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Profiling Polyphenols in Five *Brassica* species Microgreens by UHPLC-PDA-ESI/HRMS^n

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Abstract

Brassica vegetables are known to contain relatively high concentrations of bioactive compounds associated with human health. A comprehensive profiling of polyphenols from five *Brassica* species microgreens was conducted using ultra high-performance liquid chromatography photo diode array high-resolution multi-stage mass spectrometry (UHPLC-PDA-ESI/HRMS^n). A total of 164 polyphenols including 30 anthocyanins, 105 flavonol glycosides, and 29 hydroxycinnamic acid and hydroxybenzoic acid derivatives were putatively identified.The putative identifications were based on UHPLC-HRMS^n analysis using retention times, elution orders, UV/Vis spectra and high resolution mass spectra, in-house polyphenol database, and as well as literature comparisons. This study showed that these five *Brassica* species microgreens could be considered as good sources of food polyphenols.

Keywords

Microgreen; *Brassicaceae*; acylated cyanidin 3-sophroside-5-mono- and diglucosides; acylated flavonol glycosides; hydroxycinnamic acid derivatives; UHPLC-PDA-ESI/HRMS^n

INTRODUCTION

Microgreens are young edible greens produced from vegetables, herbs, or other plants, ranging in size from five to ten centimeters long including stem and cotyledons (seed-leaves). They are popular for their pretty colors, intense flavors, delicate textures and relatively high nutritional contents (1). The entire plant (seedling) is harvested at the ground level when cotyledon or seed-leaves have fully expanded and before true leaves have fully emerged.

The *Brassicacae* offers some of the most commonly consumed vegetables worldwide, which can be grown as microgreens. Five *Brassica* vegetables commonly found in the U.S. market place are red cabbage (*B. oleracea* var. *capitata*), purple kohlrabi (*B. oleracea* var. *gongylodes*), red and purple mustards (*B. juncea*), and mizuna (*B. rapa* var. *nipposinica* or

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B. juncea var. *japonica*). *Brassica* vegetables are known to be rich sources of ascorbic acid, carotenoids, glucosinolates, polyphenols, and tocopherols (2-4) which have human-health beneficial attributes reportedly involved in preventing cardiovascular diseases and some types of cancers (5-8).

Previous studies have tentatively identified phenolic compounds from 22 mature-leaf *Brassica* vegetables (9-12) and phenolic compounds have been found in tronchuda cabbage (*Brassica oleracia* var. *costata*) seeds (13) mature leaves (14) inter-nodal shoots and roots (15, 16). Twelve specific phenolic compounds have been profiled in two- to twelve-day old seedlings possessing both seed-leaves and true-leaves. The aim of the present study was to characterize and quantify the naturally occurring polyphenols in five commonly consumed *Brassicas* (mizuna, red cabbage, purple kohlrabi, red mustard and purple mustard) at their microgreen growth stage. The analyses of their native polyphenols and flavonol aglycones were performed using state-of art analytical tools: ultra high-performance liquid chromatography photo diode array high-resolution multistage mass spectrometry (UHPLC-PDA-ESI/HRMS/MS^n). Results showed that *Brassica* microgreens contained notable levels of hydroxyl cinamic acids and may contain different compounds from their true-leaves. A total of 30 anthocyanins, 105 flavonol glycosides, and 29 hydroxycinnamic acid and hydroxylbenzoic acid derivatives were tentatively identified. This is the first known reported study of polyphenol compounds in vegetables at the cotlyledonary-leaf (microgreen) stage of growth of an array of *Brassica* microgreens.

MATERIALS AND METHODS

Chemicals

Formic acid, HPLC grade Methanol and acetonitrile, were purchased from VWR International, Inc. (Clarksburg, MD). HPLC grade water was prepared from distilled water using a Milli-Q system (Millipore Lab., Bedford, MA).

Plant Materials and Sample Preparation

Five *Brassica* species, at the microgreen growth stage, were obtained from Sun Growers Organic Distributors, Inc. (San Diego, CA). All the fresh samples were lyophilized and then powdered. Powdered samples (100 mg) were extracted with 5.00 mL of methanol-water (60:40, v/v) using sonication for 60 min at room temperature, and then centrifuged at 1,000 g for 15 minutes (IEC Clinical Centrifuge, Damon/IEC Division, Needham, MA, USA). The supernatant was filtered through a 17 mm (0.45 μm) PVDF syringe filter (VWR Scientific, Seattle, WA, USA), and 10 μL of the extract was used for each HPLC injection.

UHPLC-PDA-ESI/HRMS/MS^n Conditions

The UHPLC-HRMS system used consisted of a LTQ Orbitrap XL mass spectrometer with an Accela 1250 binary Pump, a PAL HTC Accela TMO autosampler, a PDA detector (ThermoFisher Scientific, San Jose, CA), and a G1316A column compartment (Agilent, Palo Alto, CA). Separation was carried out on a Hypersil Gold AQ RP- C18 UHPLC column (200 mm × 2.1 mm i.d., 1.9 μm, ThermoFisher Scientific) with an UltraShield pre-column filter (Analytical Scientific Instruments, Richmond, CA) at a flow rate of 0.3 mL/min. The mobile phase consisted of a combination of A (0.1% formic acid in water, v/v) and B (0.1% formic acid in acetonitrile, v/v). The linear gradient was from 4% to 20% B (v/v) at 40 min, to 35% B at 60 min and to 100% B at 61 min, and held at 100% B to 65 min. The PDA was set at 520, 330 and 280 nm to record the peaks, and UV/Vis spectra were recorded from 200-700 nm.

Both positive and negative ionization modes were used and the conditions were set as follows: sheath gas at 70 (arbitrary units), aux and sweep gas at 15 (arbitrary units), spray voltage at 4.8 kV, capillary temp at 300 °C, capillary voltage at 15 V, and Tube lens at 70 V. The mass range was from 100 to 2000 amu with a resolution of 15,000, FTMS AGC target at 2e5, FT- MS/MS AGC target at 1e5, isolation width of 1.5 *amu*, and max ion injection time of 500 ms. The most intense ion was selected for the data-dependent scan to offer their MS^2 to MS^5product ions, respectively, with the a normalization collision energy at 35%.

RESULTS AND DISCUSSION

Strategies for Systematic Identification of Polyphenols from Microgreen *Brassica*

Brassicaceae polyphenol composition has been extensively investigated. The main flavonols in *Brassica* vegetables are the *O*-glycosides of quercetin, kaempferol, and isorhamnetin, (2, 17-22). The sugar moiety found in *Brassica* vegetables is glucose, occurring as mono-, di-, tri-, tetra-, and pentaglucosides (17-23). They are also commonly found acylated by different hydroxycinnamic acids. Anthocyanins are another main class of flavonoid found in *Brassica* vegetables and cyanidin is the most common anthocyanidin in colored-leaf *Brassica* vegetables (2, 24). Hydroxycinnamic acids (C6-C3) are phenolic acids characterized in *Brassica* vegetables with the most common ones being *p*-coumaric, caffeic, sinapic and ferulic acids; often found in conjugation with sugars or other hydroxycinnamic acids (2, 17-19, 21, 22).

The five *Brassica* species microgreen phenolic compounds exhibit absorbance maxima at three wavelengths (280 nm for flavonols and flavonol glycosides, 320 nm for hydroxycinnamic acid derivatives, and 520 nm for anthocyanins(2, 17-19, 21, 22).

