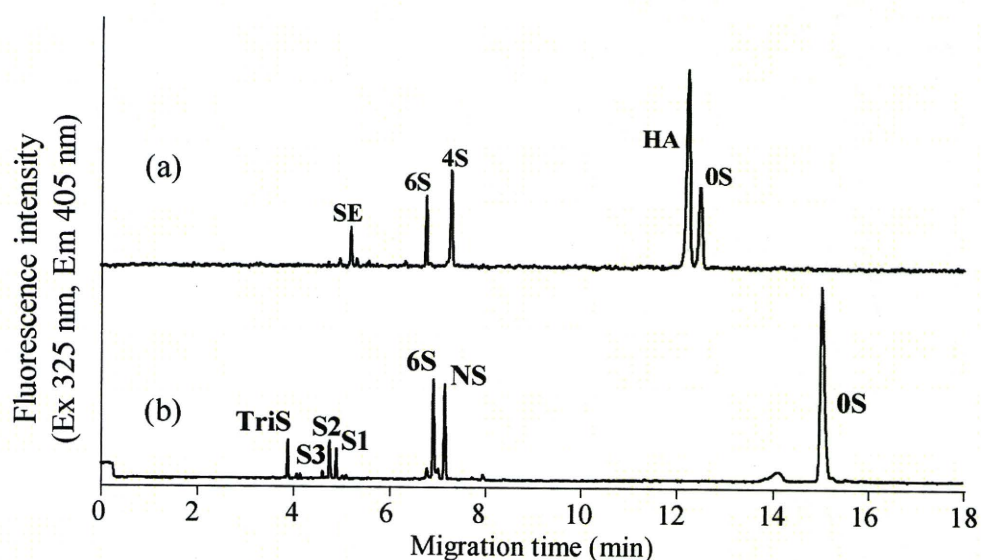
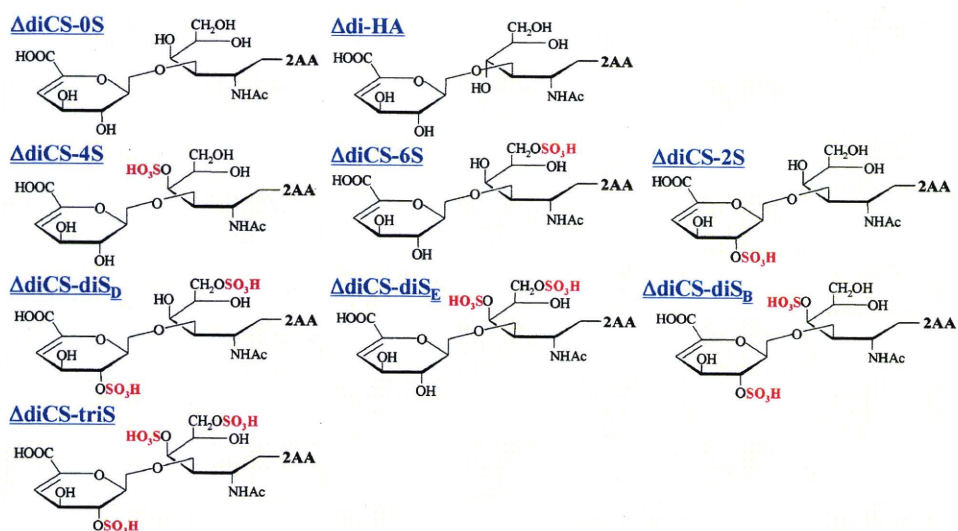


Fig.126 CE analysis of unsaturated disaccharides from HCT116 cell. Analytical conditions; Capillary, fused silica (40 cm x 50 μm.i.d). Buffer, 100 mM Tris-phosphate buffer (pH 3.0). Applied voltage, 25 kV. Injection, pressure method (1.0 psi, 10 sec). Temperature, 25 °C. Detection, He-Cd laser induced fluorescent detection (Ex: 325 nm, Em: 405 nm).

