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# Glucosinolates in Crucifer Vegetables: Broccoli, Brussels Sprouts, Cauliflower, Collards, Kale, Mustard Greens, and Kohlrabi

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*Additional index words.* *Brassica oleracea italica* group, *B. oleracea gemmifera*, *B. oleracea botrytis* group, *B. oleracea acephala* group (var. *sabellica*), *B. oleracea acephala* group, *B. juncea* var. *rugosa*, *B. oleracea gemmifera* group, *B. oleracea acephala* group (var. *selensia*).

**Abstract.** Correlation coefficients based on relative concentrations of 13 glucosinolates in the edible parts of 30 cultivars were determined. Brussels sprouts (*Brassica oleracea* L. *gemmifera* group), cauliflower (*B. oleracea* L. *botrytis* group), and either marrow-stem or smooth-leafed kale (*B. oleracea* L. *acephala* group) had similar glucosinolate patterns based on significant correlations ( $P < 0.01$ ). The glucosinolates of 'Morris Heading' collards [*B. oleracea* L. *acephala* group (var. *sabellica*)] were highly correlated with those of curly kale [*B. oleracea* L. *acephala* group (var. *selensia*)]. Mustard greens [*B. juncea* (L.) Czern. & Coss. var. *rugosa* Bailey] and the corresponding seeds were the most highly correlated of the 17 cultivars for which the edible parts and seeds were compared. Seed analyses indicated relationships among the cultivars somewhat similar to those seen for the edible portions.

Crucifer vegetables play an important role in the American diet. In 1983, the United States produced 352,000 t of fresh broccoli (*Brassica oleracea* L. *italica* group), and 259,000 t of fresh cauliflower (36). However, the naturally occurring glucosinolates (GSs) in the edible crucifers should be monitored because of their potential detrimental or beneficial effects on health. The tendency to produce goiter has been shown for cauliflower (2, 24), kale (3), kohlrabi (*B. oleracea* L. *gongylodes* group) (2), and brussels sprouts (24). As illustrated in Figs. 1 and 2, isothiocyanates (NCSs), oxazolidine-2-thiones (OZTs), and thiocyanate (SCN) ion are liberated from GSs by the action of the enzyme thioglucosidase [EC 3.2.3.1] (34). The biological activity of these GS breakdown products has been studied. Thiocyanate ion from 3-indolylmethyl-GSs (Table 1) is known to inhibit the accumulation of iodide in the thyroid gland (37) and may be a predisposing factor for goiter. Increased liver and thyroid weights in rats have been linked with 5-vinyl-OZT (27), a compound produced from 2-hydroxy-3-butenyl-GS (Fig. 2). On the other hand, the GS hydrolysis products benzyl-

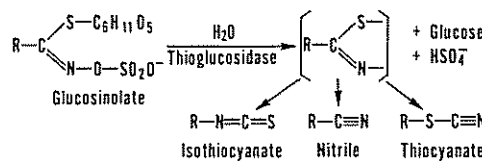


Fig. 1. Major product classes from the enzymatic hydrolysis of glucosinolates. See Table 1 for R group listing.

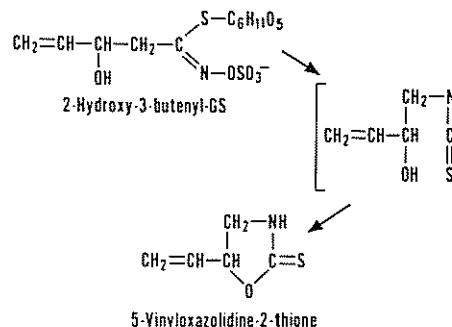


Fig. 2. Formation of an oxazolidine-2-thione from enzymatic hydrolysis of a glucosinolate common in crucifer vegetables.

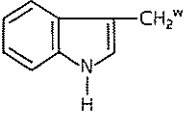
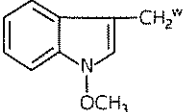
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<sup>1</sup>Retired.

and 2-phenylethyl-NCS (43) and some 3-indolyl compounds have been shown to inhibit chemical carcinogenesis in rats by stimulating mixed function oxidases in the liver and intestine (23).

