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Application of Gas Chromatography/Matrix Isolation/Fourier Transform Infrared Spectrometry to the Identification of Glucosinolates from *Brassica* Vegetables

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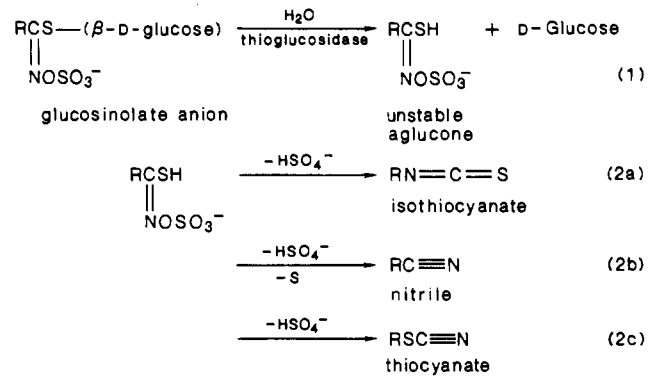
There is limited epidemiologic evidence suggesting that ingestion of *Brassica* vegetables may be associated with reduced risk of some cancers of the alimentary tract, and a number of *Brassica* constituents are known to inhibit carcinogenesis in laboratory animals. The components that are responsible for the observed protective activity and the effects of processing on them have not yet been established. An analytical method using capillary gas chromatography/matrix isolation/Fourier transform infrared spectroscopy (GC/MI/FT-IR) has been developed for characterizing a series of intact glucosinolates extracted from Brussels sprouts and rutabaga (swede). Highly resolved gas chromatograms and diagnostic MI/FT-IR spectra were obtained for different glucosinolate analogues with subtle structural differences.

Glucosinolates [RC(=$NOSO_3^-$)—S—(β-D-glucose)] occur naturally in certain families of dicotyledonous angiosperms, including edible crops in the genus *Brassica* of the Cruciferae family (Fenwick et al., 1983; Heaney and Fenwick, 1987). The breakdown products of glucosinolates possess pungent odors and biting tastes. These properties in *Brassica* vegetables such as mustard and horseradish make them desirable as condiments and relishes and in salads (e.g., radish and watercress). The nutritional value of commonly consumed Brassicas, such as cabbage, cauliflower, or Brussels sprouts, lies primarily in their high content of dietary fibers and vitamins A and C (Fenwick et al., 1983).

Some glucosinolate decomposition products have been found to inhibit the neoplastic effects of certain carcinogens (National Research Council, 1982) as well as to possess antifungal and antibacterial activities. On the other hand, adverse effects due to the occurrence of glucosinolates in feed, arising from the use of rapeseed or mustard, have been documented (Heaney and Fenwick, 1987); undesirable consequences include cytotoxicity and the tainting of poultry eggs and dairy milk. Coupled with low dietary iodine, glucosinolates have goitrogenic activity in humans.

Because of recommendations for the increased consumption of cruciferous vegetables related to their anticarcinogenicity (National Research Council, 1982), interest has increased in the physiological activities (Heaney and Fenwick, 1987) of the various aglucone products resulting from the enzymatic hydrolysis of glucosinolates (reactions 1 and 2) during food processing, cooking, or ingestion.



The myrosinase enzyme responsible for the hydrolysis of glucosinolates is now considered to have only thioglucosidase activity. The resulting unstable aglucone (reaction 1) undergoes Lossen rearrangement (Ettlinger and Lundeen, 1957) to yield various products (reaction 2), depending on the nature of the side chain (R), among other factors.

Many methods have been used to monitor both total and individual glucosinolate content of Brassicas (McGregor et al., 1983) including liquid chromatography/mass spectrometry (Hogge et al., 1987) and packed (Christensen et al., 1982) and capillary column gas chromatography/mass spectrometry (GC–MS) (Hiltunen et al., 1980; Sosulski and

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Dabrowski, 1984; Truscott et al., 1982a,b). In a recent study on the analysis of intact glucosinolates from *Brassica* vegetables, Shaw et al. (1989) reported a new analytical procedure for characterizing per(trimethylsilyl)desulfoglucosinolate analogues. Capillary GC separation using a bonded-phase, fused silica methyl silicone column with positive-ion chemical ionization MS detection and MS/MS (methane as the reagent gas) gave superior chromatography and highly diagnostic mass spectral data, from which compounds could be identified.

