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Chemical profiling of glucosinolates in cruciferous vegetables-based dietary supplements using ultra-high performance liquid chromatography coupled to tandem high resolution mass spectrometry

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ABSTRACT

The chemical profiles of glucosinolates in cruciferous vegetables-based dietary supplements (CVDS) have been established with an ultra-high performance liquid chromatography high-resolution mass spectrometry (UHPLC-HRMS) method. In total, 29 glucosinolates, including two new acylated glucosinolates, were putatively identified. The structures of the two new acylated glucosinolates were deduced as 6′-*O*-sinapoyl-4-(methylsulphinyl)-butyl glucosinolate and 6′-*O*-sinapoyl-4-(methylthio)-butyl glucosinolate, respectively. The possible fragmentation pathways of the two new glucosinolates were proposed based on their multi-stage mass spectrometry (ESI–MS^n) spectra. Furthermore, the glucosinolates in CVDS were desulfated and quantified as desulfo-glucosinolates by diode array detector. The total content of glucosinolates in CVDS varied greatly from 6.15 to 104.17 μmol/g. The chemical profiles of these CVDS also showed substantial diversity. Our study presented an effective strategy that can be used for quality control of commercial dietary supplements that contain glucosinolates.

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1. Introduction

The dietary supplement industry is slated to be the world's fastest growing market. According to Euromonitor International's statistical data, in the United States, sales of vitamins and dietary supplements increased consistently, from US$19.7 billion in 2009 to US$ 24.6 billion in 2013. Globally, the sales topped US$ 84.4 billion in 2013. Unlike pharmaceuticals, dietary supplements are not required to be standardized in the United States. Therefore, dietary supplements from different manufacturers differ significantly both in their chemical profiles and the contents of nutrients. The problem is more prominent in botanical dietary supplements, since the discrepancies in their chemical profiles originate from different species, harvesting regions and seasons of every single ingredient as well as different methods of production of the dietary supplements (Fu et al., 2009). To ensure the efficacy and safety of botanical dietary supplements, it is essential to establish suitable analytical method to ascertain their qualities.

Glucosinolates, the main categories of nutrients in cruciferous vegetables, are sulfur-containing chemicals. They could be cleaved off by the enzyme myrosinase in the plants. During food preparation and chewing, glucose groups are cleaves off from glucosinolates, and the remaining molecules quickly convert to biologically active compounds such as isothicyanates, nitriles and indoles with health promoting properties (Cheung and Kong, 2010; Manchali et al., 2012). Also, degradation of glucosinolates occur during storage or cooling to 4 °C (Crska et al., 2016).

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Table 1
Retention time, high-resolution mass of the deprotonated molecule, formula, error between calculated and measured values, MS^n diagnostic fragments, putative identification, and occurrence of the glucosinolates (GLs) in dietary supplements by UHPLC-$HRMS^n$.