As reviewed by Tookey et al. (34), the GSs in some circum-

Table 1. Glucosinolate (GS) structures.

Chemical name	Structure of R group <sup>2</sup>
1-Methylpropyl (413) <sup>y</sup>	CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>3</sub>
Allyl-GS (397)	CH <sub>2</sub> =CH-CH <sub>2</sub>
3-Butenyl-GS (411)	CH <sub>2</sub> =CH-(CH <sub>2</sub> ) <sub>2</sub>
4-Methylthiobutyl-GS (459)	CH <sub>3</sub> -S-(CH <sub>2</sub> ) <sub>4</sub>
4-Methylsulfinylbutyl-GS (475)	CH <sub>3</sub> SO(CH <sub>2</sub> ) <sub>4</sub>
2-Hydroxy-3-butenyl-GS (427)	CH <sub>2</sub> =CH-CHOHCH <sub>2</sub> <sup>x</sup>
4-Pentenyl-GS (425)	CH <sub>2</sub> =CH-(CH <sub>2</sub> ) <sub>3</sub>
5-Methylthiopentyl-GS (473)	CH <sub>3</sub> -S-(CH <sub>2</sub> ) <sub>5</sub>
5-Methylsulfinylpentyl-GS (489)	CH <sub>3</sub> -SO-(CH <sub>2</sub> ) <sub>5</sub>
2-Hydroxy-4-pentenyl-GS (441)	CH <sub>2</sub> =CH-CH <sub>2</sub> -CHOH-CH <sub>2</sub> <sup>x</sup>
2-Phenylethyl-GS (487)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>
3-Indolylmethyl-GS (487)	
3-( <i>N</i> -Methoxy)indolylmethyl-GS (516)	

<sup>2</sup> See Fig. 1<sup>y</sup> Values in parentheses indicate the molecular weight of the GS as the potassium salt.<sup>x</sup> Cyclic oxazolidine-2-thione forms if GS is hydrolyzed under conditions expected to yield isothiocyanate.<sup>w</sup> SCN ion forms as a decomposition product from unstable isothiocyanate.

stances may hydrolyze to form organic nitriles instead of NCSs (Fig. 1). They may, for example, form nitriles in the preparation of coleslaw, depending on how the cabbage (*B. oleracea* L. *capitata* group) is processed (8). In sauerkraut, a naturally fermented cabbage product, Daxenbichler et al. (10) found 1-cyano-3-methylsulfinylpropane, which is formed from a GS. Among the nitriles some are suspected and some are known to be toxic (5, 15, 26).

There has been concern that levels of naturally occurring toxicants might be increased inadvertently during the breeding to enhance desirable traits in horticultural crops (16). In view of the indicated metabolic involvement of GSs in various types of mammalian and nonmammalian (insect) (28) systems, it is important to identify broad baseline levels of GSs in various crucifer cultivars. As part of a comprehensive survey, the following brassicas were analyzed: six broccoli cultivars; six brussels sprouts; five cauliflower; five collards; five kale; one marrow-stem kale; one smooth-leafed kale; two curly kale; one kohlrabi; 'Siberian' kale, *B. napus* L.; and two mustard greens, *B. juncea* (L.) Czern. & Coss.

### Materials and Methods

**Source.** All plants were grown at the Wisconsin Agricultural Experiment Station, Madison. In 1975, all were planted in June and harvested in the following months: kohlrabi and mustard greens, July; broccoli, August; brussels sprouts, kale, and collards, September; cauliflower, October. In 1976, collards were planted in June and harvested in September; in 1978, kohlrabi and brussels sprouts were planted in May and harvested in October; in 1979, marrow-stem kale was planted in April and harvested in July.

**Preparations and analyses.** Generally three to five individual

plants were sampled by taking 100 g of the edible portions: broccoli heads, brussels sprouts buttons, cauliflower curds, and peeled kohlrabi tubers. Samples were taken from above-ground portions of collards, kale, and mustard greens. A single analysis was made of marrow-stem kale leaves and stems combined. Vegetative materials (1 to 3-cm pieces) were extracted with boiling aqueous methanol (40), the methanol was removed, and the aqueous solutions were diluted with water and frozen for the few weeks or months until analysis.

