Experimental MS-MS fragmentations series for native, methylated and synthetic macrocyclic Mcc J25.

Native and methylated native MccJ25		Native	Methylated
Series I – C-terminal y-series			
(GGAGHVPE)**YFVGIGTPISFYG**	y_{13}	1419.71	
(GGAGHVPEY)**FVGIGTPISFYG**	y_{12}	1257.64	
(GGAGHVPEYF)**VGIGTPISFYG**	y_{11}	1110.55	
(GGAGHVPEYFV)**GIGTPISFYG**	y_{10}	1011.48	
(GGAGHVPEYFVG)**IGTPISFYG**	y_{9}	954.49	
(GGAGHVPEYFVGI)**GTPISFYG**	y_{8}	841.39	
(GGAGHVPEYFVGIG)**TPISFYG**	y_{7}	784.86	
(GGAGHVPEYFVGIGT)**PISFYG**	y_{6}	683.34	697.37
(GGAGHVPEYFVGIGTP)**ISFYG**	y_{5}	586.28	600.3
(GGAGHVPEYFVGIGTPI)**SFYG**	y_{4}	473.20	487.22
(GGAGHVPEYFVGIGTPIS)**FYG**	y_{3}	386.17	400.21
(GGAGHVPEYFVGIGTPISF)**YG**	y_{2}	239.10	253.12
Series II – Internal fragments (b/a cleavage)			
(GGAGHVPEYFVGIGT)**PISFY**(G)		608.30/580.27	608.35/580.33
(GGAGHVPEYFVGIGT)**PISF**(YG)		445.24/417.25	445.26
(GGAGHVPEYFVGIGT)**PIS**(FYG)		298.17/270.17	298.19/270.19
(GGAGHVPEYFVGIGT)**PI**(SFYG)		211.14/183.15	211.14/183.15
Series III – Dehydrated (-18) N-terminal b- and a-series			
GGAGHVPEYFVGIGT(PISFYG)	b_{15}/a_{15}	1424.66/1396.67	
GGAGHVPEYFVGIG(TPISFYG)	b_{14}/a_{14}	1323.55/1295.55	
GGAGHVPEYFVGI(GTPISFYG)	b_{13}/a_{13}	1266.58/1238.63	1266.66/1238.67
GGAGHVPEYFVG(IGTPISFYG)	b_{12}/b_{12}	1153.53/1125.5	1153.58/1125.56
GGAGHVPEYFV(GIGTPISFYG)	b_{11}/a_{11}	1096.52/1068.51	1096.54/1068.55
GGAGHVPEYF(VGIGTPISFYG)	b_{10}/a_{10}	997.45/969.47	997.47/969.49
GGAGHVPEY(FVGIGTPISFYG)	b_{9}/a_{9}	850.38/822.37	850.41/822.41
GGAGHVPE(YFVGIGTPISFYG)	b_{8}/a_{8}	687.31/659.32	687.33/659.35
Series IV – Internal fragments MS^3 m/z 687 (Ion trap data)			
GGAGH(V)**PE**(YFVGIGTPISFYG)		588.2	
Internal fragments MS^3 m/z 687, MS^4 588 (Ion trap data)			
GGAG(HV)**PE**(YFVGIGTPISFYG)		451.0	
GGA(GHV)**PE**(YFVGIGTPISFYG)		394.1	
GG(AGHV)**PE**(YFVGIGTPISFYG)		323.2	
Series IV – Internal fragments MS^3 m/z 659 (Ion trap data)			
GGAGHVP(17)**E**(YFVGIGTPISFYG)		642.3	
GGAGHV(P(17))**E**(YFVGIGTPISFYG)		545.0/517.2	
GGAGH(VP(17))**E**(YFVGIGTPISFYG)		445.9/417.9	
GGAG(HVP(17))**E**(YFVGIGTPISFYG)		308.7	
GGA(GHVP(17))**E**(YF(VGIGTPISFYG)		251.8	
GG(AGHVP(17))**E**(YFVGIGTPISFYG)		180.4	
Series V – Sterically linked b- (dehydrated, -18) and y-series			
GGAGHVPEYFVGIGTP(I)**SFYG**	$b_{16}+y_{4}$	1993.91	
GGAGHVPEYFVGIGT(PI)**SFYG**	$b_{15}+y_{4}$	1896.81	
GGAGHVPEYFVGIG(TPI)**SFYG**	$b_{14}+y_{4}$	1795.83	
GGAGHVPEYFVGI(GTPI)**SFYG**	$b_{13}+y_{4}$	1738.79	1752.92
GGAGHVPEYFVG(IGTPI)**SFYG**	$b_{12}+y_{4}$	1625.68	1639.79
GGAGHVPEYFV(GIGTPI)**SFYG**	$b_{11}+y_{4}$	1568.65	1582.78
GGAGHVPEYF(VGIGTPI)**SFYG**	$b_{10}+y_{4}$	1469.61	1483.70
GGAGHVPEY(FVGIGTPI)**SFYG**	$b_{9}+y_{4}$	1322.55	1336.62
GGAGHVPE(YFVGIGTPI)**SFYG**	$b_{8}+y_{4}$	1159.53	1173.57