HRMS was used for the determination of chemical formulas. Neutral loss information from MS was used for identification of sugar moiety and acyl groups. In MS analysis, cleavage of the first glycosidic linkage is expected to take place at the *O*-glycosidic bond at the 7-position of the flavonols and the 5-position of the anthocyanins, leading to the fragmentations $[(M-H)-162]^-$ for monohexosides and $[(M-H)-324]^-$ for dihexosides (23, 25, 26). The remaining glucose moieties of the flavonoid molecule are expected to be linked to the hydroxyl group at the 3-position of the aglycone. The disaccharide moieties of the flavonoids in *Brassica* species are mainly sophorosides (2). The MS fragmentation behavior can be used for the determination of interglucoside linkage and neutral losses of 180, 162, and 120 amu indicate a sophoroside with a 1→2 inter glucoside linkage, while loss of 324 amu, and in some cases low abundance of 162 amu, corresponds to a diglucoside with a 1→6 linkage like gentiobioside (27). The saccharides (mono-, di-, tri-saccharides) and acyl groups of flavonol glycoside and their possible neutral losses in CID MS/MS analysis are listed in **Table 1**, and the basic structures of the phenolic compounds found in these five *Brassica* species microgreens are shown in **Figure 1**.

Anthocyanins

Among the five *Brassica* species microgreen red cabbage, red mustard, purple mustard, and purple kohlrabi have red to purple colored seed-leaves. UHPLC chromatograms at 520 nm revealed 30 different anthocyanins are likely responsible for this coloration (**Figure 2)**. The retention times (t_R), HRMS masses $[M]^+$ molecular formulas, errors (ppm) between theoretical and measured values, and major MS^2 and MS^3 product ions are summarized in Table 2.

In these five *Brassica* species microgreens, only cyanidin (cy) derivatives were found, which is in accordance with the other studies on *Brassicas* (24, 28-30). The anthocyanins found in red cabbage microgreens were cy-3-diglucoside-5-glucoside derivatives acylated

with different hydroxycinnamic acids at the diglucosyl moiety in the 3-position. High resolution mass spectroscopic analysis with multi stage mass fragmentation was used as an important tool for anthocyanin characterization. Among the 30 cy glycosides found in red cabbage, red mustard, purple mustard and purple kohlarabi microgreens, peak 1 at *m/z* 773.2106 ($C_{33}H_{41}O_{21}$, −1.36 mmu) was the lowest molecular weight anthocyanin and the losses of three hexosyl units were observed in MS^2 spectra, suggesting cy-3-diglucoside-5-glucoside, a typical compound reported in red cabbage.The major acylated anthocyanins were cy-3-diglucoside-5-glucoside derivatives with various acylated groups e.g. coumaroyl, feruloyl and sinapoyl connected to the diglucoside. The MS/MS of most of the molecular ions of acylated anthocyanins gave the major product ions at *m/z* 449, a cy 5-glucoside residue, and at *m/z* 611, a cy-3-diglucoside residue. The MS/MS fragments of the acylated anthocyanins allow for a rough determination of the location of the acylating groups. Peaks 12, 13 and 14 are the major anthocyanins in microgreen red cabbage, and they were identified as cyanidin 3-di-feruloyl-sophoroside-5-glucoside, cy 3-(sinapoyl) (sinapoyl)sophoroside-5-glucoside and cy 3-(sinapoyl)(feruloyl)sophoroside-5-glucoside, respectivelyUsing peak 12 as an example, HRMS gave the $[M]^+$ ion at 1125.3070, corresponding to the formula of $C_{53}H_{57}O_{27}$. Fragmentation of ion at *m/z* 1125 in positive mode produced ions at m/z 963 by loss of a glucosyl residue (162 amu) from the 5-position. The ion at *m/z* 449 was produced by a total loss of 676 amu, corresponding to a di-feruloyl-diglucosyl residue (176 + 176 + 324 amu), from the terminal 3-position

In previous study of purple kohlrabi, 12 anthocyanins have been identified. The major ones are cy 3-(feruloyl)(sinapoyl) diglucoside-5-glucoside, cy 3-(feruloyl) diglucoside-5-glucoside and cy 3-(sinapoyl)(sinapoyl) diglucoside-5-glucoside (31). In our study, the acylated anthocyanins with one malonyl group attached to the hexose of C-5 and other aromatic groups (caffeic, *p*-coumaric, sinapic or ferulic acid) attached to the C-3 glycosidic substituent were found. In the MS^2 spectra, the fragment ions at (*m/z* 1023, 993 and 963), with the two acyl groups attached to the di-hexose of C-3 are usually observed as the base peak. This fragmentation pattern was evidenced with most anthocyanins analyzed and lead to the tentative identification of cy-3-(feruloyl)(feruloyl)diglucoside-5-(malonyl)-glucoside (*m/z* 1211, peak 19), cy 3-*O*-(sinapoyl)(feruloyl)diglucoside-5-*O*-(malonyl)glucoside (*m/z* 1241, peak 20), and cy 3-*O*-(sinapoyl)(sinapoyl)diglucoside-5-*O*-(malonyl)glucoside (*m/z* 1271, peak 21). Peaks 11^a-14^a were identified as cy 3-p-(coumaroyl)sophoroside-5-(malonyl)glucoside, cy 3-*O*-(pcoumaroyl)(sinapoyl) diglucoside-5-*O*-(malonyl) glucoside, cy 3-*O*-(feruloyl)glucoside-5-*O*-(malonyl)-glucoside and cy 3-*O*-(sinapoyl)glucoside-5-*O*-(malonyl)glucoside in red mustard microgreen (10). Peaks 19 and 20, were two major anthocyanins identified in red and purple mustard. Peaks 16^b, 17^b and 18^b were identified as cy 3-(sinapoyl)(coumaroyl)-triglucoside-5-(malonyl)-glucoside, and cy 3-(coumaroyl) (sinapoyl)diglucoside-5-(malonyl)glucoside, respectively.

O-Glycosylated Flavonols and Their Acylated Derivatives

Acylated flavonoid glycosides were easily identified based on the increased mass of the parent ions and the wavelength maxima (330-336 nm) of their UV spectra (Figure 3). According to the MS^n (n=2-5) data, the aglycones of the flavonol glycosides were quercetin (Qn), kaempferol (Km), and isorhamnetin (Is). Using the strategy described previously, 105 flavonol glycosides were characterized in five microgreen vegetables (**Figure 3)**. Among them, 18 were non-acylated flavonoid glycosides, and 87 were acylated flavonoid glycosides. The compound distribution in these 5 microgreens is shown in **Table 3**. Qn 3-sophoroside-7-glucoside, Qn 3-hydroxyferuloylsophoroside-7-glucoside, Km 3-hydroxyferuloylsophoroside-7-glucoside, Km 3-sinapoylsophoroside-7-glucoside and Is 3-caffeoylsophoroside-7-glucoside, are common peaks in all five brassica species microgreens. Is 3-*O*-glucoside, Qn 3,7-di-*O*-glucoside, Km 3-pcoumaroyldiglucoside, Qn 3-

caffeoylsophoroside, Qn 3-feruloylsophoroside, Qn 3-feruloylsophoroside-7-glucoside, and Km 3-sinapoylsophoroside were found only in mizuna microgreen, while Km 3-sinapoylsophoroside-7-glucoside and Qn 3-sinapoylsophorotrioside were found only in purple kohlrabi. Red cabbage microgreens had, Km 3-*p*coumaroylsophorotrioside, Km 3-*p*-coumaroylsophoroside-7-diglucoside, km 3-hydroxyferuloylsophorotrioside-7-glucoside, Km 3-disinapoyldiglucoside-7-glucoside, Km 3-sinapoylferuloylsophoroside-7-glucoside and Qn 3-disinapoylsophorotrioside which were also found in mature red cabbage. Km 3-sophorotrioside-7-glucoside, Qn 3-caffeoylsophorotrioside-7-glucoside and Qn 3-hydroxyferuloylsophorotioside-7-glucoside only existed in microgreen of red mustard and purple mustard.