Single, 2-g samples of the various seeds were examined in 1975. The extract obtained by treating ground defatted seeds with boiling water (33) was concentrated and frozen.

Total glucose measurements [calculated as total GS (40)] were made on glucose released from extracts by hydrolysis (38) with thioglucoside glucohydrolase (myrosinase) (6), using either of the two equivalent reagents—Glucostat X4 (Eli Lilly) (41) in 1975 or Glucose Auto/Stat (Pierce) (6) in 1978 and 1979. A modification (6) of the procedure of Josefsson (20) measured independently the 3-indolylmethyl-GSs as SCN ion released after hydrolysis. Other GSs were identified and quantitated by gas-liquid chromatography of the products of hydrolysis, NCSs and OZTs (7). A schematic of the GS analysis is included in a paper by Daxenbichler et al. (9). Confirmation of the identity of aglucons from at least one cultivar of each vegetable was made by a GC-MS tandem system (32).

### Results and Discussion

In the present study, GS patterns of cultivars consist of the relative amounts of the nine GSs listed in Table 2 plus 4-pentenyl-, 5-(methylthio)pentyl-, 5-(methylsulfinyl)pentyl-, and benzyl-GS. By means of cluster analysis, correlation coefficients (based on these 13 GSs) were calculated between all possible pairs of cultivars. Those that were highly correlated in their GS patterns were grouped together. Cultivars in each group had coefficients of 0.68 or greater, because, for a simple linear correlation (*r*) based on 13 points, 0.68 is significant at the 99% confidence level (*P* < 0.01). The cluster analysis progressively separates unlike cultivars. Thus, group I and group VII are the most dissimilar; this separation supports the taxonomic viewpoint, since group I is *B. oleracea* and group VII is *B. napus*.

Broccoli, with a predominance of 4-(methylsulfinyl)butyl-GS, formed a separate group (group I). Group II included brussels sprouts, cauliflower, and contained the kale cultivars 'Maris Kestrel' (marrow stem) and 'Petland Brig' (smooth leaf). Members of this group contained predominantly 3-indolylmethyl-GS's with lower levels of allyl- and 3-(methylsulfinyl)propyl-GS. Most of the collards cultivars (18–21 in Table 2) were distinguished by high levels of 2-hydroxy-3-butenyl-GS (group 3). An exception was 'Morris Heading', whose high level of 3-(methylsulfinyl)propyl-GS made it similar to curly kale cultivars 'Dark Blue Southern' and 'Vates' (group V). The preponderance of allyl-GS in mustard greens (IV), 4-(methylthio)butyl-GS in kohlrabi (VI) and 5-(methylsulfinyl)pentyl-GS in 'Siberian' kale (VII) made their GS patterns distinctive.

When the GS determinations in seed of 17 cultivars were made and the data sorted into groups using cluster analysis, grouping of cultivars on the basis of seed analysis generally compared with that of the vegetative portions (Table 3). Broccoli (group 1), kohlrabi (group 2), mustard greens (group 4), and 'Siberian' kale (group 8) all formed separate groups. In contrast to data from the vegetative parts, seed data of brussels sprouts (groups 6 and 7) and cauliflower (group 5) were in separate groups, whereas collards and 'Petland Brig' kale were

Table 2. Glucosinolate (GS) content of vegetable cultivars.