In the present study, gas chromatography/matrix isolation/Fourier transform infrared spectrometry (GC/MI/FT-IR) (Bourne et al., 1984; Reedy et al., 1985) has been used for the first time to separate and unequivocally characterize various glucosinolate products from rutabaga (swede) and Brussels sprouts. These infrared spectral data have provided evidence on the nature and identity of the functional groups of the glucosinolate molecules and the different side chains and complement the mass spectrometry data. Specifically, the presence of a cyclic ether and of TMS (trimethylsilyl ether) groups in the glucose moiety or elsewhere, or any methylene linkage, vinyl group, or indole moiety, can be readily established. The matrix isolation spectral technique offers increased resolution and sensitivity over other infrared spectroscopic measurement techniques such as vapor phase. This is because, in GC/MI/FT-IR, the GC effluent is trapped as a cryogenic (12 K) solid of microscopic dimensions in a matrix of IR-transparent argon atoms, thus allowing signal averaging to be carried out for extended times and leading to spectra with sharper bands than those obtained at ambient temperature.

EXPERIMENTAL SECTION

Materials and Reagents. Aryl sulfatase (Type H-1 from *Helix pomatia*) and DEAE Sephadex A-25 and SP-Sephadex C-25 resins were purchased from Sigma Chemical Co. (St. Louis, MO). Pyridine (silylation grade), trimethylchlorosilane (TMCS), and *N*-methyl-*N*-(trimethylsilyl)heptafluorobutyramide (MSHFBA) were purchased from Alltech (Deerfield, IL), and methanol (Baker Analyzed grade) was purchased from J. T. Baker Chemical Co. (Phillipsburg, NJ). Distilled deionized water was used throughout this work.

A modified version by Shaw et al. (1989) of the Heaney and Fenwick method (1980) describing preparation, extraction, isolation, and derivatization of rutabaga (swede) and Brussels sprouts was used. Vegetables obtained from local markets were chopped (500 g), frozen at liquid nitrogen temperature, blended, and stored as powder at −34 °C. Extractions using 20-g portions were carried out in boiling methanol (200 mL, 15 min). Concentrated extracts were diluted with water and stored at −12 °C.

The isolation of glucosinolates involved mixing the vegetable extracts (1 mL) with an equal volume of lead and barium acetates (0.5 M), in order to precipitate the protein, and centrifuging. Glucosinolates in the supernatant were concentrated by adsorption onto a DEAE Sephadex A-25 (30-mg) microcolumn. Bound glucosinolates were enzymatically desulfated in situ by incubation overnight (20 °C) with aryl sulfatase. Desulfoglucosinolates were then eluted with distilled water and lyophilized. Desulfoglucosinolate residues were suspended in silylating reagent (100 μL of pyridine, 100 μL of MSHFBA, 10 μL of TMCS), sonicated for 3 min, quantitatively transferred to a 1-mL Reacti-Vial (Pierce, Rockport, IL), and heated to 120 °C for 20 min.

A Sirius 100 FT-IR spectrometer (Mattson Instruments, Madison, WI) equipped with a Cryolect matrix isolation interface was used. Post-GC-run infrared spectra were measured at 4-cm^{-1} resolution, and signal averaging was carried out for 2 min 43 s (300 scans). Gas chromatographic separations were performed on a Hewlett-Packard Model 5890 instrument (Avondale, PA) equipped with a flame ionization detector and a Hewlett-Packard 3392A integrator. A cross-linked methyl silicone capillary column (HP-1), 25 m × 0.2 mm (i.d.), with a 0.33-μm stationary phase (Hewlett-Packard) was used throughout this study. Helium containing 1.5% argon (Matheson Gas Products) at approximately 27 cm/s linear velocity was used as carrier gas, and helium (99.995%) at 30 mL/min was used as the makeup gas to the detector. The injection and detector temperatures were 270 °C. The carrier gas mixture was purified by using an Alltech Associates Hydro-Purge II and a heated Supelco gas purifier filter. A splitless injection mode using a 10-μL Hamilton 701N syringe was followed with injection volumes of 1–2 μL. The purge delay time was 45 s. The temperature program of Shaw et al. (1989) was used; the initial oven temperature was 210 °C with a 3-min hold, followed by a 10 °C/min ramp to 300 °C, and the oven was held at this temperature until the analysis was complete.

