Simultaneous quantification of 22 glucosinolates in 12 Brassicaceae vegetables by hydrophilic interaction chromatography-tandem mass spectrometry

Xu Liang[1], Hui Wen Lee[1], Zhifeng Li[2], Yonghai Lu[3], Li Zou[3], Choon Nam Ong[1,3]*

[1] NUS Environment Research Institute, National University of Singapore, 5A Engineering Drive 1, 117411, Singapore;

[2] College of Pharmacy, Jiangxi University of Traditional Chinese Medicine, 1688 Meilingdadao Road, 330004, Nanchang, Jiangxi Province, PR China;

[3] Saw Swee Hock School of Public Health, National University of Singapore, 12 Science Drive 2, 117549, Singapore.

Address correspondence to:

Choon Nam Ong

NUS Environment Research Institute,

National University of Singapore,

T-Lab Building #02-01, 5A Engineering Drive 1, S117411, Republic of Singapore.

Tel: +65-6516 7386

E-mail: eridir@nus.edu.sg

Table S1. MS and MS^n information of five glucosinolates

Glucosinolates	Formula	Exact Mass	$[M-H]^-$	RT (min)	MS/MS fragments	ppm
Glucoraphasatin	$C_{12}H_{21}NO_9S_3$	419.0379	418.0306	2.79	97, 259, 338	1.2
Glucosativin	$C_{11}H_{21}NO_9S_3$	407.0379	406.0306	3.45	97, 259, 326	1.2
Gluconapoleiferin	$C_{12}H_{21}NO_{10}S_2$	403.0607	402.0537	5.00	97, 120, 160, 195, 225, 259	2.0
Neoglucobrassicin	$C_{17}H_{22}N_2O_{10}S_2$	478.0716	477.0643	2.21	97, 205, 259, 446, 447	1.0
4-Methoxyglucobrassicin	$C_{17}H_{22}N_2O_{10}S_2$	478.0716	477.0643	3.29	97, 195, 291, 259, 397	1.0

Table S2. Mean levels (μg/g dry weight, mean±SD) of glucosinolates in 12 vegetables.

	Rocket salad	Watercress	Red Radish	Radish	Pakchoi	Chinese cabbage	Choysum	Brussels Spouts	Cabbage	Cauliflower	Broccoli	Kai Lan
Sinigrin	n.d.	n.d.	n.d.	n.d.	0.3±0.1	n.d.	0.3±0	1309.3±116	1889.3±202.1	331.7±51	0.2±0	320.2±88.6
Glucoiberin	n.d.	1.4±0.4	3.3±0.4	1.3±0.4	n.d.	0.2±0	n.d.	2070.4±196.4	1069.3±333.2	2176.8±61.5	10±1.5	306.6±154.3
Glucocheirolin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.5±0.7	n.d.	n.d.	2±0.8
Glucoraphasatin	n.d.	n.d.	6514.7±1050.4	5078.6±792.7	n.d.	0.5±0.1	0.6±0.1	n.d.	n.d.	n.d.	0.6±0.3	n.d.
Glucosativin	4422.4±264	n.d.	20.1±5.4	304.7±5.6	0.5±0.2	n.d.	n.d.	1.3±0.2	319.1±14.6	593.2±149.2	n.d.	3.1±0.8
Glucoerucin	467.7±62.7	0.4±0	330.3±32.2	444±107.3	0.4±0	0.6±0.1	n.d.	n.d.	299.1±8.2	304±15	0.7±0.2	0.7±0.3
Glucoraphenin	n.d.	n.d.	65.5±5.1	141.5±9.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Glucoraphanin	1799.1±31.2	5.3±1.5	27.1±3.7	53.3±7.4	42.3±15	48.3±20.7	6.8±2.2	528.1±172.8	1192.4±521.9	86.9±22.7	1418±491.6	367.6±126.9
Gluconapin	12.6±3.7	0.7±0	0.5±0.1	1±0.1	1605.9±263.4	600±155.3	739.6±21.9	670±102.1	39±4.3	19.2±1.9	0.4±0.1	847.1±135.4
Epiprogoitrin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	161.4±26.8	86.4±21.6	n.d.	n.d.	n.d.	82.3±19.3
Progoitrin	n.d.	0.6±0.2	n.d.	n.d.	595.9±81.8	556.9±104.9	507.7±70.2	3229.5±915	463.7±87.1	139.9±45.3	n.d.	2943.1±482.8
Glucoalyssin	22.9±1.2	122.3±21.4	2.3±0.4	21.3±3.6	399.1±154	110.7±20.8	154.7±62.9	4.7±1.4	n.d.	n.d.	30.5±17.1	17.1±4.8
Glucobrassicanapin	n.d.	n.d.	n.d.	n.d.	457.1±86.8	657.8±85.5	402.1±46.1	n.d.	n.d.	n.d.	n.d.	n.d.
Gluconapoleiferin	n.d.	n.d.	n.d.	n.d.	0.4±0	2±0.5	0.4±0.1	n.d.	n.d.	n.d.	n.d.	n.d.
Glucobrassicin	n.d.	504.5±100.6	149.5±27.7	3.6±0.5	117.3±38.8	513.5±29.4	168.4±41.9	1424.3±193.5	2707±170.9	835.3±220.5	490.8±138.2	31.2±8.2
Neoglucobrassicin	n.d.	n.d.	n.d.	533.5±50.2	3477.8±458.4	5162±812.3	3675.6±275.4	1802.3±235.5	4558.9±704.5	7448.1±932.3	1395.2±68	982.6±305.2
4-Methoxyglucobrassicin	835.8±51.7	2961.6±30.1	5394.6±442.2	1140.1±83.6	2402.6±338.4	3097.3±666.4	1827.2±210	4206.6±893.1	5207.8±502.9	1338.6±229.6	2491.1±187.9	495.6±79.8
4-Hydroxyglucobrassicin	890.9±159.2	1565.1±316	1273.9±64.9	2476±90	128.6±16.1	1000.1±127	65.2±9.7	2523.5±578.7	325.1±62.8	366±32.4	2965.4±362.7	642.8±135.7
Glucotropaeolin	n.d.	n.d.	n.d.	n.d.	1.1±0.1	0.3±0.1	0.5±0.1	1.9±0.4	n.d.	n.d.	0.4±0.3	0.7±0.2
Gluconasturtiin	19.1±4	8850.1±1939.9	13.9±1.6	35.6±3.5	200.9±38.3	148.1±45.8	56.6±2.5	82.3±26	30.3±6.1	12±3.3	35.3±3.8	16.1±3
Glucobarbarin	2610.7±251.9	n.d.	23.4±4.1	45.9±3.7	45.3±14.3	86.8±18.6	10.5±1.8	339.9±47.2	1445.7±275.4	n.d.	2159.3±440	552.7±206.7
Glucosinalbin	3.9±0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	11085±315	14012±2014	13819±653	10280±729	9476±567	11985±310	7778±431	18280.5±1060.6	19551±1318	13652±1217	10998±557	7611±868