Cultivar	Vegetable group <sup>1</sup>	Year grown	Glucosinolate content ( $\mu\text{mol}/100\text{ g}$ fresh wt)									Total GS <sup>2</sup>
			Allyl	3-(Methylthio)propyl	3-(Methylsulfinyl)propyl	3-Butenyl	2-Hydroxy-3-butenyl	4-(Methylthio)butyl	4-(Methylsulfinyl)butyl	2-Phenylethyl	3-Indolylmethyl <sup>3</sup>	
<b>Broccoli</b>												
1) Brase	I	1975	1.6	0.0	7.2	0.2	0.0	2.2	76.3	0.6	54.3	262.7
2) Green Comet <sup>4</sup>	I	1975	1.1	0.0	3.3	1.0	3.7	1.8	51.1	1.9	64.1	200.2
3) Green Duke <sup>5</sup>	I	1975	0.0	0.0	1.9	0.0	0.0	2.2	74.3	0.7	71.7	202.2
4) Southern Comet <sup>6</sup>	I	1975	0.0	0.0	3.6	0.1	0.3	1.1	63.7	0.2	55.6	194.4
5) Spartan Early	I	1975	0.0	0.0	1.4	0.2	0.0	1.3	29.8	0.0	42.2	102.2
6) Royal Purple <sup>7</sup>	I	1975	0.0	0.0	11.2	0.0	1.2	3.7	88.3	0.6	68.3	167.2
s <sup>8</sup> , 32 df			(0.9)		(6.3)	(0.6)	(1.9)	(1.8)	(37.2)	(1.0)	(49.4)	(144.6)
<b>Brussels sprouts</b>												
7) Cambridge No. 1	II	1978	3.9	0.0	2.4	3.3	5.7	1.2	6.1	0.4	443.3	600.6
8) Cambridge No. 3	II	1978	22.7	0.2	16.9	1.3	4.7	0.5	0.6	1.0	327.8	525.0
9) Cambridge No. 5	II	1978	12.2	0.2	13.0	0.5	1.0	0.4	0.4	1.4	469.4	584.4
10) Exhibition	II	1978	6.6	0.0	7.8	5.2	6.3	0.6	5.2	0.3	376.7	578.9
11) Jade Cross E <sup>9</sup>	II	'75, '78	13.1	tr <sup>10</sup>	11.8	12.2	25.4	0.6	22.6	1.4	373.9	563.3
12) Long Island Improved	II	1975	5.7	0.0	18.9	2.8	6.9	0.4	14.1	0.8	359.4	465.6
s, 30 df			(13.7)		(13.6)	(8.1)	(17.0)	(0.6)	(17.9)	(0.8)	(129.1)	(172.4)
<b>Cauliflower</b>												
13) Cleopatra	II	1975	14.6	2.9	22.8	0.0	0.0	0.9	0.8	0.0	104.7	160.6
14) Idol	II	1975	2.9	1.6	0.9	0.0	0.0	0.2	0.0	0.0	18.8	41.1
15) Imperial	II	1975	16.5	7.4	1.1	0.1	0.0	1.3	1.7	0.4	75.9	118.3
16) Snowball No. 16	II	1975	10.8	3.8	1.3	0.0	0.0	0.5	0.0	0.0	60.0	91.7
17) Super Snowball	II	1975	5.4	2.4	0.0	tr	0.0	0.5	0.0	tr	43.6	61.1
s, 17 df			(8.6)	(4.3)	(16.2)			(0.7)	(1.6)		(47.5)	(68.6)
<b>Collards</b>												
18) Georgian Southern Creole	III	1975	62.7	0.0	3.0	38.1	130.3	0.0	3.4	1.1	165.3	547.8
19) Georgia	III	1976	80.9	0.0	3.4	29.7	52.6	0.0	8.6	0.7	87.4	359.4
20) Vates	III	1975	197.3	0.0	2.2	13.3	54.0	0.0	0.8	5.3	150.4	600.0
21) Vates Variety No. 12	III	1976	81.8	0.0	0.0	19.7	96.7	0.0	0.0	1.0	67.3	372.1
22) Morris Heading	V	1975	62.5	0.0	49.9	5.8	16.8	0.0	13.2	2.8	67.2	316.1
s, 18 df			(110.9)		(28.4)	(23.0)	(79.6)		(16.0)	(3.2)	(73.3)	(260.2)
<b>Kale</b>												
23) Maris Kestrel (marrow stem) <sup>11,12</sup>	II	1979	12.6	0.0	8.4	0.0	0.0	0.5	0.0	1.8	46.7	64.4
24) Petland Brig (smooth leaf)	II	1975	28.7	0.0	8.8	4.1	22.5	0.0	0.7	0.8	61.4	267.8
25) Dark Blue Southern (curly)	V	1975	20.9	0.0	67.8	0.3	1.1	0.0	5.8	1.9	69.5	306.7
26) Vates (curly)	V	1975	20.6	0.0	69.3	0.0	0.0	0.0	7.7	2.2	44.2	242.8
27) Siberian ( <i>B. napus</i> ) <sup>13</sup>	VII	1975	0.0	0.0	0.0	31.3	158.1	0.9	28.9	17.5	102.3	693.9
s, 9 df <sup>14</sup>			(14.8)		(44.3)	(3.4)	(18.7)		(5.9)	(1.5)	(36.2)	(100.1)
<b>Mustard greens (<i>B. juncea</i>)</b>												
28) Greenwave	IV	1975	693.9	0.0	0.0	2.7	0.0	0.0	2.1	5.2	12.2	1140.6
29) Southern Giant Curled	IV	1975	779.4	0.0	0.0	8.5	0.0	0.0	0.0	7.6	4.2	1242.2
s, 6 df			(128.9)			(5.2)			(1.5)	(4.0)	(13.6)	(151.7)
<b>Kohlrabi</b>												
30) Early White Vienna	VI	'75, '78	0.0	9.7	2.3	0.0	0.3	33.6	4.3	1.8	27.7	86.1
s, 8 df				(9.0)	(4.2)		(0.7)	(41.3)	(6.8)	(2.2)	(17.6)	(51.1)