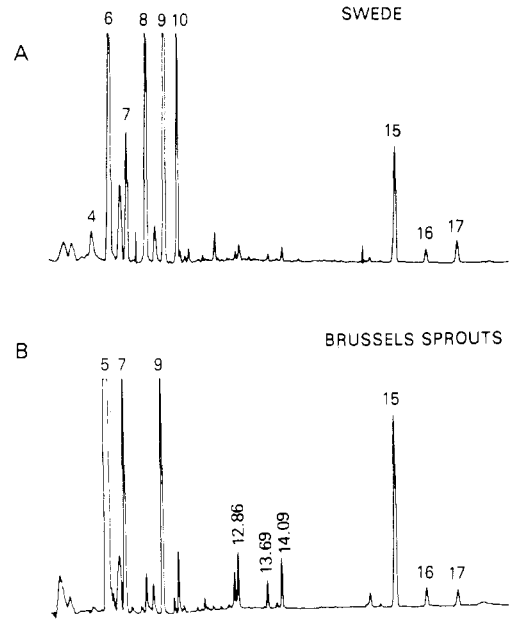

Figure 1. FID trace of per(trimethylsilyl)desulfoglucosinolates from (A) rutabaga (swede) and (B) Brussels sprouts extracts.

RESULTS AND DISCUSSION

The structures of glucosinolates with different substituents (Tables I and II) found in rutabaga (swede) and Brussels sprouts extracts were elucidated by GC/MI/FT-IR spectrometry. Parts A and B of Figure 1 show the flame ionization detector traces obtained for these extracts. The identification numbers used to label the different GC peaks are the same as those reported earlier (Shaw et al., 1989). The GC peaks due to the 3-butenyl (**7**) and 2-hydroxy-3-butenyl (**9**) glucosinolates were commonly found in the chromatograms obtained from both rutabaga and Brussels sprouts samples. The observed MI/FT-IR spectra were in many cases characteristic of subtle structural differences in the glucosinolate side chain.

Parts A and B of Figure 2 show FT-IR spectra observed for 1-methylpropyl (**6**) and 2-propenyl (**5**) glucosinolates, respectively. The most pronounced features, which are typical of all the glucosinolates investigated, are the CH_3 asymmetric stretch (2966 cm^{-1}) and the COC asymmetric stretch of the cyclic ether of the glucose ring (1167 cm^{-1}),

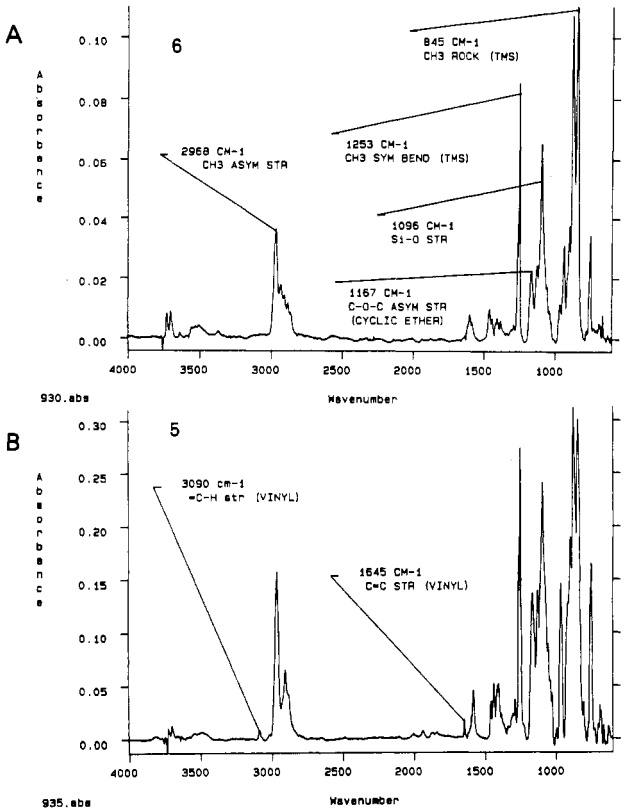

Figure 2. MI/FT-IR spectra observed for TMS derivatives of (A) 1-methylpropyl (**6**) and (B) 2-propenyl (**5**) glucosinolates in the swede and Brussels sprouts extracts, respectively.

