

Electronic Supplementary Information

Differentiation of Isomeric Ginsenosides by using Electron-Induced Dissociation Mass Spectrometry

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Figure S-1

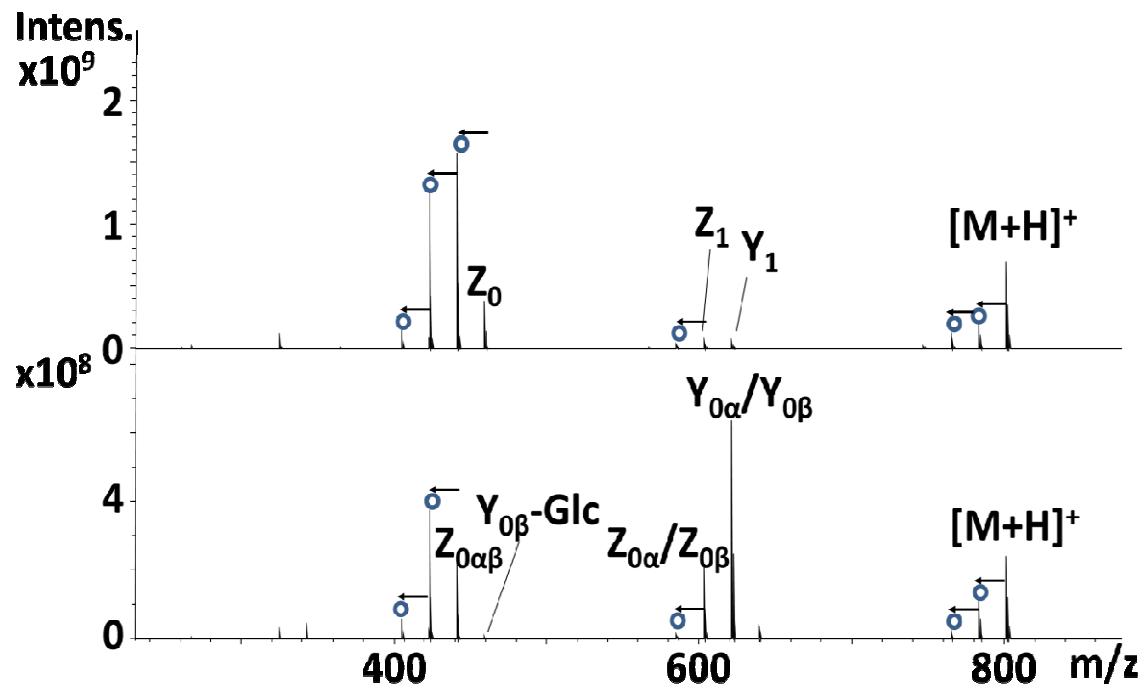


Figure S-2

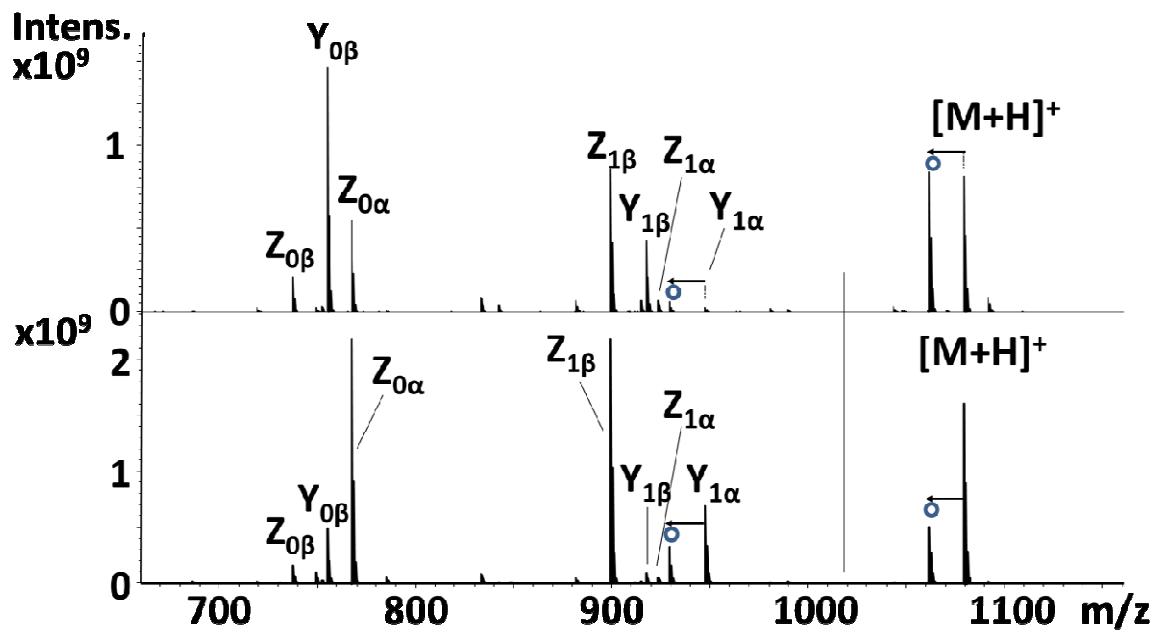


Figure S-3

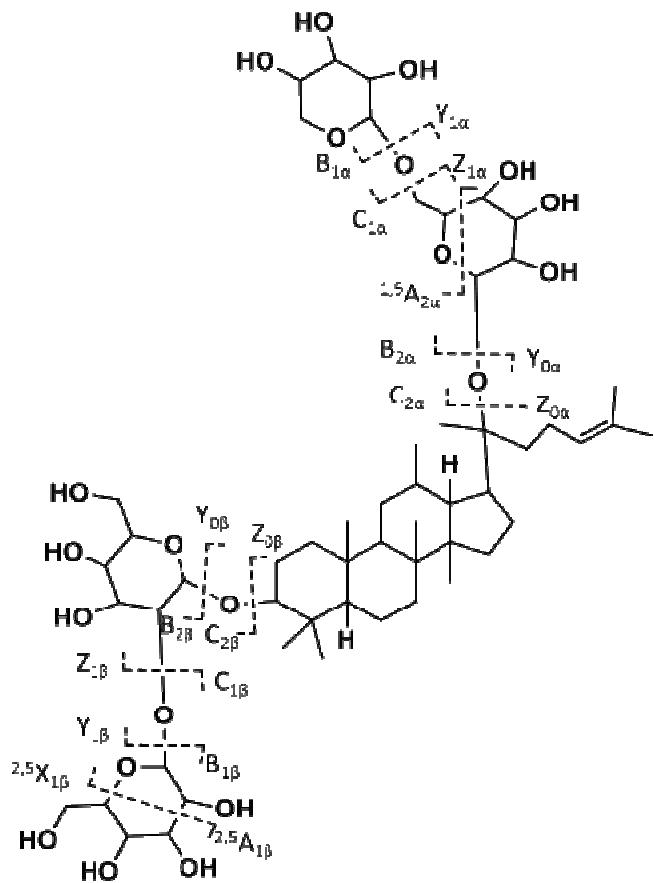


Figure S-4

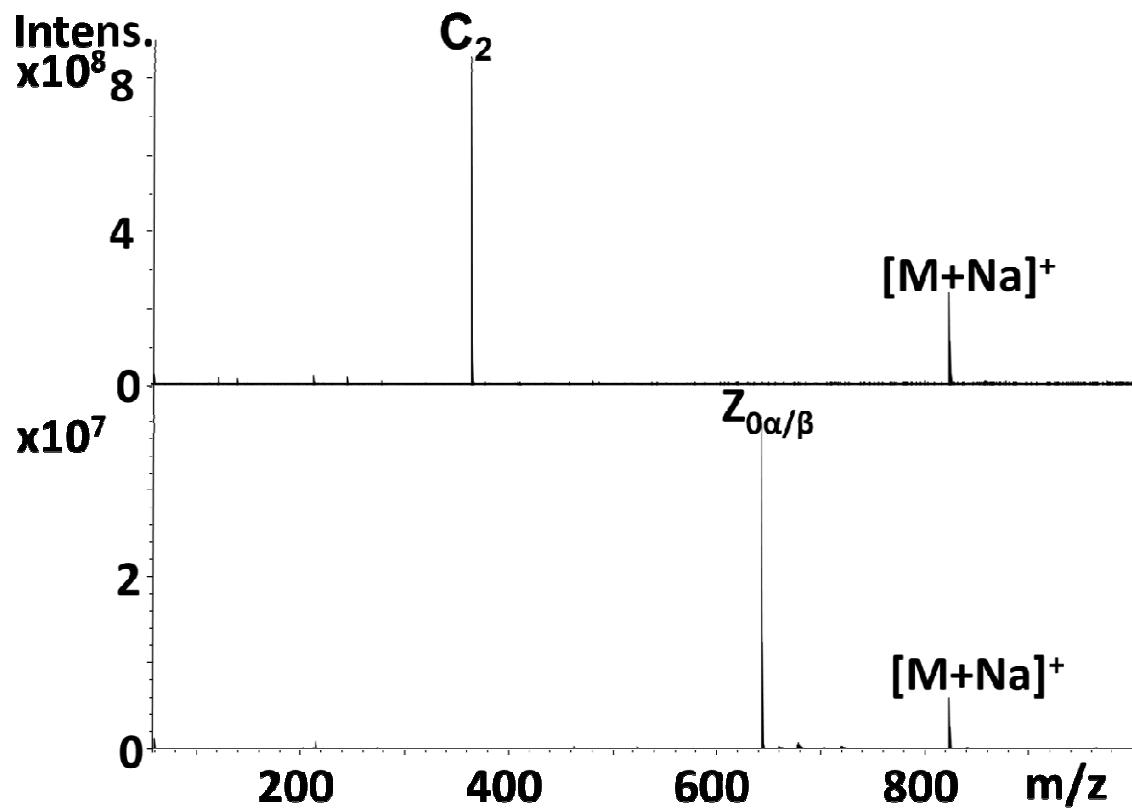


Figure S-5

The structure of Rg₁ was generated using Chem3D Pro 7.0 (Cambridge Soft, Cambridge, MA, USA). It was subjected to energy minimization by the MM2 method in Chem3D. The default values of the MM2 force field parameters in the software programs were used for all the calculations.