<sup>1</sup> Correlation coefficient of any two cultivars within a group  $\geq 0.68$ . Also included in correlation coefficient calculations are 4-pentenyl-, 5-(methylthio)pentyl-, and benzyl-GS, all present in some cultivars at low levels and 5-(methylsulfinyl)pentyl-GS present in 'Siberian' kale.

<sup>2</sup> Includes all 3-indolylmethyl-GSs detected by SCN ion analysis.

<sup>3</sup> Determined as glucose released and calculated based on an average molecular weight of 457 for GSs.

<sup>4</sup> Hybrid. All cultivars not designated are open pollinated.

<sup>5</sup> This is a broccoli marketed as a cauliflower.

<sup>6</sup> s = SD among analyses ignoring cultivars.

<sup>7</sup> tr is  $< 0.1 \mu\text{mol}/100\text{ g}$ .

<sup>8</sup> Used primarily as stock feed.

<sup>9</sup> Contains  $30.1 \mu\text{mol}/100\text{ g}$  4-pentenyl-GS,  $2.4 \mu\text{mol}$  5-(methylthio)pentyl-GS, and  $137.3 \mu\text{mol}$  5-(methylsulfinyl)pentyl-GS.

<sup>10</sup> Cultivars 23 and 27 are not included in this calculation.

grouped together. Because the total GS levels for these seeds averaged 100 times that in the vegetative parts, the seeds are reported in millimoles, rather than in micromoles, as are the vegetative parts.

When the GS patterns of the 17 seed cultivars were compared to the corresponding edible parts, only five correlation coefficients were highly significant ( $P < 0.01$ ). The similarity of the 4-(methylsulfinyl)butyl-GS levels relative to the total GSs of the two plant parts and the low level or total lack of 2-hydroxy-3-butenyl-GS for broccoli 'Green Duke' and 'Royal Purple' helped give coefficients of 0.70 and 0.81, respectively. The collards

cultivars 'Georgian Southern Creole' and 'Morris Heading' (coefficients 0.68, 0.69) were likewise similar in relative amounts of allyl-, 3-(methylsulfinyl)propyl- and 2-hydroxy-3-butenyl-GS in the vegetative parts and the seeds. 'Southern Giant Curled' mustard (1.00) had 97% of the total GS as allyl-GS in the tops and 93% in the seed.

One factor contributing to the disparity of GS patterns in the seeds and edible parts of all the cultivars was the concentration of 3-indolylmethyl-GSs. In *B. juncea*, these precursors of SCN ion were  $< 3\%$  of the total GS in either seeds or edible parts, and, in *B. napus*, as much as 20%. But in the edible parts of

Table 3. Glucosinolate (GS) content of seed cultivars.