Using MS analysis of peak a19, as an example, the deprotonated molecular ion at m/z 933 ($C_{42}H_{45}O_{24}$) lost a hexosyl group from position 7, giving the product ion at *m/z* 771. The MS^3 product ion revealed a loss of 162 amu, corresponding to a caffeoyl group, and a loss of dihexoxyl group at the 3-position (324 amu), leading to the Km aglycone (m/z 285). Thus, peak a19 was tentatively identified as Km 3-caffeoyldiglucoside-7-glucoside. Peak b13 also exhibited the deprotonated ion at *m/z* 933 but showed different fragmentation pathways. During the MS fragmentation of peak 18a, loss of 162 amu, corresponding to a hexosyl moiety at the terminal 7-position was observed. Further fragmentation of the acylated ion, *m/z* 625, gave the loss of pcoumaroyl group and the loss of a dihexosyl group, producing the Qn aglycone ion (*m/z* 301). Thus, peak b13 was assigned as Qn 3-p-coumaroyldiglucoside-7-glucoside. Using this strategy, the remaining flavonols were identified on the basis of HRMS, MS fragmentation pattern, UV maxima, and retention times as flavonols, previously characterized in the five *Brassica* species microgreens.

Derivatives of Hydroxycinnamic Acids and Hydroxybenzoic acids

Hydroxycinnamic acids and hydroxybenzoic acids are considered non-flavonoid phenolics and are characterized by their C6-C3 and C6-C structures, respectively. Most of the hydroxycinnamic acids and hydroxybenzoic acid derivatives detected in mature vegetables (17-19, 21) were also detected in our five *Brassica* species microgreens. However, our five *Brassica* species microgreens contained a greater variety and higher concentrations of cinamic acids than their mature leaf counterpart. The retention times, HRMS molecular ions $[M-H]^-$, diagnostic MS^2 and MS^3 product ions, UV λ_{max} and identification of the hydroxycinnamates, arranged by molecular weight, are listed in **Table 3**. Their peaks are eluted with the flavanol glycoside peaks, as shown in **Figure 3**. The hydroxycinnamic acids, hydoxycinnamoylquinic acids, hydroxycinnamoylmalic acids, and hydroxycinnamoyl saccharides with one to three glucosides were identified using reference compounds (designated by **) or from the literature (designated by *) **Table 3**. Sixteen of the hydroxycinnamoylsaccharides were formed from di- or triglucoses, mainly gentiobiose, with one to three hydroxycinnamoyl units. By direct comparison with reference compounds in mustard greens, peaks a36, a41, b28 and d26 (**Figure 3**) were identified as disinapoylgentiobioses. Peaks a4, b11, and c12 were identified as feruloyl-glucosides. Peaks a42, d27, and a43 were identified as sinapoyl-feuloylgentiobioses. Peak a47 and b30, identified as trisinapoylgentionbiose and feruloyl-disinapoyl-gentionbiose, are peaks common to microgreens of mizuna, purple kohlrabi, red mustard, and purple mustard. Peak d11 is only found in mizuna and was tentatively identified as sinapic acid-glucose.

Other organic acids, such as caffeoylquinic acid, ferulic acid, sinapic acid, citric acid, malic acid, and caffeoylquinic acid are organic acids common in these five microgreens. There were a number of organic acid isomers found in the five *Brassisa* microgreens and identification was based on their similar MS^2 and MS^3 spectra. However, they exhibited different retention times based on species. For example, the peaks a42, a43and d27 all had

the same $[M-H]^-$ at *m/z* 723. HRMS measurements suggested the formula of $C_{33}H_{39}O_{18}$, with the main MS^2 product ion at *m/z* 529 (M - 194, neutral loss of ferulic acid) and the main MS^3 product ions at *m/z* 223 sinapic acid). These compounds were identified as sinapoyl-ferulic acid and its isomers. Similarly, peaks a36, b28, and a41 ($[M - H]^-$ at *m/z* 753, with a main MS^2 product ion at 529 and main MS^3 product ions at 205) was identified as disinapoylgentiobiose and its isomers.

In summary, this is the first study characterizing phenolic profiles specifically in *Brassisca* species microgreens. A total of 165 phenolic compounds were tentatively identified using complementary information from UHPLC-PDA-$HRMS^n$ in negative and positive modes, revealing a large number of highly glycosylated and acylated quercetin, kaempferol, cyanidin aglycones and complex hydroxycinnamic and benzoic acids. The results showed that the *Brassica* species microgreens tended to have more complex polyphenols profiles and to contain more varieties of polyphenols compared to their mature plant counterpart. Thus, *Brassica* species microgreens could be considered a good source for polyphenols. This compositional study should serve as reference base for these five *Brassica* species microgreens and enhance their value to health agencies and consumers

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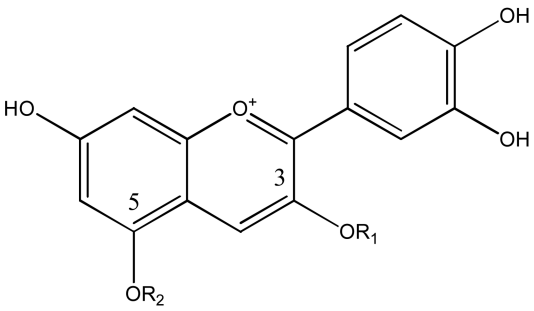
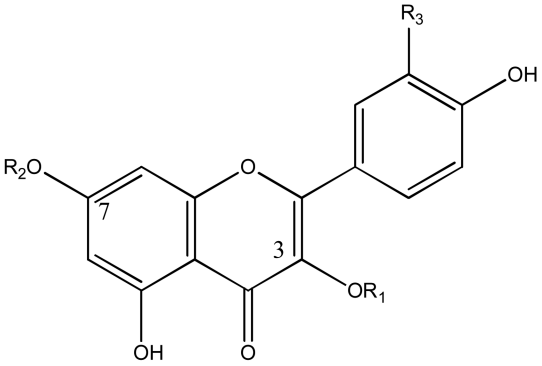


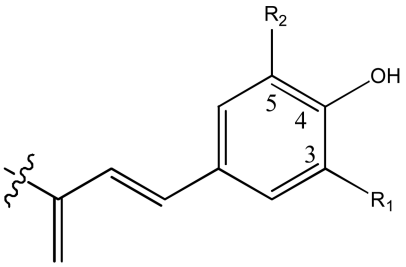
Anthocyanins

R_1 = sophorosyl, diglucosyl or triglucosyl with acyls
R_2 = glucosyl, glucosyl with malonyl



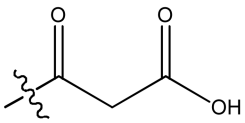
Flavonols and Flavonol glycosides

Kaempferol R_1=R_2=R_3=H (MW, 286 Da)
Quercetin R_1=R_2=H, R_3=OH (MW, 302 Da)
Isorhamnetin R_1=R_2=H, R_3=OCH_3 (MW, 316 Da)
Flavonol glycosides R_1 and/or R2 = glycosyls



Hydroxycinnamoyls

p-Coumaroyl R_1=R_2=H
Caffeoyl R_1=OH, R_2=H
Feruloyl R_1=OCH_3, R_2=H
Hydroxyferuloyl R_1=OCH_3, R_2=OH
Sinapoyl R_1=R_2=OCH_3
Flavonol glycosides R1 and/or R2 = glycosyls



Malonyl

Figure 1.
Basic chemical structures identified from five *Brassica* species microgreens.