No.	t_R (min)	$[M-H]^-$ (Da)	Formula	Error (ppm)	MS^2 diagnostic fragments (%)	MS^3 diagnostic fragments (%)	MS^4 diagnostic fragments (%)	Putative identification	Occurrence
1	1.23	422.0245	$C_{11}H_{20}O_{10}NS_3$	−0.98	358(100)	278(12), 275(29), 259(100), 180(18), 162(50)	139(100), 97(42)	Glucoiberin	B3, B7, C2, C3
2	1.26	434.0248	$C_{12}H_{20}O_{10}NS_3$	−0.68	419(100), 354(11), 291 (11), 275(18), 259(64)	402(100), 370(14), 331(17), 259(12), 257(50), 256(19), 241(26), 224(24), 157(40)		Glucoraphenin	C4, R1
3	1.27	436.0387	$C_{12}H_{22}O_{10}NS_3$	−2.43	372(100)	292(15), 275(36), 259(100), 195(11)	139(100), 97(40)	Glucoraphanin	B2, B3, B4, B5, B6, B7, C2, C3
4	1.29	424.0368	$C_{14}H_{18}O_{10}NS_2$	−0.96	344(17), 275(48), 259 (100), 246(14), 241(12), 228(13), 182(25)	199(14), 139(100), 97(33)	81(68), 80 (100)	Glucosinalbin isomer	B1, B5, B7, C1, C4, C5
5	1.50	436.0395	$C_{12}H_{22}O_{10}NS_3$	−3.70	372(100)	292(15), 275(36), 259(100), 227(11), 195(12)	139(100), 97(39)	Glucoraphanin isomer	B1, B2, B3, B5, B6, B7, C3
6	1.52	434.0247	$C_{12}H_{20}O_{10}NS_3$	−1.82	419(100), 291(11), 275 (19), 259(62)	402(100), 370(25), 331(17), 272(17), 259(17), 257(17), 241(42), 157(83)		Glucoraphenin isomer	C4, R1
7	1.53	388.0367	$C_{11}H_{18}O_{10}NS_2$	−2.86	332(68), 308(18), 275 (44), 259(100), 210(35)	139(100), 97(30)		Progoitrin	C1
8	1.65	424.0360	$C_{14}H_{18}O_{10}NS_2$	−4.13	344(16), 275(43), 259 (100), 246(11), 241(15), 182(23)	199(29), 139(100), 97(40)	81.00(100)	Glucosinalbin	B1, B5, B7, C1, C4, C5
9	1.82	372.0428	$C_{11}H_{18}O_9NS_2$	−0.07	292(16), 275(42), 259 (100), 194(13)			Gluconapin	C2
10	1.89	436.0399	$C_{12}H_{22}O_{10}NS_3$	−2.78	372(100)	292(11), 275(30), 259(100), 194(16)	199(13), 139(100), 97(28)	Glucoraphanin isomer	B2, B3, B6, C3
11	2.23	406.0312	$C_{11}H_{20}O_9NS_3$	1.61	326(14), 275(30), 259 (100), 228(17)	139(100), 97(39)		Glucoibervirin	B1, B2, B3, B5, B7, C3
12	2.39	463.0488	$C_{16}H_{19}O_{10}N_2S_2$	0.24	285(100), 267(87), 240 (13), 160(12)	97(100)		4-Hydroxyglucobrassicin	B1, B2, B3, B5, B6, B7
13	2.80	424.0380	$C_{14}H_{18}O_{10}NS_2$	0.61	344(19), 275(47), 259 (100), 246(15), 182(26)	139(100), 97(30)		Glucosinalbin isomer	B5, B7, C1, C4, C5
14	3.26	408.0432	$C_{14}H_{18}O_9NS_2$	0.82	328(12), 275(29), 259 (100), 230(14), 212(27), 166(11)			Glucotropaeolin	C2
15	3.40	420.0455	$C_{12}H_{22}O_9NS_3$	−4.40	340(14), 275(40), 259 (100), 242(14), 227(15)	139(100), 97(30)	81(100)	Glucoerucin	B1, B2, B3, B5, B6, B7, C2, C3
16	3.47	544.0625	$C_{18}H_{26}O_{12}NS_3$	0.44	464(31), 418(100), 366 (17), 351(14), 348(22), 302(47), 291(51), 275 (24), 259(77)	275(40), 259(100), 145(15)		Unknown GLs	R1
17	3.58	544.0621	$C_{18}H_{26}O_{12}NS_3$	−0.35	464(29), 418(100), 366 (16), 348(17), 302(39), 291(52), 275(24), 259 (73)	341(29), 301(29), 259(100), 241(21), 240(29), 176(14)		Unknown GLs	R1
18	3.66	418.0293	$C_{12}H_{20}O_9NS_3$	−2.96	338(14), 275(30), 259 (100), 240(13), 176(11)	199(15), 139(100), 97(38)		Glucoraphasatin	R1
19	3.85	478.0881	$C_{15}H_{28}O_{10}NS_3$	0.10	414(100)	334(15), 275(52), 259(100), 236(15), 218(13), 172(12)		Glucosiberin	C5
20	3.88	388.0739	$C_{12}H_{22}O_9NS_2$	−0.61	370(24), 344(57), 342 (29), 275(43), 259 (100), 210(14)			Glucokohlrabiin	B4, C2
21	4.36	447.0543	$C_{16}H_{19}O_9N_2S_2$	1.29	367(16), 291(26), 275 (51), 269(20), 259 (100), 205(22)	139(100), 97(30)		Glucobrassicin	B1, B2, B3, B4, B5, B6, B7, C1, C2, C3, C4, C5, R1
22	5.43	422.0589	$C_{15}H_{20}O_9NS_2$	0.89	342(16), 275(29), 259 (100), 244(22)			Gluconasturtiin	B1, B2, B3, B4, B5, B6, B7, C2, C3, C4, C5
23	5.61	434.0617	$C_{13}H_{24}O_9NS_3$	−0.29	354(14), 275(42), 259 (100), 256(17), 241(14), 192(16)			Glucoberteroin	B2, B3, B5, B6, B7, C3
24	6.09	492.1037	$C_{16}H_{30}O_{10}NS_3$	0	428(100)	348(11), 275(37), 259(100), 250(11), 232(12)		Glucohirsutin	C5
25	6.36	528.0673	$C_{18}H_{26}O_{11}NS_3$	2.14	418(100), 291(10), 275 (9), 259(27)			Unknown GLs	R1
26	6.44	528.0674	$C_{18}H_{26}O_{11}NS_3$	2.14	448(9), 418(100), 291 (7), 259(16)			Unknown GLs	R1
27	6.66	477.0650	$C_{17}H_{21}O_{10}N_2S_2$	1.45	299(14), 291(50), 281 (14), 275(61), 259(100), 235(20), 227(16)			4-methoxyglucobrassicin	B1, B2, B3, B4, B5, B6, B7, C2, R1
28	7.25	402.0902	$C_{13}H_{24}O_9NS_2$	0.96	322(11), 275(36), 259 (100), 224(14)	139(100), 97(36)		n-hexyl-GLs	B1, B2, B3, B5, B6, B7, C3, R1