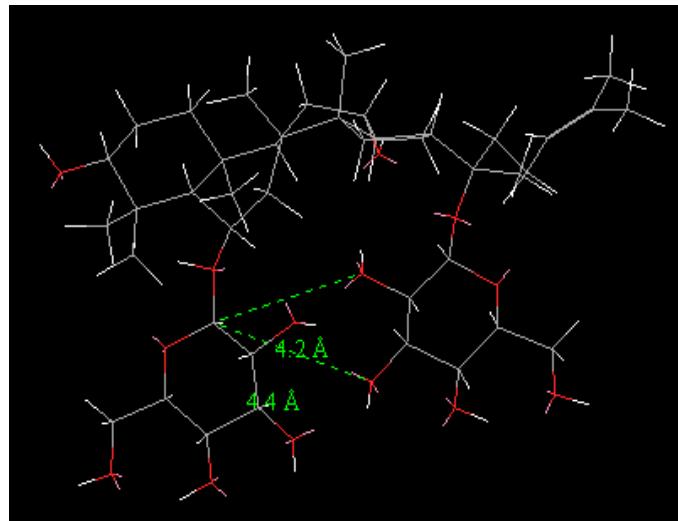


Figure S-6

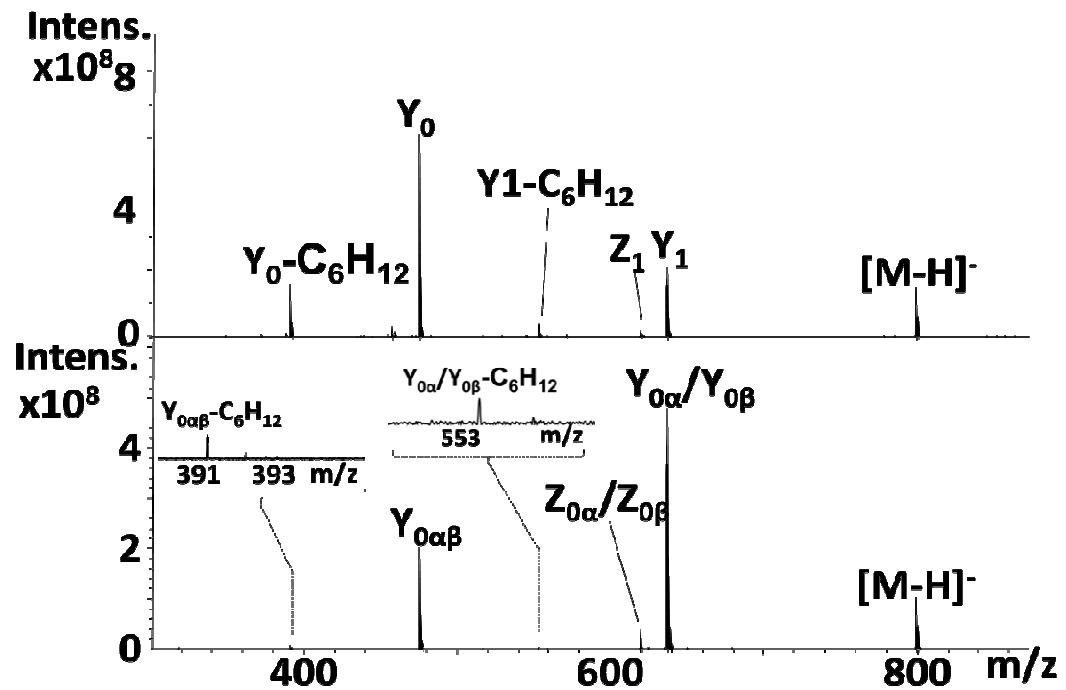
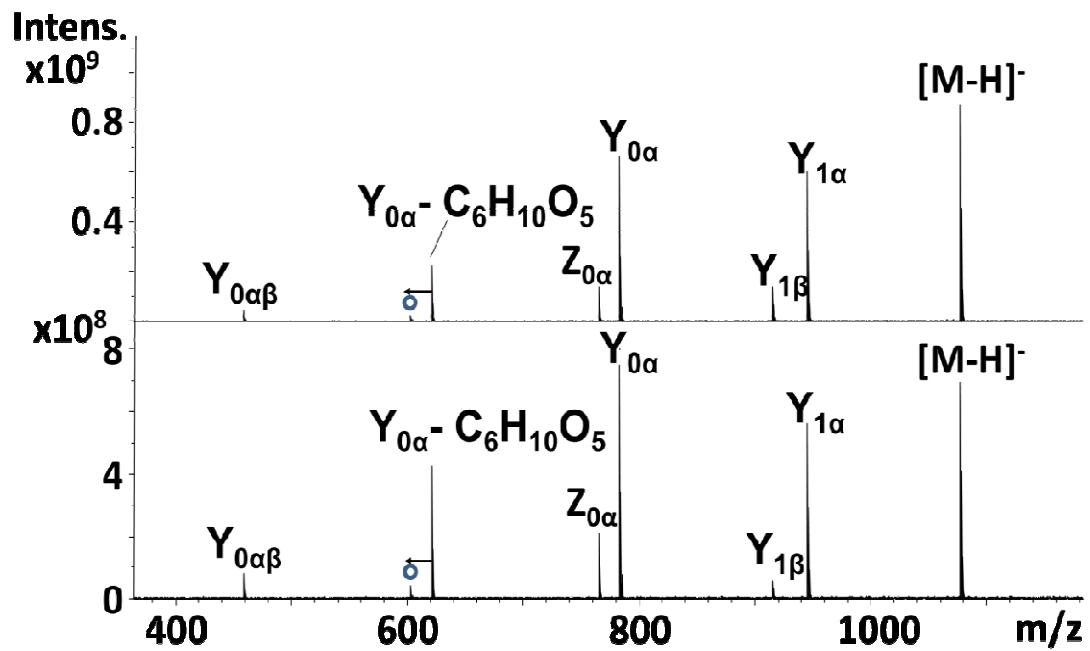


Figure S-7



Scheme S-1

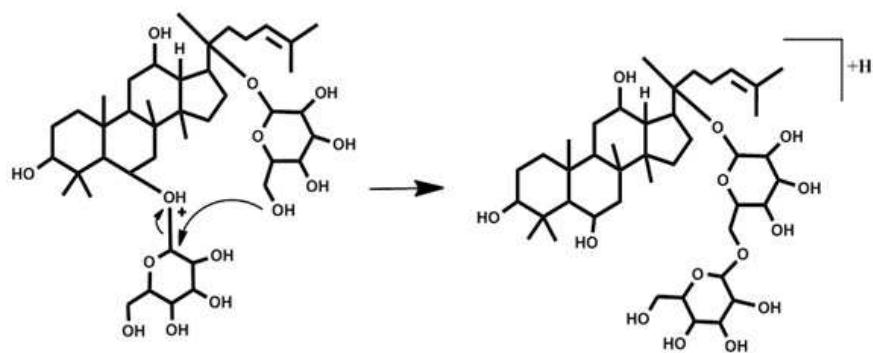


Table S-1

Expt. mass	Molecular formula	Assignment	Loss or Gain	Theo.mass	Error (ppm)	S/N
801.4995	C ₄₂ H ₇₃ O ₁₄ ⁺	[M+H]		801.4995	0.02	124490.2
800.4908	C ₄₂ H ₇₂ O ₁₄ ^{+•}	M		800.4917	-1.07	342.3
783.4883	C ₄₂ H ₇₁ O ₁₃ ⁺	[M+H-H ₂ O]		783.4889	-0.79	44.9
782.4822	C ₄₂ H ₇₀ O ₁₃ ^{+•}	[M-H ₂ O] ^{+•}		782.4811	1.41	44.6
683.437	C ₃₇ H ₆₃ O ₁₁ ⁺	^{1,5} X ₁		683.4365	0.75	14
653.4247	C ₃₆ H ₆₁ O ₁₀ ⁺	Y ₁	-H	653.4259	-1.87	29.5
637.4311	C ₃₆ H ₆₁ O ₉ ⁺	Z ₁	-H	637.4310	0.14	47.9
621.4361	C ₃₆ H ₆₁ O ₈ ⁺	Z ₁ -H ₂ O	H	621.4361	0.01	190.8
603.4258	C ₃₆ H ₅₉ O ₇ ⁺	Z ₁ -2H ₂ O	H	603.4255	0.45	60.9
