

Supplementary information

Fig. 1S. Example of ESI MS and MS/MS data for a selenized peptide with two possible S/Se substitution positions; (a) ESI MS spectrum at RT=22.5 min, (b) MS/MS fragmentation of GUELDNIMR peptide; (c) zoom of the MS/MS spectrum showing clear Se isotopic patterns of selenized fragments.

Fig. 2S Annotated fragmentation of selenized FEPCGLIQLQGMR (a,b) and MQCCQLQDVSR (c,d) peptides with both SeC/C (a,c) and SeM/M (b,d) substitution.

Table 1S. Summary of selenized peptides identified in the tryptic digest of the water soluble fraction (shotgun approach).

nr	sequence	z (modification)	RT, min		Theoretical mass, Da	Experimental mass, Da	Δ , ppm	protein	AA
			Se-peptide	S-peptide					
1	EVQDSPLDACR	2 (non alk)	15.30	15.18	1336.511	1336.519	5.77	GL19_ORYSJ	C
2	MQCCQQLQDVSR	2 (non alk)	15.48	14.63	1599.600	1599.607	4.82	GL19_ORYSJ	M
3	QYAAQLPSMCR	2 (ox; non alk)	20.14	20.13	1371.546	1371.554	5.62	GL19_ORYSJ	C
4	QLAAVDSDWCR	2 (non alk)	21.03	20.98	1367.537	1367.531	4.37	RA5_ORYSJ	C
5	QYAAQLPSMCR	2 (ox; non alk)	21.12	20.13	1371.546	1371.554	5.62	GL19_ORYSJ	M
6	IYEAHVGMSEPEVSTYR	3	21.67	20.84	2200.918	2200.919	0.42	GLGB_ORYSJ	M
7	VTYPIMADPSR	2	21.84	20.92	1296.562	1296.557	3.84	REHYA_ORYSI	M
8	FQPMFR	2 (ox)	23.28	22.62	872.3409	872.3486	8.84	GL19_ORYSJ	M
9	DAVMSTLGMTEDEK	2	24.06	23.41	1444.566	1444.563	2.20	LEA3_ORYSI	M
10	ELGATDVGHPMAEVFPGCR	3 (non alk)	26.70	26.65	2089.879	2089.883	1.69	RAG2_ORYSJ	C
11	ELGATDVGHPMAEVFPGCR	3 (non alk)	27.66	26.65	2089.879	2089.883	1.69	RAG2_ORYSJ	M
12	CQPGMGYPMSLPR	2 (ox)	28.40	28.33	1703.67	1703.666	2.45	RAG2_ORYSJ	C
13	CEAISHMLGGIYR	2	28.10	28.03	1553.656	1553.654	1.21	RA5_ORYSJ	C
14	ELGAPDVGHPMSEVFR	2, 3	28.06	27.32	1787.775	1787.774	0.38	RA5_ORYSJ	M
15	CSALNHMVGGIYR	3	28.08	28.02	1524.641	1524.639	1.49	RAG2_ORYSJ	C
16	CSALNHMVGGIYR	3	29.45	28.54	1524.641	1524.642	0.48	RAG2_ORYSJ	M
17	CEAISHMLGGIYR	2	29.53	28.67	1553.656	1553.656	0.43	RA5_ORYSJ	M
18	FEPGLIQLQGMR	2	33.16	32.02	1595.703	1595.706	1.77	SSG1_ORYSI	M
19	FNAPLAHLIMAGADVLAVPSR	3	44.10	44.01	2210.111	2210.125	5.98	SSG1_ORYSI	M
20	FGIVEGLMTTVHAITATQK	3	44.38	44.13	2064.016	2064.03	6.75	G3PC3_ORYSJ	M

Table 2S. Summary of selenized peptides identified in the tryptic digest of the GE protein spots (*cf.* Fig. 3)

Spot 1: 19 kDa globulin

peak	RT, min	Sequence	z (modifications)	Theoretical mass, Da	Experimental mass, Da	delta, ppm
A	10.81					
B	15.03	EVQDSPLDA Se CR	2 (non alk)	1336.516	1336.518	1.74
B	15.03	MQ Se CCQQLQDVSR MQC Se CCQQLQDVSR	2 (ox)	1599.604	1599.605	0.61
C	15.34	Se MQCCQQLQDVSR	2 (ox)	1599.604	1599.605	0.61
D	17.35	Se MQCCQQLQDVSR	2 (one C non alk)	1542.582	1542.583	0.83
E	19.81	QYAAQLPSM Se CR	2	1371.551	1371.553	1.77
F	20.83	QYAAQLPS Se MCR	2 (ox)	1371.551	1371.555	2.83
G	22.97	FQP Se MFR	2 (ox)	872.3448	872.3482	4.17
H	24.16	QYAAQLPS Se MCR	2 (non alk)	1314.529	1314.533	2.87