n.d. < LOD, which was replaced by LOD/2 in the following statistical analysis.

Table S3. Mean levels (μg/g fresh weight) of glucosinolates in 12 vegetables.

	Rocket salad	Watercress	Red Radish	Radish	Pakchoi	Chinese cabbage	Choysum	Brussels Spouts	Cabbage	Cauliflower	Broccoli	Kai Lan
Sinigrin	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.02	209.49	113.36	26.53	0.03	25.62
Glucoiberin	n.d.	0.08	0.16	0.08	n.d.	0.01	n.d.	331.26	64.16	174.14	1.2	24.53
Glucocheirolin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.27	n.d.	n.d.	0.16
Glucoraphasatin	n.d.	n.d.	325.73	304.72	n.d.	0.02	0.03	n.d.	n.d.	n.d.	0.07	n.d.
Glucosativin	398.02	n.d.	1.01	18.28	0.03	n.d.	n.d.	0.21	19.14	47.46	n.d.	0.25
Glucoerucin	42.09	0.03	16.51	26.64	0.02	0.03	n.d.	n.d.	17.95	24.32	0.08	0.06
Glucoraphenin	n.d.	n.d.	3.27	8.49	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Glucoraphanin	161.92	0.32	1.35	3.2	2.12	2.42	0.34	84.5	71.54	6.95	170.16	29.41
Gluconapin	1.13	0.04	0.03	0.06	80.29	30	36.98	107.19	2.34	1.53	0.05	67.77
Epiprogoitrin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.07	13.83	n.d.	n.d.	n.d.	6.58
Progoitrin	n.d.	0.04	n.d.	n.d.	29.8	27.84	25.39	516.72	27.82	11.2	n.d.	235.45
Glucoalyssin	2.06	7.34	0.11	1.28	19.95	5.53	7.73	0.76	n.d.	n.d.	3.67	1.37
Glucobrassicanapin	n.d.	n.d.	n.d.	n.d.	22.85	32.89	20.1	n.d.	n.d.	n.d.	n.d.	n.d.
Gluconapoleiferin	n.d.	n.d.	n.d.	n.d.	0.02	0.1	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Glucobrassicin	n.d.	30.27	7.48	0.22	5.86	25.67	8.42	227.89	162.42	66.83	58.9	2.49
Neoglucobrassicin	n.d.	n.d.	n.d.	32.01	173.89	258.1	183.78	288.37	273.53	595.85	167.42	78.61
4-Methoxyglucobrassicin	75.23	177.7	269.73	68.4	120.13	154.86	91.36	673.05	312.47	107.08	298.94	39.65
4-Hydroxyglucobrassicin	80.18	93.9	63.7	148.56	6.43	50	3.26	403.76	19.51	29.28	355.85	51.42
Glucotropaeolin	n.d.	n.d.	n.d.	n.d.	0.05	0.02	0.03	0.3	n.d.	n.d.	0.04	0.05
Gluconasturtiin	1.72	531.01	0.7	2.13	10.05	7.4	2.83	13.16	1.82	0.96	4.23	1.29
Glucobarbarin	234.96	n.d.	1.17	2.75	2.27	4.34	0.52	54.39	86.74	n.d.	259.12	44.21
Glucosinalbin	0.35	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	997.66	840.73	690.95	616.82	473.78	599.23	388.88	2924.88	1173.07	1092.13	1319.76	608.92

n.d. < LOD, which was replaced by LOD/2 in the following statistical analysis.