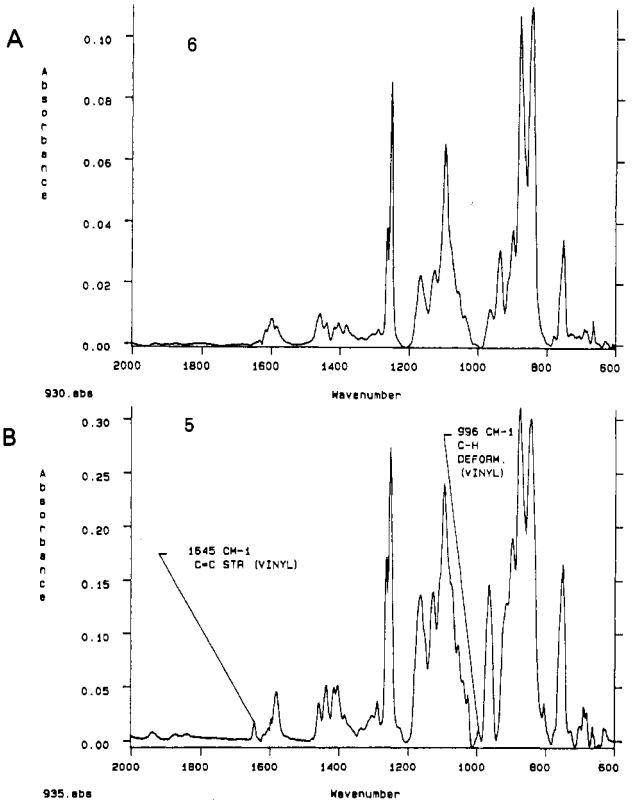

Figure 3. MI/FT-IR spectra observed for TMS derivatives of (A) 1-methylpropyl (**6**) and (B) 2-propenyl (**5**) glucosinolates in the 2000–600-cm^{-1} range.

as well as those derived from the strongly absorbing TMS groups: the TMS CH_3 symmetric scissors (1253 cm^{-1}), the SiO stretch (1096 cm^{-1}), and the TMS CH_3 rock (845 cm^{-1}). The presence of a vinyl group, as in 2-propenyl glucosinolate (**5**) (Figures 2B and 3B), was indicated by very weak yet characteristic bands at 3090 cm^{-1} (=C—H stretch), 1645 cm^{-1} (C=C stretch), and 996 cm^{-1} (=C—H deformation). A second band expected around 915-905 cm^{-1} for an RCH=CH_2 group (Alpert et al., 1973) was probably obscured by the very intense TMS bands. As expected, these vinyl bands are not found in Figure 2A or 3A.

Table I. Derivatized Glucosinolates Identified in Rutabaga and Brussels Sprouts

compd no.	systematic name	structure of side chain[a]
4	isopropyl	R′CH(CH_3)CH_3
5	2-propenyl	R′CH_2CH=CH_2
6	1-methylpropyl	R′CH(CH_3)CH_2CH_3
7	3-butenyl	R′CH_2CH_2CH=CH_2
8	4-pentenyl	R′$CH_2CH_2CH_2$CH=CH_2
9·TMS	2-[(trimethylsilyl)oxy]-3-butenyl	R′CH_2CH(OTMS)CH=CH_2
10·TMS	2-[(trimethylsilyl)oxy]-4-pentenyl	R′CH_2CH(OTMS)CH_2CH=CH_2
14	3-(methylsulfonyl)propyl	R′$CH_2CH_2CH_2(SO_2)CH_3$
15	3-indolylmethyl	R′CH_2(indole)
16·TMS	[4-[(trimethylsilyl)oxy]-3-indolyl]methyl	R′CH_2(indole-4-OTMS)
17	(4-methoxy-3-indolyl)-methyl	R′CH_2(indole-4-OMe)

[a] R′ = –C[=NO(TMS)]—S—(β-D-glucose).