563.3939	C ₃₃ H ₅₅ O ₇ ⁺	^{1,5} X ₀	-H	563.3942	-0.59	111.6
491.3729	C ₃₀ H ₅₁ O ₅ ⁺	Y ₀	-H	491.3731	-0.41	27.9
475.3777	C ₃₀ H ₅₁ O ₄ ⁺	Z ₀	-H	475.3782	-1.02	2062
457.3671	C ₃₀ H ₄₉ O ₃ ⁺	Z ₀ -H ₂ O	-H	457.3676	-1.14	297.2
439.3565	C ₃₀ H ₄₇ O ₂ ⁺	Z ₀ -2H ₂ O	-H	439.3571	-1.27	162.8
421.3463	C ₃₀ H ₄₅ O ⁺	Z ₀ -3H ₂ O	-H	421.3465	-0.46	105.8
400.7484	C ₄₂ H ₇₃ O ₁₄ ^{2+•}	[M+H] ^{2+•}		400.7495	-2.66	714.1
327.1275	C ₁₂ H ₂₃ O ₁₀ ⁺	C ₂	H	327.1286	-3.28	27.4
309.1175	C ₁₂ H ₂₁ O ₉ ⁺	B ₂	-H	309.1180	-1.65	43.4
215.1791	C ₁₆ H ₂₃ ⁺	Z ₀ -2H ₂ O-C ₁₄ H ₂₄ O ₂	-2H	215.1794	-1.52	21.9
207.1737	C ₁₄ H ₂₃ O ⁺	Z ₀ -C ₁₆ H ₂₈ O ₃	-H	207.1743	-3.10	50.5
189.1632	C ₁₄ H ₂₁ ⁺	Z ₀ -H ₂ O-C ₁₆ H ₂₈ O ₃	-H	189.1638	-3.05	28.2
143.1062	C ₈ H ₁₅ O ₂ ⁺	C ₈ H ₁₅ O ₂		143.1067	-3.19	2026.4
127.1114	C ₈ H ₁₅ O ⁺	C ₈ H ₁₅ O		127.1117	-2.69	135.7