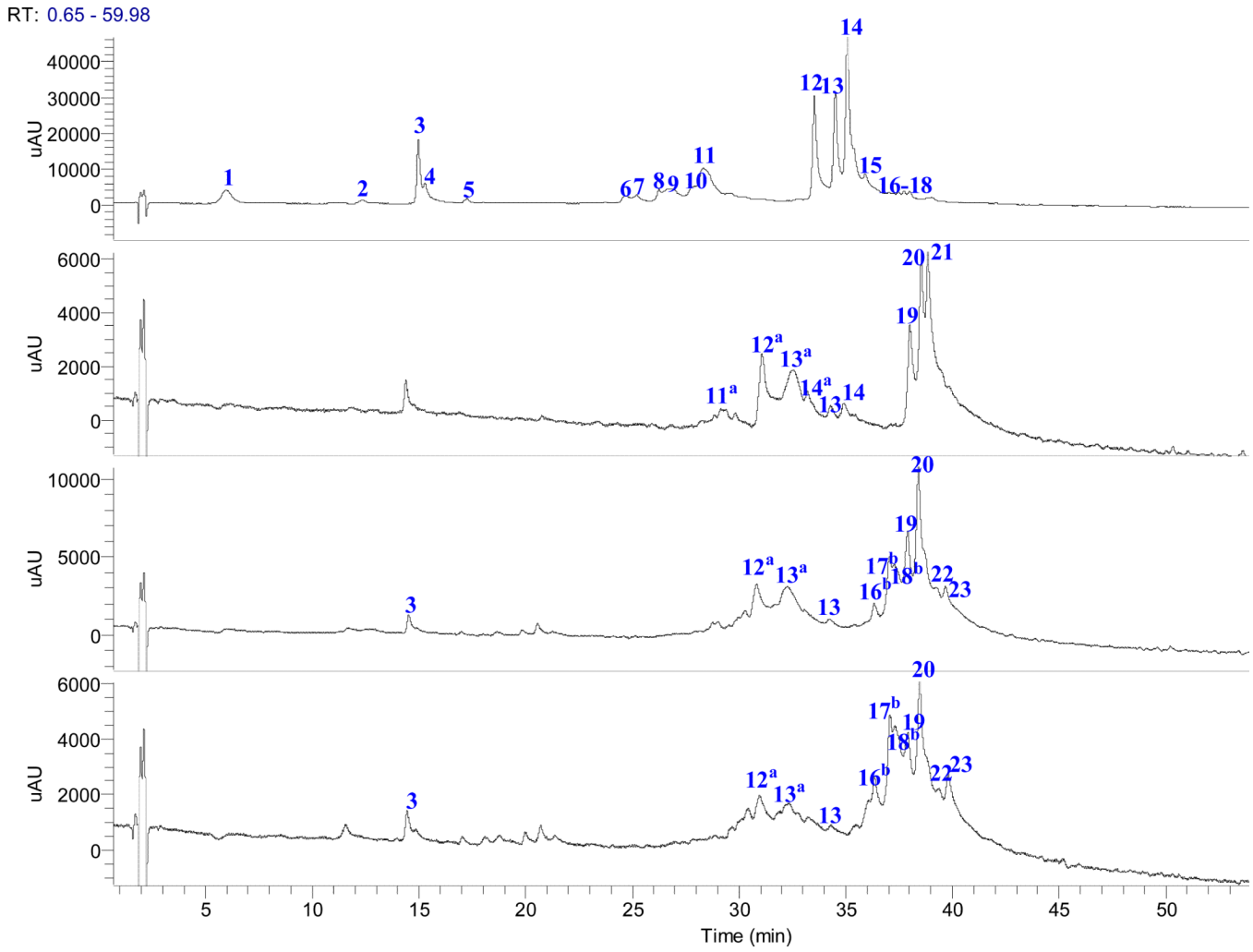


Figure 2.
The UHPLC chromatogram from five *Brassica* species microgreens: red cabbage (A), purple kohlrabi (B), red mustard (C) and purple mustard (D) under 520 nm.

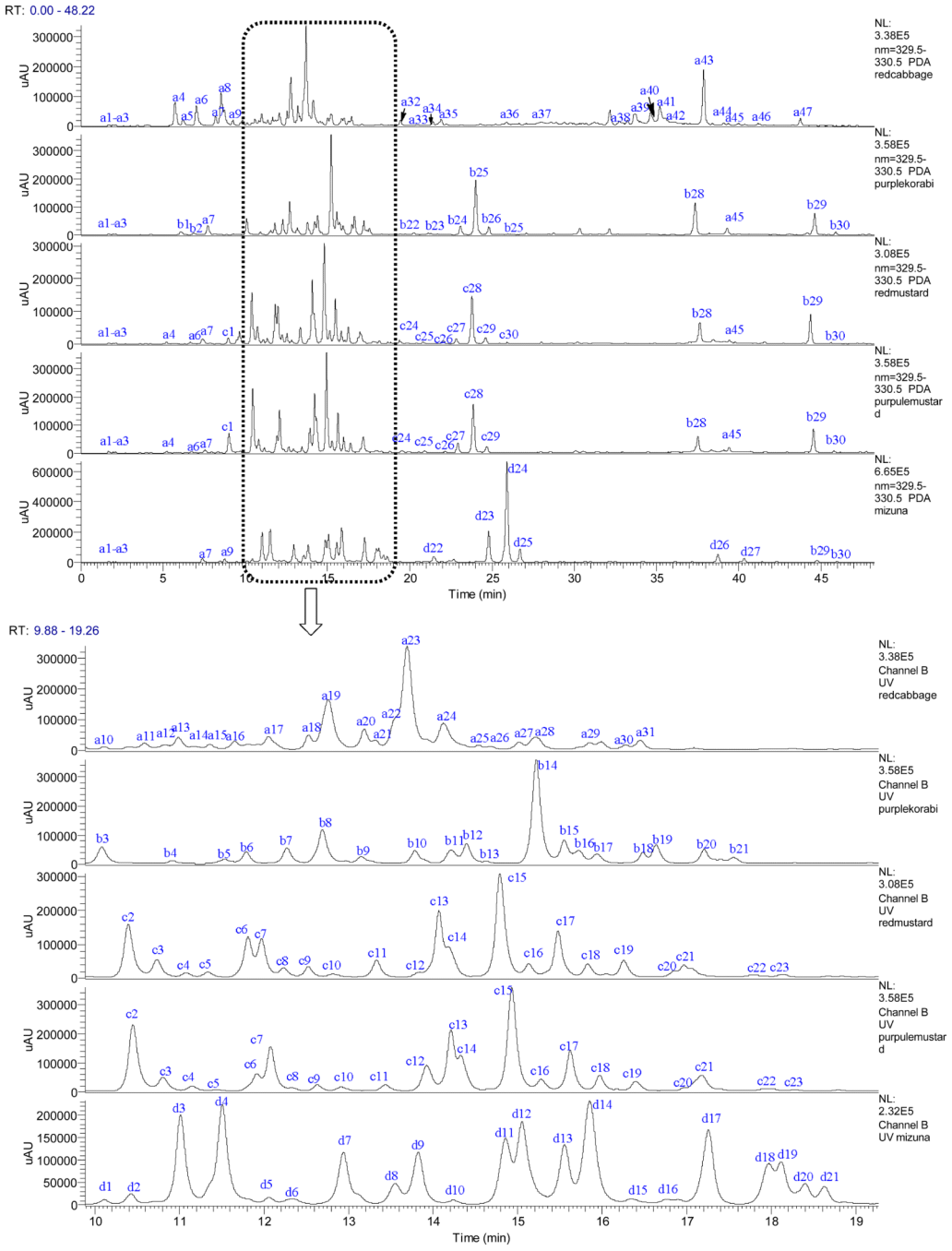


Figure 3.

The UHPLC chromatogram of five *Brassica* species microgreens: red cabbage (A), purple kohlrabi (B), red mustard (C), purple mustard (D) and mizuna (E) under 330 nm.

Table 1

Typical substitutional groups and common neutral losses of polyphenols in five *Brassica* species microgreens.