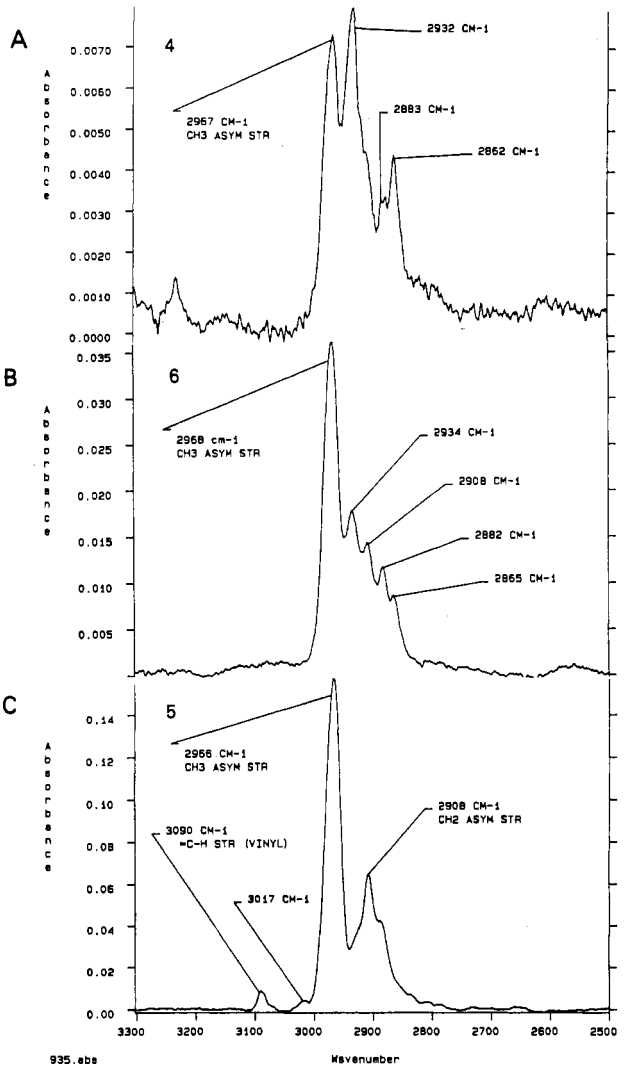

Figure 4. MI/FT-IR spectra showing the C–H stretch region for TMS derivatives of (A) isopropyl (**4**), (B) 1-methylpropyl (**6**), and (C) 2-propenyl (**5**) glucosinolates.

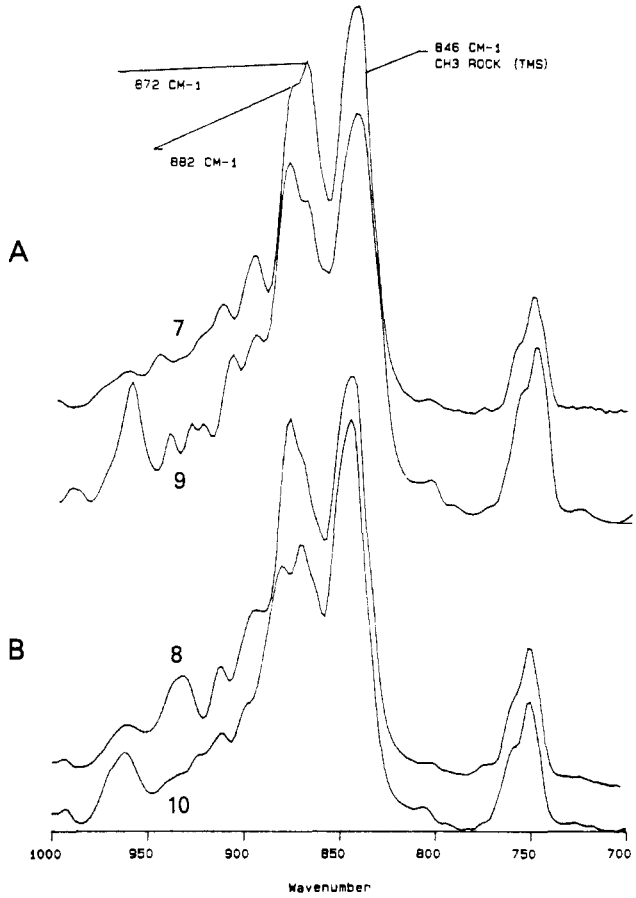

Figure 5. Expanded MI/FT-IR spectral region (1000–700 cm^{-1}) found for TMS derivatives of (A) 3-butenyl (**7**) and 2-hydroxy-3-butenyl (**9**) glucosinolate and (B) 4-pentenyl (**8**) and 2-hydroxy-4-pentenyl (**10**) glucosinolate.