Table S-2

Expt. mass	Molecular formula	Assignment	Loss or Gain	Theo.mass	Error (ppm)	S/N
801.4993	C ₄₂ H ₇₃ O ₁₄ ⁺	[M+H]		801.4995	-0.23	53091.8
783.4894	C ₄₂ H ₇₁ O ₁₃ ⁺	[M+H-H ₂ O]		783.4889	0.61	3775.4
765.4801	C ₄₂ H ₆₉ O ₁₂ ⁺	[M+H-2H ₂ O]		765.4784	2.28	561.2
744.4650	C ₃₉ H ₆₈ O ₁₃ ^{+•}	[M-C ₃ H ₄ O] ^{+•}	H	744.4654	-0.60	7
727.4617	C ₃₉ H ₆₇ O ₁₂ ⁺	^{3,5} X ₁		727.4627	-1.38	14.5
639.4460	C ₃₆ H ₆₃ O ₉ ⁺	Y ₁	H	639.4467	-1.03	40.8
621.4361	C ₃₆ H ₆₁ O ₈ ⁺	Z ₁	-H	621.4361	0.01	51.4
603.4242	C ₃₆ H ₅₉ O ₇ ⁺	Z ₁ -H ₂ O	-H	603.4255	-2.21	78.7
585.4159	C ₃₆ H ₅₇ O ₆ ⁺	Z ₁ -2H ₂ O	-H	585.4150	1.60	21.2
477.3938	C ₃₀ H ₅₃ O ₄ ⁺	Y ₀	H	477.3938	-0.08	20.3
459.3826	C ₃₀ H ₅₁ O ₃ ⁺	Z ₀	-H	459.3833	-1.46	1625.9
441.3720	C ₃₀ H ₄₉ O ₂ ⁺	Z ₀ -H ₂ O	-H	441.3727	-1.60	927.7
423.3614	C ₃₀ H ₄₇ O ⁺	Z ₀ -2H ₂ O	-H	423.3621	-1.75	728
405.3509	C ₃₀ H ₄₅ ⁺	Z ₀ -3H ₂ O	-H	405.3516	-1.67	221.7
400.7492	C ₄₂ H ₇₃ O ₁₄ ^{2+•}	[M+H] ^{2+•}		400.7495	-0.67	73.1
375.2888	C ₂₄ H ₃₉ O ₃ ⁺	Z ₀ -C ₆ H ₁₂	-2H	375.2894	-1.52	28
367.2993	C ₂₆ H ₃₉ O ⁺	Z ₀ -2H ₂ O-C ₄ H ₈	-2H	367.2995	-0.66	38.8
349.2880	C ₂₆ H ₃₇ ⁺	Z ₀ -3H ₂ O-C ₄ H ₈	-2H	349.2890	-2.80	37.6
343.1226	C ₁₂ H ₂₃ O ₁₁ ⁺	C ₂	H	343.1235	-2.59	56.1
325.1122	C ₁₂ H ₂₁ O ₁₀ ⁺	B ₂	-H	325.1129	-2.22	221.7
215.1790	C ₁₆ H ₂₁ ⁺	Z ₀ -2H ₂ O-C ₁₄ H ₂₄ O ₂	-H	215.1794	-1.98	67.2
207.1738	C ₁₄ H ₂₃ O ⁺	Z ₀ -C ₁₆ H ₂₈ O ₃	-H	207.1743	-2.62	39.5
189.1633	C ₁₄ H ₂₁ ⁺	Z ₀ -H ₂ O-C ₁₆ H ₂₈ O ₃	-H	189.1638	-2.52	73
127.1114	C ₈ H ₁₅ O ⁺	C ₈ H ₁₅ O		127.1117	-2.69	91.7
CID of [M+H] ⁺						
783.4905	C ₄₂ H ₇₁ O ₁₃ ⁺	[M+H-H ₂ O]		783.4889	2.02	607.8
765.4796	C ₄₂ H ₆₉ O ₁₂ ⁺	[M+H-2H ₂ O]		765.4784	1.63	364.9
621.4367	C ₃₆ H ₆₁ O ₈ ⁺	Z ₁	-H	621.4361	0.97	763.1
603.4259	C ₃₆ H ₅₉ O ₇ ⁺	Z ₁ -H ₂ O	-H	603.4255	0.61	851.7
585.4153	C ₃₆ H ₅₇ O ₆ ⁺	Z ₁ -2H ₂ O	-H	585.4150	0.57	477.5
459.3824	C ₃₀ H ₅₁ O ₃ ⁺	Z ₀	-H	459.3833	-1.90	1597.7
441.3719	C ₃₀ H ₄₉ O ₂ ⁺	Z ₀ -H ₂ O	-H	441.3727	-1.83	7110.4
423.3614	C ₃₀ H ₄₇ O ⁺	Z ₀ -2H ₂ O	-H	423.3621	-1.75	5618.5
405.3513	C ₃₀ H ₄₅ ⁺	Z ₀ -3H ₂ O	-H	405.3516	-0.69	1168.1