Series VI – Sterically linked b- (dehydrated, -18) and y-series

GGAGHVPEYFVGIG(T)**PISFYG**	$b_{14}+y_6$	2005.98	
GGAGHVPEYFVGI(GT)**PISFYG**	$b_{13}+y_6$	1948.95	1963.06
GGAGHVPEYFVG(IGT)**PISFYG**	$b_{12}+y_6$	1835.82	1851.00
GGAGHVPEYFV(GIGT)**PISFYG**	$b_{11}+y_6$	1778.85	
GGAGHVPEYF(VGIGT)**PISFYG**	$b_{10}+y_6$	1679.72	1693.90
GGAGHVPEY(FVGIGT)**PISFYG**	$b_{9}+y_6$	1532.73	
GGAGHVPE(YFVGIGT)**PISFYG**	b_8+y_6	1369.66	

Synthetic macrocyclic peptide. All fragments are internal.

Series I

GGAGHVPEYFVGIGTP(I)**SFYG**	1993.91
GGAGHVPEYFVGIGT(PI)**SFYG**	1896.81
GGAGHVPEYFVGIG(TPI)**SFYG**	1795.84
GGAGHVPEYFVGI(GTPI)**SFYG**	1738.79
GGAGHVPEYFVG(IGTPI)**SFYG**	1625.68
GGAGHVPEYFV(GIGTPI)**SFYG**	1568.65
GGAGHVPEYF(VGIGTPI)**SFYG**	1469.61
GGAGHVPEY(FVGIGTPI)**SFYG**	1322.55
GGAGHVPE(YFVGIGTPI)**SFYG**	1159.52
GGAGHVP(EYFVGIGTPI)**SFYG**	(1030.47)
GGAGHV(PEYFVGIGTPI)**SFYG**	933.42
GGAGH(VPEYFVGIGTPI)**SFYG**	834.39

Series II

GGAGHVPEYFVG(IGT)**PISFYG**	1835.89
GGAGHVPEYFV(GIGT)**PISFYG**	1778.85
GGAGHVPEYF(VGIGT)**PISFYG**	1679.72
GGAGHVPEY(FVGIGT)**PISFYG**	1532.73
GGAGHVPE(YFVGIGT)**PISFYG**	1369.66

Series III

GGAGHVPEYFVGIGT(PI)**SFYG**	1896.91
GGAGHVPEYFVGIGT(PIS)**FYG**	1809.84
GGAGHVPEYFVGIGT(PISF)**YG**	1662.77
GGAGHVPEYFVGIGT(PISFY)**G**	1499.70
GGAGHVPEYFVGIGT(PISFYG)	1442.66

Series IV

GGAGHV(PEYFVGIGTPI)**SFYG**	933.42
GGAGHV(PEYFVGIGTPIS)**FYG**	846.41
GGAGHV(PEYFVGIGTPISF)**YG**	699.33
GGAGHV(PEYFVGIGTPISFY)**G**	536.26
GGAGHV(PEYFVGIGTPISFYG)	479.24
G)**GAGHV**(PEYFVGIGTPISFYG	422.23
GG)**AGHV**(PEYFVGIGTPISFYG	(365.20)
GGA)**GHV**(PEYFVGIGTPISFYG	294.15

All masses are given as MH+. Masses in parantheses are overlapped or of low intensity.