

## Supporting Information

**Supporting Information Table 1.** Table of theoretical and measured b- and y-type ions, from the MS/MS spectrum shown in Figure 2B. The table was used for manual *de novo* sequencing of *V. vulgaris* peptide HGEYAM\*SIYNPLVDVWHLR as a triply-charged precursor. \*indicates oxidation.

Singly-charged b-ions <i>m/z</i> observed	Singly-charged b-ions <i>m/z</i> predicted				Singly-charged y-ions <i>m/z</i> predicted	Singly-charged y-ions <i>m/z</i> observed
	138.067	1	His	20	-	
	195.088	2	Gly	19	2266.097	
324.130	324.131	3	Glu	18	2209.075	
487.194	487.194	4	Tyr	17	2080.033	
558.231	558.231	5	Ala	16	1916.969	
705.266	705.267	6	Met*	15	1845.932	
792.298	792.299	7	Ser	14	1698.897	
905.383	905.383	8	Ile	13	1611.865	
1068.446	1068.446	9	Tyr	12	1498.781	1498.778
1182.489	1182.489	10	Asn	11	1335.717	1335.716
	1279.542	11	Pro	10	1221.674	1221.675
1392.625	1392.626	12	Leu	9	1124.622	1124.622
1491.695	1491.694	13	Val	8	1011.538	1011.583
1606.719	1606.721	14	Asp	7	912.469	912.469
1705.793	1705.790	15	Val	6	797.442	797.443
	1891.869	16	Trp	5	698.374	698.374
	2028.928	17	His	4	512.295	512.294
	2115.960	18	Ser	3	375.236	375.235
	2229.044	19	Leu	2	288.204	
	-	20	Arg	1	175.120	

Doubly-charged b-ions <i>m/z</i> observed	Doubly-charged b-ions <i>m/z</i> predicted				Doubly-charged y-ions <i>m/z</i> predicted	Doubly-charged y-ions <i>m/z</i> observed
	69.537	1	His	20	-	
	98.048	2	Gly	19	1133.552	
	162.569	3	Glu	18	1105.042	1105.042
	244.101	4	Tyr	17	1040.520	1040.520
	279.620	5	Ala	16	958.989	958.987
	353.137	6	Met*	15	923.470	923.469
	396.653	7	Ser	14	849.952	849.952
	453.195	8	Ile	13	806.436	
	534.727	9	Tyr	12	749.894	749.894
591.748	591.748	10	Asn	11	668.363	668.362
640.274	640.275	11	Pro	10	611.341	611.341
696.817	696.817	12	Leu	9	562.815	
746.351	746.351	13	Val	8	506.273	506.272
	803.865	14	Asp	7	456.739	456.738
853.397	853.399	15	Val	6	399.225	
996.438	946.438	16	Trp	5	349.691	349.690
1014.967	1014.968	17	His	4	256.651	
	1058.484	18	Ser	3	188.122	
	1115.026	19	Leu	2	144.606	
	-	20	Arg	1	88.064	

**Supporting Information Table 2.** Table of theoretical and measured b- and y-type ions, from the low energy MS/MS spectrum shown in Supporting Information Figure 4. The table was used for manual *de novo* sequencing of *V. vulgaris* peptide AIEKPFLVVYDEDGK as a triply-charged precursor.

Singly-charged b-ions <i>m/z</i> observed	Singly-charged b-ions <i>m/z</i> predicted				Singly-charged y-ions <i>m/z</i> predicted	Singly-charged y-ions <i>m/z</i> observed
	72.045	1	Lys	15	-	
	185.129	2	Gly	14	1651.858	
314.171	314.172	3	Asp	13	1538.774	
442.266	442.267	4	Glu	12	1409.732	1409.724
539.319	539.319	5	Asp	11	1281.637	1281.632
686.387	686.388	6	Tyr	10	1184.584	1184.579
799.470	799.472	7	Val	9	1037.516	1037.512
898.538	898.540	8	Val	8	924.431	924.429
997.606	997.609	9	Leu	7	825.363	825.361
1160.668	1160.672	10	Phe	6	726.295	726.293
1275.695	1275.699	11	Pro	5	563.231	563.230
1404.736	1404.741	12	Lys	4	448.204	448.204
1519.762	1519.768	13	Glu	3	319.162	
1576.778	1576.790	14	Leu	2	204.135	
	-	15	Ala	1	147.113	

Doubly-charged b-ions <i>m/z</i> observed	Doubly-charged b-ions <i>m/z</i> predicted				Doubly-charged y-ions <i>m/z</i> predicted	Doubly-charged y-ions <i>m/z</i> observed
	36.526	1	Lys	15	-	
	93.068	2	Gly	14	826.433	
	157.590	3	Asp	13	769.891	769.890
	221.637	4	Glu	12	705.370	705.368
	270.164	5	Asp	11	641.322	
	343.698	6	Tyr	10	592.796	
	400.240	7	Val	9	519.262	
	449.774	8	Val	8	462.720	
	499.308	9	Leu	7	413.185	
	580.840	10	Phe	6	363.651	
	638.353	11	Pro	5	282.120	
	702.875	12	Lys	4	224.606	
	760.388	13	Glu	3	160.085	
	788.899	14	Leu	2	102.571	
	-	15	Ala	1	74.061	