Cultivar	Seed group <sup>1</sup>	Glucosinolate content (mmol/100 g defatted meal)										
		3-Carbon side chains			4-Carbon side chains				5-Carbon side chains			Total GS <sup>4</sup>
		Allyl	3-(Methylthio)propyl	3-(Methylsulfinyl)propyl	3-Butenyl	2-Hydroxy-3-butenyl	4-(Methylthio)butyl	4-(Methylsulfinyl)butyl	4-Pentenyl	2-Phenylethyl	3-Indolylmethyl <sup>3</sup>	
<b>Broccoli</b>												
1) *Green Comet <sup>2</sup>	1	0.49	0.03	0.13	0.59	2.66	0.98	3.15	0.02	0.07	0.94	13.89
2) Green Duke <sup>2</sup>	1	0.03	0.0	0.0	0.11	0.0	2.84	8.61	0.11	0.0	0.78	16.22
5) Spartan Early	1	0.01	0.0	0.02	0.88	2.27	1.18	3.55	0.0	0.0	0.72	14.17
6) Royal Purple	1	0.06	0.37	1.45	0.05	0.0	2.61	7.22	0.06	0.06	1.28	16.39
<b>Brussels sprouts</b>												
11) Jade Cross E <sup>3</sup>	6	0.20	0.02	0.0	1.55	6.02	1.28	1.31	0.06	0.08	1.06	14.17
12) Long Island Improved	7	2.24	0.35	1.13	0.49	1.70	0.86	2.01	0.0	0.13	0.96	13.00
<b>Cauliflower</b>												
14) Idol	5	5.96	1.24	3.62	0.04	0.16	0.08	0.17	0.10	0.08	1.11	17.20
15) Imperial	5	3.99	1.18	3.39	tr <sup>4</sup>	0.08	0.21	0.47	tr	0.04	0.83	10.28
16) Snowball No. 16	5	3.85	1.04	2.90	tr	0.08	0.02	0.12	tr	0.02	1.33	12.78
17) Super Snowball	5	4.40	1.15	4.21	0.04	0.12	0.11	0.11	0.11	0.07	1.28	15.83
<b>Collards</b>												
18) Georgian Southern Creole	3	2.55	0.12	0.28	0.60	2.67	0.31	0.35	0.0	0.03	0.79	14.61
20) Vates	3	3.53	0.10	0.11	1.00	5.96	0.31	0.41	0.0	0.07	0.73	16.61
22) Morris Heading	3	6.30	0.50	1.97	0.74	2.39	0.47	0.93	0.0	0.26	0.86	21.72
<b>Kale</b>												
24) Petland Brig	3	5.44	0.30	0.73	1.19	5.08	0.64	1.11	0.0	0.08	0.90	21.72
27) Siberian ( <i>B. napus</i> ) <sup>5</sup>	8	0.10	0.0	0.0	4.10	3.97	0.15	0.55	0.53	0.22	1.12	15.61
<b>Mustard greens (<i>B. juncea</i>)</b>												
29) Southern Giant Curled	4	12.25	0.05	0.20	0.15	0.0	0.04	0.05	0.0	0.05	0.38	18.50
<b>Kohlrabi</b>												
30) Early White Vienna	2	0.05	0.40	2.74	0.05	0.19	2.41	8.59	0.03	0.21	0.57	19.39

<sup>4</sup> Any two cultivars within a group have correlation coefficients  $\geq 0.68$ .

<sup>3</sup> Includes all 3-indolylmethyl-GSs measured in SCN analysis procedure.

<sup>2</sup> Determined as glucose released and calculated based on an average molecular weight of 457 for GSs.

<sup>1</sup> Numbers correspond to those in Table 2.

<sup>5</sup> Hybrid. All cultivars not designated are open-pollinated.

<sup>tr</sup> tr is  $< 0.01 \mu\text{mol}/100 \text{ g}$ .

<sup>1</sup> Contains 0.09 mmol/100 g 5-(methylthio)pentyl-GS.

*B. oleracea* subspecies the range for collards, kale, and kohlrabi was 31–48%, for broccoli 39–56%, and for cauliflower and brussels sprouts 73–88% of total GS. In contrast to these high percentages of 3-indolylmethyl-GSs in vegetative parts of nine *B. oleracea* is the low level of 4–14% in seeds. A similar disparity has been reported for leaves and seeds of cabbage (33, 40).