Spot 7 : Glutelin type-A 1

peak	RT, min	Sequence	z (modifications)	Theoretical mass, Da	Experimental mass, Da	delta, ppm
A	10.68	QLQ Se CQNDQR	2 (non alk)	1236.4751	1236.478	2.81
B	12.3					
C	12.83	ERYQEGGYQQSQYGSG Se CPN	3	2315.8583	2315.863	2.05
C	12.83	YQEGQYQQSQYGSG Se CSN	2 (non alk)	2030.7146	2030.717	1.33
D	25.9					
E	30.44					
F	31.84	SQAGTTEFFDVSNEQFQ Se CTGVSVVR	3	2840.2156	2840.225	3.42
H	41.48					

Spot 5 : Glutelin type-A 2

peak	RT, min	Sequence	z (modifications)	Theoretical mass, Da	Experimental mass, Da	delta, ppm
A	10.68	QLQ Se CQNDQR	2 (non alk)	1236.4751	1236.478	2.81
G	32.71	GLSLLQPYASLQEQEQGQ Se MQSR	3 (ox)	2538.1618	2538.167	2.02

Spot 12 :Glutelin type-A 2

peak	RT, min	Sequence	z (modifications)	Theoretical mass, Da	Experimental mass, Da	delta, ppm
A	10.66	QLQSeCQNDQR	2	1236.475	1236.481	4.83
B	13.1	ASLQEQQGQSeMQSR	2 (ox)	1666.681	1666.684	1.51
B	13.1	EHYQEGGYQQSQYGSQSeCPN	2, 3 (non alk)	2235.8	2235.803	1.30
C	27.04					
E	32.84	GLSLLQPYASLQEQQGQSeMQSR	3 (ox)	2538.162	2538.167	2.26
F	41.68	SQAGTTEFFDVSNELFQSeCTGVSVVR	3	2825.241	2825.252	3.87

Spot 6 : Glutelin type-B 4

peak	RT, min	Sequence	z (modifications)	Theoretical mass, Da	Experimental mass, Da	delta, ppm
D	28.7	YSNTPGSeMVYIIQGR	2 (ox)	1645.7367	1645.744	4.72

Spot 2-3-4 : Granule-bound starch synthase

peak	RT, min	Sequence	z (modifications)	theoretical mass, Da	experimental mass, Da	delta, ppm
A	11.99	S SeM E EKYPGK	2	1115.4402	1115.4392	-0.86
B	14.38	TGFH SeM GR	2	852.3146	852.3188	4.97
B	14.38	GFH SeM GR	2	751.2669	751.2682	1.78
C	16.22	V SeM VISPR	2	848.4023	848.4038	1.82
D	17.55	KINW SeM K	2 (ox)	866.3918	866.3932	1.66
E		IYGPDTGV ^{DYK} DNQ SeMR	3 (ox)	1918.7964	1918.7985	1.12
F	20.01	INW SeM K	2 (ox)	738.2968	738.2984	2.22
G	20.01	N SeC MNQDLSWK	2	1342.4879	1342.4902	1.74
H	21.14	N SeM NQDLSWK	2 (ox)	1342.4879	1342.4944	4.87
I	21.14	G SeC ELDNIMR	2	1154.4293	1154.4308	1.33
J	22.44	VVGTPAYEE SeM VR		1397.6094	1397.6122	2.03
K	22.87	GCELDNI SeMR	2 (ox)	1154.4293	1154.4326	2.89
L	ND	GLIQLQG SeMR	2 (ox)	1062.5089	1062.5120	2.96
M	ND	YGTP SeC ACASTGGLVDTVIEGK	2 (ox)	2202.9370	2202.9414	2.02
N	ND	L SeM AGADVLAVPSR	2 (ox)	1459.7302	1459.7350	3.32
O	31.88	TGGLGDVLGGLPPA SeMA ANGHR	3	2007.9393	2007.9417	1.22
P	31.88	FEP SeC GLIQLQGMR	2, 3	1595.7033	1595.7058	1.59
Q	32.52	FEP SeC GLIQLQG SeMR	2, 3 (ox)	1595.7033	1595.7066	2.09
R	32.52	VAF SeC IHNISYQGR	2, 3	1611.7061	1611.7023	-2.33
S	35.60	LTGITGIVNG SeM DVSEWDPSKDK	3 (ox)	2409.0967	2409.1056	3.71
T	38.26	ATGAGMNVVFGAE SeM APWSK	2, 3 (ox)	2069.9148	2069.9218	3.40
U		GTYGEDVVFV SeC NDWHTGPLASYL K	3	2775.2083	2775.2199	4.19
V	43.72	FNAPLAHL SeM AGADVLAVPSR	2, 3/(ox)	2210.1115	2210.1228	5.13
W	45.10					