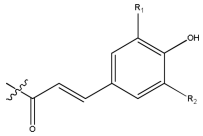
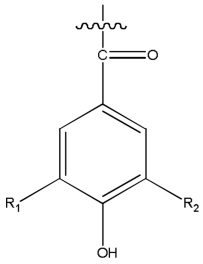
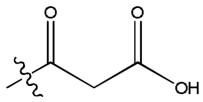
Substitutional groups	Name	Neutral Loss in HRMS
mono-saccharides	pentose (xylose, arabinose)	132.0422 ($C_5H_8O_4$)
	methyl-pentose (rhamnose) hexose (glucose, galactose)	146.0579 ($C_6H_{10}O_4$) 162.0528 ($C_6H_{10}O_5$)
di-saccharides	sophorose=2-β-D-glucopyranosyl-D-glucose gentiobiose=6-β-D-glucopyranosyl-D-glucose	324.1056 ($C_{12}H_{20}O_{10}$)
tri-saccharides	sophorotriose (2‴- β-D-glucopyranosyl-2″-β-D-glucopyranosyl-D-glucose) gentiotriose (6‴- β-D-glucopyranosyl-6″-β-D-glucopyranosyl-D-glucose)	486.1584 ($C_{18}H_{30}O_{15}$)
hydroxycinnamoyls	*p*-coumaroyl R_1=H R_2=H caffeoyl R_1=OH R_2=H	146.0347 ($C_9H_6O_2$) 162.0317 ($C_9H_6O_3$)
	feruloyl R_1=OCH_3 R_2=H sinapoyl R_1=OCH_3 R_2=OCH_3	176.0473 ($C_{10}H_8O_3$) 206.0579 ($C_{11}H_{10}O_4$)
hydroxybenzoyls	*p*-hydroxybenzoyl R_1=H R_2=H	120.0211 ($C_7H_4O_2$)
	galloyl R_1= OH R_2=OH	152.0109 ($C_7H_4O_4$)
di-carboxylic acid acyls	malonyl	86.0004 ($C_3H_2O_3$)
		

Table 2

UHPLC-HRMS-Data of anthocyanins from combines four *Brassica* species Microgreens: red cabbage, red mustard, purple mustard, mizuna and purple kohlrabi

Peak #	t_R (min)	$[M]^+$	Formula	Error (mmu)	major and important MS^2 ions	major MS^3 ion	Tentative Identification
1	5.97	773.2106	$C_{33}H_{41}O_{21}$	−1.36	611(29), 449(40), 287(100)	287(100)	cy 3-diglucoside-5-glucoside*
2	12.34	965.2528	$C_{43}H_{49}O_{25}$	−2.12	803(100), 641(20), 287(60)	287(100)	cy 3-hydroxyferuloyl-5-glucoside*
3	14.98	979.2699	$C_{44}H_{51}O_{25}$	−1.53	817(71), 449(46), 287(100)	287(100)	cy 3-(sinapoyl)-diglucoside-5-glucosides*
4	15.29	979.2708	$C_{44}H_{51}O_{25}$	−0.61	817(82), 449(52), 287(100)	287(100)	cy 3-(sinapoyl)-diglucoside-5-glucoside*
5	17.21	1141.3246	$C_{50}H_{61}O_{30}$	0.34	979(100), 449(54)	287(100)	cy 3-(glucopyranosyl-sinapoyl)diglucoside-5-glucoside*
6	24.63	919.249	$C_{42}H_{47}O_{23}$	−1.38	757(100), 449(19), 287(50)	287(100)	cy 3-(coumaroyl)sophoroside-5-glucoside*
7	25.23	1287.3597	$C_{59}H_{67}O_{32}$	−1.01	1125(100), 449(6)	963(100),	cy-3(glucosyl)(sinapoyl)(p-coumaroyl)sophorside-5-glucoside*
8	26.31	1317.369	$C_{60}H_{69}O_{33}$	−1.94	1185(100), 1155(35), 449(2)	1023(100), 449(3)	cy-3(glucosyl)(sinapoyl)(feruloyl)sophorside-5-glucoside*
9	26.97	919.249	$C_{42}H_{47}O_{23}$	−1.38	757(100), 449(19), 287(50)	287(100)	cy 3-(coumaroyl)sophoroside-5-glucoside*
10	27.71	949.2602	$C_{43}H_{49}O_{24}$	−0.66	787(100), 449(18), 287(49)	287(100)	cy 3-(feruloyl)sophoroside-5-glucoside*
11	28.31	1141.3016	$C_{53}H_{57}O_{28}$	−1.30	979(100), 449(11)	287(100)	cy 3-(caffeoyl)(sinapoyl)diglucoside-5-glucoside
11a	29.14	1005.2492	$C_{45}H_{49}O_{26}$	−1.46	757(22), 535(100), 491(10), 287(73)	287(100)	cy 3-(coumaroyl)sophoroside-5-(malonyl)glucoside
12	33.37	1125.307	$C_{53}H_{57}O_{27}$	−1.04	963(100), 449(13)	287(100)	cy 3-diferuloylsophoroside-5-glucoside*
12a	31.07	1211.3088	$C_{56}H_{59}O_{30}$	0.23	963(100), 535(81), 521(9)	287(100)	cy 3-(coumaroyl)(sinapoyl)diglucoside-5-(malonyl)glucoside*
13	34.50	1125.307	$C_{53}H_{57}O_{27}$	−1.04	963(100), 449(13)	287(100)	cy 3-diferuloylsophoroside-5-glucoside*
13a	32.56	1035.2599	$C_{46}H_{51}O_{27}$	−1.32	992(7), 787(40), 780(5), 535(100), 492(12), 449(6), 287(5)	287(100)	cy 3-(feruloyl)glucoside-5-(malonyl)-glucoside*
14	35.07	1155.3192	$C_{54}H_{59}O_{28}$	0.40	993(100), 449(9)	287(100)	cy 3-sinapoylferuloylsophoroside-5-glucoside*
14a	33.21	1065.2702	$C_{47}H_{53}O_{28}$	−1.59	817(73), 535(100), 492(2), 449(3)	287(100)	cy 3-(sinapoyl)glucoside-5-(malonyl)-glucoside*
15	35.91	1155.3192	$C_{54}H_{59}O_{28}$	0.40	993(100), 449(9)	287(100)	cy 3-(sinapoyl)(feruloyl)sophoroside-5-glucoside*
16	37.14	1185.3298	$C_{55}H_{61}O_{29}$	0.50	1023(100), 449(10)	287(100)	cy 3-(sinapoyl)(sinapoyl)sophoroside-5-glucoside*
16b	36.34	1373.3585	$C_{62}H_{69}O_{35}$	−2.89	963(100), 697(66), 653(28)	287(100)	cy 3-(sinapoyl)(coumaroyl)-triglucoside-5-(malonyl)-glucoside*

Peak #	t_R (min)	$[M]^+$	Formula	Error (mmu)	major and important MS^2 ions	major MS^3 ion	Tentative Identification
17	37.55	1155.3192	$C_{54}H_{59}O_{28}$	0.40	993(100), 449(9)	287(100)	cy 3-(sinapoyl)(feruloyl)sophoroside-5-glucoside*
17b	37.08	1197.2902	$C_{55}H_{57}O_{30}$	−2.72	949(18), 860(3), 535(100), 517(3), 491(9)	287(100)	cy 3-(caffeoyl) (sinapoyl)-xylglu-5-(malonyl) glucoside*
18	37.99	1185.3298	$C_{55}H_{61}O_{29}$	0.49	1023(100), 449(10)	287(100)	cy 3-(smapoyl)(sinapoyl)sophoroside-5-glucoside*
18b	37.37	1227.3008	$C_{56}H_{59}O_{31}$	−2.68	979(82), 535(100), 491(10)	287(100)	cy 3-(p-coumaroyl)(sinapoyl)diglucoside-5-O-(malonyl)glucoside
19	38.00	1211.3082	$C_{56}H_{59}O_{30}$	−1.46	963(91), 535(100), 491(3)	287(100)	cy-3-(feruloyl)(feruloyl)diglucoside-5-(malonyl)glucoside*
20	38.56	1241.3192	$C_{57}H_{61}O_{31}$	−1.03	1206(15), 1198(30), 993(100), 535(88), 449(8)	287(100)	cy 3-(sinapoyl)(feruloyl)diglucoside-5-(malonyl)glucoside*
21	38.85	1271.3296	$C_{58}H_{63}O_{32}$	−0.10	1023(100), 535(51), 491(7)	287(100)	cy 3-(sinapoyl)(sinapoyl)diglucoside-5-(malonyl)glucoside*
22	39.35	1241.3190	$C_{57}H_{61}O_{31}$	−0.13	993(100), 535(70), 492(13)	287(100)	cy3-(sinapoyl)(feruloyl)diglucoside-5-(malonyl)glucoside*
23	39.81	1211.3078	$C_{56}H_{59}O_{30}$	−0.77	963(86), 535(100)	287(100)	cy 3-(p-coumaroyl)(sinapoyl)diglucoside-5-(malonyl)glucoside*

*compared with literature data, cy-cyanidin

Table 3

UHPLC-HRMS-Data of flavonol glycosides and derivatives of hydroxycinnamic acids and hydroxybenzoic acids from five *Brassica* speies microgreens: red cabbage, red mustard, purple mustard, mizuna and purple kohlrabi.