**Broccoli.** In seeds of three broccoli cultivars, Ettliger (11) had seen 4-(methylsulfinyl)butyl-GS as the primary component and 4-(methylthio)butyl-GS as a secondary component, but we saw in the seed of four cultivars these two compounds as major components, with 4-(methylsulfinyl)butyl-GS dominating. These two components also were found in the vegetative parts of all cultivars. To the best of our knowledge, this is the first report of 4-(methylthio)butyl-GS in broccoli heads. The compound 2-hydroxy-3-butenyl-GS was another secondary component in the seeds of two cultivars and was present in both the seeds and head of only one of the four cultivars analyzed. 'Royal Purple', although often marketed as a cauliflower, is actually a form of heading broccoli, based on GS profiles and genetic lineage (44).

**Brussels sprouts.** The most thorough work reported on brussels sprouts was done by Heaney and Fenwick (17) on 22 unnamed cultivars and by Sones et al. (30) on 43 samples of unnamed commercial cultivars grown in the United Kingdom. Comparison of Sones' results with those of the six cultivars in this study revealed similar relative levels of allyl-, 3-butenyl-, 2-hydroxy-3-butenyl-, and 3-methylsulfinylpropyl-GS. However, Sones found the level of 3-indolylmethyl-GSs to be less than half the total of these four GSs, whereas our data showed 3-indolylmethyl-GSs were 11 times the total of the same GSs. Levels of SCN ion precursors are known to vary throughout the

growing season (21), but it is likely that some of the cultivars used by Sones have a different genetic base than those reported here. The 4-(methylsulfinyl)butyl-GS was present in the six cultivars in our study and also was isolated from brussels sprouts by Gmelin and Virtanen (13) as a phenyl-thiourea in an amount corresponding to 11  $\mu\text{mol}/100 \text{ g}$  GS.

**Cauliflower.** Allyl-, 3-(methylthio)propyl, 3-(methylsulfinyl)propyl-, and 3-indolylmethyl-GS were present in all five cultivars of cauliflower curd and were the major GSs in their seeds as well. Sones et al. (31) found GS patterns for 27 European cultivars similar to those reported here for U.S. cultivars, except that their cultivars had low levels of 2-hydroxy-3-butenyl-GS, whereas ours had none. In contrast to broccoli heads, cauliflower curds have more allyl-GS, some 3-(methylthio)propyl-GS, and lack the high level of 4-(methylsulfinyl)butyl-GS contained in broccoli.

**Collards.** To our knowledge, this is the first report of the GS content of collard leaves. They have up to twice the total GS content as curly kale cultivars 25 and 26 in Table 2. Higher contents of allyl-, 3-butenyl-, and 2-hydroxy-3-butenyl-GS in collards distinguish them from kale.

**Kales.** Curly kale ('Dark Blue Southern' and 'Vates') is primarily for human consumption, whereas marrow-stem kale ('Maris Kestrel') is largely for animal fodder, and smooth-leaved kale ('Petland Brig') is for both. 'Siberian' kale, primarily a stock feed, belongs to *Brassica napus* rather than *B. oleracea*.

Increased thyroid weight and decreased iodine concentration in ruminant animals grazing kale can be prevented by iodine supplement (1). Virtanen et al. (42) observed similar results in rats fed SCN ion, which is a primary GS product in kale. In assessing 'Siberian' kale as a feed, it should be recognized that

the high levels of 2-hydroxy-3-butenyl- (158  $\mu\text{mol}/100\text{ g}$ ) and of 5-(methylsulfinyl)pentyl-GS (137  $\mu\text{mol}/100\text{ g}$ ) could be deleterious because of the stability of their nitriles in the rumen (12), and because the derivative 1-cyano-2-hydroxy-3-butene causes liver and kidney damage in rats (26). The 5-(methylsulfinyl)pentyl-GS was not present in the edible portions of *B. oleracea* or *B. juncea* vegetables and thus was not included in Table 2.