CS and HA unsaturated disaccharides



HS unsaturated disaccharides

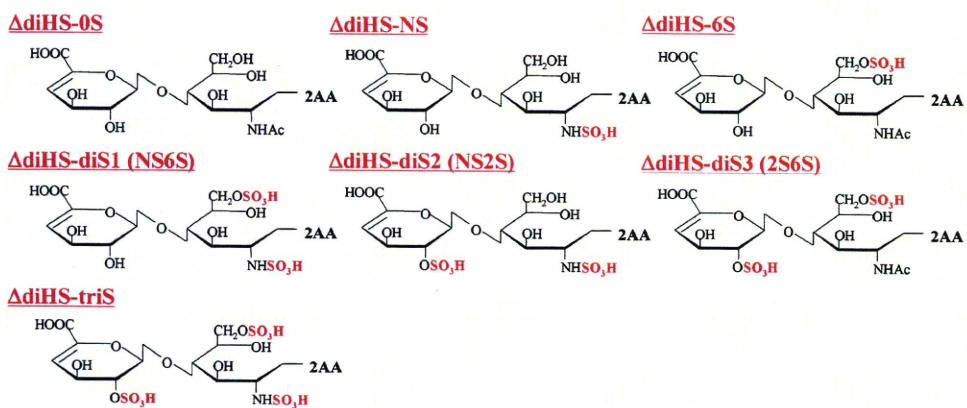


Fig.127 Structures of unsaturated disaccharides from CS and HS.

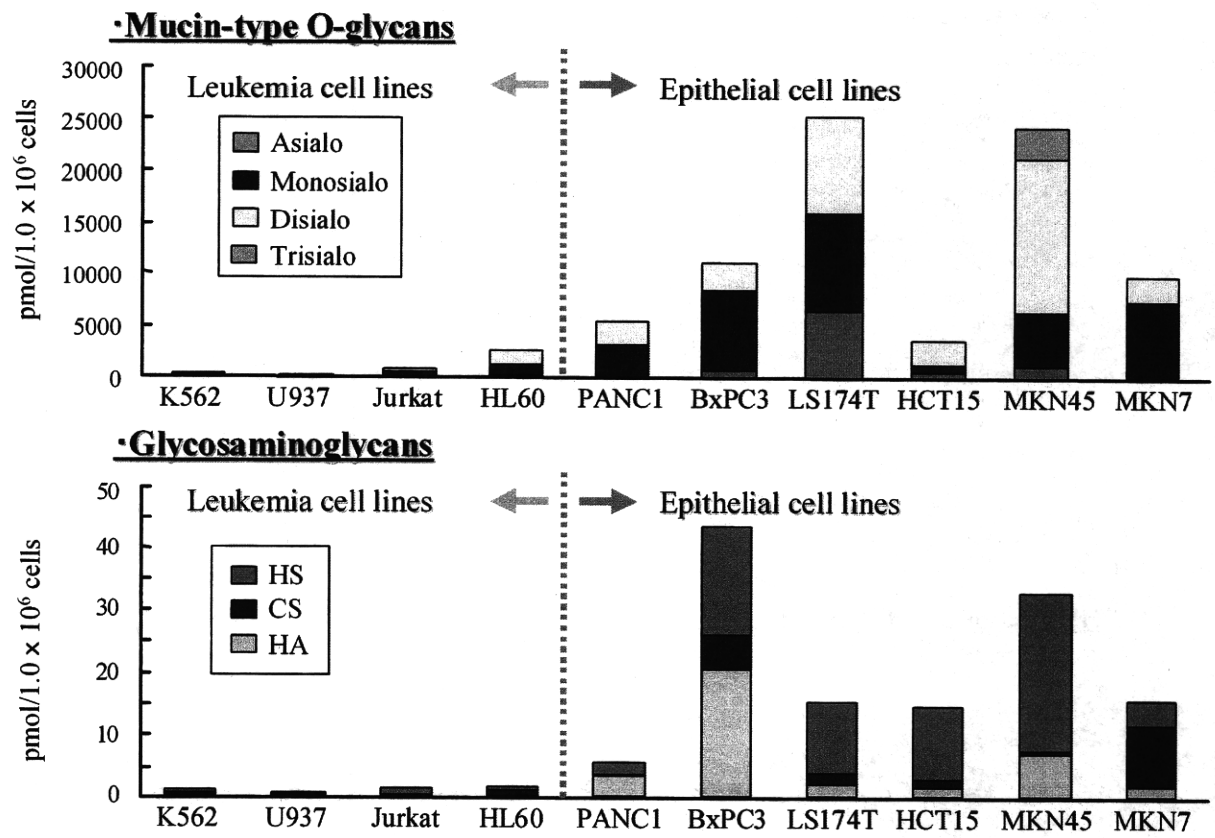
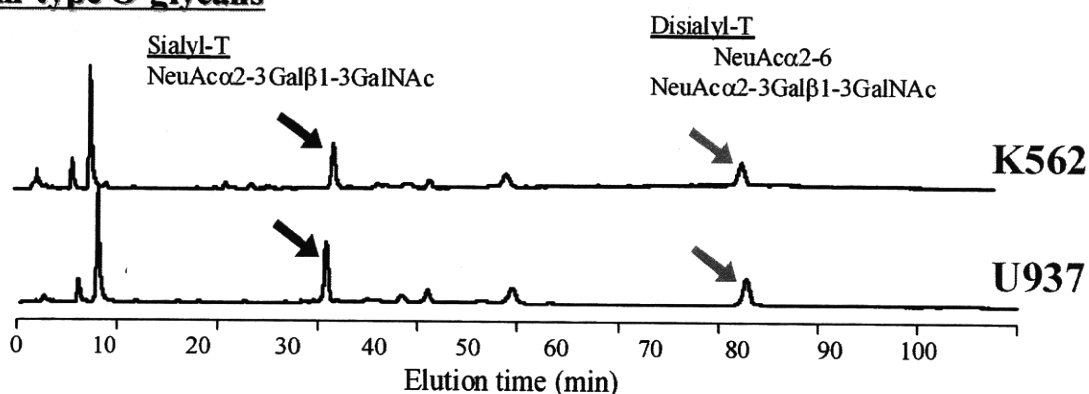