Table S-3

Expt. mass	Molecular formula	Assignment	Loss or Gain	Theo.mass	Error (ppm)	S/N
801.4993	C ₄₂ H ₇₃ O ₁₄ ⁺	[M+H]		801.4995	-0.23	15716.8
800.4917	C ₄₂ H ₇₂ O ₁₄ ⁺ •	M ⁺ •		800.4917	0.06	37.6
783.4893	C ₄₂ H ₇₁ O ₁₃ ⁺	[M+H-H ₂ O]		783.4889	0.49	471.7
765.4772	C ₄₂ H ₆₉ O ₁₂ ⁺	[M+H-2H ₂ O]		765.4784	-1.51	10.8
639.4454	C ₃₆ H ₆₃ O ₉ ⁺	Y _{0α/β}	H	639.4467	-1.97	47.2
621.4356	C ₃₆ H ₆₁ O ₈ ⁺	Z _{0α/β}	-H	621.4361	-0.80	815.6
603.4245	C ₃₆ H ₅₉ O ₇ ⁺	Z _{0α/β} -H ₂ O	-H	603.4255	-1.71	119.8
459.3816	C ₃₀ H ₅₁ O ₃ ⁺	Y _{0α/β} -Glc		459.3833	-3.75	8.2
458.3756	C ₃₀ H ₅₀ O ₃ ⁺ •	Y _{0α/β} •-Glc		458.3754	0.33	24.6
441.3718	C ₃₀ H ₄₉ O ₂ ⁺	Z _{0αβ}	-2H	441.3727	-2.05	205.6
423.3614	C ₃₀ H ₄₇ O ⁺	Z _{0αβ} -H ₂ O	-2H	423.3621	-1.75	345.4
405.3508	C ₃₀ H ₄₅ ⁺	Z _{0αβ} -2H ₂ O	-2H	405.3516	-1.92	74.2
400.7509	C ₄₂ H ₇₃ O ₁₄ ^{2+•}	[M+H] ^{2+•}		400.7492	4.24	34.4
384.3384	C ₂₇ H ₄₄ O ⁺ •	[M -2Glc]		384.3387	-0.69	40.3
343.1228	C ₁₂ H ₂₃ O ₁₁ ⁺	C ₂	H	343.1235	-1.98	77.3
325.1120	C ₁₂ H ₂₁ O ₁₀ ⁺	B ₂	-H	325.1129	-2.84	56.6
215.1789	C ₁₆ H ₂₁ ⁺	Z _{0αβ} -H ₂ O-C ₁₄ H ₂₆ O	-H	215.1794	-2.26	16.2
207.1736	C ₁₄ H ₂₃ O ⁺	Z _{0αβ} -C ₁₆ H ₂₆ O	-H	207.1743	-3.44	25.3
189.1633	C ₁₄ H ₂₁ ⁺	Z _{0αβ} -H ₂ O-C ₁₆ H ₂₆ O	-H	189.1638	-2.42	25.9
127.1114	C ₈ H ₁₅ O ⁺	C ₈ H ₁₅ O		127.1117	-2.61	23.2
CID of [M+H] ⁺						
783.4902	C ₄₂ H ₇₁ O ₁₃ ⁺	[M+H-H ₂ O]		783.4889	1.63	413.4
765.4794	C ₄₂ H ₆₉ O ₁₂ ⁺	[M+H-2H ₂ O]		765.4784	1.37	269.7
621.4356	C ₃₆ H ₆₁ O ₈ ⁺	Z _{0α/β}	-H	621.4361	-0.80	2541.7
603.4253	C ₃₆ H ₅₉ O ₇ ⁺	Z _{0α/β} -H ₂ O	-H	603.4255	-0.38	847.8
585.4149	C ₃₆ H ₅₇ O ₆ ⁺	Z _{0α/β} -2H ₂ O	-H	585.4149	-0.11	173.2
459.3830	C ₃₀ H ₅₁ O ₃ ⁺	Y _{0α/β} -Glc		459.3833	-0.59	169.7
441.3721	C ₃₀ H ₄₉ O ₂ ⁺	Z _{0αβ}	-2H	441.3727	-1.38	953.8
423.3615	C ₃₀ H ₄₇ O ⁺	Z _{0αβ} -H ₂ O	-2H	423.3621	-1.52	1736.4
405.3511	C ₃₀ H ₄₅ ⁺	Z _{0αβ} -2H ₂ O	-2H	405.3516	-1.18	809.4

Table S-4

Expt. mass	Molecular formula	Assignment	Loss or Gain	Theo.mass	Error (ppm)	S/N
1079.5997	C ₅₃ H ₉₁ O ₂₂ ⁺	[M+H]		1079.5995	-0.14	3778.1
1061.5891	C ₅₃ H ₈₉ O ₂₁ ⁺	M-H ₂ O		1061.5898	0.67	3792.8
947.5574	C ₄₈ H ₈₃ O ₁₈ ⁺	Y _{1α}	H	947.5584	1.06	128.6
929.5468	C ₄₈ H ₈₁ O ₁₇ ⁺	Z _{1α}	-H	929.5470	0.19	286.8
917.5468	C ₄₇ H ₈₁ O ₁₇ ⁺	Y _{1β}	H	917.5468	-0.03	1988.3
899.5363	C ₄₇ H ₇₉ O ₁₆ ⁺	Z _{1β}	-H	899.5363	0.04	3990.8
767.4940	C ₄₂ H ₇₁ O ₁₂ ⁺	Z _{0α}	-H	767.4934	-0.79	2911.5
755.4940	C ₄₁ H ₇₁ O ₁₂ ⁺	Y _{0β}	H	755.4929	-1.46	7833.1
737.4834	C ₄₁ H ₆₉ O ₁₁ ⁺	Z _{0β}	-H	737.4831	-0.46	1124
CID of [M+H] ⁺ of Rc						
1079.5993	C ₅₃ H ₉₁ O ₂₂ ⁺	[M+H]		1079.5995	-0.33	6671.3
1061.5906	C ₅₃ H ₈₉ O ₂₁ ⁺	M-H ₂ O		1061.5898	1.43	2062.8
947.5573	C ₄₈ H ₈₃ O ₁₈ ⁺	Y _{1α}	H	947.5584	-0.10	2760.2
929.5468	C ₄₈ H ₈₁ O ₁₇ ⁺	Z _{1α}	-H	929.5470	-0.03	1301.3
917.5471	C ₄₇ H ₈₁ O ₁₇ ⁺	Y _{1β}	H	917.5468	0.30	371.7
899.5360	C ₄₇ H ₇₉ O ₁₆ ⁺	Z _{1β}	-H	899.5363	-0.29	8577.6
767.4930	C ₄₂ H ₇₁ O ₁₂ ⁺	Z _{0α}	-H	767.4934	-1.31	9851.8
755.4939	C ₄₁ H ₇₁ O ₁₂ ⁺	Y _{0β}	H	755.4929	-0.14	2202.9