Besides the very weak =C—H stretch bands observed above 3000 cm^{-1} for glucosinolates containing unsaturated carbon atoms (Figure 4C), the CH_3 asymmetric stretch band around 2966 cm^{-1} was consistently present in all the glucosinolate spectra (Figure 4A–C). A second band that fell in the narrow range of 2909–2906 cm^{-1} is probably due to the CH_2 asymmetric stretch, since it was absent only from the spectrum of isopropyl glucosinolate (**4**), which does not have a methylene group on the glucosinolate side chain (Table I; Figure 4A). Of all the glucosinolates investigated, only isopropyl (**4**) and 1-methylpropyl (**6**) glucosinolates (parts A and B, respectively of Figure 4), which contain saturated aliphatic hydrocarbon side chains, exhibited atypical glucosinolate spectra with several resolved bands in the CH stretch region.

The TMS derivatives of 2-hydroxy-3-butenyl (**9**) and 2-hydroxy-4-pentenyl (**10**) glucosinolates exhibited differences in the fingerprint region that distinguished them from their 3-butenyl (**7**) and 4-pentenyl (**8**) glucosinolate analogues, respectively. Inspection of an expanded spectral region observed for the 3-butenyl pair (**7** and **9**) (Figure 5A) or the 4-pentenyl pair (**8** and **10**) (Figure 5B) shows that such differences include, for example, the variation in relative intensity of the 882- and 872-cm^{-1} bands.

3-Indolylmethyl glucosinolate (**15**) exhibited an additional band of medium intensity at 1456 cm^{-1} due to the skeletal in-plane vibrations of the C=C double bonds of the fused aromatic ring in indole (Figures 6 and 7A). The spectrum of the 3-methylindole standard measured in KBr exhibited only two intense bands in the fingerprint region around 1450 and 740 cm^{-1} (Aldrich, 1981). The second resonance expected around 740 cm^{-1} for a 1,2-disubstituted benzene ring was probably obscured by more intense TMS bands in **15**.

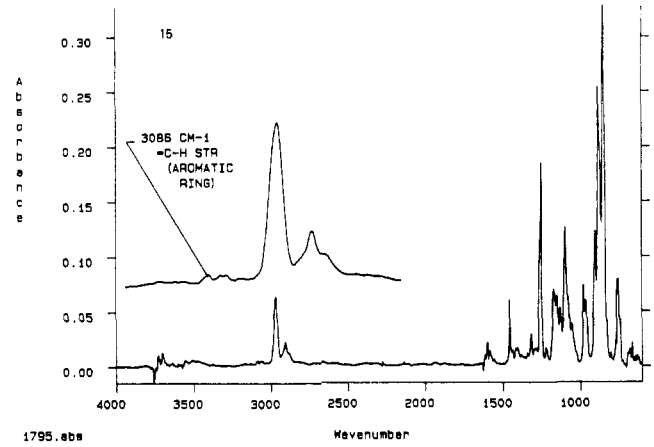

Figure 6. MI/FT-IR spectrum obtained for 3-indolylmethyl glucosinolate TMS derivative.