Peak.No.	t_R(min)	[M-H]-	Formula	Error (mmu)	major and important MS^2 ions	MS^3 ion	Tentative Identification
a1	1.66	133.0143	$C_4H_5O_5$	0.40	241(83), 153(100)	115(100)	malic acid*
a2	1.98	191.0192	$C_6H_7O_7$	−0.53	173(22), 111(100)	67(100)	citric acid*
a3	3.37	205.0349	$C_7H_9O_7$	−0.48	173(61), 159(6), 143(11), 111(100)		methyl citric acid
b1	5.56	503.1398	$C_{21}H_{27}O_{14}$	−0.83	341(100), 179(9)	179(100)	courmaroyl-di-glucoside
a4	5.71	355.1029	$C_{16}H_{19}O_9$	−1.56	217(59), 193(100), 175(40)	134(100)	feruloyl-glucose
b2	5.93	353.0870	$C_{16}H_{17}O_9$	−0.80	191(100), 179(43), 135(8)	173(100)	caffeoyl-quinic acid
5a	6.12	299.0768	$C_{13}H_{15}O_8$	−0.44	239(90), 179(71), 137(100)		salicyloyl-glucose*
a6	6.21	547.1671	$C_{23}H_{31}O_{15}$	0.47	223(100)	208(100)	sinapoyl-gentiobiose*
a7	7.18	447.0557	$C_{20}H_{15}O_{12}$	−1.12	357(38), 275(55), 259(100)	139(100)	rhamnosyl-ellagic acid
a8	8.32	787.1942	$C_{33}H_{39}O_{22}$	1.45	625(100)	300(100)	qn 3-diglucoside-7-glucoside*
a9	9.20	787.1920	$C_{33}H_{39}O_{22}$	−1.85	625(100)	300(100)	qn 3-diglucoside-7-glucoside*
c1	9.68	933.2486	$C_{39}H_{49}O_{26}$	−0.79	771(100)	591(100)	km 3-sophorotrioside-7-glucoside
b3	10.06	787.1916	$C_{33}H_{39}O_{22}$	−2.25	625(100)	300(100)	qn 3-sophoroside-7-glucoside*
d1	10.09	845.2113	$C_{39}H_{41}O_{21}$	−3.28	683(100), 477(15), 315(6)	353(100)	is 3-sinapoylglucoside-7-glucoside*
a10	10.11	771.1978	$C_{33}H_{39}O_{21}$	−1.13	609 (100)	285(100)	km 3-sophoroside-7-glucoside*
d2	10.43	817.2015	$C_{34}H_{41}O_{23}$	−2.91	609(100), 447(34)	447(100)	km 3-diglucoside-7-glucoside with HCOOH
c2	10.45	1141.2889	$C_{49}H_{57}O_{31}$	1.07	979 (100), 949(93), 787(72)	787(100)	qn 3-hydroxyferuloylsophorotioside-7-glucoside*
a11	10.59	979.2349	$C_{43}H_{47}O_{26}$	−1.23	817(98), 787(100), 625(59)	625(100)	qn 3 hydroxyferuloylsophoroside-7-glucoside*
c3	10.80	1111.2760	$C_{48}H_{55}O_{30}$	−2.13	949(100), 787(30)	787(100)	qn 3-caffeoylsophorotrioside-7-glucoside*
a12	10.82	979.2333	$C_{43}H_{47}O_{26}$	−2.80	817(98), 787(100), 625(59)	625(100)	qn 3 hydroxyferuloylsophoroside-7-glucoside*
b4	10.92	787.1906	$C_{33}H_{39}O_{22}$	−3.25	625(100)	300(100)	qn 3-sophoroside-7-glucoside*
d3	10.97	979.2359	$C_{43}H_{47}O_{26}$	−0.20	817(92), 787(100), 625(51)	625(100)	qn 3 hydroxyferuloylsophoroside-7-glucoside*

Peak.No.	t_R(min)	[M-H]-	Formula	Error (mmu)	major and important MS^2 ions	MS^3 ion	Tentative Identification
a13	10.99	949.2256	$C_{42}H_{45}O_{25}$	0.06	787(100), 625(22)	625(100)	qn 3-caffeoylsophoroside-7-glucoside*
c4	11.11	1111.2749	$C_{48}H_{55}O_{30}$	−3.46	949(100), 787(29)	787(100)	qn 3-caffeoylsophorotrioside-7-glucoside*
a14	11.12	949.2231	$C_{42}H_{45}O_{25}$	−2.44	787(100), 625(20)	625(100)	qn 3-caffeoylsophoroside-7-glucoside*
c5	11.31	1111.2762	$C_{48}H_{55}O_{30}$	−2.16	949(100), 787(29)	787(100)	qn 3-caffeoylsophorotrioside-7-glucoside*
a15	11.36	1111.2780	$C_{48}H_{55}O_{30}$	−0.36	949(100), 787(30)	787(100)	qn 3-caffeoylsophorotrioside-7-glucoside*
d4	11.47	949.2234	$C_{42}H_{45}O_{25}$	−2.14	787(100), 625(20)	625(100)	qn 3-caffeoylsophoroside-7-glucoside*
b5	11.53	609.1447	$C_{27}H_{29}O_{16}$	−1.41	489(7), 447(100), 285(10)	285(100)	km 3-diglucoside
a16	11.65	1111.2761	$C_{48}H_{55}O_{30}$	−2.26	949(100), 788(34), 625(36)	625(100)	qn 3-caffeoylsophorotrioside-7-glucoside*
b6	11.81	771.1976	$C_{33}H_{39}O_{21}$	−1.33	609(100)	285(100)	km 3-sophoroside-7-glucoside*
c6	11.92	787.1942	$C_{33}H_{39}O_{22}$	1.45	625(100)	300(100)	qn 3-sophoroside-7-glucoside*
a17	12.05	963.2385	$C_{43}H_{47}O_{25}$	−2.69	801(100), 609(2)	609(100)	km 3-hydroxyferuloylsophoroside-7-glucoside*
d5	12.07	1111.2766	$C_{48}H_{55}O_{30}$	−1.76	949(100), 787(38)		qn 3-caffeoylsophorotrioside-7-glucoside*
c7	12.08	979.2349	$C_{43}H_{47}O_{26}$	−1.23	817(98), 787(100), 625(59)	625(100)	qn 3 hydroxyferuloylsophoroside-7-glucoside*
b7	12.25	979.2329	$C_{43}H_{47}O_{26}$	−3.21	817(95), 787(100), 625(55)	625(100)	qn 3 hydroxyferuloylsophoroside-7-glucoside*
c8	12.28	1125.2937	$C_{49}H_{57}O_{30}$	−0.28	963(100)	771(100)	km 3-hydroxyferuloylsophorotrioside-7-glucoside*
d6	12.37	949.2234	$C_{42}H_{45}O_{25}$	−2.14	787(100), 625(20)	625(100)	qn 3-caffeoylsophoroside-7-glucoside*
a18	12.53	977.2541	$C_{44}H_{49}O_{25}$	−2.80	831(43), 771(100), 625(21)	301(100)	qn 3 sophoroside-7-sinapoylrhamoside
c9	12.63	1095.2826	$C_{48}H_{55}O_{29}$	−0.28	975(2), 933(100), 809(7)	771(100)	km 3-caffeoylsophorotrioside-7-glucoside*
b8	12.69	949.2236	$C_{42}H_{45}O_{25}$	−1.94	787(100), 625(20)	625(100)	qn 3-caffeoylsophoroside-7-glucoside*
a19	12.72	933.2289	$C_{42}H_{45}O_{24}$	−1.73	771(100)	609(100)	km 3-caffeoyldiglucoside-7-glucoside
c10	12.91	547.1671	$C_{23}H_{31}O_{15}$	0.47	223(100)	208(100)	sinapoylgentiobiose*
d7	12.94	963.2381	$C_{43}H_{47}O_{25}$	−3.09	801(100)	609(100)	km 3-hydroxyferuloylsophoroside-7-glucoside*
b8	13.15	1111.2760	$C_{48}H_{55}O_{30}$	−2.13	949(100), 787(30)	787(100)	qn 3-caffeoylsophorotrioside-7-glucoside*
a20	13.18	1095.2797	$C_{48}H_{55}O_{29}$	−3.42	949(84), 933(100), 787(45)	787(100)	qn 3-p-coumaroyltriglucoside-7-glucoside