Allyl- and 3-(methylsulfinyl)propyl-GS have been documented previously in marrow-stem kale (4, 13, 19) and, together with 3-indolylmethyl-GSs, are the major GSs in this subspecies. Low levels of 2-hydroxy-3-butenyl-GS have been seen in marrow-stem kale (19), but none was found in our sample of 'Maris Kestrel', a cultivar of marrow-stem.

The same three predominant GSs in 'Maris Kestrel' (marrow stem kale) also predominate in 'Dark Blue Southern' and 'Vates' (curly kales) and have been observed by Michajlovskij et al. (25) to be prominent in kale for human consumption. We measured only 0–1  $\mu\text{mol}/100\text{ g}$  2-hydroxy-3-butenyl-GS in curly kale, but 22  $\mu\text{mol}/100\text{ g}$  in the smooth-leafed kale 'Petland Brig'.

The greater variability of GS patterns among kale cultivars than for other vegetables covered in our study reflects the diverse origins of kales as a group of brassicas (44).

**Mustard.** Since the seeds of mustard are used widely for oil and for table condiment mustards, previous research has concentrated on GSs of the seeds. In the leaves of two cultivars (Table 2) grown in the United States for their green leaves, allyl-GS (694–779  $\mu\text{mol}/100\text{ g}$ ) accounted for 97% of the GSs, while 3-butenyl- and 2-phenylethyl-GS each fell into the 0.4–1.1% range (3–8  $\mu\text{mol}/100\text{ g}$ ). The level of allyl-GS or its hydrolysis product allyl-NCS is important in light of the reported mutagenicity (45) for both of these compounds and because of the activity of allyl-GS as a feeding and ovipositing stimulant for certain insects (28). Seven oriental mustard-green cultivars previously analyzed (18) had considerably lower levels of allyl-GS (157–414  $\mu\text{mol}/100\text{ g}$ ) than the U.S. cultivars, whereas the butenyl-GS was as high as 9% of the total GSs (6–41  $\mu\text{mol}/100\text{ g}$ ), and the 2-phenylethyl-GS ranged between 1 and 6  $\mu\text{mol}/100\text{ g}$ . The 4-(methylsulfinyl)butyl- and benzyl-GS (see below) have not been previously reported in *B. juncea* greens.

**Kohlrabi.** Unlike any of the other vegetables, the predominant GSs in kohlrabi, a *B. oleracea* variety, were 3-(methylthio)propyl- and 4-(methylthio)butyl-GS, along with 3-indolylmethyl-GSs. Interestingly, the seed contained higher levels of the corresponding sulfinyl compounds than of the two methylthio compounds, and 4-(methylsulfinyl)butyl-GS was the GS present in the largest amount in the seed.

Initially, a component was misidentified as 4-(methylsulfonyl)butyl-NCS in all the vegetables reported in this paper except mustard greens. The compound had a similar retention time on both GC columns to that of this NCS. Subsequent work with capillary GC-MS established that the compound was 3-indolylacetone nitrile, unexpected among the GS hydrolysis products. We previously misidentified small amounts of the same nitrile in turnips and rutabagas (6) and in cabbage, as demonstrated by MS analysis of extracts from 'Market Prize' (*B. oleracea* ssp. *capitata* L. f. *alba* DC.) (40) and 'Red Danish' [*B. oleracea* ssp. *capitata* f. *rubra* (L.) Thell.] (39). This nitrile also has been observed by Linser et al. (21) in brussels sprouts buttons, cauliflower heads, and savoy cabbage leaves [*B. oleracea* ssp. *sabauda* (L.)].

Four newly identified 3-indolyl compounds, 4-hydroxy-3-in-

dolylmethyl-, 4-methoxy-3-indolylmethyl-, 5-hydroxy-3-indolylmethyl-, and 5-methoxy-3-indolylmethyl-GS, occur in crucifers (15, 31, 37) and may well be contributing to the SCN<sup>-</sup> ion measurements of the vegetables reported here. Regarding 3-indolylmethyl- and 3-(*N*-methoxy)indolylmethyl-GS, the former predominates in brussels sprouts buttons, cauliflower curds, and marrow-stem kale leaves, while in the edible part of broccoli the latter predominates (19).

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