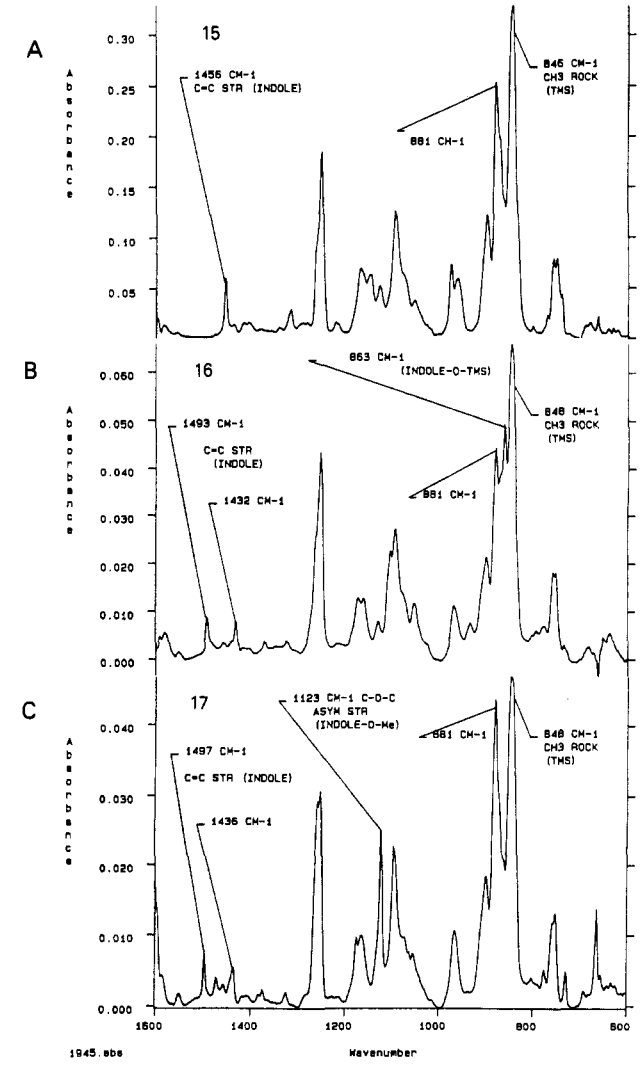

Figure 7. MI/FT-IR spectra showing the 1600–600-cm^{-1} region for TMS derivatives of (A) 3-indolylmethyl (**15**), (B) (4-hydroxy-3-indolyl)methyl (**16**), and (C) (4-methoxy-3-indolyl)-methyl (**17**) glucosinolate.

Figure 7B shows the spectrum of the TMS derivative of (4-hydroxy-3-indolyl)methyl glucosinolate (**16**). A band at 863 cm^{-1} highly characteristic of the unique TMS group on indole was observed. (4-Methoxy-3-indolyl)methyl glucosinolate (**17**) also exhibited another characteristic

Table II. Observed Frequencies (cm^{-1}) for Per(trimethylsilyl)desulfoglucosinolates

assignment	standards			swede					Brussels sprouts					
	9.29,[a] 5[b]	14.47, 14	17.30, 15	8.74, 4	9.22, 6	9.70, 7	10.24, 8	10.76, 9	11.12, 10	9.26, 5	9.70, 7	10.74, 9	17.28, 15	18.18, 16	19.06, 17	intens
=CH str	3090		3086			3086	3083	3086	3086	3090	3086	3086	3086			vw[c]
			3065										3065			vw
			3034										3034			vw
	3018		3026				3020		3019	3018		3020	3026			vw
CH_3 asym str	2966	2967	2967	2967	2968	2966	2966	2965	2965	2966	2966	2965	2967	2967	2966	m
CH_2 asym str	2907	2907	2908		2908	2907	2909	2908	2906	2907	2907	2908	2908	2907	2908	w
C=C str (vinyl)	1645					1647	1647	1650	1647	1645	1647	1650				vw
C=C str (indole)			1456										1456	1493	1497	w
O=S=O sulfone		1325														m
TMS, CH_3 sym str	1253	1253	1252	1253	1253	1253	1253	1252	1252	1253	1253	1252	1252	1254	1252	s
C—O—C asym (cyclic ether)	1164	1167	1170	1168	1167	1167	1164	1164	1162	1164	1167	1164	1170	1173	1173	m
														1159	1164	m
O=S=O (sulfone)		1148														m
C—O—C asym str (ether/indole)															1123	s
TMS, SiO str	1096	1095	1096	1096	1096	1096	1096	1096	1095	1096	1096	1096	1096	1094	1095	s
=CH def (vinyl)	996					1000	994	993	993	996	1000	993				vw
TMS, CH_3 rock	845	846	846	845	845	846	846	846	845	845	846	846	846	863[d]	848	vs

[a] GC retention time (±0.01 min). [b] Compound number. [c] v = very; w = weak; m = medium; s = strong. [d] TMS attached to indole.