Peak.No.	t_R(min)	[M-H]-	Formula	Error (mmu)	major and important MS^2 ions	MS^3 ion	Tentative Identification
a21	13.32	1095.2826	$C_{48}H_{55}O_{29}$	−0.28	975(2), 933(100), 809(7)	771(100)	km 3-caffeoylsophorotrioside-7-glucoside*
c11	13.44	625.1410	$C_{27}H_{29}O_{17}$	−0.04	463(8), 343(16), 301(100)	179(100)	qn diglucoside*
a22	13.52	1155.3022	$C_{50}H_{59}O_{31}$	−2.38	993(100), 950(41), 787(39)		qn 3-sinapoyltriglucoside-7-glucoside
d8	13.58	961.2592	$C_{44}H_{49}O_{24}$	−2.84	623(72), 609(100), 592(27)	257(100)	km 3-sophoroside-7-sinapoylrhamnoside
a23	13.69	993.2493	$C_{44}H_{49}O_{26}$	−2.45	801(13), 787(100)	607(100)	qn 3-sinapoylsophoroside-7-glucoside*
d9	13.77	933.2275	$C_{42}H_{45}O_{24}$	−3.13	771(100)	609(100)	km 3-caffeoyldiglucoside-7-glucoside
b10	13.78	963.2391	$C_{43}H_{47}O_{25}$	−2.09	801(100)	609(100)	km 3-hydroxyferuloylsophoroside-7-glucoside*
c12	13.92	355.1029	$C_{16}H_{19}O_9$	−1.56	217(59), 193(100), 175(40)	134(100)	feruloylglucose*
a24	14.12	1125.2937	$C_{49}H_{57}O_{30}$	−0.28	963(100)	771(100)	km 3-hydroxyferuloylsophorotrioside-7-glucoside*
b11	14.21	355.1029	$C_{16}H_{19}O_9$	−1.56	217(59), 193(100), 175(40)	134(100)	feruloylglucose*
d10	14.21	933.2283	$C_{42}H_{45}O_{24}$	−2.24	787(10), 771(100), 625(11)	625(100)	km 3-caffeoyldiglucoside-7-glucoside
c13	14.21	1155.3028	$C_{50}H_{59}O_{31}$	−1.78	993(100), 950(29), 788(30)		qn 3-sinapoyltriglucoside-7-glucoside
c14	14.33	1155.3023	$C_{50}H_{59}O_{31}$	−2.28	993(100), 950(29), 788(30)		qn 3-sinapoyltriglucoside-7-glucoside
b12	14.39	933.2306	$C_{42}H_{45}O_{24}$	−0.03	787(14), 771(100), 625(11)	625(100), 607(8)	qn 3-p-coumaroyldiglucoside-7-glucoside*
a25	14.52	1095.2810	$C_{48}H_{55}O_{29}$	−2.45	949(100), 933(38), 771(62), 625(40)		km 3-caffeoyl-triglucoside-7-glucoside
b13	14.61	933.2280	$C_{42}H_{45}O_{24}$	−2.63	771(100)	609(100)	km 3-caffeoyl-diglucoside-7-glucoside
a26	14.67	1095.2811	$C_{48}H_{55}O_{29}$	−2.35	949(100), 933(38), 932(6), 787(6), 771(62)		km 3-caffeoyl-triglucoside-7-glucoside
d11	14.89	385.1137	$C_{17}H_{21}O_{10}$	−0.32	247(52), 223(100), 205(55)	164(100)	sinapic acid-glucose
c15	14.91	993.2486	$C_{44}H_{49}O_{26}$	−3.15	831(99), 787(100), 769(6), 625(44)	625(100)	qn 3-sinapoylsophorotrioside*
a27	15.01	1139.3093	$C_{50}H_{59}O_{30}$	−0.32	977(100)	771(100)	km 3-sinapoylsophorotrioside-7-glucoside*
d12	15.04	993.2481	$C_{44}H_{49}O_{26}$	−3.65	831(100), 787(94), 769(6), 625(45)		qn 3-sinapoyldiglucoside-7-glucoside
a28	15.21	977.2535	$C_{44}H_{49}O_{25}$	−2.24	815(100), 609(3)	609(100)	km 3-sinapoylsophoroside-7-glucoside*
b14	15.22	993.2496	$C_{44}H_{49}O_{26}$	−2.15	831(99), 787(100), 769(6), 625(44)	625(100)	qn 3-sinapoyltriglucoside
c16	15.27	963.2387	$C_{43}H_{47}O_{25}$	−2.49	801(100), 609(2)	609(100)	km 3-hydroxyferuloylsophoroside-7-glucoside*
b15	15.55	963.2381	$C_{43}H_{47}O_{25}$	−3.09	801(100), 787(45), 625(26)	625(100)	km 3-hydroxyferuloylsophoroside-7-glucoside*
d13	15.55	963.2374	$C_{43}H_{47}O_{25}$	−3.79	801(100), 787(47), 625(25)		km 3-hydroxyferuloylsophoroside-7-glucoside*