Table S-5

EID of [M+Na] ⁺ of Rf							
Expt. mass	Molecular formula	Assignment	Loss or Gain	Metal adduct	Theo.mass	Error (ppm)	S/N
823.4816	C ₄₂ H ₇₂ O ₁₄	M		Na ⁺	823.4814	0.21	23872
766.4476	C ₃₉ H ₆₇ O ₁₃ •	M-C ₃ H ₅ O•	H	Na ⁺	766.4474	0.28	16.4
739.3879	C ₃₆ H ₆₀ O ₁₄	M-C ₆ H ₁₂	-H	Na ⁺	739.3875	0.50	30.9
723.3937	C ₃₆ H ₆₀ O ₁₃	M-C ₆ H ₁₂ O		Na ⁺	723.3926	1.50	17.6
703.4388	C ₃₈ H ₆₄ O ₁₀	^{0,2} X ₁		Na ⁺	703.4392	-0.52	6
695.3622	C ₃₄ H ₅₆ O ₁₃	M-C ₈ H ₁₆ O	-H	Na ⁺	695.3613	1.28	29.5
689.4241	C ₃₇ H ₆₂ O ₁₀	^{1,5} X ₁		Na ⁺	689.4235	0.84	29.4
681.3460	C ₃₃ H ₅₄ O ₁₃	M-C ₉ H ₁₈ O	-2H	Na ⁺	681.3457	0.50	39.2
643.4185	C ₃₆ H ₆₀ O ₈	Z ₁	-H	Na ⁺	643.4180	0.71	21
585.2888	C ₂₇ H ₄₆ O ₁₂	M-C ₁₆ H ₂₆ O ₂		Na ⁺	585.2881	1.11	27.8
571.2727	C ₂₆ H ₄₄ O ₁₂	M-C ₁₇ H ₂₈ O ₂		Na ⁺	571.2725	0.35	29.6
497.3606	C ₃₀ H ₅₀ O ₄	Y ₀	-H	Na ⁺	497.3601	0.94	26.8
481.3653	C ₃₀ H ₅₀ O ₃	Z ₀	-H	Na ⁺	481.3652	0.17	50.1
441.3730	C ₃₀ H ₄₉ O ₂	Z ₀ -H ₂ O (H)	-H		441.3727	0.66	44.5
423.3624	C ₃₀ H ₄₇ O	Z ₀ -2H ₂ O (H)	-H		423.3621	0.61	128.4
405.3522	C ₃₀ H ₄₅	Z ₀ -3H ₂ O(H)	-H		405.3516	1.53	33.7
365.1055	C ₁₂ H ₂₂ O ₁₁	C ₂	H	Na ⁺	365.1054	0.19	571.2
245.0632	C ₈ H ₁₄ O ₇	^{1,3} A ₂		Na ⁺	245.0632	0.11	289.9
203.0527	C ₆ H ₁₂ O ₆	C ₁	H	Na ⁺	203.0526	0.45	52.9
201.0370	C ₆ H ₁₀ O ₆	C ₁	-H	Na ⁺	201.0370	0.20	211.2
CID of [M+Na] ⁺							
823.4816	C ₄₂ H ₇₂ O ₁₄	M		Na ⁺	823.4814	0.21	168.9
365.1053	C ₁₂ H ₂₂ O ₁₁	C ₂	H	Na ⁺	365.1054	-0.36	912.6

Table S-6

EID of [M+Na] ⁺ of Rg _i							
Expt. mass	Molecular formula	Assignment	Loss or Gain	Metal adduct	Theo.mass	Error (ppm)	S/N
823.4816	C ₄₂ H ₇₂ O ₁₄	M		Na ⁺	823.4814	0.21	25464.3
766.4476	C ₃₉ H ₆₇ O ₁₃ •	M-C ₃ H ₅ O•	H	Na ⁺	766.4474	0.28	118.7
723.3931	C ₃₆ H ₆₀ O ₁₃	M -C ₆ H ₁₂ O		Na ⁺	723.3926	0.67	73.2
703.4389	C ₃₈ H ₆₄ O ₁₀	^{0,2} X _{0β}		Na ⁺	703.4392	-0.38	26.8
689.4235	C ₃₇ H ₆₂ O ₁₀	^{1,5} X _{0β}		Na ⁺	689.4235	-0.03	76.1
659.4130	C ₃₆ H ₆₀ O ₉	Y _{0α/β}	-H	Na ⁺	659.4130	0.07	205.6
643.4180	C ₃₆ H ₆₀ O ₈	Z _{0α/β}	-H	Na ⁺	643.4180	-0.06	1146.1
575.3552	C ₃₁ H ₅₂ O ₈	Z _{0α/β} -C ₅ H ₈		Na ⁺	575.3554	-0.42	655.5
533.3083	C ₂₈ H ₄₆ O ₈	Z _{0α} -C ₈ H ₁₄	-H	Na ⁺	533.3085	-0.35	111.6
519.3289	C ₂₈ H ₄₈ O ₇	Z _{0α/β} -H ₂ O-C ₈ H ₁₀	2H	Na ⁺	519.3292	-0.63	234.9
477.2816	C ₂₅ H ₄₂ O ₇	Z _{0β} -C ₁₁ H ₁₈ O		Na ⁺	477.2823	-1.41	32.6
463.3541	C ₃₀ H ₄₈ O ₂	Z _{0αβ}	-2H	Na ⁺	463.3547	-1.19	93
397.3073	C ₂₅ H ₄₂ O ₂	Z _{0αβ} -C ₅ H ₈	H	Na ⁺	397.3077	-1.01	201.7
203.0523	C ₆ H ₁₂ O ₆	C _{1α/β}	H	Na ⁺	203.0526	-1.52	820.8
201.0366	C ₆ H ₁₀ O ₆	C _{1α/β} -H ₂	-H	Na ⁺	201.0370	-1.79	679.1
CID of [M+Na] ⁺							
823.4816	C ₄₂ H ₇₂ O ₁₄	M		Na ⁺	823.4814	0.21	196.6
643.4175	C ₃₆ H ₆₀ O ₈	Z _{0α/β}	-H	Na ⁺	643.4180	-0.84	1379.2