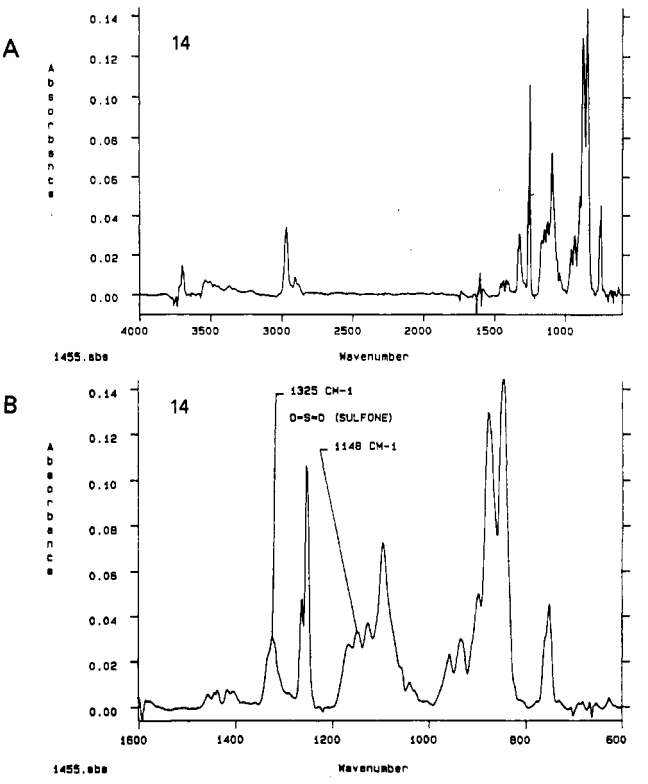

Figure 8. MI/FT-IR spectra observed for 3-(methylsulfonyl)-propyl glucosinolate TMS derivative (**14**) in the ranges (A) 4000–600 cm^{-1} and (B) 1600–600 cm^{-1}.

band at 1123 cm^{-1} attributed to the additional ether substituent on indole (Figure 7C). Parts A and B of Figure 8 show the spectra of 3-(methylsulfonyl)propyl glucosinolate (**14**) with bands at 1325 and 1148 cm^{-1} characteristic of the sulfone moiety.

Unlike thiocyanate RSC≡N or isothiocyanate RN=C=S groups, which exhibit very intense bands, absorption arising from the –S(R′)C=N– function in the TMS derivatives of glucosinolates [R″S(R′)C=NO($SiMe_3$)] was essentially lost.

The 3-methylsulfinyl glucosinolate standard, which is known to be unstable, gave rise to three GC peaks under our experimental conditions. On the other hand, the two unidentified GC components found in the Brussels sprouts extract that eluted at 13.69 and 14.09 min gave rise to FT-IR spectra identical with those obtained for two of the decomposition products of 3-methylsulfinyl glucosinolate. Since these results were reproducible, the presence of the 3-methylsulfinyl glucosinolate in Brussels sprouts can be inferred. The structural elucidation of these unknown products is the subject of further investigation.

In conclusion, this paper demonstrates that GC/MI/FT-IR is a practical technique for identifying glucosinolates. TMS derivatives of 10 different glucosinolates isolated from swede or Brussels sprouts were separated by capillary GC and characterized by MI/FT-IR. Subtle structural variations on the side chain were documented. Observed FT-IR bands were consistent with the presence of particular functional groups such as vinyl (3090, 1645, and 996 cm^{-1}) or indole (1456, or 1493 and 1432 cm^{-1}) (Table II). Structural assignments based on FT-IR data are in agreement with those found by mass spectrometry (Shaw et al., 1989).

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Separation and Identification of Glucosinolates from *Brassica* Vegetables Using High-Performance Capillary Gas Chromatography (GC)–Positive-Ion Chemical Ionization Mass Spectrometry (PICIMS) and GC–PICIMS/MS

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A new, general-purpose analytical procedure for identification of desulfoglucosinolates from *Brassica* vegetables has been developed by combining high-performance capillary gas chromatography (HPCGC) with positive-ion chemical ionization mass spectrometry (PICIMS) and PICIMS/MS. HPCGC on a 25 m × 0.2 mm Ultra 1 WCOT fused silica column gave highly reproducible base-line separation of alkyl, alkenyl, hydroxyalkenyl, aryl, and indole desulfoglucosinolates as their per(trimethylsilyl)desulfoglucosinolate analogues. PICIMS and PICIMS/MS of these compounds using methane as the reagent gas gave conventional and daughter ion mass spectra in which the major ions were highly diagnostic of the glucosinolate structure.

Glucosinolates (1) are an important class of β-D-thioglucosides whose natural occurrence is limited to several plant families within the dicotyledonous angiosperms. Although approximately 100 glucosinolates (Kjaer and Skrydstrup, 1987) have been identified in the Cruciferae family, only a few of these (ca. 20) appear to be associated with the economically important genus *Brassica* (Fenwick et al., 1983).

Recently, monitoring endogenous levels of these compounds in existing and new plant varieties has become of interest because of the physiological activities of the associated breakdown products (isothiocyanate, nitrile thiocyanate, and oxazolidine-2-thiones) following endogenous, enzyme-mediated hydrolysis in disrupted, un-

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