Fig.128 Comparison of the amounts of O-glycans expressed on cancer cells.

•Mucin-type O-glycans



•Glycosaminoglycans (CS)

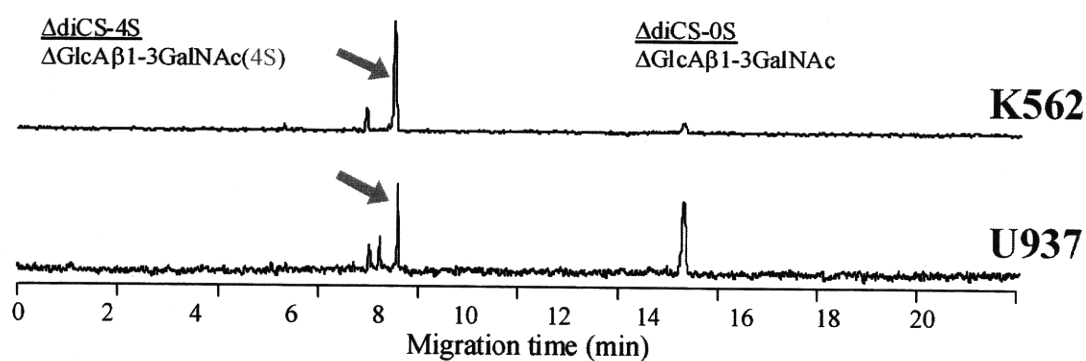


Fig.129 CE analysis of unsaturated disaccharides from K562 and U937 cell. Analytical conditions; Capillary, fused silica (40 cm x 50 μ m.i.d). Buffer, 100 mM Tris-phosphate buffer (pH 3.0). Applied voltage, 25 kV. Injection, pressure method (1.0 psi, 10 sec). Temperature, 25 $^{\circ}$ C. Detection, He-Cd laser induced fluorescent detection (Ex: 325 nm, Em: 405 nm).