Table S-7

EID of [M-H] ⁻ of Rf						
Expt. mass	Molecular formula	Assignment	Loss or Gain	Theo.mass	Error(ppm)	S/N
799.4851	C ₄₂ H ₇₁ O ₁₄ ⁻	[M-H]		799.4849	0.21	154601.2
798.4772	C ₄₂ H ₇₀ O ₁₄ ^{..}	[M-2H]		798.4771	0.12	472.7
715.3912	C ₃₆ H ₅₉ O ₁₄ ⁻	M-C ₆ H ₁₂	-H	715.3910	0.24	66.1
672.3727	C ₃₄ H ₅₆ O ₁₃ ^{..}	M-C ₈ H ₁₅ O [.]		672.3726	0.09	50.5
671.3656	C ₃₄ H ₅₅ O ₁₃ ⁻	M-C ₈ H ₁₆ O	-H	671.3648	1.17	30.5
657.3502	C ₃₃ H ₅₃ O ₁₃ ⁻	M-C ₉ H ₁₈ O		657.3492	1.57	101.2
637.4328	C ₃₆ H ₆₁ O ₉ ⁻	Y ₁	H	637.4321	1.09	5247.9
619.4221	C ₃₆ H ₅₉ O ₈ ⁻	Z ₁	-H	619.4215	0.90	101.8
561.2915	C ₂₇ H ₄₅ O ₁₂ ⁻	M-C ₁₅ H ₂₆ O ₂		561.2917	-0.27	37.5
475.3789	C ₃₀ H ₅₁ O ₄ ⁻	Y ₀	H	475.3793	-0.81	1494
391.2847	C ₂₄ H ₃₉ O ₄ ⁻	Y ₀ -C ₆ H ₁₂		391.2854	-1.75	58.2
339.0924	C ₁₂ H ₁₉ O ₁₁ ⁻	C ₂	-H	339.0933	-2.61	103.3
321.0818	C ₁₂ H ₁₇ O ₁₀ ⁻	B ₂	-3H	321.0827	-2.87	80.7
221.0660	C ₈ H ₁₃ O ₇ ⁻	^{1,3} A ₂		221.0667	-3.06	37.6
179.0554	C ₆ H ₁₁ O ₆ ⁻	C ₁	H	179.0561	-3.98	181.4
161.0449	C ₆ H ₉ O ₅ ⁻	B ₁	-H	161.0455	-4.02	594.6
CID of [M-H] ⁻						
799.4853	C ₄₂ H ₇₁ O ₁₄ ⁻	[M-H]		799.4849	0.46	665.4
637.4315	C ₃₆ H ₆₁ O ₉ ⁻	Y ₁	H	637.4321	-0.95	1136.9
619.4212	C ₃₆ H ₅₉ O ₈ ⁻	Z ₁	-H	619.4215	-0.55	103.7
553.3376	C ₃₀ H ₄₉ O ₉ ⁻	Y ₁ -C ₆ H ₁₂		553.3382	-1.10	135.4
475.3784	C ₃₀ H ₅₁ O ₄ ⁻	Y ₀	H	475.3793	-1.86	4005.6
391.2844	C ₂₄ H ₃₉ O ₄ ⁻	Y ₀ -C ₆ H ₁₂		391.2854	-2.51	992

Table S-8

EID of [M-H] ⁻ of Rg ₁						
Expt. mass	Molecular formula	Assignment	Loss or Gain	Theo.mass	Error (ppm)	S/N
799.4853	C ₄₂ H ₇₁ O ₁₄ ⁻	[M-H]		799.4849	0.46	34630.6
798.4779	C ₄₂ H ₇₀ O ₁₄ ^{2-•}	[M-2H]		798.4771	1.00	115.4
709.4523	C ₃₉ H ₆₅ O ₁₁ ⁻	^{1,4} X _{0α/β}		709.4532	-1.32	5.8
679.4418	C ₃₈ H ₆₃ O ₁₀ ⁻	^{0,2} X _{0α/β}		679.4427	-1.28	14.7
637.4315	C ₃₆ H ₆₁ O ₉ ⁻	Y _{0α/β}	H	637.4321	-0.95	14502.2
619.4211	C ₃₆ H ₅₉ O ₈ ⁻	Z _{0α/β}	-H	619.4215	-0.71	598.1
559.3986	C ₃₄ H ₅₅ O ₆ ⁻	^{2,4} X _{0α/β} -Glc		559.4004	-3.24	11.6
510.3195	C ₂₈ H ₄₆ O ₈ ^{•-}	Z _{0α} -C ₈ H ₁₄		510.3198	-0.59	16.7
475.3783	C ₃₀ H ₅₁ O ₄ ⁻	Y _{0αβ}	2H	475.3793	-2.07	1964.6
391.2835	C ₂₄ H ₃₉ O ₄ ⁻	Y _{0αβ} -C ₆ H ₁₂	-H	391.2854	-4.81	27.3
179.0553	C ₆ H ₁₁ O ₆ ⁻	C _{1α/β}	H	179.0561	-4.53	100.7
161.0448	C ₆ H ₉ O ₅ ⁻	B _{1α/β}	-H	161.0455	-4.64	159.9
CID of [M-H] ⁻						
799.4852	C ₄₂ H ₇₁ O ₁₄ ⁻	[M-H]		799.4849	0.34	1105.2
637.4315	C ₃₆ H ₆₁ O ₉ ⁻	Y _{0α/β}	H	637.4321	-0.95	6120
619.4209	C ₃₆ H ₅₉ O ₈ ⁻	Z _{0α/β}	-H	619.4215	-1.04	437.1
553.3372	C ₃₀ H ₄₉ O ₇ ⁻	Y _{0α/β} -C ₆ H ₁₂		553.3382	-1.82	20.8
475.3785	C ₃₀ H ₅₁ O ₄ ⁻	Y _{0αβ}	H	475.3793	-1.65	2914
391.2844	C ₂₄ H ₃₉ O ₄ ⁻	Y _{0αβ} -C ₆ H ₁₂		391.2854	-2.51	72.9