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Peak.No.	t_R(min)	[M-H]-	Formula	Error (mmu)	major and important MS^2 ions	MS^3 ion	Tentative Identification
c17	15.63	1139.3103	$C_{50}H_{59}O_{30}$	0.56	977(100), 771(3)	771(100)	km 3-sinapoylsophorotrioside-7-glucoside*
b16	15.72	963.2391	$C_{43}H_{47}O_{25}$	−2.09	801(100), 787(45), 625(26)	625(100)	km 3-hydroxyferuloylsophoroside-7-glucoside*
d14	15.82	933.2283	$C_{42}H_{45}O_{24}$	−2.33	787(10), 771(100), 625(11)	625(100)	km 3-caffeoyldiglucoside-7-glucoside
a29	15.87	947.2429	$C_{43}H_{47}O_{24}$	−2.28	827(2), 785(100), 609(2)	609(100)	km 3-feruloylsophoroside-7-glucoside*
b17	15.93	933.2280	$C_{42}H_{45}O_{24}$	−2.63	788(10), 771(100), 625(11)	625(100)	km 3-caffeoyldiglucoside-7-glucoside
c18	15.93	1109.2946	$C_{49}H_{57}O_{29}$	−4.06	947(100)	771(100)	km 3-feruloylsophorotrioside-7-glucoside
a30	16.28	917.2318	$C_{42}H_{45}O_{23}$	−4.26	755(100)	609(100)	km 3-p-coumaroylsophoroside-7-glucoside*
d15	16.36	1095.2805	$C_{48}H_{55}O_{29}$	−2.95	933(100), 787(28)		km 3-caffeoyltriglucoside-7-glucoside
c19	16.39	977.2535	$C_{44}H_{49}O_{25}$	−2.24	815(100), 609(3)	609(100)	km 3-sinapoylsophoroside-7-glucoside*
a31	16.47	1079.2852	$C_{48}H_{55}O_{28}$	−3.33	755(100), 609(12)	609(100)	km 3-p-coumaroylsophoroside-7-diglucoside
b18	16.48	1139.3065	$C_{50}H_{59}O_{30}$	−3.16	977(100)	771(100)	km 3-sinapoylsophorotrioside-7-glucoside*
b19	16.63	977.2542	$C_{44}H_{49}O_{25}$	−2.64	815(100)	609(100)	km 3-sinapoylsophoroside-7-glucoside*
d16	16.76	609.1441	$C_{27}H_{29}O_{16}$	−2.01	489(13), 447(100), 285(19)	284(100)	km 3-glucoside-7-glucoside**
c20	16.93	947.2429	$C_{43}H_{47}O_{24}$	−2.28	827(2), 785(100), 609(2)	609(100)	km 3-feruloylsophoroside-7-glucoside*
c21	17.17	639.1566	$C_{28}H_{31}O_{17}$	2.08	519(10), 477(100), 315(12)	314(100)	is 3-glucoside-7-glucoside*
b20	17.20	947.2439	$C_{43}H_{47}O_{24}$	−2.38	785(100)	609(100)	km 3-feruloylsophoroside-7-glucoside*
d17	17.25	977.2535	$C_{44}H_{49}O_{25}$	−3.34	815(100), 771(10)	609(100)	km 3-sinapoylsophoroside-7-glucoside*
b21	17.55	917.2328	$C_{42}H_{45}O_{23}$	−2.91	755(100)	609(100)	km 3-p-coumaroylsophoroside-7-glucoside
d18	17.97	947.2429	$C_{43}H_{47}O_{24}$	−3.38	785(100)	609(100)	km 3-feruloylsophoroside-7-glucoside*
c22	18.03	551.1753	$C_{26}H_{31}O_{13}$	−1.71	389(100), 341(6)	341 (100)	ferulic acid-rhamnosylglucose with a 48 amu group
d19	18.12	947.2449	$C_{43}H_{47}O_{24}$	−1.38	785(100)	609(100)	km 3-feruloylsophoroside-7-glucoside*
c23	18.28	993.2473	$C_{44}H_{49}O_{26}$	−4.49	801(13), 787(100)	607(100)	qn 3-sinapoylsophoroside-7-glucoside*
d20	18.36	639.1548	$C_{28}H_{31}O_{17}$	−1.87	519(11), 477(100), 315(12)	314(100)	is 3-glucoside-7-glucoside
d21	18.63	917.2330	$C_{42}H_{45}O_{23}$	−2.71	755(100)	609(100)	km 3-p-coumaroyldiglucoside-7-glucoside
b22	19.13	625.1382	$C_{27}H_{29}O_{17}$	−2.82	505(21), 463(37), 445(55), 301(60), 300(100)		qn 3-diglucoside
a32	19.40	935.2444	$C_{42}H_{47}O_{24}$	−1.88	773(100), 755(29), 663(52), 285(30)	285(100)	km aglycone with 7 glucoside and 3 acyl glucosyls

Peak.No.	t_R(min)	[M-H]-	Formula	Error (mmu)	major and important MS^2 ions	MS^3 ion	Tentative Identification
a33	20.43	625.1414	$C_{27}H_{29}O_{17}$	0.60	505(18), 463(17), 445(54), 300(100)	271(100)	qn 7-sophoroside*
b23	21.28	639.1548	$C_{28}H_{31}O_{17}$	−2.9	315(100), 300(16)		is 3-diglucoside
a34	21.40	965.2516	$C_{49}H_{41}O_{21}$	1.02	803(100), 785(24), 693(48), 667(9), 285(21)	285(100)	km 3-caffeoyldiglucoside-7-glucoside
d22	21.48	933.2271	$C_{42}H_{45}O_{24}$	−3.53	787(10), 771(100), 625(11)	625(100)	km 3-caffeoyldiglucoside-7-glucoside
a35	21.90	935.2436	$C_{42}H_{47}O_{24}$	−2.68	773(100), 756(31), 663(55), 637(10), 285(24)	285(100)	km aglycone with 7 glucoside and 3 acyl glucosyls
c24	22.16	831.1997	$C_{38}H_{39}O_{21}$	0.93	625(100)	300(100)	qn 3-sinapoylsophoroside*
b24	23.13	193.0506	$C_{10}H_9O_4$	−0.03	178(19), 149(50), 134(100)	106(100)	ferulic acid**
b25	24.01	223.0607	$C_{11}H_{11}O_5$	−2.23	208(8), 179(11), 164(100)	149(100)	sinapic acid**
d23	24.79	193.0502	$C_{10}H_9O_4$	−0.43	178(25), 149(55), 134(100)	106(100)	ferulic acid**
b26	24.92	593.1503	$C_{27}H_{29}O_{15}$	−1.51	447(100)	284(100)	km 3-glucoside-7-rhanmoside
d24	25.86	223.0607	$C_{11}H_{11}O_5$	−0.50	208(8), 179(11), 164(100)	149(100)	sinapic acid isomer
b27	26.17	977.2536	$C_{44}H_{49}O_{25}$	−3.24	815(100), 653(14)	653(100)	km 3-sinapoylsophoroside-7-glucoside*
d25	26.69	223.0607	$C_{11}H_{11}O_5$	−2.23	208(8), 179(11), 164(100)	149(100)	sinapic acid isomer
a36	32.77	753.2253	$C_{34}H_{41}O_{19}$	0.73	529(100)	205(100)	disinapoylgentiobiose*
a37	33.68	1123.2886	$C_{53}H_{55}O_{27}$	−4.47	961(100), 755(20)	755(100)	km 3-hydroxyferuloylsophorotrioside-7-glucoside*
a38	34.63	1153.2981	$C_{54}H_{57}O_{28}$	1.32	991(100), 785(20)	785(100)	km 3-sinapoylferuloylsophoroside-7-glucoside*
a39	35.20	1183.3081	$C_{55}H_{59}O_{29}$	−5.62	1021(100), 816(19)	815(100)	km 3-disinapoyldiglucoside-7-glucoside
a40	35.52	1183.3086	$C_{55}H_{59}O_{29}$	−5.20	977(22), 959(7), 815(100), 609(14), 591(7)	609(100)	km 3-sinapoyldiglucoside-7-sinapoylglucoside
b28	37.34	753.2253	$C_{34}H_{41}O_{19}$	0.73	529(100)	205(100)	disinapoylgentiobiose*
a41	37.86	753.2253	$C_{34}H_{41}O_{19}$	0.73	529(100)	205(100)	disinapoylgentiobiose*
d26	38.81	753.2258	$C_{34}H_{41}O_{19}$	1.39	529(100)	223(100)	disinapoylgentiobiose*
a42	39.11	723.2144	$C_{33}H_{39}O_{18}$	0.29	529(100), 499(21)	223(100)	sinapoyl-feruloylgentiobiose*
a43	39.35	723.2125	$C_{33}H_{39}O_{18}$	−1.69	529(100), 499(21)	223(100)	sinapoyl-feruloylgentiobiose*
a44	39.99	1199.3057	$C_{55}H_{59}O_{30}$	−3.96	993(100, -206), 787(12)	787(100)	qn 3-disinapoylsophorotrioside
d27	40.41	723.2120	$C_{33}H_{39}O_{18}$	−2.19	529(100), 499(21)	223(100)	sinapoyl-feruloylgentiobiose
a45	43.75	959.2830	$C_{45}H_{51}O_{23}$	0.35	735(100), 529(7), 511(11)	529(100)	trisinapoylgentionbiose*

Peak.No.	t_R(min)	[M-H]-	Formula	Error (mmu)	major and important MS^2 ions	MS^3 ion	Tentative Identification
a47	44.67	959.2798	$C_{45}H_{51}O_{23}$	−2.87	735(100), 529(10), 511(13)	223(100)	trisinapoylgentionbiose*
b30	45.98	929.2695	$C_{44}H_{49}O_{22}$	−2.63	705(100), 511(6)	499(100)	feruloyl-disinapoyl-gentionbiose

km- kaempferol, qn-quercetin, is-isorhamnetin

* identified with literature data

** with reference standards