Table S-9

EID of [M-H] ⁻ of Rb ₂						
Expt. mass	Molecular formula	Assignment	Loss or Gain	Theo.mass	Error (ppm)	S/N
1077.5848	C ₅₃ H ₈₉ O ₂₂ ⁻	[M-H]		1077.5851	-0.28	89222.9
1076.5814	C ₅₃ H ₈₈ O ₂₂ ⁻	[M-2H]		1076.5773	3.83	10.0
1007.5057	C ₄₈ H ₇₉ O ₂₂ ⁻	M-C ₅ H ₁₀	-H	1007.5068	-1.14	50.3
945.5434	C ₄₈ H ₈₁ O ₁₈ ⁻	Y _{1α}	H	945.5428	0.59	6.9
915.5324	C ₄₇ H ₇₉ O ₁₇ ⁻	Y _{1β}	H	915.5323	0.14	5.1
897.5199	C ₄₇ H ₇₇ O ₁₆ ⁻	Z _{1β}	-H	897.5217	-2.02	5.0
866.5010	C ₄₆ H ₇₄ O ₁₅ ⁻	Z _{1β} -CH ₃ O [•]	-H	866.5033	-2.68	5.1
855.5115	C ₄₅ H ₇₅ O ₁₅ ⁻	Y _{1β} -C ₂ H ₄ O ₂		855.5111	0.41	16.3
823.4843	C ₄₄ H ₇₁ O ₁₄ ⁻	^{2,5} X _{1β}		823.4849	-0.77	19.4
812.4933	C ₄₃ H ₇₂ O ₁₄ ⁻	^{1,5} X _{0α}		812.4928	0.67	13.3
783.4899	C ₄₂ H ₇₁ O ₁₃ ⁻	Y _{0α}	H	783.4900	-0.15	105.1
765.4804	C ₄₂ H ₆₉ O ₁₂ ⁻	Z _{0α}	-H	765.4795	1.24	30.2
697.4169	C ₃₇ H ₆₁ O ₁₂ ⁻	Y _{1α} Z _{1β} -C ₅ H ₈	H	697.4169	0.07	48.9
657.3880	C ₃₄ H ₅₇ O ₁₂ ⁻	Z _{0α} -C ₈ H ₁₂	H	657.3856	3.73	16.8
621.4377	C ₃₆ H ₆₁ O ₈ ⁻	Y _{0α} Y _{1β}	2H	621.4372	0.82	5.0
309.0824	C ₁₁ H ₁₈ O ₁₀ ⁻	C _{2α}	-H	309.0827	-1.04	247.2
293.0876	C ₁₁ H ₁₇ O ₉ ⁻	B _{2α}	-H	293.0878	-0.70	45.0
291.0718	C ₁₁ H ₁₅ O ₉ ⁻	B _{2α}	-3H	291.0722	-1.22	38.8
249.0608	C ₉ H ₁₃ O ₈ ⁻	^{0,2} A _{2α}	-H	249.0616	-3.18	5.0
179.0561	C ₆ H ₁₁ O ₆ ⁻	C _{1β}	H	179.0561	-0.07	21.9
161.0456	C ₆ H ₉ O ₅ ⁻	B _{1β}	-H	161.0455	0.33	60.9
159.0300	C ₆ H ₇ O ₅ ⁻	B _{1β}	-3H	159.0299	0.65	30.1
149.0457	C ₅ H ₉ O ₅ ⁻	C _{1α}	H	149.0455	1.03	78.8
131.0352	C ₅ H ₇ O ₄ ⁻	B _{1α}	-H	131.0350	1.66	22.0
CID of [M-H] ⁻						
945.5429	C ₄₈ H ₈₁ O ₁₈ ⁻	Y _{1α}	H	945.5428	0.06	1442
915.5321	C ₄₇ H ₇₉ O ₁₇ ⁻	Y _{1β}	H	915.5323	-0.19	339.6
783.4899	C ₄₂ H ₇₁ O ₁₃ ⁻	Y _{0α}	H	783.4900	-0.15	1845.3
765.4793	C ₄₂ H ₆₉ O ₁₂ ⁻	Z _{0α}	-H	765.4795	-0.20	393.2
621.4372	C ₃₆ H ₆₁ O ₈ ⁻	Y _{0α} Y _{1β}	2H	621.4372	0.01	722.1
603.4264	C ₃₆ H ₅₉ O ₇ ⁻	Y _{0α} Y _{1β} -H ₂ O	2H	603.4266	-0.38	75.7
459.3844	C ₃₀ H ₅₁ O ₃ ⁻	Y _{0αβ}	2H	459.3844	0.07	154.2

Table S-10

Expt. mass	Molecular formula	Assignment	Loss or Gain	Theo.mass	Error (ppm)	S/N
1077.5848	C ₅₃ H ₈₉ O ₂₂ ⁻	[M-H]		1077.5851	-0.28	91113.4
1076.5814	C ₅₃ H ₈₈ O ₂₂ ⁻	[M-2H]		1076.5773	3.83	13.3
1007.5085	C ₄₈ H ₇₉ O ₂₂ ⁻	M-C ₅ H ₁₀	-H	1007.5068	1.64	43.3
945.5447	C ₄₈ H ₈₁ O ₁₈ ⁻	Y _{1α}	H	945.5428	1.97	147.7
915.5341	C ₄₇ H ₇₉ O ₁₇ ⁻	Y _{1β}	H	915.5323	1.99	60.9
866.5021	C ₄₆ H ₇₄ O ₁₅ ⁻	Z _{1β} -CH ₃ O [•]	-H	866.5033	-1.41	5.1
823.4877	C ₄₄ H ₇₁ O ₁₄ ⁻	^{2,5} X _{1β}		823.4849	3.36	17.8
783.4914	C ₄₂ H ₇₁ O ₁₃ ⁻	Y _{0α}	H	783.4900	1.77	106.8
765.4800	C ₄₂ H ₆₉ O ₁₂ ⁻	Z _{0α}	-H	765.4795	0.72	47.2
697.4176	C ₃₇ H ₆₁ O ₁₂ ⁻	Y _{1α} Z _{1β} -C ₅ H ₈	H	697.4169	1.07	55.9
657.3831	C ₃₄ H ₅₇ O ₁₂ ⁻	Z _{0α} -C ₈ H ₁₂	H	657.3856	-3.73	19.0
621.4380	C ₃₆ H ₆₁ O ₈ ⁻	Y _{0α} Y _{1β}	2H	621.4372	1.30	18.0
311.0983	C ₁₁ H ₁₉ O ₁₀ ⁻	C _{2α}	H	311.0984	-0.23	24.9
309.0813	C ₁₁ H ₁₇ O ₁₀ ⁻	C _{2α}	-H	309.0827	-4.59	225.5
293.0879	C ₁₁ H ₁₇ O ₉ ⁻	B _{2α}	-H	293.0878	0.32	59.3
291.0723	C ₁₁ H ₁₅ O ₉ ⁻	B _{2α}	-3H	291.0722	0.49	55.4
249.0612	C ₉ H ₁₃ O ₈ ⁻	^{0,2} A _{2α}	-H	249.0616	-1.57	5.3
221.0666	C ₈ H ₁₃ O ₇ ⁻	^{0,3} A _{2α}		221.0667	-0.34	25.4
179.0561	C ₆ H ₁₁ O ₆ ⁻	C _{1β}	H	179.0561	-0.07	23.4
161.0456	C ₆ H ₉ O ₅ ⁻	B _{1β}	-H	161.0455	0.33	49.4
159.0299	C ₆ H ₇ O ₅ ⁻	B _{1β}	-3H	159.0299	0.02	31.3
149.0455	C ₅ H ₉ O ₅ ⁻	C _{1α}	H	149.0455	-0.32	76.6
131.0350	C ₅ H ₇ O ₄ ⁻	B _{1α}	-H	131.0350	0.14	5.5
CID of [M-H] ⁻						
945.5431	C ₄₈ H ₈₁ O ₁₈ ⁻	Y _{1α}	H	945.5428	-0.55	464.6
915.5323	C ₄₇ H ₇₉ O ₁₇ ⁻	Y _{1β}	H	915.5323	0.28	330.4
783.4900	C ₄₂ H ₇₁ O ₁₃ ⁻	Y _{0α}	H	783.4900	0.03	34.8
765.4791	C ₄₂ H ₆₉ O ₁₂ ⁻	Z _{0α}	-H	765.4795	-0.02	499
621.4371	C ₃₆ H ₆₁ O ₈ ⁻	Y _{0α} Y _{1β}	2H	621.4372	-0.46	140.5
603.4269	C ₃₆ H ₅₉ O ₇ ⁻	Y _{0α} Y _{1β} -H ₂ O	2H	603.4266	-0.15	376
459.3844	C ₃₀ H ₅₁ O ₃ ⁻	Y _{0αβ}	2H	459.3844	0.45	38.3